KARPAGAM ACADEMY OF HIGHER EDUCATION

(Deemed University Established Under Section 3 of UGC Act 1956)

COIMBATORE-21

DEPARTMENT OF CHEMISTRY

M.Sc Chemistry Syllabus

ELECTIVE-III Semester-III
16CHP305A POLYMER CHEMISTRY 4H 4C

Instruction Hours/week:L: 4 T:0 P:0 Marks: Internal:40 External: 60 Total:100

Scope

Polymer Chemistry frames much of our understanding of the natural world and continues to bring new technologies that are useful to every aspect of human life. Polymer Chemistry is an exciting and challenging course, which helps us to understand the various aspects of compounds used in our day to day life. Polymer chemistry interfaces with a myriad of other disciplines and fields. It is fundamental to understand other areas of chemistry, biology and medicine. Due to highly prized nature of Polymer chemistry and its diverse topics, it lays the foundation for extremely productive and exciting career in variety of disciplines as pharmaceutical, agrochemical, mineralogy, molecular biology, biotechnology, nanotechnology, polymer technology, teaching research, scientific publication and so on. The importance of this subject would not diminish over time, so it will remain a promising career path. This course presents the basic principles of polymerization, coordination polymerization, determination of molecular weight of polymers, properties of polymers.

Programme outcome

Students will be able,

1. To learn about the basic concepts of kinetics and mechanism of polymerization.
2. To learn about the coordination polymerization.
3. To understand the Molecular weight of the polymers and their properties.
4. To learn about the processing of polymers.

Programme learning outcome

Students are learn the basic concepts and mechanism of different types of polymerization methods. They are also got the knowledge about new techniques of polymer process. Students are understand the different molecular weight determination methods.

Methodology

Blackboard teaching, Powerpoint presentation and group discussion.

UNIT – I

Polymer Basic Concepts: Monomers, repeat units, degree of polymerization, Linear, branched and network Polymers. Condensation Polymerization: Mechanism of stepwise polymerization. Kinetics and statistics of linear stepwise polymerization. Addition polymerization : Free radical, cationic and anionic polymerization. Polymerization conditions. Polymerization in homogeneous and heterogeneous systems.

UNIT – II

Co-ordination Polymerization: Kinetics, mono and bimetallic mechanism of co-ordination polymers. Zeigler Natta catalyst, co-polymerization: Block and graft co-polymers, kinetics of copolymerization. Types of co-polymerization. Reactivity ratio.

UNIT–III

Molecular Weight and Properties: Polydispersion – average molecular weight concept, number, weight and viscosity average molecular weights. Measurement of molecular weights. Viscosity, light scattering, osmotic and ultracentrifugation methods. Polymer structure and physical properties – crystalline melting point Tm. The glass transition temperature.Determination of Tg. Relationship between Tm and Tg.

UNIT – IV

Polymer Processing: Plastics, elastomers and fibres. Compounding, processing techniques: calendering, die casting, rotational casting, film casting, injection moulding, blow moulding extrusion, moulding, thermoforming, foaming, reinforcing and fibre spinning.

UNIT – V

Properties of Commercial Polymers: Polyethylene, polyvinyl chloride, polyamides, polyesters, phenolic resins, epoxy resins and silicone polymers. Functional polymers, Fire retarding polymers and electrically conducting polymers. Biomedical polymers – contact lens, dental polymers, artificial heart, kidney, skin and blood cells.

SUGGESTED BOOKS:

1. Billmeyer, F.W., 2003. Text Book of Polymer Science. III Edition, John Wiley, New York.
2. Gowariker, V. R., N. V. Viswanathan and J. Sreedhar, 1986. Polymer Science, New Age International Private Ltd., New Delhi.
3. Alcock H. R and F. W. Lamber, 1981. Contemporary Polymer Chemistry, Prentice Hall, Englewood Cliffs, NJ.
4. Flory, P. J., 1953. Principles of Polymer Chemistry, Cornell University Press, New York.
5. Odian, G., 1981. Principles of Polymerization. II Edition, John Wiley & Sons, New York.

KARPAGAM ACADEMY OF HIGHER EDUCATION

(Deemed University Established Under Section 3 of UGC Act 1956)

COIMBATORE-21

DEPARTMENT OF CHEMISTRY

LECTURE PLAN

POLYMER CHEMISTRY

Name of the Faculty:	Ms. B. Prabha	Department	: CHEMISTRY
Semester	: III	Year	: II
Course Code	: 16CHP305A		

UNIT-1

Polymer Basic Concepts **Total hours: 12**

S.NO	LECTURE DURATION	TOPICS TO BE COVERED	SUPPORT MATERIALS
1.	**1**	Monomers, repeat units, degree of polymerization	**T1: 19-22,; T2: 4-5 ,239 T1: 96-98; T2: 139-141**
2.	**1**	Linear, branched and network polymers	**T1: 142-143; T2: 5-8, T1: 142-143**
3.	**1**	Condensation polymerization: Mechanism of stepwise polymerization	**T2: 25-26, 26-32**
4.	**1**	Kinetics of linear step wise polymerization	**T2: 33-35**
5.	**1**	Statistics of linear step wise polymerization	**T2: 35-38**
6.	**1**	Addition polymerization: Free radical,	**T1: 105,116-120; T2: 50-53, 85-88, 89-90**
7.	**1**	Cationic polymerization	**T1: 105,116-120; T2: 50-53, 85-88, 89-90**
8.	**1**	anionic polymerization	**T1: 105,116-120; T2: 50-53, 85-88, 89-90**
9.	**1**	Polymerization conditions	**T2: 126**
10.	**1**	Polymerization in homogenous and heterogeneous systems	**T2: 127-133**
11.	**1**	Polymerization in homogenous and heterogeneous systems	**T2: 127-133**
12.	**1**	Discussion of important questions	

Text book:

T1: Gowariker, V. R., N. V. Viswanathan and J. Sreedhar, 1986. Polymer Science, *New Age International* Private Ltd., New Delhi.

T2: Billmeyer, F.W., 2003. Text Book of Polymer Science. III Edition, John Wiley, New York.

Reference book

R1: M.S Bhatnagar,2004, " A text book of polymers". Ist Edition, S.Chand & Company.

UNIT-2

Co-ordination Polymerization **Total no. of hours: 12**

S.NO	LECTURE DURATION	TOPIC TO BE COVERED	SUPPORT MATERIALS
1.	**1**	Co-ordination polymerization	**T2: 91**
2.	**1**	Kinetics of co-ordination polymerization	**T2: 94-96**
3.	**1**	Mono metallic mechanism of co-ordination polymers	**T1: 47-52; T2: 92-93**
4.	**1**	bimetallic mechanism of co-ordination polymers	**T1: 47-52; T2: 92-93**
5.	**1**	Ziegler Natta catalyst	**T1: 46; T2: 91-94**
6.	**1**	Co-polymerization: Block	**T1: 120-122; T2: 142-144**
7.	**1**	graft co-polymers	**T1: 120-122; T2: 142-144**
8.	**1**	Kinetics of copolymerization	**T1: 101,107-108**
9.	**1**	Types of co-polymerization	**T1: 103-106, T2: 182,206**
10.	**1**	Reactivity ratio	**T1: 106-107**
11.	**1**	Reactivity ratio	**T1: 106-107**
12.	**1**	Discussion of important questions	

Text book:

T1: Gowariker, V. R., N. V. Viswanathan and J. Sreedhar, 1986. Polymer Science, *New Age International* Private Ltd., New Delhi.

T2: Billmeyer, F.W., 2003. Text Book of Polymer Science. III Edition, John Wiley, New York.

Reference book

R1: M.S Bhatnagar,2004, " A text book of polymers". Ist Edition, S.Chand & Company.

UNIT -3

Molecular Weight and Properties **Total no. of hours: 12**

S.NO	LECTURE DURATION	TOPIC TO BE COVERED	SUPPORT MATERIALS
1	**1**	Polydispersion- Average molecular weight concept, number	**T1:86-88,**
2	**1**	Weight and viscosity average molecular weights	**T1: 89-92,**
3	**1**	Measurements of molecular weights	**T2: 208-213, 198**
4	**1**	viscosity	**T2: 208, T1: 404-408**
5	**1**	light scattering	**T2: 208, T1: 413- 419**
6	**1**	Osmotic method	**T2: 205-206, T1: 392-401**
7	**1**	Ultracentrifugation methods	**T2: 207, T1: 409-413**
8	**1**	Polymer structure and physical properties- Crystalline melting point T_m	**T1: 100-104; T2:331-336**
9	**1**	The glass transition temperature T_g	**T2: 337**
10	**1**	Determination of T_g.	**T1: 423-426**
11	**1**	Relation between T_m and T_g.	**T2: 337-340**
12	**1**	Discussion of important questions	

Text book:

T1: Gowariker, V. R., N. V. Viswanathan and J. Sreedhar, 1986. Polymer Science, *New Age International* Private Ltd., New Delhi.

T2: Billmeyer, F.W., 2003. Text Book of Polymer Science. III Edition, John Wiley, New York

Reference book

R1: M.S Bhatnagar,2004, " A text book of polymers". Ist Edition, S.Chand & Company.

UNIT -4

Polymer Processing **Total no. of hours: 12**

S.NO	LECTURE DURATION	TOPIC TO BE COVERED	SUPPORT MATERIALS
1	**1**	Plastics, elastomers and fibres.	**T1: 14,221, 225, 429,229,449 T2: 351, 371,486,471-475**
2	**1**	Compounding	**T1: 450-451**
3	**1**	Process techniques: Calendering,	**T1: 452-453; T2:464-466**
4	**1**	Die casting	**T1: 453-454; T2:464-466**
5	**1**	rotational casting, film casting	**T1: 454-456; T2: 465-466**
6	**1**	injection moulding, blow moulding	**T1: 457-462; T2: 458-461, 461-464**
7	**1**	Extrusion moulding	**T1: 457-462; T2: 458-461, 461-464**
8	**1**	Thermoforming	**T1: 462-464; T2: 467-469**
9	**1**	Foaming	**T1: 462-464; T2: 467-469**
10	**1**	Reinforcing	**T1: 465-469**
11	**1**	Fiber spinning	**T1: 470-474; T2: 491-496**
12	**1**	Discussion of important questions	

Text book:

T1: Gowariker, V. R., N. V. Viswanathan and J. Sreedhar, 1986(2014 re-print). “Polymer Science”, *New Age International* Private Ltd., New Delhi.

T2: Billmeyer, F.W., 2008(Re-print). “Text Book of Polymer Science”. III Edition, John Wiley, New York.

Reference book

R1: M.S Bhatnagar,2004, “ A text book of polymers”. Ist Edition, S.Chand & Company.

UNIT -5

Properties of Commercial Polymers **Total no. of hours: 12**

S.NO	LECTURE DURATION	TOPIC TO BE COVERED	SUPPORT MATERIALS
1	**1**	Polyethylene, Polyvinyl chloride	**T1: 215-217, 236-238, 227-229**
2	**1**	Polyamides	**T1: 215-217, 236-238, 227-229**
3	**1**	Polyesters and Silicon polymers	**T1: 221-223,255-256; T2: 442-445,448-450**
4	**1**	Phenolic resins, Epoxy resins	**T1: 251-254; T2: 436-440,445-446**
5	**1**	Functional polymers, Fire retarding Polymers	W_1
6	**1**	Electrically conducting polymers	W_1
7	**1**	Bio-medical polymers- contact lens, dental polymers	W_2
8	**1**	Artificial heart, kidney, skin and blood cells.	W_2
9	**1**	Revision and Discussion of Possible Questions	
10	**1**	Recapitulation and discussion of Previous year question	
11	**1**	Recapitulation and discussion of Previous year question	
12	**1**	Recapitulation and discussion of Previous year question	

Text book:

T1: Gowariker, V. R., N. V. Viswanathan and J. Sreedhar, 1986. Polymer Science, *New Age International* Private Ltd., New Delhi.

T2: Billmeyer, F.W., 2003. Text Book of Polymer Science. III Edition, John Wiley, New York

Reference book

R1: M.S Bhatnagar,2004, " A text book of polymers". Ist Edition, S.Chand & Company.

Web Address:

W$_1$: https://en.wikipedia.org/wiki/Fire-safe_polymers or Functional or Electrically conducting polymers

W$_2$: https://biomedical polymers/applications.

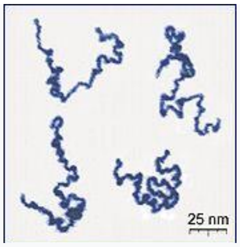
UNIT-1

Polymer Basic Concepts

Monomers, repeat units, degree of polymerization, Linear, branched and network Polymers. Condensation Polymerization: Mechanism of stepwise polymerization. Kinetics and statistics of linear stepwise polymerization. Addition polymerization : Free radical, cationic and anionic polymerization. Polymerization conditions. Polymerization in homogeneous and heterogeneous systems.

INTRODUCTION

Polymer



Appearance of real linear polymer chains as recorded using an atomic force microscope on a surface, under liquid medium. Chain contour length for this polymer is ~204 nm; thickness is ~0.4 nm.

IUPAC definition

Substance composed of macromolecules. Applicable to substance macromolecular in nature like cross-linked systems that can be considered as one macromolecule.

A **polymer** (/ˈpɒlɪmər/; Greek *poly-*, "many" + *-mer*, "parts") is a large molecule, or macromolecule, composed of many repeated subunits. Because of their broad range of properties, both synthetic and natural polymers play essential and ubiquitous roles in everyday life. Polymers range from familiar synthetic plastics such as polystyrene to natural biopolymers such as DNA and proteins that are fundamental to biological structure and function. Polymers, both natural and synthetic, are created via polymerization of many small molecules, known as monomers. Their consequently large molecular mass relative to small molecule compounds produces unique physical properties, including toughness, viscoelasticity, and a tendency to form glasses and semicrystalline structures rather than crystals.

The term "polymer" derives from the ancient Greek word πολύς (*polus*, meaning "many, much") and μέρος (*meros*, meaning "parts"), and refers to a molecule whose structure is composed of multiple repeating units, from which originates a characteristic of high relative molecular mass and attendant properties. The units composing polymers derive, actually or conceptually, from molecules of low relative molecular mass. The term was coined in 1833 by Jöns Jacob Berzelius, though with a definition distinct from the modern IUPAC definition. The modern concept of polymers as covalently bonded macromolecular structures was proposed in 1920 by Hermann Staudinger, who spent the next decade finding experimental evidence for this hypothesis.

Polymers are studied in the fields of biophysics and macromolecular science, and polymer science (which includes polymer chemistry and polymer physics). Historically, products arising from the linkage of repeating units by covalent chemical bonds have been the primary focus of polymer science; emerging important areas of the science now focus on non-covalent links. Polyisoprene of latex rubber is an example of a natural/biological polymer, and the polystyrene of styrofoam is an example of a synthetic polymer. In biological contexts, essentially all biological macromolecules—i.e., proteins (polyamides), nucleic acids (polynucleotides), and polysaccharides—are purely polymeric, or are composed in large part of polymeric components—e.g., isoprenylated/lipid-modified glycoproteins, where small lipidic molecules and oligosaccharide modifications occur on the polyamide backbone of the protein.

The simplest theoretical models for polymers are ideal chains.

Monomer

A **monomer** (/ˈmɒnəmər/ ***MON**-ə-mər*) (*mono-*, "one" + *-mer*, "part") is a molecule that, as a unit, binds chemically or supramolecularly to other molecules to form a supramolecularpolymer. Large numbers of monomer units combine to form polymers in a process called polymerization. It is a small molecule of an organic substance. A double bond exist between the individual molecule which is weak. Molecules of a small number of monomer units (up to a few dozen) are called oligomers. The term "monomeric protein" may also be used to describe one of the proteins making up a multiprotein complex.

Biopolymer groupings, and the types of monomers that create them:

- For *lipids* (Diglycerides, triglycerides)*****, the monomers are **glycerol and fatty acids**.
- For *proteins* (Polypeptides), the monomers are **amino acids**.

Repeat unit

A **repeat unit** or **repeating unit** is a part of a polymer whose repetition would produce the complete polymer chain (except for the end-groups) by linking the repeat units together successively along the chain, like the beads of a necklace.

A repeat unit is sometimes called a *mer* or *mer unit*. "Mer" originates from the Greek word "meros," which means part. The word polymer derives its meaning from this, which means "many mers." A repeat unit (or mer), is not to be confused with the term monomer, which refers to the small molecule from which a polymer is synthesized.

One of the simplest repeat units is that of the addition polymer polyvinyl chloride, $-[CH_2-CHCl]_n-$, whose repeat unit is $-[CH_2-CHCl]-$. In this case the repeat unit has the same atoms as the monomer vinyl chloride $CH_2=CHCl$. When the polymer is formed, the C=C double bond in the monomer is replaced by a C-C single bond in the polymer repeat unit, which links by two new bonds to adjoining repeat units.

In condensation polymers (see examples below), the repeat unit contains fewer atoms than the monomer or monomers from which it is formed.

The subscript "n" denotes the degree of polymerisation, that is, the number of units linked together. The molecular mass of the repeat unit, M_R, is simply the sum of the atomic masses of the atoms within the repeat unit. The molecular mass of the chain is just the product nM_R. Other than monodisperse polymers, there is normally a molar mass distributioncaused by chains of different length.

In copolymers there are two or more types of repeat unit, which may be arranged in alternation, or at random, or in other more complex patterns.

Degree of polymerization

The **degree of polymerization**, or **DP**, is the number of monomeric units in a macromolecule or polymer or oligomer molecule.

For a homopolymer, there is only one type of monomeric unit and the *number-average* degree of polymerization is given by $DP_n = X_n = M_n / M_0$, where M_n is the number-average molecular weight and M_0 is the molecular weight of the monomer unit. For most industrial purposes, degrees of polymerization in the thousands or tens of thousands are desired. This number does not reflect the variation in molecule size of the polymer that typically occurs, it only represents the mean number of monomeric units.

Some authors, however, define DP as the number of repeat units, where for copolymers the repeat unit may not be identical to the monomeric unit. For example, in nylon-6,6, the repeat unit contains the two monomeric units —$NH(CH_2)_6NH$— and —$OC(CH_2)_4CO$—, so that a chain of 1000 monomeric units corresponds to 500 repeat units. The degree of polymerization or chain length is then 1000 by the first (IUPAC) definition, but 500 by the second.

Classification of polymers:

copolymer - a polymer prepared from more than one monomer

addition polymer - a polymer that consists of a repeat unit equivalent to its monomer - generally vinyl polymers, e.g., polyethylene, or ring-opening polymers, e.g., poly(ethylene oxide)

condensation polymer - a polymer that differs from its monomer(s) by the elimination of a small molecule during polymerization (Carothers' original definition) e.g., polyamides and polyesters

the definition has been expanded to include any polymer that incorporates new functional group(s) in the chain that were not present in the monomers
(to allow inclusion of polyurethanes)

Descriptions of polymer structure:

linear polymer - a polymer consisting of a single continuous chain of repeat units

branched polymer - a polymer that includes side chains of repeat units connecting onto the main chain of repeat units (different from side chains already present in the monomers)

crosslinked polymer - a polymer that includes interconnections between chains, either formed during polymerization (by choice of monomer) or after polymerization (by adding a specific reagent)

network polymer - a crosslinked polymer that includes numerous interconnections between chains such that the entire sample is (or could be) a single molecule

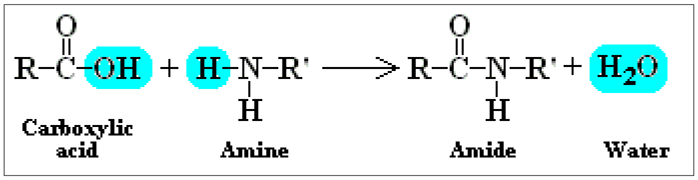
Condensation polymerization

The monomers that are involved in condensation polymerization are not the same as those in addition polymerization. The monomers for condensation polymerization have two main characteristics:.

- ⇨ Instead of double bonds, these monomers have functional groups (like alcohol, amine, or carboxylic acid-groups).
- ⇨ Each monomer has at least two reactive sites, which usually means two functional groups.

The Amide Linkage:

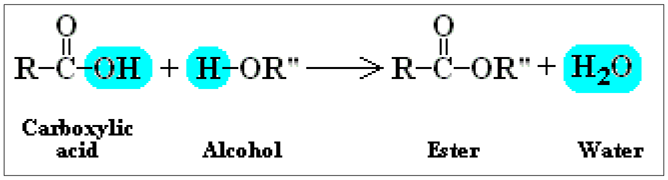
When a carboxylic acid and an amine react, a water molecule is removed, and an amide molecule is formed.



Because of this amide formation, this bond is known as an *amide linkage*.

The Ester Linkage:

When a carboxylic acid and an alcohol react, a water molecule is removed, and an ester molecule is formed.



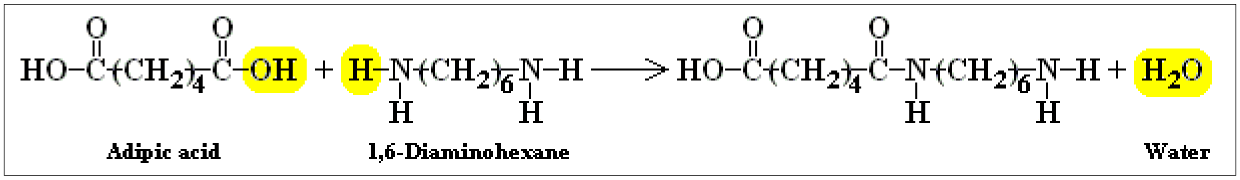
Because of this ester formation, this bond is known as an *ester linkage*.

Monomers involved in condensation polymerization have functional groups. These functional groups combine to form amide and ester linkages. When this occurs, a water molecule in removed. Since water is removed, we call these reactions condensation reactions (water condenses out.). When a condensation reaction involves polymerization, we call it *condensation polimarization*.

Examples: **The Mechanism of Condensation Polymerization**

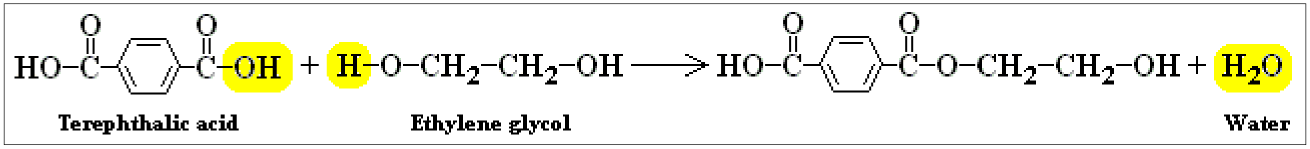
That the monomers are joined by condensation polymerization have two functional groups. You also know (from Part 6) that a carboxylic acid and an amine can form an amide linkage, jand a carboxylic acid and an alcohol can form an ester linkage. Since each monomer has two reactive sites, they can form long-chain polymers by making many amide or ester links. Let's look at two examples of common polymers made from the monomers we have studied.

Example 1:
A carboxylic acid monomer and an amine monomer can join in an amide linkage.

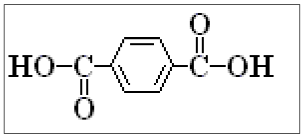


As before, a water molecule is removed, and an amide linkage is formed. Notice that an acid group remains on one end of the chain, which can react with another amine monomer. Similarly, an amine group remains on the other end of the chain, which can react with another acid monomer. Thus, monomers can continue to join by amide linkages to form a long chain. Because of the type of bond that links the monomers, this polymer is called a polyamide. The polymer made from these two six-carbon monomers is known as nylon-6,6. (Nylon products include hosiery, parachutes, and ropes.)

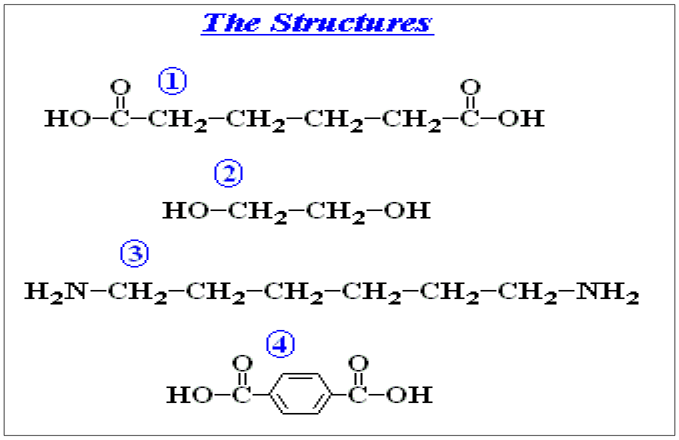
Example 2:
A carboxylic acid monomer and an alcohol monomer can join in an ester linkage.

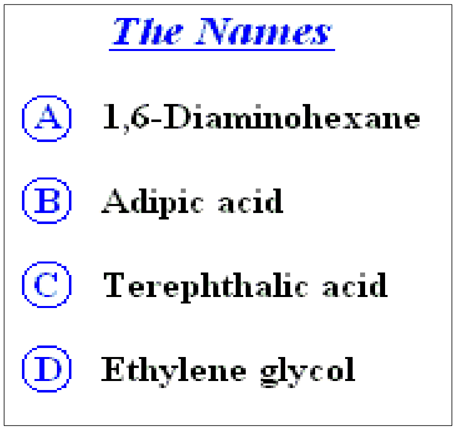


A water molecule is removed as the ester linkage is formed. Notice the acid and the alcohol groups that are still available for bonding.



Because the monomers above are all joined by ester linkages, the polymer chain is a polyester. This one is called PET, which stands for poly(ethylene terephthalate). (PET is used to make soft-drink bottles, magnetic tape, and many other plastic products.)





The Names

Ⓐ 1,6-Diaminohexane

Ⓑ Adipic acid

Ⓒ Terephthalic acid

Ⓓ Ethylene glycol

Stepwise polymerization

A number of different chemical reactions may be used to synthesize polymeric materials by step polymerization. These include esterification, amidation, the formation of urethanes, aromatic substitution, and others. Polymerization usually proceeds by the reactions between two different functional groups, for example, hydroxyl and carboxyl groups, or isocyanate and hydroxyl groups.All step polymerizations fall into two groups depending on the type of monomer(s)employed. The first involves two different bifunctional and/or polyfunctional monomers in which each monomer possesses only one type of functional group. (A polyfunctional monomer is a monomer with more than one functional group per molecule. A bifunctional monomeris one with two functional groups per molecule.) The second involves a single monomer containing both types of functional groups. The synthesis of polyamides illustrates both groups of polymerization reactions. Thus polyamides can be obtained from the reaction of diamines with diacids.

$$nH_2N\text{-}R\text{-}NH_2 + nHO_2C\text{-}R'\text{-}CO_2H \rightarrow \text{-(-NH-R-NHCO-R'-CO-)-}_nOH + (2n-1)H_2O$$

or from the reaction of amino acids with themselves:

$$nH_2N\text{-}R\text{-}CO_2H \rightarrow H\text{-(-NH-R-CO-)-}_nOH + (n-1)H_2O$$

The two groups of reaction can be represented in a general manner by the equations

$$nA\text{-}A + nB\text{-}B \rightarrow \text{-(-A-AB-B-)-}_n$$

$$nA\text{-}B \rightarrow \text{-(-A-B-)-}_n$$

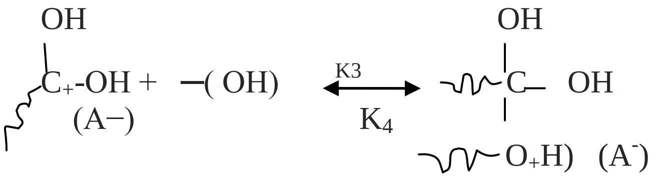
where A and B are the two different types of functional groups. The characteristics of these two polymerization reactions are very similar. The successful synthesis of high polymers (i.e., polymer of sufficiently high molecular weight to be useful from the practical viewpoint) using any step polymerization reaction generally is more difficult than the corresponding small molecule reaction, since high polymers can be achieved only at very high conversions (>98–99%). A conversion of 90%, which would be considered excellent for the synthesis of ethyl acetate or methyl benzamide, is a disaster for the synthesis of the corresponding polyester or polyamide. The need for very high conversions to synthesize high polymer places several stringent requirements on any reaction to be used for polymerization—a favorable equilibrium and the absence of cyclization and other side reactions. These stringent requirements are met by a relatively small fraction of the reactions familiar to and used by chemists to synthesize small molecules. An additional requirement for achieving high molecular weights is the need for the A and B functional groups to be present at very close to stoichiometric amounts.

Kinetics of Stepwise Polimerisation:

Consider the polyesterification of a diacid and a diol to illustrate the general form of the kinetics of a typical step polymerization. Simple esterification is a well-known acidcatalyzed reaction and polyesterification follows the same course [Otton and Ratton, 1988; Vancso-Szmercsanyi and Makay-Bodi, 1969]. The reaction involves protonation of the carboxylic acid,

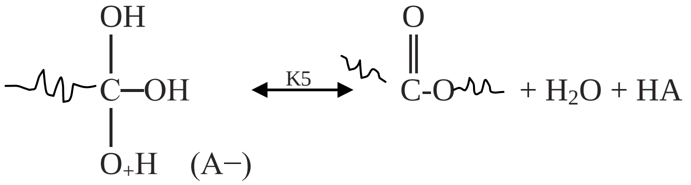
$$\sim(C\text{-OH}) + HA \underset{K2}{\overset{K1}{\longleftrightarrow}} \text{—}(HO\text{-}C_{+}\text{-OH}(A^{-}) \qquad 1$$

followed by reaction of the protonated specie with the alcohol to yield the ester



$$\sim\overset{OH}{\underset{(A-)}{C_{+}}}\text{-OH} + \text{—(OH)} \underset{K_4}{\overset{K3}{\longleftrightarrow}} \sim\overset{OH}{\underset{\sim O_{+}H)\ (A^{-})}{C}}\text{— OH} \qquad 2$$

II



$$\sim\overset{OH}{\underset{O_{+}H\quad(A-)}{C}}\text{—OH} \overset{K5}{\longleftrightarrow} \sim\overset{O}{\overset{\|}{C}}\text{-O}\sim + H_2O + HA \qquad 3$$

In the above equations and are used to indicate all acid or alcohol species in the reaction mixture (i.e., monomer, dimer, trimer, . . . , n-mer). Species I and II are shown in the form of their associated ion pairs since polymerization often takes place in organic media of low polarity. (A^-) is the negative counter ion derived from the acid HA. Polyesterifications, like many other step polymerizations, are equilibrium reactions. However, from the practical viewpoint of obtaining high yields of high-molecular-weight product such polymerizations are run in a manner so as to continuously shift the equilibrium in the direction of the polymer. In the case of a polysterification this is easily accomplished by removal of the water that is a by-product of the reaction species II (Eq. 3).

Under these conditions the kinetics of polymerization can be handled by considering the reactions in Eqs. 2 and 3 to be irreversible.

The rate of a step polymerization is conveniently expressed in terms of the concentrations of the reacting functional groups. Thus the polyesterification can be experimentally followed by titrating for the unreacted carboxyl groups with a base. The rate of polymerization Rp can then be expressed as the rate of disappearance of carboxyl groups -d[COOH]/dt. For the usual polyesterification, the polymerization rate is synonomous with the rate of formation of species II; that is, k_4 is vanishingly small (since the reaction is run under conditions that drive Eqs. 2 and 3 to the right), and k_1, $k_{2,}$ and k_5 are large compared to k_3. An expression for the reaction rate can be obtained following the general procedures for handling a reaction scheme with the characteristics described [Moore and Pearson, 1981]. The rate of polymerization is given by

$R= -d[COOH]/dt = k_3[C^+ (OH)_2][OH]$ 4

Where [COOH], [OH], and $[C^+ (OH)_2]$ represent the concentrations of carboxyl, hydroxyl, and protonated carboxyl (**I**) groups, respectively. The concentration terms are in units of moles of the particular functional group per liter of solution. Equation 4 is inconvenient in that the concentration of protonated carboxylic groups is not easily determined experimentally. One can obtain a more convenient expression for Rp by substituting for $C^+ (OH)_2$ from the equilibrium expression

$K = k_1/k_2 = [C^+(OH)_2] / [COOH][HA]$ 5

for the protonation reaction (Eq. 1). Combination of Eqs. 4 and 5 yields

$-d[COOH]/dt = k_3K[COOH][OH][HA]$ 6

Two quite different kinetic situations arise from Eq. 6 depending on the identity of HA, that is, on whether a strong acid such as sulfuric acid or p-toluenesulfonic acid is added as an external catalyst.

Self-Catalyzed Polymerization

In the absence of an externally added strong acid the diacid monomer acts as its own catalyst for the esterification reaction. For this case [HA] is replaced by [COOH] and Eq. 6 can be written in the usual form [Flory, 1953]

$-d[COOH]/dt = k[COOH]^2 [OH]$ 7

where K and k3 have been combined into the experimentally determined rate constant k. Equation 2-18 shows the important characteristic of the self-catalyzed polymerization- the reaction is third-order overall with a second-order dependence on the carboxyl concentration. The second-order dependence on the carboxyl concentration is comprised of two first-order dependencies—one for the carboxyl as the reactant and one as the catalyst.

For most polymerizations the concentrations of the two functional groups are very nearly stoichiometric, and Eq. 7 can be written as

$-d[M]/dt = k[M]^3$ 8a

Or

$-d[M]/[M]^3 = kdt$ 8b

where [M] is the concentration of hydroxyl groups or carboxyl groups.

Integration of Eq. 8b yields

$$2kt = 1/[M]^2 - 1/[M_0]^2 \qquad 9$$

where $[M_0]$ is the initial (at t = 0) concentration of hydroxyl or carboxyl groups. It is convenient at this point to write Eq. 9 in terms of the extent or fraction of reaction p defined as the fraction of the hydroxyl or carboxyl functional groups that has reacted at time t. p is also referred to as the extent or fraction of conversion. (The value of p is calculated from a determination of the amount of unreacted carboxyl groups.) The concentration [M] at time t of either hydroxyl or carboxyl groups is then given by

$$[M] = [M_0] - [M_0]p = [M_0](1-p) \qquad 10$$

Combination of Eqs. 9 and 10 yields

$$1/(1-p)^2 = 2[M_0]^2kt+1 \qquad 11$$

Experimental Observations

Equation 11 indicates that a plot of $1/(1-p)^2$ versus t should be linear. This behavior has been generally observed in polyesterifications. Figure 2-1 shows the results for the polymerization of diethylene glycol, (HOCH2CH2)2O, and adipic acid [Flory, 1939; Solomon, 1967and 1972]. The results are typical of the behavior observed for polyesterifications. Although various authors agree on the experimental data, there has been considerable disagreement on the interpretation of the results. At first glance the plot does not appear to exactly follow the relationship. The experimental points deviate from the third-order plot in the initial region below 80% conversion and in the later stages above 93% conversion. These deviations led various workers [Amass, 1979; Fradet and Marechal, 1982a,b; Solomon, 1967, 1972] to suggest alternate kinetic expressions based on either 1- or 3 /2-order dependencies of

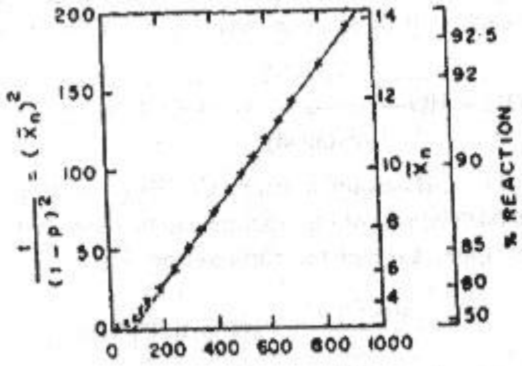


Fig. 2. Plot showing $1/(1-p)^2$ or ($\overline{X}_n$) vs time for self catalyzed polyesterification of diethylene glycol with adipic acid at 166°C.

the reaction rate on the carboxyl concentration, that is, 2- and 2(1/ 2)-order dependencies according to

$$-d[COOH]/dt = k[COOH][OH] \qquad 12a$$

And

$$-d[COOH]/dt = k[COOH]^{3/2}[OH] \qquad 12b$$

However, a critical evaluation shows that both kinetic possibilities leave much to be desired. The experimental rate data fits Eq. 12a well only in the region between 50 and 86% conversion with an excessively poor fit above 86% conversion. On the other hand, a plot according to Eq. 12b fits reasonably well up to about 80% conversion but deviates badly above that point. Neither of the two alternate kinetic plots comes close to being as useful as the third-order plot in Fig. 2-1. The third-order plot fits the experimental data much better than does either of the others at the higher conversions. The fit of the data to the third-order plot is reasonably good over a much greater range of the higher conversion region. The region of high conversion is of prime importance, since, high-molecular-weight polymer is obtained only at high conversions. From the practical viewpoint, the low conversion region of the kinetic plot is of little significance.

External Catalysis of Polymerization

The slow increase in molecular weight was mistakenly thought originally to be due to the low reactivity of functional groups attached to large molecules. It is, however, simply a consequence of the third-order kinetics of the direct polyesterification reaction. The realization of this kinetic situation led to the achievement of high-molecular-weight products in reasonable reaction times by employing small amounts of externally added strong acids (such as sulfuric acid or p-toluenesulfonic acid) as catalysts. Under these conditions, [HA] in Eq. 2-17 is the concentration of the catalyst. Since this remains constant throughout the course of the polymerization, Eq. 2-17 can be written as,

$$-d[M]/dt = K' [M]^2 \qquad 13$$

where the various constant terms in Eq. 11 have been collected into the experimentally determinable rate constant K′. Equation 13 applies to reactions between stoichiometric concentrations of the diol and diacid. Integration of Eq. 13 yields

$$K' t = 1/[M] - 1/[M_0] \qquad 14$$

Combining Eqs. 14 and 10 yields the dependence of the degree of polymerization on reaction time as

$$[M_o]k't = 1/(1-p) - 1 \qquad 15$$

Or

$$X\overline{n} = 1 + [M_o]k't \qquad 15b$$

Data for the polymerization of diethylene glycol with adipic acid catalyzed by p-toluene sulfonic acid are shown in Fig. 2-2. The plot follows Eq. 15 with the degree of polymerization increasing linearly with reaction time. The much greater rate of increase of Xn with reaction time in the catalyzed polyesterification (Fig. 2-2) relative to the uncatalyzed reaction (Fig. 2-1) is a general and most significant phenomenon. The polyesterification becomes a much more economically feasible reaction when it is catalyzed by an external acid. The selfcatalyzed polymerization is not a useful reaction from the practical viewpoint of producing high polymers in reasonable reaction times.

Equations 2-27 and 2-33 and Fig. 2-2 describe the much greater difficulty of performing a successful polymerization compared to the analogous small-molecule reaction (such as the synthesis of ethyl acetate from acetic acid and ethanol).

Consider the case where one needs to produce a polymer with a degree of polymerization of 100, which is achieved only at 99% reaction. Running the polymerization to a lower conversion such as 98%, an excellent conversion for a small-molecule synthesis, results in no polymer of the desired molecular weight. Further, one must almost double the reaction time (from _450 min to 850 min in (Fig. 2-2) to achieve 99% reaction and the desired polymer molecular weight. For the small molecule reaction one would not expend that additional time to achieve only an additional 1% conversion. For the polymerization one has no choice other than to go to 99% conversion. The nonlinearity in the initial region of Fig. 2-2 is, like that in Fig. 2-1, a characteristic of esterifications in general and not of the polymerization reaction. The general linearity of the plot in the higher conversion region is a strong confirmation of the concept of functional group reactivity independent of molecular size. Figure 2-2 shows that the polyesterification.

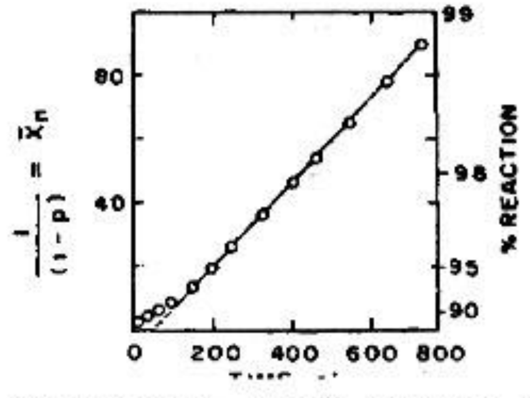


Fig. 3. Plot showing 1/(1 — p) or $\overline{X}_n$ vs time for polycondensation of diethylene glycol and adipic acid at 109 °C using 0.4 mole, % p-toluene sulphonic acid as the catalyst[4,5].

continues its second-order behavior at least up to a degree of polymerization of 90 corresponding to a molecular weight of _10,000. There is no change in the reactivities of the hydroxyl and carboxyl groups in spite of the large increase in molecular size (and the accompanying large viscosity increase of the medium). Similar results have been observed in many other polymerizations. Data on the degradation of polymers also show the same effect. Thus in the acid hydrolysis of cellulose there is no effect of molecular size on hydrolytic reactivity up to a degree of polymerization of 1500 (molecular weight 250,000) [Flory, 1953]. The concept of functional group reactivity independent of molecular size has been highly successful in allowing the kinetic analysis of a wide range of polymerizations and reactions of polymers. Its validity, however, may not always be quite rigorous at very low or very high conversions.

Addition polymerization

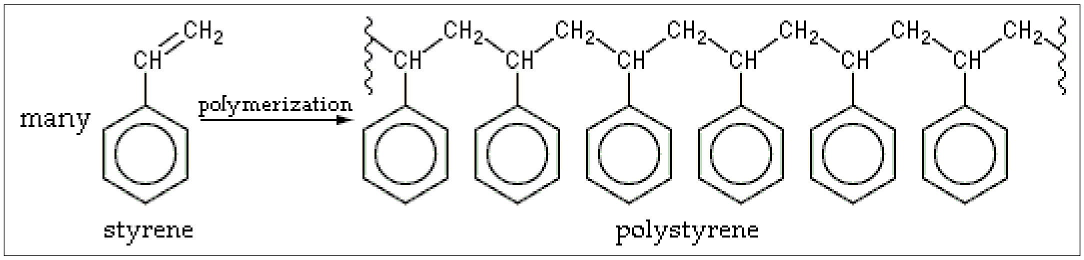
Polymers are long chain giant organic molecules are assembled from many smaller molecules called **monomers**. **Polymers** consist of many repeating monomer units in long chains. A polymer is analogous to a necklace made from many small beads (monomers). Many monomers are alkenes or other molecules with double bonds which react by **addition** to their unsaturated double bonds.

The electrons in the double bond are used to bond two monomer molecules together. This is represented by the red arrows moving from one molecule to the space between two molecules where a new bond is to form. The formation of polyethylene from ethylene (ethene) may be illustrated in the graphic on the left as follows. In the complete polymer, all of the double bonds have been turned into single bonds. No atoms have been lost and you can see that the monomers have just been joined in the process of addition. A simple representation is -[A-A-A-A-A]-. Polyethylene is used in plastic bags, bottles, toys, and electrical insulation.

- **LDPE - Low Density Polyethylene:** The first commercial polyethylene process used peroxide catalysts at a temperature of 500 C and 1000 atmospheres of pressure. This yields a transparent polymer with highly branched chains which do not pack together well and is low in density. LDPE makes a flexible plastic. Today most LDPE is used for blow-molding of films for packaging and trash bags and flexible snap-on lids. LDPE is recyclable plastic #4.
- **HDPE - High Density Polyethylene:** An alternate method is to use Ziegler-Natta aluminum titanium catalysts to make HDPE which has very little branching, allows the strands to pack closely, and thus is high density. It is three times stronger than LDPE and more opaque. About 45% of the HDPE is blow molded into milk and disposable consumer bottles. HDPE is also used for crinkly plastic bags to pack groceries at grocery stores. HDPE is recyclable plastic #2.

Examples

- **PVC** (polyvinyl chloride), which is found in plastic wrap, simulated leather, water pipes, and garden hoses, is formed from vinyl chloride ($H_2C=CHCl$). The reaction is shown in the graphic on the left. Notice how every other carbon must have a chlorine attached.
- **Polypropylene:** The reaction to make polypropylene ($H_2C=CHCH_3$) is illustrated in the middle reaction of the graphic. Notice that the polymer bonds are always through the carbons of the double bond. Carbon #3 already has saturated bonds and cannot participate in any new bonds. A methyl group is on every other carbon.
- **Polystyrene:** The reaction is the same for polystrene where every other carbon has a benzene ring attached. Polystyrene (PS) is recyclable plastic #6. In the following illustrated example, many styrene monomers are polymerized into a long chain polystyrene molecule. The squiggly lines indicate that the polystyrene molecule extends further at both the left and right ends.



- Blowing fine gas bubbles into liquid polystyrene and letting it solidify produces *expanded polystyrene*, called *Styrofoam* by the Dow Chemical Company.
- **Polystyrene with DVB:** Cross-linking between polymer chains can be introduced into polystyrene by copolymerizing with ***p*-divinylbenzene** (**DVB**). DVB has vinyl groups (-CH=CH_2) at each end of its molecule, each of which can be polymerized into a polymer chain like any other vinyl group on a styrene monomer.

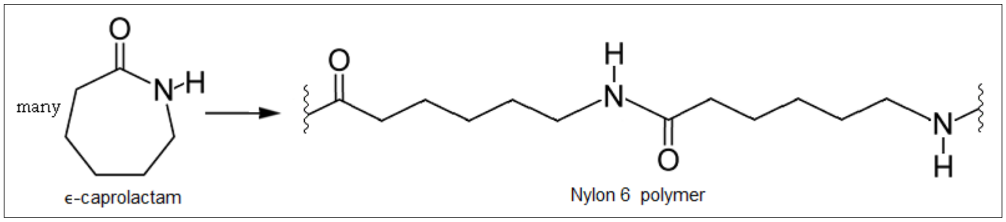
Polymers from conjugated dienes usually give elastomer polymers having rubber-like properties.

Addition homopolymers from conjugated dienes

Monomer	Polymer name	Trade name	Uses
H_2C=CH-C(CH_3)=CH_2	polyisoprene	natural or some synthetic rubber	applications similar to natural rubber
H_2C=CH-CH=CH_2	polybutadiene	polybutadiene synthetic rubber	select synthetic rubber applications
H_2C=CH-CCl=CH_2	polychloroprene	Neoprene	chemically-resistant rubber

Ring opening polymerization

In this kind of polymerization, molecular rings are opened in the formation of a polymer. Here epsilon-caprolactam, a 6-carbon cyclic monomer, undergoes ring opening to form a Nylon 6 homopolymer, which is somewhat similar to but not the same as Nylon 6,6 alternating copolymer.



Cationic polymerization

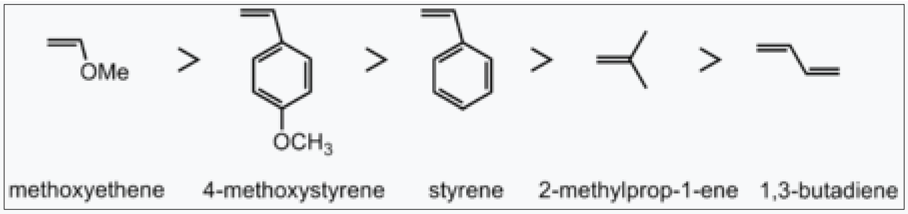
Cationic polymerization is a type of chain growth polymerization in which a cationic initiator transfers charge to a monomer which then becomes reactive. This reactive monomer goes on to react similarly with other monomers to form a polymer. The types of monomers necessary for cationic polymerization are limited to olefins with electron-donating substituents and heterocycles. Similar to anionic polymerization reactions, cationic polymerization reactions are very sensitive to the type of solvent used. Specifically, the ability of a solvent to form free ions will dictate the reactivity of the propagating cationic chain. Cationic polymerization is used in the production of polyisobutylene (used in inner tubes) and poly(N-vinylcarbazole) (PVK).

Monomers

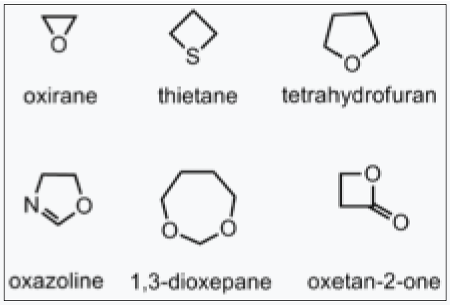
Monomer scope for cationic polymerization is limited to two main types: olefins and heterocyclic monomers. Cationic polymerization of both types of monomers occurs only if the overall reaction is thermally favorable. In the case of olefins, this is due to isomerization of the monomer double bond; for heterocycles, this is due to release of monomer ring strain and, in some cases, isomerization of repeating units. Monomers for cationic polymerization are nucleophilic and form a stable cation upon polymerization.

Olefins

Cationic polymerization of olefin monomers occurs with olefins that contain electron-donating substituents. These electron-donating groups make the olefin nucleophilic enough to attack electrophilic initiators or growing polymer chains. At the same time, these electron-donating groups attached to the monomer must be able to stabilize the resulting cationic charge for further polymerization. Some reactive olefin monomers are shown below in order of decreasing reactivity, with heteroatom groups being more reactive than alkyl or aryl groups. Note, however, that the reactivity of the carbenium ion formed is the opposite of the monomer reactivity.[5]



Heterocyclic monomers



Heterocyclic monomers that are cationically polymerized are lactones, lactams, and cyclic amines. Upon addition of an initiator, cyclic monomers go on to form linear polymers. The reactivity of heterocyclic monomers depends on their ring strain. Monomers with large ring strain, such as oxirane, are more reactive than 1,3-dioxepane which has considerably less ring strain. Rings that are six-membered and larger are less likely to polymerize due to lower ring strain.

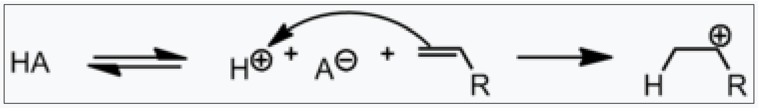
Synthesis

Initiation

Initiation is the first step in cationic polymerization. During initiation, a carbenium ion is generated from which the polymer chain is made. The counterion should be non-nucleophilic, otherwise the reaction is terminated instantaneously. There are a variety of initiators available for cationic polymerization, and some of them require a coinitiator to generate the needed cationic species.[7]

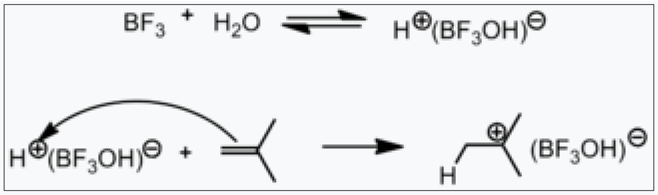
Classical protonic acids

Strong protic acids can be used to form a cationic initiating species. High concentrations of the acid are needed in order to produce sufficient quantities of the cationic species.
The counterion (A^-) produced must be weakly nucleophilic so as to prevent early termination due to combination with the protonated olefin. Common acids used are phosphoric, sulfuric, fluro-, and triflic acids. Only low molecular weight polymers are formed with these initiators.



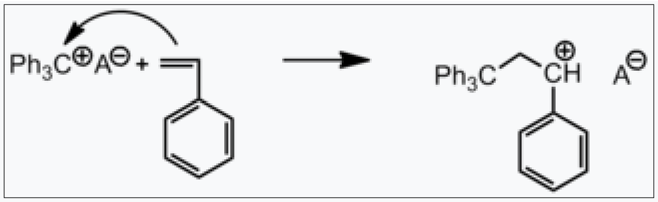
Lewis acids/Friedel-Crafts catalysts

Lewis acids are the most common compounds used for initiation of cationic polymerization. The more popular Lewis acids are $SnCl_4$, $AlCl_3$, BF_3, and $TiCl_4$. Although these Lewis acids alone are able to induce polymerization, the reaction occurs much faster with a suitable cation source. The cation source can be water, alcohols, or even a carbocation donor such as an ester or an anhydride. In these systems the Lewis acid is referred to as a coinitiator while the cation source is the initiator. Upon reaction of the initiator with the coinitiator, an intermediate complex is formed which then goes on to react with the monomer unit. The counterion produced by the initiator-coinitiator complex is less nucleophilic than that of the Brønsted acid A^- counterion. Halogens, such as chlorine and bromine, can also initiate cationic polymerization upon addition of the more active Lewis acids.[1]



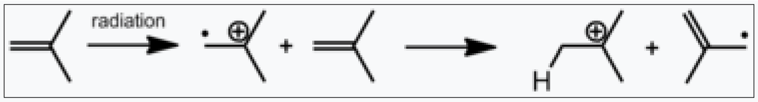
Carbenium ion salts

Stable carbenium ions are used to initiate chain growth of only the most reactive olefins and are known to give well defined structures. These initiators are most often used in kinetic studies due to the ease of being able to measure the disappearance of the carbenium ion absorbance. Common carbenium ions are trityl and tropylium cations.



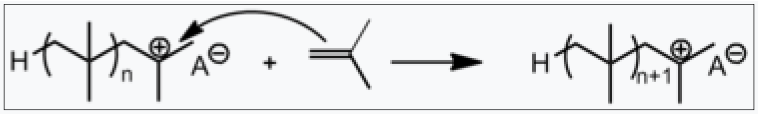
Ionizing radiation

Ionizing radiation can form a radical-cation pair that can then react with a monomer to start cationic polymerization. Control of the radical-cation pairs are difficult and often depend on the monomer and reaction conditions. Formation of radical and anionic species are often observed.



Propagation

Propagation proceeds via addition of monomer to the active species, i.e. the carbenium ion. The monomer is added to the growing chain in a head-to-tail fashion; in the process, the cationic end group is regenerated to allow for the next round of monomer addition.



Effect of temperature

The temperature of the reaction has an effect on the rate of propagation. The overall activation energy for the polymerization (E) is based upon the activation energies for the initiation (E_i), propagation (E_p), and termination (E_t) steps:

$$E = E_i + E_p - E_t$$

Generally, is larger than the sum of and , meaning the overall activation energy is negative. When this is the case, a decrease in temperature leads to an increase in the rate of propagation. The converse is true when the overall activation energy is positive.

Chain length is also affected by temperature. Low reaction temperatures, in the range of 170–190 K, are preferred for producing longer chains. This comes as a result of the activation energy for termination and other side reactions being larger than the activation energy for propagation. As the temperature is raised, the energy barrier for the termination reaction is overcome, causing shorter chains to be produced during the polymerization process.

Effect of solvent and counterion

The solvent and the counterion (the gegen ion) have a significant effect on the rate of propagation. The counterion and the carbenium ion can have different associations according to intimate ion pair theory; ranging from a covalent bond, tight ion pair (unseparated), solvent-separated ion pair (partially separated), and free ions (completely dissociated).

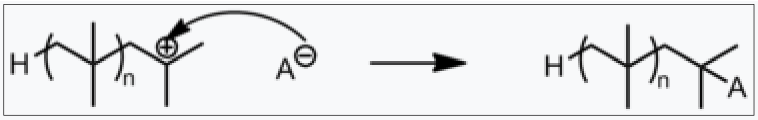
〜〜〜RXcovalent 〜〜〜R+
X−
tight ion pair 〜〜〜R+
/X−
solvent-separated
ion pair 〜〜〜R+
+X−
free ions

The association is strongest as a covalent bond and weakest when the pair exists as free ions.[6] In cationic polymerization, the ions tend to be in equilibrium between an ion pair (either tight or solvent-separated) and free ions. The more polar the solvent used in the reaction, the better the solvation and separation of the ions. Since free ions are more reactive than ion pairs, the rate of propagation is faster in more polar solvents.

The size of the counterion is also a factor. A smaller counterion, with a higher charge density, will have stronger electrostatic interactions with the carbenium ion than will a larger counterion which has a lower charge density. Further, a smaller counterion is more easily solvated by a polar solvent than a counterion with low charge density. The result is increased propagation rate with increased solvating capability of the solvent.

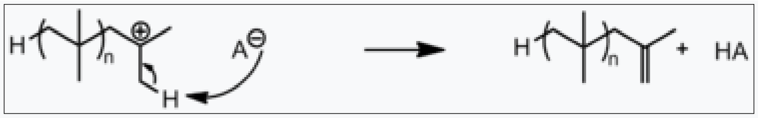
Termination

Termination generally occurs via unimolecular rearrangement with the counterion. In this process, an anionic fragment of the counterion combines with the propagating chain end. This not only inactivates the growing chain, but it also terminates the kinetic chain by reducing the concentration of the initiator-coinitiator complex.



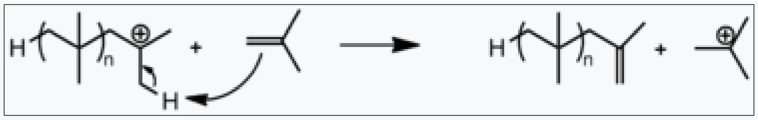
Chain transfer

Chain transfer can take place in two ways. One method of chain transfer is hydrogen abstraction from the active chain end to the counterion. In this process, the growing chain is terminated, but the initiator-coinitiator complex is regenerated to initiate more chains.



Chain transfer by hydrogen abstraction to the counterion

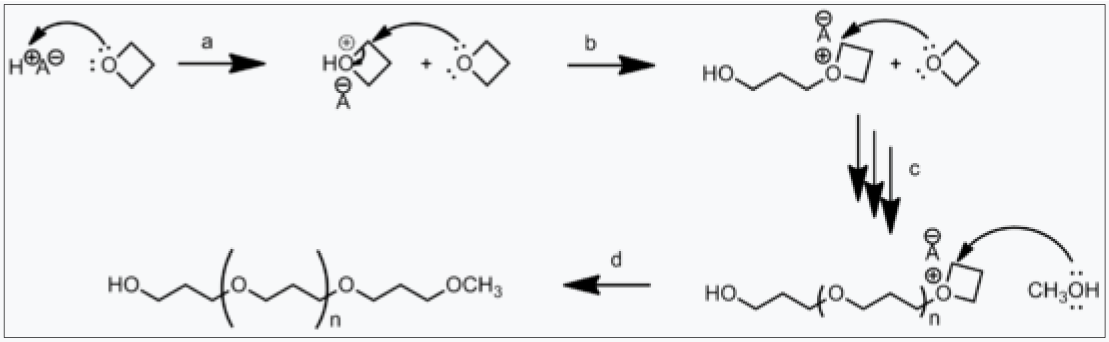
The second method involves hydrogen abstraction from the active chain end to the monomer. This terminates the growing chain and also forms a new active carbenium ion-counterion complex which can continue to propagate, thus keeping the kinetic chain intact.



Chain transfer by hydrogen abstraction to the monomer

Cationic ring-opening polymerization

Cationic ring-opening polymerization follows the same mechanistic steps of initiation, propagation, and termination. However, in this polymerization reaction, the monomer units are cyclic in comparison to the resulting polymer chains which are linear. The linear polymers produced can have low ceiling temperatures, hence end-capping of the polymer chains is often necessary to prevent depolymerization.



Cationic ring-opening polymerization of oxetane involving (a and b) initiation, (c) propagation, and (d) termination with methanol

Kinetics

The rate of propagation and the degree of polymerization can be determined from an analysis of the kinetics of the polymerization. The reaction equations for initiation, propagation, termination, and chain transfer can be written in a general form:

$I^+ + M \xrightarrow{k_i} M^+$

$M^+ + M \xrightarrow{k_p} M^+$

$M^+ \xrightarrow{k_t} M$

$M^+ + M \xrightarrow{k_{tr}} M + M^+$

In which I^+ is the initiator, M is the monomer, M^+ is the propagating center, and k_i, k_p, k_t, and k_{tr} are the rate constants for initiation, propagation, termination, and chain transfer, respectively. For simplicity, counterions are not shown in the above reaction equations and only chain transfer to monomer is considered. The resulting rate equations are as follows, where brackets denote concentrations:

$$\text{Rate (initiation)} = k_i\,[I^+][M]$$

$$\text{Rate (propagation)} = k_p\,[M^+][M]$$

$$\text{Rate (termination)} = k_t\,[M^+]$$

Rate (chain transfer) = k_{tr} $[M^+][M]$

Assuming steady-state conditions, i.e. the rate of initiation = rate of termination

$$M^+ = \frac{k_i[I^+][M]}{k_t}$$

This equation for $[M^+]$ can then be used in the equation for the rate of propagation

$$rate(propagation) = \frac{k_p k_i [M]^2 [I^+]}{k_t}$$

From this equation, it is seen that propagation rate increases with increasing monomer and initiator concentration.

The degree of polymerization, X_n, can be determined from the rates of propagation and termination.

$$X_n = \frac{rate\ (propagation)}{rate\ (termination)} = \frac{k_p[M]}{k_t}$$

If chain transfer rather than termination is dominant, the equation for X_n becomes

$$X_n = \frac{rate\ (propagation)}{rate\ (chain\ transfer)} = \frac{k_p}{k_{tr}}$$

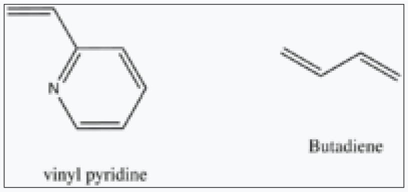
Anionic addition polymerization

Anionic addition polymerization is a form of chain-growth polymerization or addition polymerization that involves the polymerization of vinyl monomers with strong electronegative groups. This polymerization is carried out through a carbanion active species. Like all chain-growth polymerizations, it takes place in three steps: chain initiation, chain propagation, and chain termination. Living polymerizations, which lack a formal termination pathway, occur in many anionic addition polymerizations. The advantage of living anionic addition polymerizations is that they allow for the control of structure and composition.

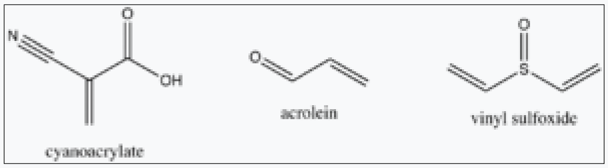
Anionic polymerizations are used in the production of polydiene synthetic rubbers, solution styrene/butadiene rubbers (SBR), and styrenic thermoplastic elastomers.

Monomer characteristics

In order for polymerization to occur with vinyl monomers, the substituents on the double bond must be able to stabilize a negative charge. Stabilization occurs through delocalizationof the negative charge. Because of the nature of the carbanion propagating center, substituents that react with bases or nucleophiles either must not be present or be protected.



Vinyl monomers with substituents that stabilize the negative charge through charge delocalization, undergo polymerization without termination or chain transfer.[4] These monomers include styrene, dienes, methacrylate, vinyl pyridine, aldehydes, epoxide, episulfide, cyclic siloxane, and lactones. Polar monomers, using controlled conditions and low temperatures, can undergo anionic polymerization. However, at higher temperatures they do not produce living stable, carbanionic chain ends because their polar substituents can undergo side reactions with both initiators and propagating chain centers. The effects of counterion, solvent, temperature, Lewis base additives, and inorganic solvents have been investigated to increase the potential of anionic polymerizations of polar monomers.[4] Polar monomers include acrylonitrile, cyanoacrylate, propylene oxide, vinyl ketone, acrolein, vinyl sulfone, vinyl sulfoxide, vinyl silane and isocyanate.



Solvent

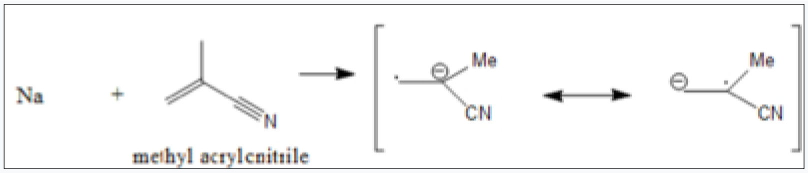
The solvent used in anionic addition polymerizations are determined by the reactivity of both the initiator and carbanion of the propagating chain end. Anionic species with low reactivity, such as heterocyclic monomers, can use a wide range of solvents.

Initiation

The reactivity of initiators used in anionic polymerization should be similar to that of the monomer that is the propagating species. The pKa values for the conjugate acids of the carbanions formed from monomers can be used to deduce the reactivity of the monomer. The least reactive monomers have the largest pKa values for their corresponding conjugate acid and thus, require the most reactive initiator. Two main initiation pathways involve electron transfer (through alkali metals) and strong anions.

Initiation by electron transfer

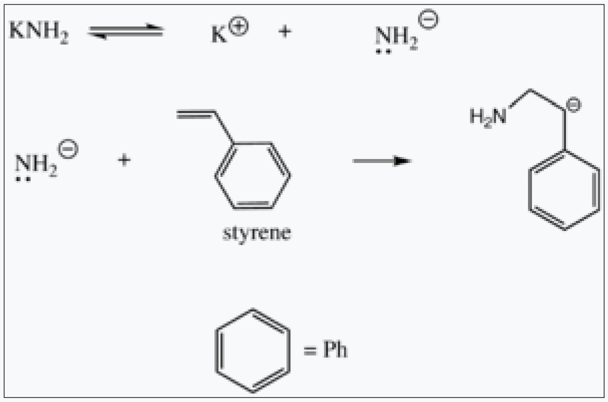
Szwarc and coworkers studied the initiation of polymerization through the use of aromatic radical-anions such as sodium naphthenate. In this reaction, an electron is transferred from the alkali metal to naphthalene. Polar solvents are necessary for this type of initiation both for stability of the anion-radical and to solvate the cation species formed. The anion-radical can then transfer an electron to the monomer.



Initiation can also involve the transfer of an electron from the alkali metal to the monomer to form an anion-radical. Initiation occurs on the surface of the metal, with the reversible transfer of an electron to the adsorbed monomer.

Initiation by strong anions

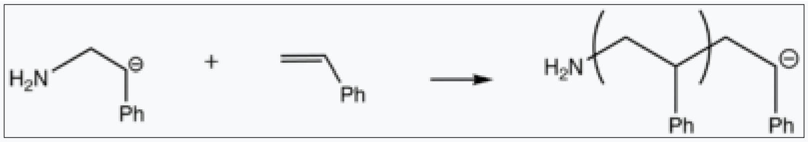
Nucleophilic initiators include covalent or ionic metal amides, alkoxides, hydroxides, cyanides, phosphines, amines and organometallic compounds (alkyllithium compounds and Grignard reagents). The initiation process involves the addition of a neutral (B:) or negative (B:-) nucleophile to the monomer.



The most commercially useful of these initiators has been the alkyllithium initiators. They are primarily used for the polymerization of styrenes and dienes.

Monomers activated by strong electronegative groups may be initiated even by weak anionic or neutral nucleophiles (i.e. amines, phosphines). Most prominent example is the curing of cyanoacrylate, which constitutes the basis for superglue. Here, only traces of basic impurities are sufficient to induce an anionic addition polymerization or zwitterionic addition polymerization, respectively.

Propagation



Propagation in anionic addition polymerization results in the complete consumption of monomer. It is very fast and occurs at low temperatures. This is due to the anion not being very stable, the speed of the reaction as well as that heat is released during the reaction. The stability can be greatly enhanced by reducing the temperatures to near 0˚C. The propagation rates are generally fairly high compared to the decay reaction, so the overall polymerization rates is generally not affected.

Termination

Anionic addition polymerizations have no formal termination pathways because proton transfer from solvent or other positive species does not occur. However, termination can occur through unintentional quenching due to trace impurities. This includes trace amounts of oxygen, carbon dioxide or water. Intentional termination can occur through the addition of water or alcohol. Another method of termination, chain transfer, can occur when an agent can act as a Brønsted acid. In this case, the pKa value of the agent is similar to the conjugate acid of the propagating carbanionic chain end. Spontaneous termination occurs because the concentration of carbanion centers decay over time and eventually results in hydride elimination. Polar monomers are more reactive because they are stabilized by their polar substituents. These polar substituents can react with nucleophiles which results in termination as well as side reactions that compete with both initiation and propagation.

Kinetics

The kinetics of anionic addition polymerization depend on whether or not a termination pathway occurs.

In general, the reaction mechanism for living anionic addition polymerization are as follows:

$I^- + M \xrightarrow{k_{init}} M^-$

$M^- + M \xrightarrow{k_{prop}} M^-$

where I = initiator, k_{init} = the initiation reaction rate constant, M = monomer, M^-= propagating species, and k_{prop} = the propagation reaction rate constant.

As most polymerizations of this type do not have a termination pathway, the rate of polymerization is the rate of propagation:

Rate (prop) = $k_p\,[M^-][M]$

where k_p is the rate of constant of propagation, $[M^-]$ is the total concentration of propagating centers, and [M] is the concentration of monomer. Since there is no termination pathway in living polymerizations, the concentration of propagating centers is equal to the concentration of initiator ([I]). Thus,

rate (prop) = $k_p\,[I][M]$

The degree of polymerization, X_n is also affected by no termination pathway. It is the ratio of concentration of reacted monomer ($[M]_o$) to initiator($[I]_o$) times the percent conversion *p*. In this case, the chain length (ν) is equal to X_n.

$$v = \frac{[M]_0}{[I]_0}p$$

When conversion, *p* = 1 (100% conversion), chain length is simply the ratio of reacted monomer to initiator. $v = \frac{[M]_0}{[I]_0}$.

Kinetics: termination due to impurities

When termination occurs due to impurities, the impurities must be taken into account in determining the reaction rate. The reaction mechanisms would begin the same as that of a living anionic addition (initiation and propagation). However, there would now be a termination step to account for the effect of the impurities on the reaction.

$M^- + HX \xrightarrow{k_{term}} M\text{-}H + X^-$

where M^-= propagating species, HX = impurity and k_{term} = the termination reaction rate constant.

Using the steady-state approximation, the rate of propagation becomes

$$rate(prop) = \frac{k_{init}k_{prop}[I][M]^2}{k_{term}[H-X]}$$

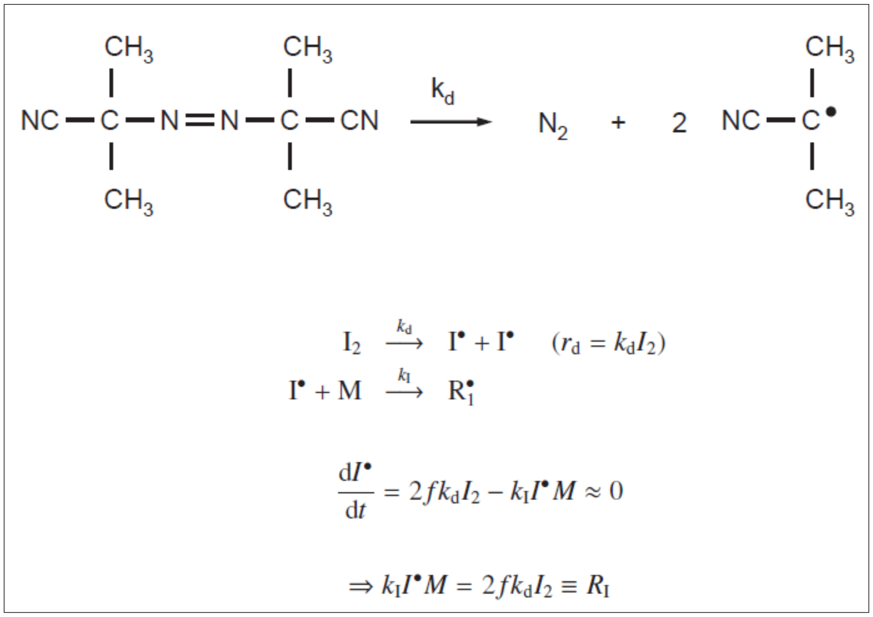
Since

$$V = \frac{rate(prop)}{rate(term)} = \frac{k_{prop}[M]}{k_{term}[H-X]}$$

Thus chain length and rate of propagation are negatively impacted by the presence of impurities in the reaction.

Free-Radical polymerization

Initiation The initiation reaction produces free radicals. There are several ways to do this: • Chemical initiation The decomposition of the initiator (e.g. AIBN) forms free radicals:



$$I_2 \xrightarrow{k_d} I^\bullet + I^\bullet \qquad (r_d = k_d I_2)$$

$$I^\bullet + M \xrightarrow{k_I} R_1^\bullet$$

$$\frac{dI^\bullet}{dt} = 2fk_dI_2 - k_I I^\bullet M \approx 0$$

$$\Rightarrow k_I I^\bullet M = 2fk_dI_2 \equiv R_I$$

where *f* is the initiator efficiency, typically *f* = [0.5, 1]. Note that in order to ensure a continuous production of radicals all over the process, 1/*k*d should be larger than the characteristic time of the polymerization reaction. Examples of the decomposition characteristic time, τd for some commercial initiators are:

Acetyl peroxide 2 h 80 ◦C
Cumyl peroxide 12 h 110 ◦C
t-Butyl hydroperoxide 45 h 150 ◦C
Since this is a first order process, τd = 1/*k*d.

- Thermal initiation: thermal decomposition of the monomer (e.g. styrene).

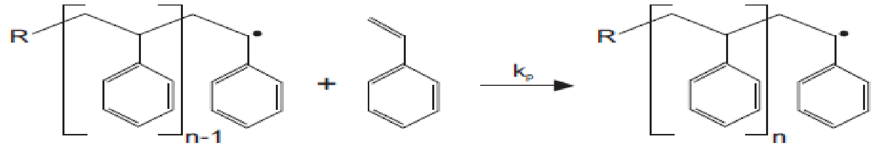
This represents a danger, for example during monomer transportation, since it may lead to undesired polymerization of the monomer. For this reason, inhibitors (scavengers of radicals) are usually added to the monomers before storage. This causes the occurrence of a non reproducible induction period when such monomers are polymerized.

- Initiation by radiation

The decomposition of the initiator is caused by light or another source of radiation. Since this method is quite expensive, it is only applied to polymerization systems operating at very low temperatures.

Propagation

Propagation is the addition of a monomer molecule to a radical chain.



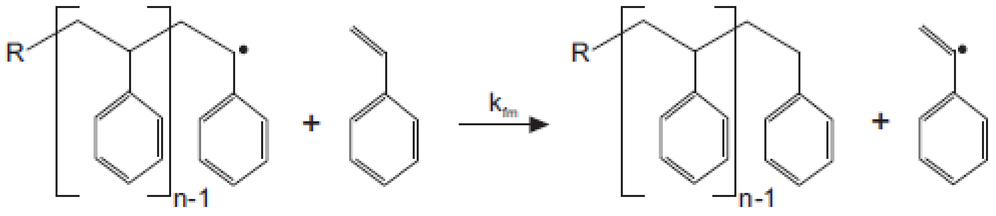
$$R_n^\bullet + M \xrightarrow{k_p} R_{n+1}^\bullet \qquad (r_p = k_p R_n^\bullet M)$$

Chain Transfer

- Chain transfer to monomer

$$R_n^\bullet + M \xrightarrow{k_{fm}} P_n + R_1^\bullet \qquad (r = k_{fm} R_n^\bullet M)$$

The reactants are the same as for the propagation reaction, but the activation energy is much larger. Accordingly, *k*fm is usually at least 103 times smaller than *k*p. This reaction



leads to the formation of a polymer chain with a terminal double bond. This can induce chain branching through the terminal double bond propagation reaction.

- Chain transfer to chain transfer agent

$$R_n^\bullet + S \xrightarrow{k_{fs}} P_n + R_1^\bullet \qquad (r = k_{fs} R_n^\bullet S)$$

A chain transfer agent, S is a molecule containing a weak bond that can be broken to lead to radical transfer, similarly as in the case of monomer above (e.g. CCl4, CBr4, mercaptans).

- Chain transfer to polymer

$$\mathrm{R}_n^\bullet + \mathrm{P}_m \xrightarrow{k_{\mathrm{fp}}} \mathrm{P}_n + \mathrm{R}_m^\bullet \qquad \left(r = k_{\mathrm{fp}} R_n^\bullet \left(m P_m\right)\right)$$

In this reaction the growing radical chain, R• *n* extracts a hydrogen from the dead chain, P*m*. Since this extraction can occur on any of the *m* monomer units along the chain, the rate of this reaction is proportional to the length of P*m*.

General observations on the role of chain transfer reactions:

- The concentration of radicals is not affected and therefore the rate of monomer consumption is also unchanged.
- The growth of polymer chains is stopped and therefore shorter chains are produced.
- Each transfer event leaves a different end-group on the chain that can be detected (NMR, titration) so as to identify and quantify the corresponding chain transfer reaction.
- Nonlinear (branched) polymer chains are produced: directly by chain transfer to polymer or indirectly through the propagation of the terminal double bond left by a chain transfer to monomer event.

Text book:

T1: Gowariker, V. R., N. V. Viswanathan and J. Sreedhar, 1986. Polymer Science, *New Age International* Private Ltd., New Delhi.

T2: Billmeyer, F.W., 2003. Text Book of Polymer Science. III Edition, John Wiley, New York.

Reference book

R1: M.S Bhatnagar,2004, " A text book of polymers". Ist Edition, S.Chand & Company.

Possible Questions

Multiple choice questions (Each Carry 1 Marks)

1. In step polymerization the reactivity of a functional group depends on?
a. **The collision frequency of the group** b. diffusion rate of the whole molecule
c. Nature of the functional group d. Size of the group
2. The alkyl resins are condensation polymers obtained from dibasic acids and
a. phenol b. formaldehyde c. Acetaldehyde d. Glycol
3. Reactivity of a functional group depends on ?
a. Collision frequency b. diffusion rate c. Size d.Molecular weight
4. In a polymer chain the functional group has appreciable mobility due to
a. the conformational rearrangements b. different stereochemical forms
c. Tautomeric arrangements d. Optical activity

5. The polyesterification becomes a much more economically feasible reaction when it is catalyzed by an ?
a. Base **b. Acid** c. Alkali d.Neutral
6. Example for radical sources for the polymerization reactions?
a. **Peroxides** b. Epoxides c. Nitrenes d. Carbenes
7. A surface of titanium atom is bonded with ?
a. Five chlorines b. Six chlorines c.Three chlorines d. Two chlorines
8. In free radical vinyl polymerization
a. The electrons in the pi bond split up b. The electrons in the sigma bond split up
c. Non bonding electrons are used d. Electrons from the functional group splits.
9. The general linearity of the plot in the higher conversion region is a strong confirmation of the concept of functional group reactivity independent of?
a. Frequency b. Molecular Weight c. Density **d. Molecular size**
10. In the acid hydrolysis of cellulose there is no effect of?
a. Frequency b. Molecular weight c. Density **d. Molecular size**
11. Isotactic polymerization depends intimately on the?
a. Crystal structure of the initiator surface b. Surface area of the initiator
c. Volume of the initiator d. Concentration of the initiator
12. In isotactic polymerization the polymerization occurs at active sites found on the?
a. Edges (surfaces) of elementary sheets of the crystal b. Edges of the basal planes
c. Corners of the basal planes d. Inside the pores of the catalyst
13. Which find extensive use as radical sources?
a. Peroxides b. Epoxides c. Nitrenes d. Carbenes
14. The enantiomorphic site control model attributes stereo control in ?
a. Isoselective polymerization b. Isotactic polymerization
c. Free radical polymerization d. Ionic polymerization
15. The C─N bond dissociation energy is?
a. ~ 190 kJ mol $-^{1}$ b. ~ 390 kJ mol $-^{1}$ **c. ~ 290 kJ mol $-^{1}$** d. ~ 360 kJ mol $-^{1}$
16. The various initiators are used at different temperatures depending on their rates of
a. Reaction **b. Decomposition** c. Composition d. Entropy
17. The azo(bis-isobutyro)nitrile (AIBN) is commonly used at?

a. 60-70 ^{O}C **b. 50–70^{O}C** c. 80-90 ^{O}C d. 40-50 ^{O}C

18. Teflon is a polymer of the monomer or Teflon is obtained by the polymerisation of ?
    a. Monofluroethene b. Difluroethene c. Trifluroethene **d. Tetrafluroethene**
19. Which of the following is an example of condensation polymer?
    a. PVC b. Polyamide **c. Terylene** d. Polyester
20. Two trimers react together to form
    a. Trimer **b. Hexamer** c. Monomer d. Heptamer

Questions (Each Carry 6 Marks)

1. Explain the kinetics of step growth polymerisation?
2. Write a note on condensation polymerization?
3. What are the types of addition polymers?
4. Write a note on i) Monomer ii) Repeat unit iii) Polymer?
5. Explain the mechanism of step-growth polymerization?
6. Write a note on free radical addition polymerization?
7. Write a note on linear, branched and crosslinked polymers ?
8. Explain the polymerization in homogenous and heterogenous systems ?
9. Explain the step-growth polymerization and its types?
10. Write a note on conditions of polymerization?

Compulsory Questions (Each Carry 10 Marks)

1. Explain in brief the types of addition polymerization and derive the kinetic equation for anionic polymerization?
2. Briefly explain the kinetics and mechanism of Step-Growth Polymerisation?

16CHP305A
Karpagam Academy of Higher Education
Coimbatore-21
(For the Candidates admitted on 2016 Onwards)
III-Semester
Polymer Chemistry

Questions	**Opt-1**	**Opt-2**	**Opt-3**	**Opt-4**	**Answers**
Unit 1- Objective questions for online examination (Each carry 1 mark)					
Which is obtained from the reaction of diamines with diacids?	Polyamides	polyester	Acrylicfibre	poly vinyl chloride	Polyamides
In step polymerization the reactivity of a functional group depends on?	The collision frequency of the group	b. diffusion rate of the whole molecule	Nature of the functional group	Size of the group	The collision frequency of the group
The alkyl resins are condensation polymers obtained from dibasic acids and	phenol	formaldehyde	Acetaldehyde	Glycol	Phenol
Reactivity of a functional group depends on ?	Collision frequency	diffusion rate	Size	Molecular weight	Collision frequency
In a polymer chain the functional group has appreciable mobility due to	the conformational rearrangements	different stereochemical forms	Tautomeric arrangements	Optical activity	The conformational rearrangements
The first step in the reaction of the diol and diacid monomer is to form ?	dimer	trimer	Pentamer	Tetramer	Dimer
The rate of a step polymerization is conveniently expressed in terms of the	Concentrations of the reacting functional groups.	concentration of the monomeric	Concentration of monomer and the solvent	Concentration of the functional groups and monomers	Concentration of the functional groups and monomers
A dimer reacts with a monomer to give	Trimer	Dimer	Pentamer	Tetramer	Trimer
In thermal catalyzed polymerizations the most widely used mode of generating radicals to initiate polymerization ?	Homolytic dissociation of initiators	Heterolytic dissociation of initiators	Decomposition of the initiator	Association of the initiator	Homolytic dissociation of initiators
The Polyesterification of a diol and a diacid will illustrate the general kinetics of a typical ?	Step polymerization	Ionic polymerization	Radical polymerization	Self catalysted polymerization	Step polymerization
The carboxyl concentration is comprised of two first-order dependencies, one for the carboxyl as the reactant and another one as?	Product	Reactant	Reagent	Catalyst	Catalyst
The polyesterification becomes a much more economically feasible reaction when it is catalyzed by an ?	Base	Acid	Alkali	Neutral	Acid
Example for radical sources for the polymerization reactions?	Peroxides	Epoxides	Nitrenes	Carbenes	Peroxides
A titanium atom at the surface is bonded by?	Five chlorines	Six chlorines	Three chlorines	Two chlorines	Five chlorines
In free radical vinyl polymerization	The electrons in the pi bond split up	The electrons in the sigma bond split up	Non bonding electrons are used	Electrons from the functional group splits.	The electrons in the pi bond split up
The general linearity of the plot in the higher conversion region is a strong confirmation of the concept of functional group reactivity independent of?	Frequency	Molecular Weight	Density	Molecular size	Molecular size

In the acid hydrolysis of cellulose there is no effect of ?	Frequency	Molecular wight	Density	Molecular size	Molecular size
Isotactic polymerization depends intimately on the ?	Crystal structure of the initiator surface	Surface area of the initiator	Volume of the initiator	Concentration of the initiator	Crystal structure of the initiator surface
In isotactic polymerization the polymerization occurs at active sites found on the ?	Edges (surfaces) of elementary sheets of the crystal	Edges of the basal planes	Corners of the basal planes	Inside the pores of the catalyst	Edges (surfaces) of elementary sheets of the crystal
Which find extensive use as radical sources?	Peroxides	Epoxides	Nitrenes	Carbenes	Peroxides
The enantiomorphic site control model attributes stereo control in ?	Isoselective polymerization	Isotactic polymerization	Free radical polymerization	Ionic polymerization	Isoselective polymerization
The C─N bond dissociation energy is?	~ 190 kJ mol -^{1}	~ 390 kJ mol -^{1}	~ 290 kJ mol -^{1}	~ 360 kJ mol -^{1}	~ 290 kJ mol -^{1}
The various initiators are used at different temperatures depending on their rates of	Reaction	Decomposition	Composition	Entropy	Decomposition
The azobisisobutyronitrile (AIBN) is commonly used at?	60-70 ^{O}C	50–70^{O}C	80-90 ^{O}C	40-50 ^{O}C	50–70^{O}C
Teflon is a polymer of the monomer or Teflon is obtained by the polymerisation of ?	Monofloroethene	Difloroethene	Trifloroethene	Tetrafloroethene	Tetrafloroethene
Which of the following is an example of condensation polymer?	PVC	Polyamide	Terylene	Polyester	Terylene
two trimers react together to form	Trimer	Hexamer	Monomer	Heptamer	Hexamer
Ionic vinyl polymerizations are very similar to	Free radical vinyl polymerizations	Step polymerizations	Self catalysted vinyl polymerization	Free radical polymerizations	Free radical vinyl polymerizations
A tetramer reacts with a trimer to form	Trimer	Dimer	Pentamer	Heptamer	Heptamer
A pentamer reacts with a trimer to form	Trimer	Dimer	Pentamer	Octamer	Octamer
Monomer concentration decreases steadily throughout reaction in?	Step polymerization	Ionic polymerization	Radical polymerization	Self catalysted polymerization	Ionic polymerization
Polymer molecular weight rises steadily throughout reaction in ?	Step polymerization	Ionic polymerization	Radical polymerization	Self catalysted polymerization	Step polymerization
In which step of cationic polymerization follows the first order kinetics	Initiation	propagation	termination	transfermation	termination
A simple termination or chain transfer depending to	chain growth	degree of polymerization	kinetics	polymer deformation	degree of polymerization
The temperature would decreases the	molecular weight of polymer	chain formation	initiator	monomer	molecular weight of polymer
In the radical polymerization, the propagation rate depends on	monomer	concentration of monomer radical	concentration of catalyst	reaction rate	concentration of monomer radical
In Cationic vinyl polymerization electron flow is ?	Same direction	Same and opposite direction	Opposite direction	Same or opposite direction	Opposite direction
Ionic polymerization necessarily carry along a?	Counter ion	Cation	Anion	Cation or anion	Counter ion
The fraction of the radicals produced in the homolysis reaction that initiate polymer chains is defined as?	Initiator efficiency	High efficiency	Low efficiency	Closer efficiency	Initiator efficiency
A dimer react with another dimer to form a	Trimer	Dimer	Pentamer	Tetramer	Tetramer
In most polymerizations, the second step is?	Much faster than the first step	Much slower than the first step	Less faster than the first step	Slower than the first step	Much faster than the first step

Which is impossible under any and all reaction conditions if it does not pass the test of thermodynamic feasibility?	Cationic vinyl polymerization	Ionic polymerization	Polymerization	Wastage reactions	Polymerization
which of the following is a example of bifunctional monomer	methyl isonate	acetylene	malic acid	glycine	glycine
Which of the following is the functionality of Gallic acid	monofunctional	bifunctional	tetra functional	tri functional	tetra functional
Monomers show high selectivity towards?	Cationic initiators	Cationic and anionic initiators	Ionic initiators	Anionic initiators	Ionic initiators
Most monomers will undergo polymerization with a radical initiator, although at?	Varying rates	Reliable rates	Stable rates	Positive rates	Varying rates
Polymerization is possible only if the free-energy difference -G between monomer and polymer is?	Positive	Negative	Both negative and positive	Neither negative nor positive	Negative
The property of fabric which influences drape the most is?	Tensile	Compressional	Shear	Surface	Shear
The Q–e scheme is best considered as an empirical approach to placing monomer reactivity on a?	Qualitative basis	Quantitative basis	Qualitative radical	Quantitative radical	Quantitative basis
To remove the residual metals, a process referred as ?	Ashing	Reashing	Ashing and reashing	Deashing	Deashing
3,4-Difluorophenylamine is a weaker base than ?	Phenylamine	Phenylacetate	Phenol	Henepthyl alcohol	Phenylamine
What method would you use to synthesize a triblock copolymer?	Free radical polymerization	Anionic polymerization	Using a Ziegler Natta catalyst	Condensation polymerization	Free radical polymerization
Suspension free radical polymerization of styrene would be preferred over bulk polymerization to overcome the problem of ?	Branching	Cross-linking	Stereo-isomerism	Polymeric impurities	Branching
Polymers are ?	Large molecule	Small molecule	Small chain molecule	Large chain molecule	Large chain molecule
Polymers are high molecular weight in the range of ?	10^4 to 10^7	10^3 to 10^7	10^2 to 10^7	10^5 to 10^7	10^3 to 10^7
Tetramer + monomer is ?	Trimer	Dimer	Pentamer	Tetramer	Pentamer
Which one is not a polymer?	Carbohydrates	Proteins	Carboxylic acid	Nucleic acid	Carboxylic acid
Due to the presence of carbon atom in polymers all large biological molecules are made of ?	Ionic bond	Covalent bond	Triple bond	Metalic bond	Covalent bond
Amino acids are building blocks of ?	Carbohydrates	Proteins	Carboxylic acid	Lipids	Proteins
polyethylene is ?	Colourless liquid	Colourless gas	Gas	Liquid	Colourless gas

UNIT – II

Co-ordination Polymerization

Co-ordination Polymerization: Kinetics, mono and bimetallic mechanism of co-ordination polymers. Zeigler Natta catalyst, co-polymerization: Block and graft co-polymers, kinetics of copolymerization. Types of co-polymerization. Reactivity ratio.

Coordination polymerization

Coordination polymerisation is a form of addition polymerization in which monomer adds to a growing macromolecule through an organometallic active center. The development of this polymerization technique started in the 1950s with heterogeneous Ziegler-Natta catalysts based on titanium tetrachloride and an aluminium co-catalyst such as methylaluminoxane. Coordination polymerization has a great impact on the physical properties of vinyl polymers such as polyethylene and polypropylene compared to the same polymers prepared by other techniques such as free-radical polymerization. The polymers tend to be linear and not branched and have much higher molar mass. Coordination type polymers are also stereoregular and can be isotactic or syndiotactic instead of just atactic. This tacticity introduces crystallinity in otherwise amorphous polymers. From these differences in polymerization type the distinction originates between low-density polyethylene (LDPE), high-density polyethylene (HDPE) or even ultra-high-molecular-weight polyethylene (UHMWPE).

Polymerizations catalysed by metallocenes occur via the Cossee-Arlman mechanism. The active site is usually anionic but cationic coordination polymerization also exists.

In many applications Ziegler-Natta polymerization is succeeded by metallocene catalysis polymerization. This method is based on homogeneous metallocene catalysts such as the Kaminsky catalyst discovered in the 1970s. The 1990s brought forward a new range of post-metallocene catalysts.

Typical monomers are nonpolar ethylene and propylene. The development of coordination polymerization that enables copolymerization with polar monomers is more recent. Examples of monomers that can be incorporated are methyl vinyl ketones methyl acrylate and acrylonitrile.

Kinetics

A case of heterogeneous polymerization.

It is defined : H is the surface of the transition-metal compound,

AR is the metal alkyl,

M is the monomer,

M_X is the polymer.

Adsorption of metal alkyl from solution to form the active site

$$H + AR \xrightleftharpoons{K_1} H-AR$$

Adsorption of M from solution

$$H + M \xrightleftharpoons{K_2} M-H$$

Initiation

$$M-H-AR \xrightarrow{K_i} H-A-M-R$$

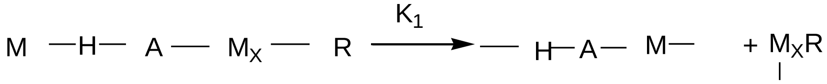
Propagation

$$M - H - A - M_X - R \xrightarrow{K_P} H - M_{X+1} - R$$

Termination
(transfer)

$$M - H - A - M_X - R \xrightarrow{K_{tr}} H - A - M - R + M_X$$

Termination
(monomer forms an inactive site)



$$M - H - A - M_X - R \xrightarrow{K_1} - H - A - M - + \underset{|}{M_X}R$$

It is assumed that the process occurs in Langmuir isotherm condition and it is defined that :

Θ_A and Θ_M are the fractions of the available surface covered by AR and M respectively,

[C*] is the concentration of growing chains,

Then the overall rate can be determined.

$$\theta_A = \frac{K_1 \ [AR]}{1 + K_1 \ [AR] + K_2 \ [M]} \qquad \theta_M = \frac{K_2 \ [M]}{1 + K_1 \ [AR] + K_2 \ [M]}$$

The overall rate :

$$R_O = -\frac{d\,[M]}{dt} = (k_p + k_{tr})\, \theta_M \ [C^*]$$

Assume that [C*] reaches steady state so that the initiation rate is similar to the termination rate.

$$k_i\, \theta_A\, \theta_M = k_t \ [C^*] \ \theta_M$$

The overall rate :

$$R_o = -\frac{d\,[M]}{dt} = \frac{(k_p + k_{tr})\, k_i}{k_t} \ \frac{K_1 K_2 \,[AR]\,[M]}{(1 + K_1 \ [AR] + K_2 \ [M]\,)^2}$$

Ziegler–Natta catalysis and polymerization

Historical Development of Ziegler–Natta Initiators

Various mechanisms have been proposed to explain the stereoselectivity of Ziegler- Natta initiators [Boor, 1979; Carrick, 1973; Corradini et al., 1989; Cossee, 1967; Ketley, 1967a,b; Tait and Watkins, 1989; Zambelli and Tosi, 1974]. Most mechanisms contain considerable details that distinguish them from each other but usually cannot be verified. In this section the mechanistic features of Ziegler–Natta polymerizations are considered with emphasis on those features that hold for most initiator systems.

The major interest will be on the titanium–aluminum systems for isoselective polymerization, more specifically, $TiCl_3$ with $Al(C_2H\ 5)_2Cl$ and $TiCl_4$ with $Al(C_2H\ 5)_3$—probably the most widely studied systems, and certainly the most important systems for industrial polymerizations. Before proceeding with the mechanistic consideration it is useful to

review the evolution of the Ti-Al initiator system for industrial applications. The original initiator used by Ziegler for ethylene polymerization was obtained in situ as a precipitate on mixing the components $TiCl_4$ and $Al(C_2H\ 5)_3$ in a hydrocarbon solvent. The mixture was used directly for initiating polymerization. Natta, recognizing that the major product of the reaction was b-$TiCl_3$ (brown in color), explored various methods of preforming it outside the polymerization system, for example, by reduction of TiCl4 with hydrogen, aluminum, and various alkylaluminum compounds. The stereoselectivity of these early initiator systems was low with isotactic indices of only 20–40% for polypropene. The isotactic index, a measure of the isotactic content of a polymer, is the percentage of the sample insoluble in a hydrocarbon solvent such as boiling n-heptane. This is not as informative a technique as high-resolution NMR since insoluble molecules may contain some syndiotactic and atactic sequences and soluble molecules may contain some isotactic sequences. It does, however, give a simple measure of isotacticity that is usually within about 10% of the value obtained from NMR,
especially for highly isotactic samples.

There was a dramatic increase in stereoselectivity when the α-, δ-,or γ-crystalline form of $TiCl_3$ (all violet in color) was used directly. The early generations of industrial processes used $TiCl_3$ together with $Al(C_2H\ 5)_3$ and/or $Al(C_2H\ 5)_2Cl$. Over a two decade period starting in the late 1950s, the isotactic indices for polypropene increased to the low 90 percentile range. The initiator activity was enhanced by various ball milling and heat treatments of the initiator components before and after mixing. Ball milling involves mechanical grinding and not only increases surface area but also facilitiates reactions between the initiator components.

However, the activities were too low to allow the polymer products to be used without purification (by treatment with base or acid) to remove the residual metals, a process referred to as deashing. Also, optimization of the physical properties of the product often required removal of the atactic fraction. The initiator systems were inefficient with less than 1% of the Ti being active in polymerization. The later generations of initiators, starting in the late 1970s, increased initiator efficiency and activity without sacrificing stereoselectivity [Bohm, 2001; Busico and Cipullo, 2001; Cecchin et al., 2001; Chadwick, 2001; Chadwick et al., 2001; Chien et al., 1982; Hu and Chien, 1988]. The effective surface area of the active component of the initiator system was increased by close to 2 orders of magnitude by using $MgCl_2$ as a solid support in which $TiCl_4$ is finely dispersed. Stereoselectivity was kept high and actually increased by the addition of electron-donor additives.

A typical recipe for a present-day superactive or high-mileage initiator system involve ball milling of $MgCl_2$ (or the alkoxide) and TiCl4 followed by the addition of $Al(C_2H\ 5)_3$ with an electron donor (such as dialkyl phthalate and alkoxysilane) usually added in each step of preparation. Activity is 50–200 kg polymer per gram of initiator system. Typically, the initiator system is no more than 2–4% Ti, which makes the activity about 1500–6000 kg polymer per gram of Ti. The high activity not only minimizes initiator and production costs but also avoids the costly task of initiator removal from the polymer product (except possibly for food- and medical-grade products). Isotactic indices for polypropene have been increased to 98% or higher with (mmmm) pentad fractions up to 98% and higher. This not only improves the product’s physical properties but also avoids the need to remove the a tactic fraction.

Chemical Nature of Propagating Species

Some early polymerizations reported as Ziegler–Natta polymerizations were conventional free-radical, cationic, or anionic polymerizations proceeding with low stereoselectivity.Some Ziegler–Natta initiators contain components that are capable of initiating conventional ionic polymerizations of certain monomers, such as anionic polymerization of methacrylates by alkyllithium and cationic polymerization of vinyl ethers by $TiCl_4$. Most Ziegler–Natta components participate in a complex set of reactions involving alkylation and reduction of the transition-metal component by the group I–III component as shown below for $TiCl_4 + AlR_3$:

$TiCl_4 + AlR_3 \longrightarrow TiCl_3 R + AlR_2 Cl$

$TiCl_4 + AlR2Cl \longrightarrow TiCl_3R + AlRCl_2$

$TiCl3R + AlR_3 \longrightarrow TiCl_2 R_2 + AlRCl_2$

$TiCl_3 R \longrightarrow TiCl_3 + R\bullet$

$TiCl_3 + AlR_3 \longrightarrow TiCl_2 R + AlR_2 Cl$

$R\bullet \longrightarrow$ combination + disproportionation

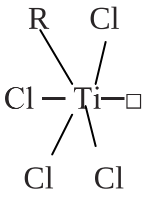
Radicals produced in Eq. 8-31 are capable of initiating radical polymerizations with some monomers, for example, vinyl chloride.The mechanism for the tereoselective polymerization of a-olefins and other nonpolar alkenes is a p-complexation of monomer and transition metal (utilizing the latter's d-orbitals) followed by a four-center anionic coordination insertion process in which monomer is inserted into a metal–carbon bond as described in Fig. 8-10. Support for the initial p-complexation has come from ESR, NMR, and IR studies [Burfield, 1984]. The insertion reaction has both cationic and anionic features. There is a concerted nucleophilic attack by the incipient carbanion polymer chain end on the a-carbon of the double bond together with an electrophilic attack by the cationic counterion on the alkene p-electrons.The anionic character of the polymerization is consistent with the polymerization rate decreasing in the order ethylene > propene > 1-butene [Bier, 1961; Boor, 1967].

The reverse order is expected for a polymerization involving the conversion of a monomer into the corresponding carbocation. For addition of a carbanion to the monomers, attack occurs at the a-carbon to form the less substituted (and more stable) carbanion. Further, a-substituents sterically hinder the approach of a carbanion and/or counterion with the result that reactivity decreases with increasing substituent size. Evidence for the anionic nature of propagation also comes from studies in which labeled methanol is used to terminate chain growth. The terminated polymer is radioactive when $CH_3 O_3 H$ is used, while termination by $^{14}CH_3 OH$ yields a nonradioactive polymer.

Mechanism of Isoselective Propagation

A variety of structures have been proposed for the active species in Ziegler–Natta initiator systems [Allegra, 1971; Arlman and Cossee, 1964; Corradini et al., 1989; Natta, 1960a,b; Patat and Sinn, 1958; Rodriguez and van Looy, 1966; Tait and Watkins, 1989].

Structure XX is generally considered as the active species formed from titanium chloride and alkylaluminum components..



The Cl in the structure represents an unoccupied (vacant) site of the octahedral titanium complex. XX represents an active titanium site at the surface of a $TiCl_3$ crystal after modification by reaction with the alkylaluminum component. The titanium atom shares four chloride ligands with its neighboring titanium atoms and has an alkyl ligand (incorporated via exchange of alkyl from the alkylaluminum for chloride) and a vacant orbital.

There are molecular mechanics calculations that indicate dimeric Ti_2Cl_6 may be the active species instead of monomeric $TiCl_3$ [Monaco et al., 2000]. Other proposals for the active species include bimetallic species that contain both titanium and aluminum [Liu et al., 2002]. To simplify matters, our discussions will center on the monomeric and monometallic titanium species, especially since the mechanistic details of stereoselectivity and activity are essentially the same for both monomeric and dimeric titanium species as well as titanium–aluminum species. The high-mileage supported initiators previously mentioned involve a species similar to XX as part of a mixed titanium–magnesium–chloride lattice, usually involving Mg-Cl-Ti bonds. Ti and Mg are interchangeable within the metal lattice.

Figure 8-11 shows the proposed mechanism for isoselective propagation. Monomer coordinates at the vacant site of titanium, resulting in a four-center transition state and subsequent insertion of monomer into the polymer–transition metal bond. The insertion is referred to as migratory insertion since the polymer chain migrates from its original site to that occupied by monomer. The whole polymer chain does not migrate, only the active end of the polymer chain migrates. This follows the principle of least nuclear motions. For the polymer chain to remain at its original coordination site after monomer insertion, all or at least most of the polymer chain atoms must move, specifically back away from the coordination site. For Cossee-Arlman mechanism, .

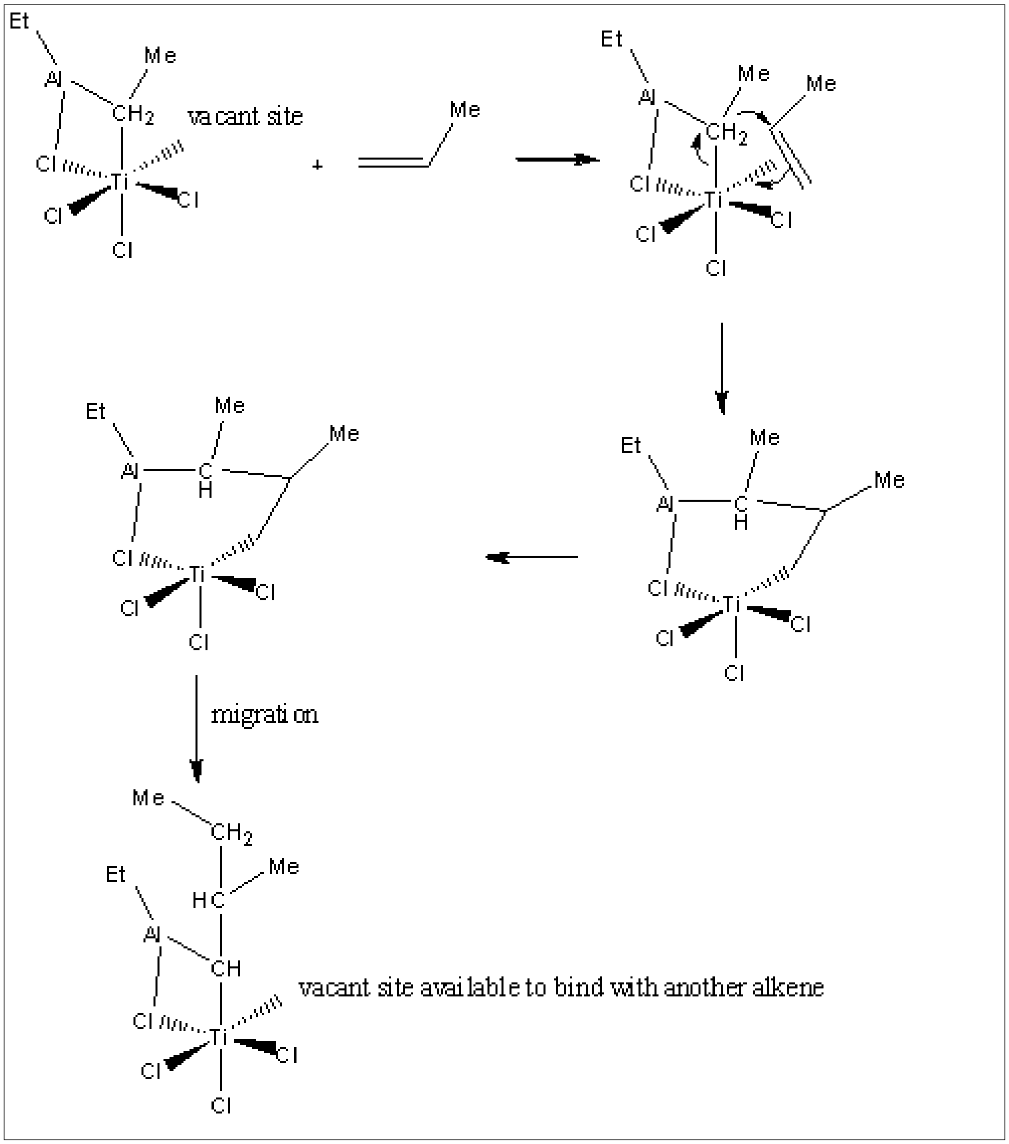
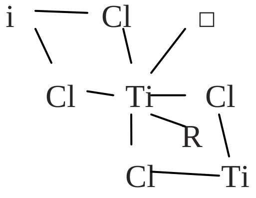


Fig. Mechanism for catalyst site control model of isoselective polymerization. migratory insertion only the atoms of the first few repeat units move. This regenerates a vacant site with its configuration opposite from the original vacancy.

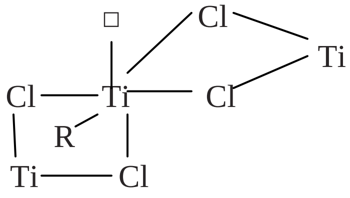
If propagation continued with this species, the result might be syndioselective propagation. Isoselective propagation requires migration of the polymer chain to its original position with regeneration of the original configuration of the vacant site, often referred to as back skip or back-flip. The chain migrates twice for insertion of each monomer unit, and the overall process can also be regarded as a site epimerization. This mechanism, referred to as the Cossee-Arlman mechanism, is based on the observed stereoselectivity and molecular modeling tudies [Arlman and Cossee, 1964; Ewen, 1999; Rappe et al., 2000; Resconi et al., 2000]. A variation on this mechanism involves a lowering of the transition state barrier to insertion by an a-agostic interaction, specifically, an attractive interaction between titanium and a hydrogen on the first carbon attached to Ti.

Isotactic polymerization depends intimately on the crystal structure of the initiator surface.For a coordination lattice, as opposed to a molecular crystal lattice, the crystal contains a number of ligand vacancies in order to achieve overall electrical neutrality of the crystal. a-TiCl$_3$ crystals are made up of elementary crystal sheets of alternating titanium and chlorine layers aligned along the principal crystal axis [Natta et al., 1961a,b,c,d]. Figure 8-12 is a representation of a portion of the crystal [Corradini et al., 1989]. The titanium and chlorine atoms are represented by solid black and open spheres, respectively. The titaniums are at the octahedral interstices of the chlorine lattice while chlorines are hexagonally close-packed. Every third titanium in the lattice is missing, that is, there is a vacancy in between pairs of titanium atoms. Vacancies are represented by & in Fig. 8-12.

Polymerization occurs at active sites found on the edges (surfaces) of elementary sheets of the crystal and not in the basal planes. This is supported by microscopic observations of polymer growth at the crystal edges [Cossee, 1967; Kollar et al., 1968a,b; Rodriguez and van Looy, 1966]. A titanium atom at the surface is bonded to only five chlorines instead of six because of the imposed requirement of electroneutrality. Of the five chlorines, four are more strongly bonded since they are bridged to other titanium atoms. The fifth, nonbridged chlorine may be replaced by an alkyl group when the titanium component interacts with the group I–III component. The octahedral vacancy remains as a vacancy.Neighboring metal atoms (bridged by two chlorines) have opposite chirality [Allegra, 1971]. The two enantiomeric titaniums can be represented as XXI and XXII where one of the chlorine ligands has been replaced by R via alkylation by the group I–III metal component.Propagation occurs by coordination of monomer at the vacancy, migratory insertion into the Ti__R bond, and migration of the newly formed bond to regenerate the vacancy in the original configuration. Considering either XXI or XXII, coordination of monomer can occur through either of the two monomer enantiofaces (si or re), which results in two diastereomeric transition states. The two diasteromeric states give rise to the two possible placements of monomer units in the polymerchain—meso and racemo [Corradini et al., 1984,1985; Zambelli et al., 1978, 1980].



XXI



XXII

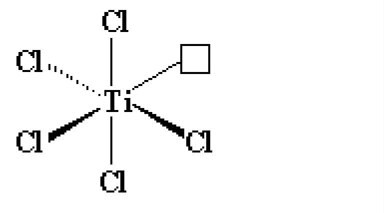
The driving force for isoselective propagation results from steric and electrostatic interactions between the substituent of the incoming monomer and the ligands of the transition metal. The chirality of the active site dictates that monomer coordinate to the transition metal vacancy primarily through one of the two enantiofaces. Actives sites XXI and XXII each yield isotactic polymer molecules through nearly exclusive coordination with the re and si monomer enantioface, respectively, or vice versa. That is, we may not know which enantioface will coordinate with XXI and which enantioface with XXII, but it is clear that only one of the enantiofaces will coordinate with XXI while the opposite enantioface will coordinate with XXII.

This is the catalyst (initiator) site control or enantiomorphic site control model for isoselective polymerization.

The enantiomorphic site control model attributes stereocontrol in isoselective polymerization to the initiator active site with no influence of the structure of the propagating chain end. The mechanism is supported by several observations:

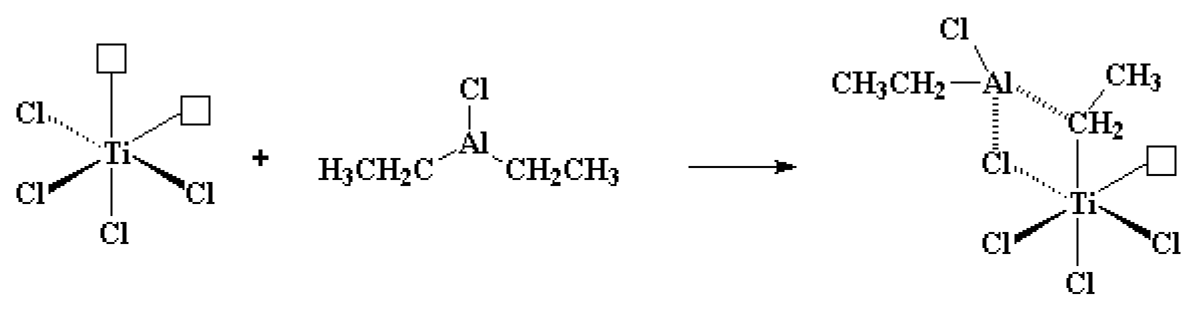
1. ^{13}C NMR of isotactic polypropene shows the main error is pairs of racemic dyads instead of isolated racemic dyads (Table 8-3) [Heatley et al., 1969; Resconi et al., 2000; Wolfsgruber et al., 1975]. A stereoerror in the addition of a monomer molecule is immediately corrected when stereocontrol is by the chiral active site. If stereocontrol was due to the propagating chain end, an error would continue to propagate in an isotactic manner to yield a polymer, referred to as an isotactic stereoblock, containing long isotactic all-R and all-S stereoblocks on each side of the error.
2. ^{13}C NMR of ethylene-propene copolymers of low ethylene content produced by initiators that yield isotactic polypropene shows that the isotactic propene units on each side of an ethylene unit have the same configuration (i.e., all-R or all-S) [Zambelli et al., 1971, 1978, 1979]. For stereocontrol by the propagating chain end, the amount of polymer in which the polypropene blocks on either side of an ethylene unit have the same configuration would equal that in which the blocks have the opposite configuration.
3. Statistical analysis of the stereochemical sequence distributions (Table 8-3 and Sec. 8-16) also supports the enantiomorphic site control model.

Isotactic Polymerization Mechanism



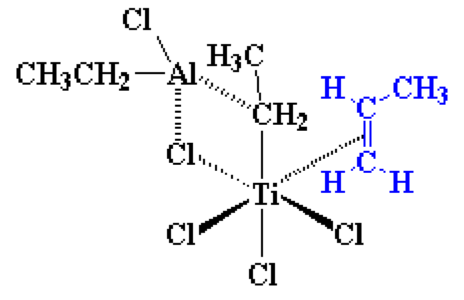
A surface titanium has an empty orbital.

Suface titanium wants to fill its orbitals. But first, $Al(C_2H_5)_2Cl$ enters the picture. It donates one of its ethyl groups to the impoverished titanium, but kicks out one of the chlorines in the process. We still have an empty orbital. But more about that in a moment.



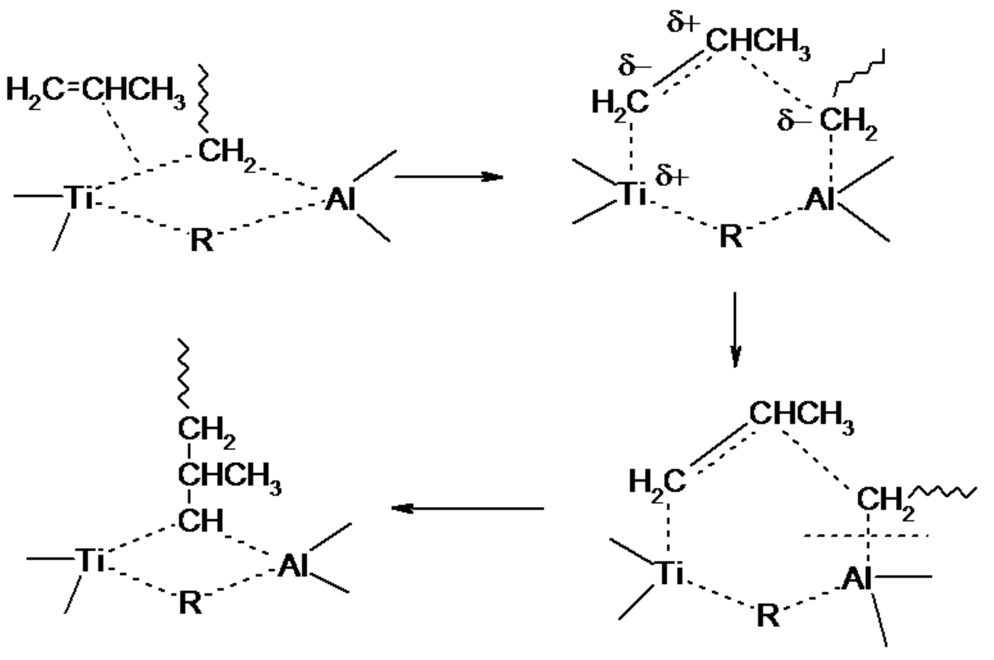
As you can see in this picture, the aluminum has a hard time letting go. It stays coordinated, though not covalently bonded, to the CH_2 carbon atom of the ethyl group it just donated to the titanium. Not only that, but it also coordinates itself to one of the chlorine atoms adjacent to the titanium. But titanium still has one empty orbital left to be filled.

So then a vinyl monomer like propylene comes along. There are two electrons in the π-system of a carbon-carbon double bond. Those electrons can be used to fill the empty orbital of the titanium. We say that the propylene and the titanium form a *complex*, and we draw it like this:



The π-electrons from propylene end up filling titanium's empty orbital.

Natta- Bimetallic Polymerization mechanism



Copolymerization

Copolymerization of ethylene and α-olefins have been demonstrated soon after the discovery that Ziegler-Natta catalysts homopolymerize α-olefins. Copolymers have gained much interest in polymer field due to their elastomeric characteristics. Therefore, many research works were carried out to prepare better catalyst systems and to obtain more interesting elastomeric copolymers. The properties of the copolymers formed can be controlled by operating conditions, chemical composition and physical state of catalyst and comonomers structure. The most important copolymer is prepared from ethylene and propylene. The production of ethylene-propylene copolymers were traditionally carried out with homogenous Ziegler-Natta catalyst based on vanadium compounds. The application of the Ziegler-Natta heterogenous catalytic system based on titanium compounds for the production of copolymers has recently become more important, due to high activity of the catalyst systems and low production costs. The best coordinated anionic type catalyst suitable for the production of ethylene-propylene copolymers are obtained by reaction of alklyaluminium compounds with transition metals such as vanadium, chromium, niobium and titanium. Recently, Soga and coworkers53 successfully copolymerized ethylene and propylene using a soluble chromium catalytic system composed of $Cr(C_{17}H_{35}COO)_3$ and $AlEt_2Cl$. The catalytic system produced random copolymer with a narrow molecular weight distribution.

Kinetics of Copolymerization

Although radical copolymerization has been more extensively studied and is more important than ionic copolymerization, we will consider the general case without specification as to whether the mode of initiation is by a radical, anionic, or cationic species. Copolymerization of the two monomers leads to two types of propagating species—one with M_1 at the propagating end and the other with M_2. These can be represented by M_1^* and M_2^* where the asterisk represents either a radical, a carbocation, or a carbanion as the propagating species depending on the particular case. If it is assumed that the reactivity of the propagating species is dependent only on the monomer unit at the end of the chain (referred to as the end or ultimate unit), four propagation reactions are then possible. Monomers M_1 and M_2 can each add either to a propagating chain ending in M_1 or to one ending in M_2, that is,

$$M_1^* + M_1 \xrightarrow{K11} M_1^* \qquad 1$$

$$M_1^* + M_2 \xrightarrow{k12} M_2^* \qquad 2$$

$$M_2^* + M_1 \xrightarrow{k21} M_1^* \qquad 3$$

$$M_2^* + M_2 \xrightarrow{K22} M_2^* \qquad 4$$

where k_{11} is the rate constant for a propagating chain ending in M_1 adding to monomer M_1, k_{12} that for a propagating chain ending in M_1 adding to monomer M_2, and so on. The propagation of a reactive center by addition of the same monomer (i.e., Reaction1-4) is often referred to as homopropagation or self-propagation; propagation of a reactive center by addition of the other monomer (Reactions 2 and 3) is referred to as cross propagation or a crossover reaction. All propagation reactions are assumed to be irreversible.

Monomer M_1 disappears by Reactions 1 and 3, while monomer M_2 disappears by Reactions 6-3 and 6-5. The rates of disappearance of the two monomers, which are synonymous with their rates of entry into the copolymer, are given by

$$-d[M_1]/dt = k_{11}[M_1^*][M_1] + k_{21}[M_2^*][M_1] \qquad 5$$

$-d[M_2]/dt = k_{12}[M_1 *][M_2] + k_{22}[M_2*][M_2]$ 6

Dividing Eq. 6-6 by Eq. 6-7 yields the ratio of the rates at which the two monomers enter the copolymer, that is, the copolymer composition, as

$d[M_1]/d[M_2] = (k_{11}[M_1*][M_1] + k_{21}[M_2*][M_1]) / (k12[M_1*][M_2] + k_{22}[M_2*][M_2])$ 7

In order to remove the concentration terms in M1* and M2* from Eq. 7, a steady-state concentration is assumed for each of the reactive species M1* and M2* separately. For the concentrations of M1* and M2* ro remain constant, their rates of interconversion must be equal. In other words, the rates of Reactions 2 and 3 must be equal:

$K_{21}[M_2*][M_1*] = k_{12}[M_1*][M_2]$ 8

Equation 8 can be rearranged and combined with Eq. 7 to yield

$d[M_1] / d[M_2]=((k_{11}k_{21}[M_2*][M_1]^2 / k_{12}[M_2])+k_{21}[M_2*][M_1])/k_{22}[M_2*][M_2] + k_{21}[M2*][M_1]$ 9

Dividing the top and bottom of the right side of Eq. 6-10 by $k_{21}[M2*][M_1]$ and combining the result with the parameters r_1 and r_2, which are defined by

$r_1=k_{11}/k_{12}$ and $r_2=k_{22} / k_{21}$ 10

one finally obtains

$d[M_1] / d[M_2] = [M_1] (r_1[M_1] + [M_2]) / [M_2] ([M_1] + r_2 [M_2])$ 11

Equation 11 is known as the copolymerization equation or the copolymer composition equation. The copolymer composition, $d[M_1] = d[M_2]$, is the molar ratio of the two monomer units in the copolymer. $d[M_1] = d[M_2]$ is expressed by Eq. 6-12 as being related to the concentrations of the two monomers in the feed, $[M_1]$ and $[M_2]$, and the parameters r_1 and r_2. The parameters r_1 and r_2 are termed the monomer reactivity ratios. Each **r** as defined above in Eq. 6-11 is the ratio of the rate constant for a reactive propagating species adding tis own type of monomer to the rate constant for its additon of the other monomer.The tendency of two monomers to copolymerize is noted by r values between zero and unity. An r_1 value greater than unity means that M_1* preferentially adds M_1 instead of M_2, while an r_1 value less than unity means that M_1* preferentially adds M_2. An r_1 value of zero would mean that M_1 is incapable of undergoing homopolymerization.

The copolymerization equation can also be expressed in terms of mole fractions instead of concentrations. If f_1 and f_2 are the mole fractions of monomers M_1 and M_2 in the feed, and F_1 and F_2 are the mole fractions of M_1 and M_2 in the copolymer, then

$f_1 = 1 - f_2 = [M_1] / ([M_1] + [M_2])$ 12

and

$F_1 = 1 - F_2= d[M_1] / (d[M_1] + d[M_2])$ 13

Combining Eqs. 12 and 13 with above Eq. yields

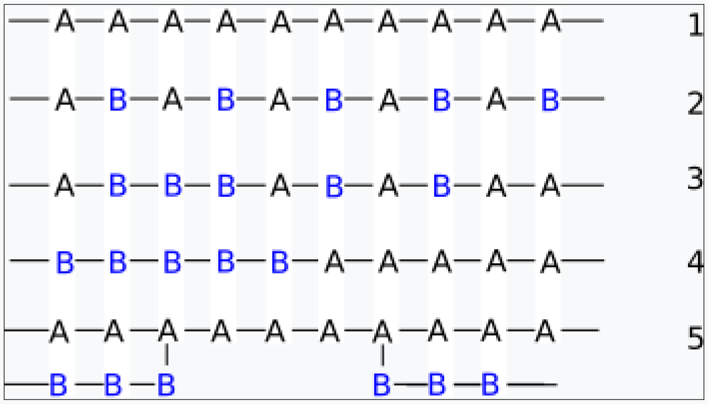
$F_1 = (r_1f_1^2 + f_1f_2) / (r_1f_1^2 +2f_1f_2 + r_2 f_2^2)$

or

$f_1 / f_2 = f_1(r_1f_1+ f_2) / f_2\ (r_2f_2+ f_1)$ 14

The equation 14 gives the copolymer composition as the mole fraction of monomer M_1 in the copolymer and is often more convenient to use than the previous form of the copolymerization equation.

Types of copolymers



Different types of copolymers

Since a copolymer consists of at least two types of constituent units (also structural units), copolymers can be classified based on how these units are arranged along the chain.[3] These include:

- **Alternating copolymers** with regular alternating A and B units (structure 2 in diagram)
- **Periodic copolymers** with A and B units arranged in a repeating sequence (e.g. $(A\text{-}B\text{-}A\text{-}B\text{-}B\text{-}A\text{-}A\text{-}A\text{-}A\text{-}B\text{-}B\text{-}B)_n$)
- **Statistical copolymers** are copolymers in which the sequence of monomer residues follows a statistical rule. If the probability of finding a given type monomer residue at a particular point in the chain is equal to the mole fraction of that monomer residue in the chain, then the polymer may be referred to as a truly **random copolymer**[4] (structure 3).
- **Block copolymers** comprise two or more homopolymer subunits linked by covalent bonds (structure 4). The union of the homopolymer subunits may require an intermediate non-repeating subunit, known as a **junction block**. Block copolymers with two or three distinct blocks are called **diblock copolymers** and **triblock copolymers**, respectively.

Copolymers may also be described in terms of the existence of or arrangement of **branches** in the polymer structure. **Linear copolymers** consist of a single main chain whereas **branched copolymers** consist of a single main chain with one or more polymeric side chains.

Other special types of branched copolymers include **star copolymers**, **brush copolymers**, and **comb copolymers**. In gradient copolymers the monomer composition changes gradually along the chain.

A **terpolymer** is a copolymer consisting of three distinct monomers. The term is derived from *ter* (Latin), meaning thrice, and polymer.

- **Stereoblock copolymers**

A special structure can be formed from one monomer where now the distinguishing feature is the tacticity of each block.

Statistical copolymers

Statistical copolymers are dictated by the reaction kinetics of the two chemically distinct monomer reactants, and are commonly referred to interchangeably as “random” in the polymer literature. As with other types of copolymers, random copolymers can have interesting and commercially desirable properties that blend those of the individual homopolymers. Examples of commercially relevant random copolymers include rubbers made from styrene-butadiene copolymers and resins from styrene-acrylic or methacrylic acidderivatives.[6] Copolymerization is particularly useful in tuning the glass transition temperature, which is important in the operating conditions of polymers; it is assumed that each monomer occupies the same amount of free volume whether it is in a copolymer or homopolymer, so the glass transition temperature falls between the Tg of each homopolymer and is dictated by the mole or mass fraction of each component.

A number of parameters are relevant in the composition of the polymer product; namely, one must consider the reactivity ratio of each component. Reactivity ratios describe whether the monomer reacts preferentially with a segment of the same type or of the other type. For example, a reactivity ratio that is less than one for component 1 indicates that this component reacts with the other type of monomer more readily. Given this information, which is available for a multitude of monomer combinations in the “Wiley Database of Polymer Properties”, the Mayo-Lewis equation can be used to predict the composition of the polymer product for all initial mole fractions of monomer. This equation is derived using the Markov model, which only considers the last segment added as affecting the kinetics of the next addition; the Penultimate Model considers the second-to-last segment as well, but is more complicated than is required for most systems. When both reactivity ratios are less than one, there is an azeotropic point in the Mayo-Lewis plot. At this point, the mole fraction of monomer equals the composition of the component in the polymer.

There are several ways to synthesize random copolymers. The most common synthesis method is free radical polymerization; this is especially useful when the desired properties rely on the composition of the copolymer rather than the molecular weight, since free radical polymerization produces relatively disperse polymer chains. Free radical polymerization is less expensive than other methods, and produces high-molecular weight polymer quickly. Several methods offer better control over dispersity. Anionic polymerization can be used to create random copolymers, but with several caveats: if carbanions of the two components do not have the same stability, only one of the species will add to the other. Additionally, anionic polymerization is expensive and requires very clean reaction conditions, and is therefore difficult to implement on a large scale.[5] Monodisperse random copolymers are also synthesized by ″living″ controlled radical polymerization methods, such as atom-transfer radical-polymerization (ATRP), nitroxide mediated radical polymerization(NMP), or Reversible addition−fragmentation chain-transfer polymerization (RAFT). These methods are favored over anionic polymerization because they can be performed in conditions similar to free radical polymerization. The reactions require longer experimentation periods than free radical polymerization, but still achieve reasonable reaction rates.

Graft copolymers

Graft copolymers are a special type of branched copolymer in which the side chains are structurally distinct from the main chain. The illustration (structure 5) depicts a special case where the main chain and side chains are composed of distinct homopolymers. However, the individual chains of a graft copolymer may be homopolymers or copolymers. Note that different copolymer sequencing is sufficient to define a structural difference, thus an A-B diblock copolymer with A-B alternating copolymer side chains is properly called a graft copolymer.

For example, suppose we perform a free-radical polymerization of styrene in the presence of polybutadiene, a synthetic rubber, which retains one reactive C=C double bond per residue. We get polystyrene chains growing out in either direction from some of the places where there were double bonds, with a one-carbon rearrangement. Or to look at it the other way around, the result is a polystyrene backbone with polybutadiene chains growing out of it in both directions. This is an interesting copolymer variant in that one of the ingredients was a polymer to begin with.

As with block copolymers, the quasi-composite product has properties of both "components". In the example cited, the rubbery chains absorb energy when the substance is hit, so it is much less brittle than ordinary polystyrene. The product is called high-impact polystyrene, or HIPS.

Block copolymers

One kind of copolymer is called a "block copolymer". Recently the terminology "block polymer" has been used. Block copolymers are made up of blocks of different polymerizedmonomers and is usually made by first polymerizing styrene, and then subsequently polymerizing methyl methacrylate (MMA) from the reactive end of the polystyrene chains. This polymer is a "diblock copolymer" because it contains two different chemical blocks. Triblocks, tetrablocks, multiblocks, etc. can also be made. Diblock copolymers are made using living polymerization techniques, such as atom transfer free radical polymerization (ATRP), reversible addition fragmentation chain transfer (RAFT), ring-opening metathesis polymerization (ROMP), and living cationic or living anionic polymerizations.[11] An emerging technique is chain shuttling polymerization.

The "**blockiness**" of a copolymer is a measure of the adjacency of comonomers vs their statistical distribution. Many or even most synthetic polymers are in fact copolymers, containing about 1-20% of a minority monomer. In such cases, blockiness is undesirable.

Copolymer Composition

Terminal Model; Monomer Reactivity Ratios

The instantaneous copolymer composition—the composition of the copolymer formed at very low conversions (about <5%)—is usually different from the composition of the comonomer feed from which the copolymer is produced, because different monomers have differing tendencies to undergo copolymerization. It was observed early that the relative copolymerization tendencies of monomers often bore little resemblance to their relative rates of homopolymerization [Staudinger and Schneiders, 1939]. Some monomers are more reactive in copolymerization than indicated by their rates of homopolymerization; other monomers are less reactive. Further, and most dramatically, a few monomers, such as maleic anhydride and stilbene undergo facile copolymerization with radical initiation, although they have very little or no tendency to undergo homopolymerization.

The composition of a copolymer thus cannot be determined simply from a knowledge of the homopolymerization rates of the two monomers. The determinants of copolymerization composition have been elucidated by several workers by assuming the chemical reactivity of the propagating chain (which may be a free radical, carbocation, or carbanion) in a copolymerization is dependent only on the identity of the monomer unit at the growing end and independent of the chain composition preceding the last monomer unit [Alfrey and Goldfinger, 1944; Mayo and Lewis, 1944; Wall, 1944; Walling, 1957]. This is referred to as the firstorder Markov or terminal model of copolymerization. Consider the case for the copolymerization of the two monomers M_1 and M_2.

Q–e Scheme

Various attempts have been made to place the radical–monomer reaction on a quantitative basis in terms of correlating structure with reactivity. Success in this area would give a better understanding of copolymerization behavior and allow the prediction of the monomer reactivity ratios for comonomer pairs that have not yet been copolymerized. A useful correlation is the Q – e scheme of Alfrey and Price [1947], who proposed that the rate constant for a radical–monomer reaction, for example, for the reaction of $M_1\bullet$ radical with M_2 monomer, be written as

$$K_{12} = P_1Q_2 \exp(-e_1e_2) \qquad 15$$

where P_1 represents the intrinsic reactivity of $M_1\bullet$ radical, Q_2 represents the intrinsic reactivity of M_2 monomer, e_1 represents the polarity of $M_1\bullet$ radical, and e_2 represents the polarity of M_2 monomer. By assuming that the same e value applies to both a monomer and its corresponding radical (i.e., e_1 defines the polarities of M_1 and $M_1\bullet$, while e_2 defines the polarities of M_2 and $M_2\bullet$), one can write expressions for k_{11}, k_{22}, k_{21} analogous to Eq. 15. These can be appropriately combined to yield the monomer reactivity ratios in the forms

$$r_1 = Q_1/ Q_2 \exp[-e_1(e_1 - e_2)] \qquad 16$$

$$r_2 = Q_2/ Q_1 \exp[-e_2(e_2 - e_1)] \qquad 17$$

which correlate monomer–radical reactivity with the parameters Q_1, Q_2, e_1, and e_2. The basis of the Q–e scheme (Eqs. 15 to 17) is the theoretically unsatisfactory suggestion that the alternating tendency is due to ground-state electrostatic interactions between permanent charges in the monomer and radical [Price, 1948].

Although there have been attempts to place it on a solid theoretical basis [Colthup, 1982; O'Driscoll and Yonezawa, 1966], the Q–e scheme is best considered as an empirical approach to placing monomer reactivity on a quantitative basis. Monomer reactivity is separated into the parameter Q, which describes the resonance factor (and to a slight extent the steric factor) present in the monomer, and the parameter e, which describes the polar factor.

Consider now the use of the Q–e shceme to predict monomer reactivity ratios. Values of Q and e have been assigned to monomers on the basis of their r values and the arbitrarily chosen reference values of Q = 1 and e = - 80 for styrene [Greenley, 1989b, 1999]. Table 6-7 shows the average Q and e values for some common monomers. The practical success of the Q–e scheme in predicting the r_1 and r_2 values for comonomer pairs not previously copolymerized has been limited in its quantitative aspects. The reason for this is that the Q and e values for a monomer are not unique values for both experimental and theoretical reasons. The precision of the calculated Q and e values is often poor as a result of inaccuracies in the experimentally determined r values. Further, the Q and e values for a monomer vary considerably depending on the monomer with which it is copolymerized as a result of inherent deficiencies of the Q–e scheme. It does not explicitly take into account steric factors that may affect monomer reactivity ratios for certain radical–monomer combinations. The assumption of the same e value for a monomer and its corresponding radical is also inadequate. Attempts to refine the Q–e scheme by using separate e values for monomer and radical have not been successful.

In spite of these deficiencies the Q–e scheme is a reasonable qualitative and even semi quantitative approach to the effect of structure on monomer reactivity. It can be used to give a general idea of the behavior to be expected from a comonomer pair that has not been studied. The Q–e values can be used to more quantitatively discuss reactivity data such as those in Table 6-4 and 6-6. The monomers are lined up in Table 6-6 in order of their e values. This order defines the polarities of the various monomers. The relative importance of resonance and polar factors in determining monomer reactivity can be discussed by considering the data in Table 6-4 in terms of the Q and e values of the monomers.

The various reference radicals can be divided into two groups: one composed of the relatively unreactive radicals and the other composed of reactive radicals. For the reactive radicals, such as vinyl chloride and vinyl acetate, monomer reactivity depends on Q with k_{12} increasing with increasing Q and polar effects are too subtle to discern. The unreactive radicals from styrene and, 3-butadiene show the same trends except that one can discern the polar effects. There is enhanced reactivity of these radicals (processing negative e values) toward a onomer such as acrylonitrile with relatively high positive e values. The resonance factor is, however, more important than the polar factor; the former determines the magnitude of monomer reactivity. Thus monomer reactivities toward the 1,3-butadiene and styrene radicals fall into two groups—one group of monomers with high Q values and high reactivities and another group with low Q values and low reactivities.

A number of useful generalizations are possible regarding which pairs of monomers will copolymerize and the behavior to be expected. Copolymerization proceeds poorly with monomers whose Q values are very different, since copolymer formation would require the energetically unfavorable conversion of a resonance-stabilized radical to a less stabilized radical and vice versa . Thus vinyl chloride and vinyl acetate do not copolymerize well with styrene or 1,3-butadiene. Copolymerization is more suitable between monomers of similar Q values, preferably high Q values, for example, styrene and 1,3-butadiene. Ideal copolymerization occurs between two monomers having similar Q and e values, for example, styrene–1,3-butadiene, vinyl chloride–vinyl acetate, and acrylonitrile–methyl acrylate. The tendency toward alternation is greatest for monomers having the same Q values with high e values of opposite sign.

TABLE: Q and e Values for Monomersa; a Data from Greenley [1989b, 1999].

Monomer	**Q**	**e**

Ethyl vinyl ether	0.018	-1.80
Propene	0.009	-1.69
N-Vinylpyrrolidone	0.088	-1.62
n-Butyl vinyl ether	0.038	-1.50
p-Methoxystyrene	1.53	-1.40
Isobutylene	0.023	-1.20
Vinyl acetate	0.026	-0.88
α-Methylstyrene	0.97	-0.81
Styrene	1.00	-0.80
Isoprene	1.99	-0.55
1,3-Butadiene	1.70	-0.50
Ethylene	0.016	0.05
Vinyl chloride	0.056	0.16
Vinylidene chloride	0.31	0.34
Methyl methacrylate	0.78	0.40
Acrylamide	0.23	0.54
Methacrylic acid	0.98	0.62
Methyl acrylate	0.45	0.64
Methacrylonitrile	0.86	0.68
Vinyl fluoride	0.008	0.72
4-Vinylpyridine	2.47	0.84
Acrylic acid	0.83	0.88
Methyl vinyl ketone	0.66	1.05
Diethyl maleate	0.053	1.08
Acrylonitrile	0.48	1.23
Tetrafluoroethylene	0.032	1.63
Diethyl fumarate	0.25	2.26
Fumaronitrile	0.29	2.73
Maleic anhydride	0.86	3.69

Text book:

T1: Gowariker, V. R., N. V. Viswanathan and J. Sreedhar, 1986. Polymer Science, *New Age International* Private Ltd., New Delhi.

T2: Billmeyer, F.W., 2003. Text Book of Polymer Science. III Edition, John Wiley, New York.

Reference book

R1: M.S Bhatnagar,2004, " A text book of polymers". Ist Edition, S.Chand & Company.

POSSIBLE QUESTIONS

Multiple choice questions (Each Carry 1 Marks)

1. The polyethene polymer formed by the addition polymerisation process using the Ziegler-Natta catalyst is a?
a**. High density and high melting point** b. Low density and high melting point
c. High density and low melting point d. Low density and low melting point
2. The catalyst used for the Ziegler–Natta polymerizations?
a. $TiCl_3$ with $Al(C_2H_5)_2Cl$ b. BCl_3 with $Al(C_2H_5)_2Cl$ c. $TiCl_3$ with $Fe(C_2H_5)_2Cl$
d. TiF_3 with $Al(C_2H_5)_2F$
3. Melting Point of Low Density Polyethylene (LDPE) is?
a. ~115º C b. ~116 ºC c. ~117ºC d.~118ºC
4. Which polymer is not an copolymer?
a. CCDDDCCDDDCCD **b. AAAAAAAAAAA** c. BBBBBBBAAAAAAA
d. CCCDDCCCDDCCC
5. The metal in the co-catalyst is come from
a. I to III b. III to IV c. IV and V **d. IV-VIII**
6. $R-Ti-Cl_4$ is an
a. bi-metallic catalyst **b. mono metallic catalyst** c. tri metallic catalyst
d. alkyl catalyst
7. Monometallic mechanism proposed by
a. Natta **b. Cossee** c. Robert d. Wilson
8. The Ti metal have a ---- number of co-ordination
a. 5 b. 4 c. 7 d. 6
9. Ti halide is acting as a
a. adsorbate b. co-catalyst c. secondary catalyst **d. Surface catalyst**
10. In the zieglar-natta catalyst the aluminium halide ------- on Ti halide
a. chemisorbed b. physisorbed c. bonded d. absorped
11. The insertition of monomer in the alternative spatial arrangement form the
a. isotactic polymer **b. syndiotactic polymer** c. copolymer d. radical polymer
12. Which of the following is not depend on the formation of vaccant sites
a. coming monomeric unit b. chlorine atom of catalyst c. substituent of monomer unit
d. Transition metal atom
13. Which is the step to form the activesite catalyst in co-ordination polymerization
a. initiation b. propagation c. termination d. transfermation
14. In the monometallic mechanism monmer attacks the
a. Ti-Cl bond b. Al-R bond **c. Ti-R bond** d. Al-Cl bond
15. Who fractionated the vinyl chloride-vinyl acetate co-polymer
a. Cossee b. Natta **c. Staudinger** d. Zieglar
16. Two or more monomers are combined to form
a. Co-ordination polymer **b. Co-polymer** c. Crystalline polymer d. Homo polymer
17. The polymer production in the co-polymerisation depends on the
a. anyone monomer unit **b. reactivity ratio** c. reaction path d. two monomers
18. The reactivity ratio is represented as
a. r1 b. r2 **c. r1/r2** d. m1/m2
19. [m1] and [m2] represents the

a. mole fraction b. molar concentration c. molecular mass d. number of moles

20. The plot between r1(assumed values) Vs r2 (calculated values) is drawn in the method of

a. Mayo-Lewis method b. Fineman-Rose method c. Lewis method d. molecular method

Questions (Each carry 6 Marks)

1. Derive the kinetic equation of co-ordination polymerization?
2. Explain the kinetics of co-polymerisation?
3. What is Co-polymer and explain its types?
4. Explain the most useful co-ordination catalyst?
5. Explain the types of co-polymerisation?
6. What is Zieglar-Natta catalyst explain it briefly?
7. Give an account about reactivity ratio?
8. Derive the kinetic equation of co-polymerization?
9. What is reactivity ratio and explain it concepts?
10. How to determine the reactivity ratio of the polymers?

Compulsory Questions (Each carry 10 Marks)

1. Explain the mono and bi metallic mechanism of co-ordination catalyst?
2. Explain the influence of reactivity ratio in the co-polymerization?

16CHP305A
Karpagam Academy of Higher Education
Coimbatore-21
(For the Candidates admitted on 2016 Onwards)
III-Semester
Polymer Chemistry

Questions	**Opt-1**	**Opt-2**	**Opt-3**	**Opt-4**	**Answers**
Unit 2- Objective questions for online examination (Each carry 1 mark)					
The alternating copolymer contains ?	2 monomer units	3 monomer units	4 monomer units	1 monomer units	2 monomer units
The copolymer is not an?	Alloy	Trimer	Monomer	Initiator	Alloy
The polyethene polymer formed by the addition polymerisation process using the Ziegler- Natta catalyst is a?	High density and high melting point	Low density and high melting point	High density and low melting point	Low density and low melting point	High density and high melting point
The catalyst used for the Ziegler–Natta polymerizations?	$TiCl_3$ with $Al(C_2H\ 5)_2Cl$	BCl_3 with $Al(C_2H\ 5)_2Cl$	$TiCl_3$ with $Fe(C_2H\ 5)_2Cl$	TiF_3 with $Al(C_2H\ 5)_2F$	$TiCl_3$ with $Al(C_2H\ 5)_2Cl$
Melting Point of Low Density Polyethylene (LDPE) is?	~115^{o} C	~116 ^{o}C	~117^{o}C	~118 ^{o}C	~115^{o} C
Which polymer is not an copolymer?	CCDDDCCDDDCCD	AAAAAAAAAAA	BBBBBBBAAAAAAA	CCCDDCCCDDCCC	AAAAAAAAAAA
Which, speeds up the oxidation process in polymerization?	Heat	Catalyst	Initiator	Reactants	Heat
Highly unsaturated polymers are much more sensitive to ?	Reduction	Addition	Oxidation	Redox	oxidation
Stability of a polymer depends on?	Physical structure	Chemical properties	Physical properties	Chemical structure	Chemical structure
Most polymers are?	Thermally stable	Physically stable	Chemically stable	Unstable	Thermally stable
Carbon Black and other colorants may also protect plastics from the effects of?	Temperature	Melting point	Pressure	Light	Light
Ultraviolet absorber is?	2-hydroxyphenyl benzotriazoles	Hydroxybenzophenones	Hindered amines	Benzophenones	Hydroxybenzophenones
Any of a group of substances that are used in plastics to impart viscosity, flexibility, softness to the finished product is defined as?	Light stabilizers	Colouarants	Plasticizers	Flame retardents	Plasticizers
Which of the following is used to form a stereo regular polymer	co-polymer	Acid catalyst	Zieglar-natta catalyst	alkyl catalyst	Zieglar-natta catalyst
higher alpha olefins form the	isotactic polymer	syndiotactic polymer	stereo polymer	copolymer	isotactic polymer
Polymerization reaction done by the presence of organo-metallic compounds is	co-ordinaion polymerisation	co-polymerization	addition polymerisation	chain polymerization	co-ordinaion polymerisation
In the zieglar-natta catalyst, the alkyl metals from group	I to III	III to IV	IV and V	IV-VIII	I to III
The metal in the co-catalyst is come from	I to III	III to IV	IV and V	IV-VIII	IV-VIII
R-Ti-Cl_4 is an	bi-metallic catalyst	mono metallic catalyst	tri metallic catalyst	alkyl catalyst	mono metallic catalyst
Monometallic mechanism proposed by	natta	cossee	Robert	Wilson	cossee
The Ti metal have a ---- number of co-ordination	5	4	7	6	5
Ti halide is acting as a	adsorbate	co-catalyst	secondary catalyst	Surfae catalyst	Surfae catalyst
In the zieglar-natta catalyst the aluminium halide ------- on Ti halide	chemisorbed	physisorbed	bonded	absorption	chemisorbed
In the Zieglar-natta catalyst, the Ti halide have a	vacant d-orbital	vacant p-orbital	filled d-orbitals	filled p-orbitals	vacant d-orbital
Which of the following is the active site of the zieglar-natta catalyst	metal in I-III group	metal in I group	metal in IV-VIII group	only in II group metal	metal in IV-VIII group

In the bi metallic mechanism forms the	bi-complex	intermediate compound	intermediate ion	Catalyst	bi-complex
Which of the following metal is not present in the zieglar-natta catalyst	Ti	Mo	V	Li	Li
The metal present in the zieglar-natta catalyst is	non-metal	semi metal	taransition metal	radio-active metal	taransition metal
Which of the following is used for the stereo-regular polymer	zieglar-natta catalyst	Acid catalyst	basic catalyst	intermediate	zieglar-natta catalyst
The insertition of monomer in the same spatial arrangement form the	isotactic polymer	syndiotactic polymer	copolymer	radical polymer	isotactic polymer
The insertition of monomer in the alternative spatial arrangement form the	isotactic polymer	syndiotactic polymer	copolymer	radical polymer	syndiotactic polymer
which of the following is not depent on the formation of vaccant sites	coming monomeric unit	chlorine atom of catalyst	substituent of monomer unit	Transition metal atom	Transition metal atom
In the syndiotactic polymer, the substituent monomer units are insert in the	alternative sites	same position	opposit position	regular postion	alternative sites
In the isotactic polymer, the monomer insertition in the --- spatial arrangements	Same direction	opposite direction	alternative direction	either same or alternative	Same direction
Which is the step to form the activesite catalyst	initiation	propagation	termination	transfermation	propagation
In the monometallic mechanism monmer attacks the	Ti-Cl bond	Al-R bond	Ti-R bond	Al-Cl bond	Ti-R bond
Who fractionated the vinyl chloride-vinyl acetate co-polymer	Cossee	natta	Staudinger	Zieglar	Staudinger
Two or more monomers are combined to form	co-ordination polymer	co-polymer	crystalline polymer	homo polymer	co-polymer
The polymer production in the co-polymerisation depends on the	anyone monomer unit	reactivity ratio	reaction path	two monomers	reactivity ratio
The reactivity ration is represented as	r1	r2	r1/r2	m1/m2	r1/r2
The r1>1 means the preference of the add	M_1 monomer	M_2 monomer	either M1 or M2	neither M1 nor M2	M_1 monomer
The r2 > 1 prefer the addition of	M_1 monomer	M_2 monomer	either M1 or M2	neither M1 nor M2	M_2 monomer
The two monomers in the co-polymerisation have same prefernce of addition to produce	ideal co-polymer	alternative co-polymer	block polymer	non-ideal polymer	ideal co-polymer
In the ideal co-polymer, the reactivity ratio is equal to	1	0	not equal to 0	not equal to unity	1
In the alternating co-polymer, the reactivity ratio is equal to	0	1	not equal to 0	above 1	0
In which of the following condition form the block co-polymer	r1/r2 = 1	r1/r2 = 0	r1,r2<1	r1,r2>1	r1,r2>1
The over all rate of co-polymerization depends on the	inition step only	propagation step only	termination step only	both inition and termination	both inition and termination
Most of the graft polymers are formed by	chain polymerization	co-ordination polymerization	radical polymerization	Ionic polymerization	radical polymerization
[m1] and [m2] represents the	mole fraction	molar concentration	molecular mass	number of moles	mole fraction
the plot between r1(assumed values) Vs r2 (calculated values) is drawn in the method of	Mayo-Lewis method	Finemann-Rose method	Lewis method	molecular method	Mayo-Lewis method
equation belongs to the	Mayo-Lewis method	Finemann-Rose method	Lewis method	molecular method	Finemann-Rose method
the slope of graph in the fineman-ross method give the value of	M	P	r1	r2	r1
In the fineman-Ross method, the ordinate intercept give the	r1 value	negative r1 value	negative r2 value	positive r1 value	negative r2 value

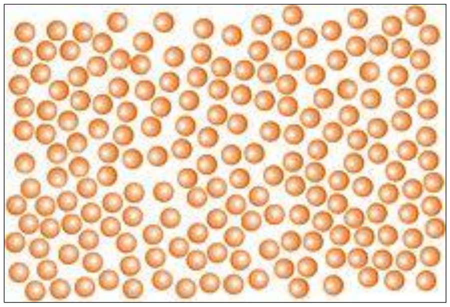
Which of the following condition make the M1 radical prefers to add M2 monomer and the M2 radical prefer to add M1 monomer	r1/r2 = 0	r1,r2<1	r1,r2>1	r1=r2=0	r1=r2=0
Which of the following condition make the both M1 and M2 radical have same preference for M1 and M2 monomers	r1=r2 = 1	r1,r2<1	r1,r2>1	r1=r2=0	r1=r2 = 1
The composition of two monomers are constant means it forms	azeotropic co-polymerisation	an azeotropic co-polymerisation	alternating co-polymerization	block co-polymer	azeotropic co-polymerisation
Which of the following conditions form the M1 richer co-polymer	r1,r2<1	r1,r2>1	r1=r2=0	r1>1 , r2<1	r1>1 , r2<1
The condition r1<1 and r2>1 condition preferse the	M1 radical prefer to M1 monomer	M2 radical prefer to the M2 monomer	M1 radical prefer to M2 monomer and M2 radical prefer the M1 monomer	M1 radical prefer to M1 and monomer and M2 radical prefer the M1 and M2 monomer	M1 radical prefer to M2 monomer and M2 radical prefer the M1 monomer
The r1 is less than r2, the azeotropic composition should be	increases	decreases	constant	first increases then decreases	decreases
The r1 < 1 and r2 > 1 condition to form the polymer richer in	M1 monomer	M2 monomer	M1 radical	M2 radical	M2 monomer

UNIT–III

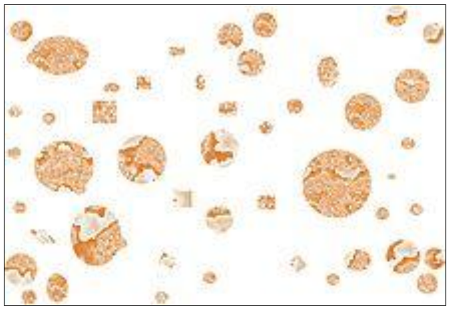
Molecular Weight and Properties

Molecular Weight and Properties: Polydispersion – average molecular weight concept, number, weight and viscosity average molecular weights. Measurement of molecular weights. Viscosity, light scattering, osmotic and ultracentrifugation methods. Polymer structure and physical properties – crystalline melting point Tm. The glass transition temperature.Determination of Tg. Relationship between Tm and Tg.

Polydispersion



A uniform (monodisperse) collection



A non-uniform (polydisperse) collection

In physical and organic chemistry, the **dispersity** is a measure of the heterogeneity of sizes of molecules or particles in a mixture. A collection of objects is called **uniform** if the objects have the same size, shape, or mass. A sample of objects that have an inconsistent size, shape and mass distribution is called **non-uniform**. The objects can be in any form of chemical dispersion, such as particles in a colloid, droplets in a cloud, crystals in a rock, or polymer macromolecules in a solution or a solid polymer mass. Polymers can be described by molecular mass distribution; a population of particles can be described by size, surface area, and/or mass distribution; and thin films can be described by film thickness distribution.

IUPAC has deprecated the use of the term ***polydispersity index***, having replaced it with the term *dispersity*, represented by the symbol *Đ* (pronounced D-stroke) which can refer to either molecular mass or degree of polymerization. It can be calculated using the equation $Đ_M = M_w/M_n$, where M_w is the weight-average molar mass and M_n is the number-average molar mass. It can also be calculated according to degree of polymerization, where $Đ_X = X_w/X_n$, where X_w is the weight-average degree of polymerization and X_n is the number-average degree of polymerization. In certain limiting cases where $Đ_M = Đ_X$, it is simply referred to as *Đ*. IUPAC has also deprecated the terms *monodisperse*, which is considered to be self-contradictory, and *polydisperse*, which is considered redundant, preferring the terms *uniform* and *non-uniform* instead.

The **dispersity index**, or formerly polydispersity index (**PDI**), or heterogeneity index, or simply dispersity (***Đ***), is a measure of the distribution of molecular mass in a given polymer sample. Đ (PDI) of a polymer is calculated:

PDI = M_w / M_n

Where M_w is the weight average molecular weight and M_n is the number average molecular weight. M_n is more sensitive to molecules of low molecular mass, while M_w is more sensitive to molecules of high molecular mass. The dispersity indicates the distribution of individual molecular masses in a batch of polymers. Đ has a value equal to or greater than 1, but as the polymer chains approach uniform chain length, Đ approaches unity

Since molecular weight is central to the entire polymer field, students in this short course are assumed to understand the need for measuring polymer molecular weight and to be familiar, from textbooks or course notes, with the basic principles underlying the most common molecular weight measurement techniques - light scattering, osmometry, GPC, end group analysis, and intrinsic viscosity. For some polymer samples, textbook familiarity with a method and an instrument manual are all that is needed to make a meaningful measurement. For others, matters are not so simple, especially if a target polymer is of a new chemistry and/or not a linear neutral homopolymer that dissolves in an ordinary solvent.

After going through common methods in some detail, “problem” polymers and a few less common measurement methods will be discussed. In this first handout, principles and terminology associated with molecular weight and its distribution will be overviewed.

Methods - Some variation of the following table [adapted from Elias et al., Adv. Polym. Scil**11** (1973), 111] is cited in many introductory polymer textbooks. This table lists measurement methods by type (A=absolute, R=relative, E=equivalent), by applicable molecular weight range, and if a specific mean molecular weight value is determined, by the type of average produced.

	Method	**Type**	**Molecular Weight Range, g/mol**	**Mean Value Measured**
1.	Membrane osmometry	A	10^4-10^6	M_n
2.	Ebullioscopy (boiling point elevation)	A	$<10^4$	M_n
3.	Cryoscopy (freezing point depression)	A	$<10^4$	M_n
4.	Isothermal distillation	A	$<10^4$	M_n
5.	Vapor Phase osmometry	A*	$<10^5$	M_n
6.	End group analysis	E	$<10^5$	M_n

7.	Static light scattering	A	10^2-10^8	M_w
8.	Sedimentation equilibrium	A	$<10^6$	M_w, M_z, $M_{z=1}$
9.	Sedimentation in a density gradient	A	$>10^5$	depends
10.	Sedimentation velocity/diffusion	A	10^3-10^8	depends
11.	Solution viscosity	R	10^2-10^8	M_η
12.	Gel Permeation Chromatography	R	10^2-10^7	different values

"absolute" – the measurement is directly related to the molecular weight without assumptions about chemical and/or physical properties of the polymer

"equivalent" – the chemical structure of the polymer must be known to obtain molecular weight

"relative" – the quantity measured depends on the physical structure of the tested polymer and so a calibration curve relating measurement and molecular weight values must be known *a priori*; typically, this molecular weight calibration is established by companion measurements on a series narrow molecular weight polydispersity standards of the same chemical and physical structure as the tested polymer

Classification of Methods -

Calibration: The terms "absolute", "relative", and "equivalent" are not always distinct. GPC, for example, may be absolute or relative, depending on the method of calibration. Vapor phase osmometry, as presented in the method's underlying theory, is an absolute method, but in actual practice, the instrument requires calibration with a standard compound of known molecular weight, making the method relative. Even an absolute method such as mass spectrometry is usually calibrated by molecular weight standards.

Molecular Weight Range: Molecular weight ranges for each method are limited by constraints unique to that method. These limits will be discussed separately as methods are introduced.

Molecular Weight Averages: The common molecular weight averages (M_n, M_w, M_z, M_{z+1}) are well understood by polymer students; they are associated with increasingly higher moments of the molecular weight distribution. However, students often do not grasp why different experimental methods are sensitive to different averages.

1.3 *Why Different Methods Provide Different Molecular Weight Averages*

If the quantity measured by a given method directly manifests the number of polymer molecules - but not their molecular weights - this quantity can only be used to deduce M_n.

As an example, consider vapor phase osmometry. In a thermodynamically ideal solution, vapor pressure π is lowered by kT/V as each nonvolatile solute molecule of molecular mass M is added to volume V of volatile solvent. The lowered vapor pressure $\Delta\pi$ of N polymer solutes is thus NkT/V, a combination independent of M but dependent on N. Upon writing this product in terms of c, the mass concentration of the solutes, M merges as a measurable parameter,

$$\boxed{\Delta\pi = \frac{N}{V}kT = \frac{c}{M}kT}$$

so that

$$\boxed{M = \frac{c}{\Delta\pi}kT}$$

For the polydisperse molecular weight case, suppose that N_i polymers of molecular weight M_i are added to the solvent, each molecular weight fraction i in the mixture present at mass concentration c_i. Only the total mass concentration c $[=\sum c_i]$ is known and only $\Delta\pi$ measured, the latter parameter summing contribution kT/V from each molecule irrespective of M_i,

$$\boxed{\Delta\pi = \frac{kT}{V}\sum N_i}$$

Applying the formula previously analyzed for monodisperse M now yields

$$\boxed{\frac{ckT}{\Delta\pi} = \frac{V\sum c_i}{\sum N_i} = \frac{\sum Vc_i}{N_i} = \frac{\sum N_i M_i}{\sum N_i} = M_n}$$

This is the “true” average molecular weight as the word “average” is used in nontechnical contexts.

In essence, vapor phase osmometry allows a “count” of the number of molecules in a known mass of polymer. The same concept of molecular counting applies to all colligative property-based measurements (colligative properties are measured in osmometry, freezing point depression, boiling point elevation, etc.), which detect the solvent activity in the presence of solute.

Contrarily, other methods manifest not just the number of dissolved molecules but also their molecular weight.Consider static light scattering. In the absence of optical interference, each polymer molecule dissolved in a fixed volume of solution contributes equally to the measured quantity, the reduced scattered intensity R (R=Rayleigh factor or ratio),

$$\boxed{R = \frac{\mathrm{N}}{\mathrm{V}}\mathrm{k} = \frac{\mathrm{c}}{\mathrm{M}}k}$$

where k is a molecular contrast factor (reflecting the optical contrast between polymer and solvent surroundings, the property ultimately responsible for all light scattering phenomena). Without inter- and intramolecular interference of scattered light, k is given by the Rayleigh scattering formula,

$$\boxed{k = \frac{16\pi^2\alpha^2 n_o{}^4}{\lambda_o{}^4}}$$

wheren_o is the solvent refractive index, λ_o is the wavelength of incident light in vacuum, and α is the molecular polarizability.

If all subunits of a linear polymer (i.e., its repeat units) contribute equally to the polymer's net polarizability, as expected for a homopolymer, α is proportional to M: a longer polymer scatters more light than a shorter one. It then follows from the above formulas that the reduced scattered intensity R is proportional to the product of c and M.

$$R=KcM$$

where the proportionality constant K is known as the optical constant; it has no dependence on M. By simple rearrangement,

$$\boxed{M = \frac{R}{Kc}}$$

Contrasting vapor phase osmometry with light scattering, the contribution of individual molecules to the measured signals are quite distinct,

$$\boxed{\Delta\pi = \frac{\mathrm{N}}{\mathrm{V}}kT \quad \text{vs.} \quad R = \frac{\mathrm{N}}{\mathrm{V}}\mathrm{M}^2 K}$$

In light scattering, each molecule contributes to the overall measurement according to the square of its molecular weight. In osmometry, all molecules contribute equally, independently of molecular weight.Turning to the analogous polydisperse molecular weight case, and using the same notation as before, contributions to R by each molecular weight fraction simply add,

$R = K\sum c_i M_i$

The M formula for the monodisperse sample now yields

$$\frac{R}{Kc} = \frac{\sum c_i M_i}{\sum c_i} = \frac{\sum N_i M_i{}^2}{\sum N_i M_i} = M_w$$

In essence, light scattering “sums” the product of the number of polymer molecules multiplied by the square of their molecular weight.

One could naively imagine a measurement method exactly intermediate to the two just evaluated, i.e., a method based on a property sensitive to the product of N and M. This product, however, is simply the total mass of polymer; it could not be employed to calculate M.

Because in vapor phase osmometry and similar techniques each molecule contributes to the overall measurement a constant, universal quantity independent of chemistry or structure, these techniques require, at least in theory, no calibration. As the previous discussion reveals, light scattering does require calibration, i.e., the value of K must be known to calculate M from R.

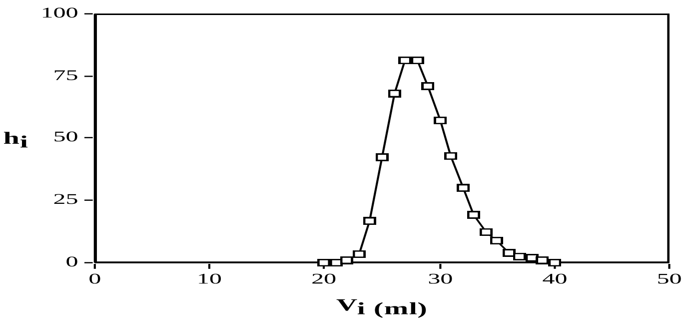
K is typically obtained by measuring the refractive index increment dn/dc as polymer is added to solvent, and as a consequence, I would prefer the light scattering method instead be termed the light scattering-refractive index method. The standard formula for K is written,

$$\boxed{K = \frac{4\pi^2 n_o^2}{\lambda_o^4 N_A}\left(\frac{dn}{dc}\right)^2}$$

This formula, offering K via measurement of dn/dc, is derived through an optical model that supposes a polymer consists of independent, identical, and isotropic scattering sites immersed an optically homogeneous medium of infinite extent. The scattering from such sites is then proportional to the square of the scattering site-solvent optical mismatch [~$(dn/dc)^2$], while the contribution from such sites to solution refraction index is linearly proportional to the same quantity [~(dn/dc]. These assumptions, due to Debye, are far from obvious. The local symmetry of a polymer chain is cylindrical, not spherical (i.e., not isotropic); also, the interaction of light with a single scattering site could be influenced by neighboring scattering sites. If one represents the chain as an optically mismatched cylinder rather than a string of isotropic, optically independent scattering sites, a slightly different prefactor appears in the theoretical formula for K. The difference can be associated with depolarized light scattering, which fortunately, is usually small for high M polymers.

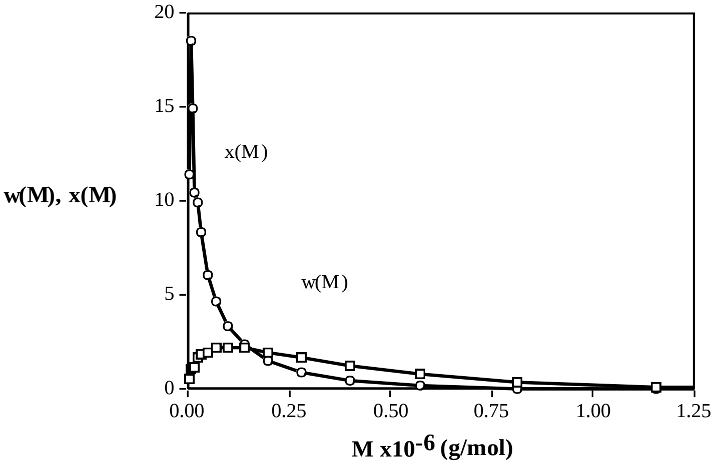
Molecular Weight Distributions -

Consider ways that this molecular weight distribution might be graphically presented. Most commonly, the distribution is shown as the raw GPC trace, which is given next. A single, well-defined molecular weight peak is noted. [To define the molecular weight distribution better, there should be more data points spread over the peak; I didn’t want to do more hand calculations, so the table has only enough data to illustrate trends clearly.]



Despite this sample's large PDI, the peak looks relatively narrow. This trace, termed the chromatogram, is by itself is pretty meaningless, since we don't know how M_i and $V_i$are related: the poorer the molecular weight separation, for example, the narrower is the chromatogram peak. Notwithstanding this trivial fact, raw GPC traces are frequently cited when arguing for low polydispersity.

In this instance, the relationship between M_i and V_i is known by a calibration with polystyrene standards, so we can do much better than the chromatogram. Given below are the weight and number fraction distributions derived above.



These bear no resemblance to the raw trace, and the significant polydispersity of the sample is amply evident. Indeed, the x(M) curve shows that the most common polymer species has a molecular weight of 7,200 g/mol even though M_n and M_w both exceed 100,000 g/mol. Approximately 10% of the molecules by weight have molecular weights in excess of 800,000 g/mol, while 10% by weight have molecular weights less than 50,000 g/mol. The value of M_n falls slightly above the maximum of w(M), whereas the value of M_w lies well above this maximum, a fact commonly mentioned in introductory polymer texts. The difference between x(M) and w(M) simply manifests that it takes many small chains to balance the mass of a few larger chains. By number, the short chains dominate, while by weight, the converse is true.

Surveying a whole year of Macromolecules, one is likely to never see a x(M) curve and just a handful of w(M) curves.

In most polymer situations, greatest interest lies in the logarithmic spread of M. This is the case, for example, if we are interested in the power law exponents of polymer physics, where an increase from 10,000 g/mol to 100,000 g/mol leads to property changes comparable to those for an increase from 100, 000 g/mol to 1,000,000 g/mol. Unfortunately, the logarithmic spread of M is too often incorrectly displayed in a plot that simply switches the x-axis variable from M to log M, leaving the y-axis magnitude unchanged. [Unfortunately, my name is listed on a paper with such an error; I didn't see the paper until it was too late to make a correction.]

To make the logarithmic plot properly, one must recognize that the plotted functions are distributions. Thus, the y-axis variable reflects the number of occurrences per unit change of x-axis variable. Here, for example, w(M)dM represents the number of chains with M in the range between M and M+dM. In logarithmic form, the y-axis variable must represent the number of chains with log M in the range between log M and log M+dlogM. The y-axis variable in a logarithmic plot of a distribution thus has a different functional form than the y-axis variable in a linear plot of this same distribution. To avoid the spontaneous creation of chains in converting plotting formats, the new y-axis variable y′ must be related to the old y-axis variable y by,

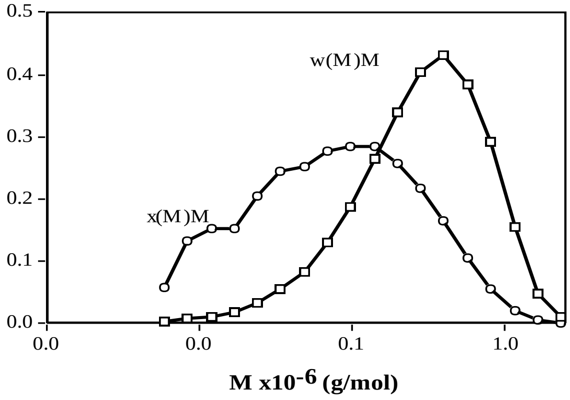
$$y\,dx = y'd\log(x)$$

Solving,

$$y' = yx$$

Thus, to present the weight fraction distribution in its logarithmic form, one must plot w(M)M vs. log M. Similarly, x(M), the number fraction distribution, must be plotted as x(M)M vs. log M. Don't simply check the log(x) box in the plotting software!

For the distribution of the example, these plots are given next.



The peak in the logarithmic weight fraction distribution is at 430,000 g/mol, well above M_w. This value nicely corresponds to the "peak molecular weight" M_p defined by the maximum of the GPC trace. When plotted in linear rather than logarithmic form, the peak is at 80,000 g/mol, which is quite different. M_p, although often used in GPC characterization, has no fundamental significance unless the distribution of molecular weights is very narrow. Loose definition of M_p creates confusion. This parameter usually represents the molecular weight position of the peak in the GPC trace.

Because the calibration curve in GPC offers an almost semi-logarithmic relationship between V_i and M_i, the function w(M)M, the weight fraction distribution in its logarithmic form, appears similar to a horizontal reflection of the original GPC trace.

End Group Method

The molecular weight of polymers which have an end group amenable to analysis could be principally analyzed by an end-group assay [42]. The biggest drawback of this method is the decrease in sensitivitywith an increased chain length. The first measurements with this method were performed by Staudinger and Eder and gave determination limits of about 15,000 g·mol−1. Weber and Husemann treated cellulose with an alkaline copper sulfate solution to oxidize aldehydes to aldonic acids. Afterwards, they determined the so-called "*Monosezahl*" (number of glucose units per carboxyl group). With this method, they were able to determine molecular weights up to 200,000 g·mol^{-1}. However, due to processing, cellulose usually already contains oxidized end groups and additional carbonyl groups. Hence, a direct relationship between carboxyl groups (aldonic acid) and molecular weight determined with a high rate of accuracy.

Osmotic Pressure

Osmometry is among the methods for determining molecular mass which rely on colligative properties (from the Latin word *colligere*for "collect"), meaning that only the number of dissolved molecules influences the properties of a solution [46]. In addition, the osmotic pressure, boiling point elevation, vapor pressure reduction, and the freezing point depression are based on colligative properties. Out of the four colligative methods, only membrane osmometry (MO) is of interest for cellulosic samples.

However, vapor pressure osmometry (VPO) is superior for analyzing samples with $M_n < 20{,}000$ g·mol^{-1}. This is because the diffusion of low molecular weight molecules through the membrane limits the utility of membrane osmometry for this especially low molecular weight region. Only a few publications address the use of VPO experiments on directly-dissolved cellulose and these will be discussed at the end of this chapter.

Since the osmotic pressure of a solution depends on molecular weight and concentration *c*, the following equation can be used to determine the number average of the molecular weight

$$\boxed{\frac{\Pi}{c} = RT\left(\frac{1}{M_n} + A_2 c + A_3 c^2 + \cdots\right)}$$

whereΠ is the osmotic pressure, c is the solute concentration, R is the ideal gas constant, T the temperature, Mn is the number average, and $A2$ and $A3$ are the second and third virial coefficients. The most common method of osmometry is membrane osmometry. In membrane osmometry, the osmotic pressure is measured directly using a semi-permeable membrane [42]. In experiments, the osmotic pressure must be measured at several different concentrations. By extrapolating the Π/c versus c plot to zero, the intercept gives the molecular weight, whereas slope yields $A2$. Note, that $A2$ is an empirical constant for a given solute/solvent system and it depends on the temperature. It represents the interaction of a single molecule with the solvent. For the fundamental theory of osmometry.

Using osmometry for cellulose molecular weight determination creates a few problems. First, the osmotic pressure is inversely proportional to molecular weight, so molecules with a high molecularweight contribute very little. Therefore, the sample must be free of low molecular compounds when applying osmometry. This is especially true for salts and, therefore, for aqueous cellulose solutions. This is the main reason that osmometry is ordinarily used with cellulose derivatives in organic solvents.

In most cases, cellulose-based membranes such as cellophane or bacterial cellulose are used for membrane osmometry. However, these membranes are not completely resistant against solvents used for cellulose. Hence, the usual cellophane membrane gels which are used in an osmometer would dissolve in, for example, cuen solutions.

Working with those membranes, they measured the molecular weights of two cellulose samples directly. Since cellulose in cuen behaves as a polyelectrolyte, they faced another problem beyond membrane instability. However, by proper conditioning of the membranes, the polyelectrolyte character of the solution can be compensated and allow for a valid measurement. Immergut's paper is one of the few dealing with the direct osmometry of pure cellulose.

This method continues to play a minor role today, even for derivatized cellulose.

It is worth noting that osmometry was originally used to determine the relationship between intrinsic viscosity and molecular weight. It has been shown that under mild conditions, the degradation during cellulose nitration is negligible. In his pioneering work, Staudinger used the osmometry of cellulose nitrates in acetone to determine the constant $Kcm$of the Staudinger Equation:

$$\log \eta_r = K_{cm} * M * c$$

where$\eta r$is the relative viscosity (see Chapter 2.4), M is the molecular weight, and $Kcm$is the molecular weight-concentration constant. The Staudinger equation was later the basis for the Mark-Houwinkequation (see Chapter 2.4).

Using VPO instruments with increased sensitivity, Kamide*et al*. detected an upper limit of 1 × 105 g·mol^{-1}. Compared with the results for cellulose acetate obtained by MO and SEC, VPO values differed by only a small percentage.

Ultracentrifugation

When polymer chemistry was in its early stages in the 1920s, analytical ultracentrifugation experiments played an important role. Svedberg introduced two analytical ultracentrifugation methods: the sedimentation velocity method and the sedimentation equilibrium method [56]. The sedimentation velocity method (performed at, for example, 70,000 RPM) provides information on the physical homogeneity of a sample, its conformation, interaction or co-sedimentation, and flexibility information.

The sedimentation equilibrium, which is carried out at lower rotor speeds such as 15,000 RPM, yields information on absolute weight averages (*Mw*, and *Mz*) and molecular weight distributions.

Ultracentrifugation is also capable of measuring the molecular charge in polysaccharides. Diffusion parameters can also be obtained by ultracentrifugation experiments; however, strictly speaking, diffusion has nothing to do with ultracentrifugation, though it is very closely connected to the theoretical and practical background. See Vollmert [57] for a detailed theoretical discussion.

The first studies of cellulose in which ultracentrifugation was used were performed by Stamm between 1926 and 1930. Stamm investigated cellulose dissolved in cuprammonium (tetraaminecopper(II) sulfate) and cellulose xanthogenate in diluted alkali solutions. He and his coworkersinvestigated the state of dispersion of cellulose in cuprammonium solutions. They found diffusioncoefficients of cellulose and also claimed that cellulose was uniform with a molecular weight of 55,000 ± 7000 $g \cdot mol^{-1}$. However, they realized that under an oxygen atmosphere, the cellulose is degraded.

A typical equilibrium run time was 190 h; therefore, severe degradation of the molecule during the measurements can be assumed.

Gralén and Svedberg measured cellulose in cuprammonium solutions under a nitrogen atmosphere.

In the area of synthetic polymers, ultracentrifugation experiments have been nearly completely replaced by other techniques. For biopolymers, especially cellulose, ultracentrifugation still plays a minor role in analytics. Two recent review articles published by Harding *et al.* discuss the possibilities of ultracentrifugation experiments in polysaccharide analysis today; especially in combination with SEC and MALLS, it can provide complementary information such as the heterogeneity of materials. Like SEC-MALLS, the sedimentation equilibrium method provides a molecular weight distribution, although there is no column or separation device and therefore no limitations concerning the column’s medium inertness or available pore sizes.

Today, the ultracentrifuge is used to obtain fundamental biophysical information about solutions of cellulose rather than to determine molecular weight. In his perspective papers, however, Harding demonstrated that sedimentation equilibrium is a powerful and valuable independent check on the results generated with other methods such as SEC-MALLS experiments.

Viscosity Method

Polymers are, in general, less soluble than their corresponding monomers. Dissolving polymers in solvents leads to an increase in viscosity; the longer the average chain length of the polymer molecules, the more the viscosity changes (known as positive viscosity). The viscosity of a solution can be easily measured; therefore, viscosity measurements are widely used in determining the average DP of cellulose.

In 1930, Hermann Staudinger was the first to recognize an empirical relationship between the relative magnitude of the increase in viscosity and the molecular weight of the polymer [27]. The simplest method for determining the viscosity of a polymer solution is by capillary viscometry, using the Ubbelohde U-tube viscometer. Here, the flow time t of the polymer solution and of pure solvent $t_0$are recorded. The ratio of the flow time of a polymer solution t to that of pure solvent is equal to the ratio of their viscosities ($\eta/\eta 0$) if their densities are equal. This is only feasible for dilute solutions (in which density differences level out). Because unity is the lower limit of the relative viscosity η*r*, the specific viscosity η*sp*is more useful, as it depicts the relative increase brought about by the dissolved polymer.

Relating the specific viscosity to concentration gives the reduced viscosity. The intrinsic viscosity is expressed as the limit of the reduced viscosity at zero concentrations. The inherent viscosity is given as the natural logarithm of the relative viscosity divided by the concentration. At concentration zero the inherent viscosity becomes equal to the intrinsic viscosity. Thus, either the extrapolation of the reducedviscosity or the inherent viscosity gives the intrinsic viscosity:

$$\text{Relative Viscosity: } \eta_r = \frac{\eta}{\eta_0}$$

$$\text{Specific Viscosity: } \eta_{sp} = \frac{\eta - \eta_0}{\eta_0} = \eta_r - 1$$

$$\text{Reduced Viscosity: } \eta_{red} = \frac{\eta_{sp}}{c}$$

$$\text{Intrinsic Viscosity: } [\eta] = \lim_{c \to 0} \frac{\eta_{red}}{c}$$

$$\text{Inherent Viscosity: } \eta_{inh} = \frac{\ln \eta_r}{c}$$

For a given polymer-solvent pair the intrinsic viscosity is a unique function of molecular mass. The Mark-Houwink (or Kuhn-Mark-Houwink-Sakurada) equation then relates the molecular weight of the polymer plus solvent at a specified temperature to the intrinsic viscosity

$$[\eta] = K_v M^v$$

Kv(or sometimes *KM*) and *v* (sometimes notated *a*) must be established by calibrating with polymers of known molecular weights. Once this has been performed, only [η] will give the molecular weight for an unknown molecule, which is normally done by plotting log [η] against log *M* and subsequent interpolation.

For a theta solvent, *v* = 0.5, and as the solvent becomes thermodynamically better, *v* increases. For most practical systems, these values can be found in data handbooks. The extrapolation factors for cellulose to zero concentration are also listed. Under these assumptions, it is possible to calculate the intrinsic viscosity by measuring only one concentration of the sample. Molecular weights derived via the

Mark-Houwink equation and viscometry yield the viscosity average molar mass [*Mv*], which is given by:

$$M_v = \left[\frac{\sum n_i M_i^{1+v}}{\sum n_i M_i}\right]^{1/v}$$

where*ni*is the number of molecules of molar mass *Mi*and the exponent *v* is the exponent of the Mark-Houwink equation. It should be noted that the viscosity average is not an absolute average and depends on solvent and/or temperature; therefore, viscosity measurements yield relative values. *Mv*is not a fixed quantity—it depends on *v*. If *v* becomes unity, viscosity and weight average are equal; *Mv*lies therefore, in between *Mn* and *Mw* in magnitude but will be usually closer to *Mw*.

Viscometry is the leading method for determining average molecular weight in industrial applications. As a standalone method, it delivers *Mv*values, typically by using an Ubbelohde capillary viscometer. In industrial applications, the measurement of [η] provides a quick and easy route to the molecular weight. For viscosity measurements, a minimum requirement is the knowledge of the dependence of [η] *on* (*M*).

The solvent most commonly used for viscometry measurements is the complex-forming solvent cuen, largely because of its rapidity and simplicity in dissolving cellulose. One drawback of cuen lies in the cuen solution's high alkalinity, which may induce degradation reactions at oxidized functionalities.

Cellulose solutions in cuen are not very stable, and the solubility for cellulose with high molecular weight (DP > 5000) is relatively poor.

Viscometry was actually one of the first methods used to determine polymer molecular weights.

It was Hermann Staudinger who applied viscometry to cellulose analytics in the 1930s. Staudinger described the *Km* value (for the Staudinger equation) of cellulose in cuen with 1×10^{-4}; in 1938 he published the *Km* values for cellulose in Schweizer's Reagent as 5×10^{-4}.

It is important to remember that *Kv*and *v* are empirical constants. There are several standard methodsfor estimating the degree of polymerization of a cellulose sample from its intrinsic viscosity in cuensolution. In process control practices in industrial environments, the intrinsic viscosity is often estimated from a single viscosity measurement. There are several published warnings when using such standard methods. Evans *et al*. showed that the Mark-Houwink-Sakurada (MHS) equations used in the SCAN.

The relationship between intrinsic viscosity and the DP (or the molecular weight) is very often derived from osmometric measurements of cellulose trinitratesamples in acetone. Such measurements date back to very early experiments and should be evaluated with modern methods. It is commonly assumed that the molecular weight average determined by viscosity is very close to *Mw* and that *Mv*therefore is an approximation of *Mw*. In fact, *Mv*can often be very far from *Mw*, depending on the MHS parameters used and on the molecular weight distribution of the sample. Only if the sample is very narrowly distributed or if uniform standards are used can *Mv*be used as an approximation of *Mw*. MHS parameters found in the literature can be excessively variable, with *Kv*values ranging from 0.42 to 1.87 and *v* values ranging from 0.771 to 0.905.

In spite of these factors, viscometry remains a primary method for obtaining cellulose molecular weight averages because it does not require calibration. It is also a feasible method for monitoring cellulose degradation during process steps, which results in relative data. This is mainly because it does not require advanced equipment, the method is relatively simple, and it is specifically recommended by industrial standards. It is essential to remember that the parameters for the Mark-Houwink equations arespecified for cellulose and that it is problematic to use such parameters for samples with, for example, high lignin or hemicellulose content.

The equations also depend on the expected DP range; a DP larger than 950 requires a different equation than the equation used for lower DPs. According to the current knowledge, there is no equation available for cellulose with a large oligomeric portion, so the cuen-DP values in such cases may be prone to error. It is standard practice to use linear fits for data when drawing a *log* [*n*]-*log Mw* plot. In general, there is no justification for the linearity, and it is questionable whether such fits are applicable forcellooligomers or samples containing oligomers in such high amounts.

Thus far, most Mark-Houwink equations for cellulose were established for cellulose in cuen or cadoxen solutions [68–70] because these solvents demonstrate beneficial properties for the rapid dissolution of cellulose. However, the instability of cellulose in this solvent must be noted, as should the limited dissolving power for very large molecules.

. The viscosity of cellulose in NMMO, a very important solvent within the technology sector, was first measured by Eckelt*et al*., who reported the following equation

$$\boxed{log\ (\frac{[\eta]}{\mathrm{ml} * g^{-1}}) = -1.465 + 0.735\ log\ M}$$

The Kuhn Mark-Houwink plot for cellulose in NMMO·H2O shows a non-linear behavior of the fit. After reaching a critical value, the straight line deviates. Thus far, this study is the only paper in which the cellulose viscosity in NMMO solutions is addressed. For analytical purposes, this solvent system has no practical importance because of the elevated temperature it requires.

Light Scattering Methods

Scattering methods are some of the most popular methods for determining molecular weight averages *Mw*. The fundamentals of the light scattering phenomena were expounded by Lord Rayleigh in 1871.

Light scattering (LS) is one of the few absolute methods that provide access to molecular weight and structure. Light scattering is often used as a tandem technique together with separation using SEC [74]. As a standalone technique, it delivers the weight average *Mw*, the corresponding z-average square radii $< r_2 g > z$, and the second virial coefficient *A*2 of cellulose. Since it is an absolute method, it does not require calibration. One limitation of the LS method is that for a given concentration *c* (g·mL^{-1}), the scattered light signal is proportional to *c* × *Mw*, such that molecules below a few thousand g·mol^{-1}need relatively high concentrations in order to produce a detectable signal. Raising the concentration of, for example, a broad distributed sample, leads to problems, especially in the SEC portion of the process in which cellulose is analyzed. Dust will also scatter light and contribute to the intensity; therefore, dust has to be removed using ultra-fine filters or centrifugation prior to measurements. The source of radiation is, in most cases, visible light from a laser; therefore, using colored solvents (e.g., Cu- and Fe-containing complexes) is challenging and cellulose is often derivatized and dissolved in an organic solvent or colorless solvent instead. Thus far, DMAc/LiCl is the solvent of choice for an LS experiment coupled to an SEC.

Measuring cellulosic samples with fluorescence activity (e.g., pulp with high lignin content) also poses some challenges. Due to the laser excitation, even small amounts of fluorophores will disrupt a measurement. There are two types of LS experiments: the batch mode and the chromatographic (online) measurement. In the batch mode (off-line), MALLS detector can be used as a standalone instrument to characterize an unfractionated polymer sample; the online use of an LS detector is described in

In this static light scattering experiment (SLS), a vertically polarized (laser) light is scattered by the macromolecules of a polymer in solution. The scattered light is detected by a photometer or a photodiode: either one photometer is used to encircle the sample in a horizontal plane or several photodiodes are placed around the measurement cell, which detects the scattered light from several positions and angles.

The ratio:

$$R_\theta = \frac{I_{scattered}}{I_{incident}}$$

depends on:

- The concentration of solution *c*;
- The specific refractive increment obtained at chemical equilibrium *dn*/*dc* or, more accurately, (*dn*/*dc*)μ;
- The molecular weight of dissolved particles (*M*);
- Scattering angle θ.

The scattering intensity is dependent on the angle and reflects the diminution of the light intensity by intra-particular interference. For light scattering experiments, the Zimm equation forms for calculating the molecular weight:

$$\frac{K^* c}{R(\theta, c)} = \frac{1}{M_w P(\theta)} + 2A_2 c$$

Where *K** is the optical constant, *R*(θ, *c*) is the excess Rayleigh ratio of the solution as a function ofscattering angle θ and concentration *c*, *Mw* is the molar mass weight average, *P*(θ) is the angular dependence of the scattered light, *A*2 is the second virial coefficient, and *c* is the concentration of the solute.

The optical constant is described by the following equation:

$$K^* = \frac{4 * \pi^2 (dn/dc)^2 n_0^2}{N_a \lambda_0^4}$$

Where *dn*/*dc* is the specific refractive increment at chemical equilibrium, *Na* is the Avogadro's Number, λ_0 is the wavelength of the incident light, and *n*0 is the solvent refractive index.

The measured data can be extrapolated to zero concentration and zero-degree scattering angle, which can be achieved for the batch mode by using the so-called Zimm-plot to derive three valuable quantities: the weight average *Mw*, the second virial coefficient of osmotic pressure *A*2 (both with extrapolation to zero angle), and the radius of gyration (z-average) by extrapolating the concentration to zero. The specific refractive increment at chemical equilibrium must be measured separately by using a differential refractometer.

Polymer morphology

Polymer morphology generally describes the arrangement and microscale ordering of polymer chains in space.

Crystallinity

When applied to polymers, the term *crystalline* has a somewhat ambiguous usage. In some cases, the term *crystalline* finds identical usage to that used in conventional crystallography. For example, the structure of a crystalline protein or polynucleotide, such as a sample prepared for xray crystallography, may be defined in terms of a conventional unit cell composed of one or more polymer molecules with cell dimensions of hundreds of angstroms or more.

A synthetic polymer may be loosely described as crystalline if it contains regions of three-dimensional ordering on atomic (rather than macromolecular) length scales, usually arising from intramolecular folding and/or stacking of adjacent chains. Synthetic polymers may consist of both crystalline and amorphous regions; the degree of crystallinity may be expressed in terms of a weight fraction or volume fraction of crystalline material. Few synthetic polymers are entirely crystalline.

The crystallinity of polymers is characterized by their degree of crystallinity, ranging from zero for a completely non-crystalline polymer to one for a theoretical completely crystalline polymer. Polymers with microcrystalline regions are generally tougher (can be bent more without breaking) and more impact-resistant than totally amorphous polymers.

Polymers with a degree of crystallinity approaching zero or one will tend to be transparent, while polymers with intermediate degrees of crystallinity will tend to be opaque due to light scattering by crystalline or glassy regions. Thus for many polymers, reduced crystallinity may also be associated with increased transparency.

Chain conformation

The space occupied by a polymer molecule is generally expressed in terms of radius of gyration, which is an average distance from the center of mass of the chain to the chain itself. Alternatively, it may be expressed in terms of pervaded volume, which is the volume of solution spanned by the polymer chain and scales with the cube of the radius of gyration.

Phase behavior

Melting point

The term *melting point*, when applied to polymers, suggests not a solid–liquid phase transition but a transition from a crystalline or semi-crystalline phase to a solid amorphous phase. Though abbreviated as simply T_m, the property in question is more properly called the crystalline melting temperature. Among synthetic polymers, crystalline melting is only discussed with regards to thermoplastics, as thermosetting polymers will decompose at high temperatures rather than melt.

Glass transition temperature

A parameter of particular interest in synthetic polymer manufacturing is the glass transition temperature (T_g), at which amorphous polymers undergo a transition from a rubbery, viscous liquid, to a brittle, glassy amorphous solid on cooling. The glass transition temperature may be engineered by altering the degree of branching or crosslinking in the polymer or by the addition of plasticizer

Glass transition

The **glass–liquid transition** or **glass transition** for short is the reversible transition in amorphous materials (or in amorphous regions within semicrystalline materials) from a hard and relatively brittle "glassy" state into a viscous or rubbery state as the temperature is increased. An amorphous solid that exhibits a glass transition is called a glass. The reverse transition, achieved by supercooling a viscous liquid into the glass state, is called vitrification.

The **glass-transition temperature** T_g of a material characterizes the range of temperatures over which this glass transition occurs. It is always lower than the melting temperature, T_m, of the crystalline state of the material, if one exists.

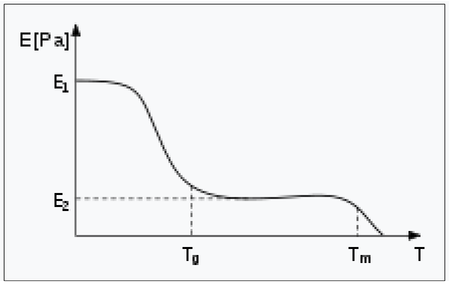
Hard plastics like polystyrene and poly(methyl methacrylate) are used well below their glass transition temperatures,that is in their glassy state. Their T_g values are well above room temperature, both at around 100 °C (212 °F). Rubber elastomers like polyisoprene and polyisobutylene are used above their T_g, that is, in the rubbery state, where they are soft and flexible.

Despite the change in the physical properties of a material through its glass transition, the transition is not considered a phase transition; rather it is a phenomenon extending over a range of temperature and defined by one of several conventions. Such conventions include a constant cooling rate (20 kelvins per minute (36 °F/min)) and a viscosity threshold of 10^{12} Pa·s, among others. Upon cooling or heating through this glass-transition range, the material also exhibits a smooth step in the thermal-expansion coefficient and in the specific heat, with the location of these effects again being dependent on the history of the material.

Relationship between T_g and T_m

In polymers the glass transition temperature, T_g, is often expressed as the temperature at which the Gibbs free energy is such that the activation energy for the cooperative movement of 50 or so elements of the polymer is exceeded. This allows molecular chains to slide past each other when a force is applied. From this definition, we can see that the introduction of relatively stiff chemical groups (such as benzene rings) will interfere with the flowing process and hence increase T_g. The stiffness of thermoplastics decreases due to this effect (see figure.) When the glass temperature has been reached, the stiffness stays the same for a while, i.e., at or near E_2, until the temperature exceeds T_m, and the material melts. This region is called the rubber plateau.

In ironing, a fabric is heated through this transition so that the polymer chains become mobile. The weight of the iron then imposes a preferred orientation. T_g can be significantly decreased by addition of plasticizers into the polymer matrix. Smaller molecules of plasticizer embed themselves between the polymer chains, increasing the spacing and free volume, and allowing them to move past one another even at lower temperatures. The "new-car smell" is due to the initial outgassing of volatile small-molecule plasticizers (most commonly known as phthalates) used to modify interior plastics (e.g., dashboards) to keep them from cracking in the cold of winter weather. The addition of nonreactive side groupsto a polymer can also make the chains stand off from one another, reducing T_g. If a plastic with some desirable properties has a T_g that is too high, it can sometimes be combined with another in a copolymer or composite material with a T_g below the temperature of intended use. Note that some plastics are used at high temperatures, e.g., in automobile engines, and others at low temperatures.



Stiffness versus temperature

In viscoelastic materials, the presence of liquid-like behavior depends on the properties of and so varies with rate of applied load, i.e., how quickly a force is applied. The silicone toy Silly Putty behaves quite differently depending on the time rate of applying a force: pull slowly and it flows, acting as a heavily viscous liquid; hit it with a hammer and it shatters, acting as a glass.

On cooling, rubber undergoes a *liquid-glass transition*, which has also been called a *rubber-glass transition*.

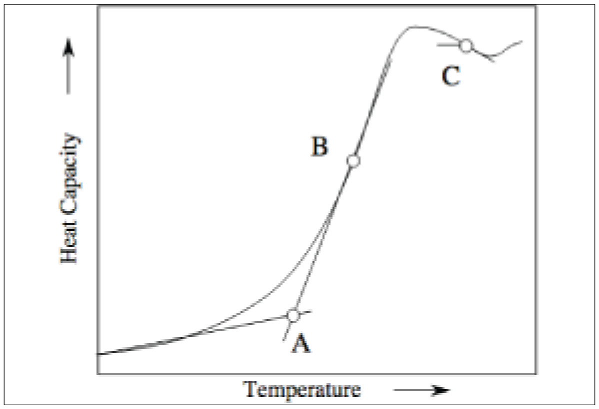
Determination of T_g

The glass transition temperature (Tg) of a polymer adhesive is actually a range of temperatures during which the solid polymer material experiences some substantial changes in its physical properties (transitions from glassy to rubbery solid).

Differential Scanning Calorimetry (DSC)

The basic concept of this method is that as a polymer transitions from a glassy to a rubbery state, one of the physical properties of the material that substantially changes is its heat capacity - the amount of heat it takes to raise the temperature of the material by one degree.

A DSC gradually adds more and more heat to a sample of a polymer material and at the same time measures how much the material changes its temperature as a result. When the polymer reaches the lower end of its glass transition temperature its heat capacity will spike up and the DSC will use this information to ultimately estimate the glass transition temperature of the material (Tg is point B on the graph below).



Estimating the Tg of a material using a DSC is a cost effective method, however, it is not always accurate. Many materials will only have a small increase in heat capacity, making the transition hard to identify.

Thermo Mechanical Analysis (TMA)

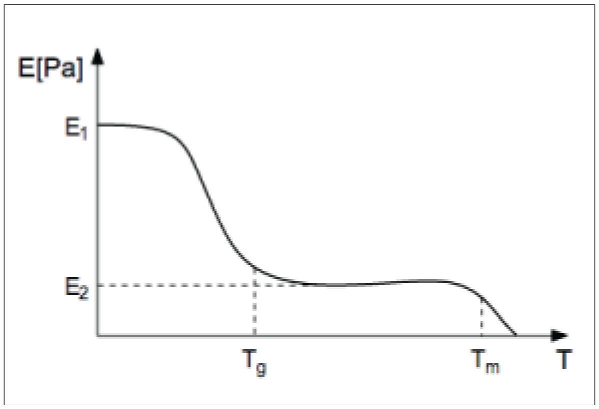
TMA estimates the glass transition temperature of a material by tracking its coefficient of thermal expansion (CTE). In many cases the CTE of a polymer material will increase 3-5x as it transitions from the glassy to the rubbery state.

Similar to DSC testing, TMA involves slowly adding heat to a sample material and simulataneously tracking changes in physical properties. In the case of TMA, the physical dimensions of the material are tracked and the Tg is identified as the temperature where there is a dramatic change in these dimensions.

TMA testing is slightly more involved than DSC testing, however, this method generally yields more accurate results.

Dynamic Mechanical Analysis (DMA)

One of the most immediate and obvious differences between a glassy and a rubbery material is of course the stiffness. DMA testing uses this fundmental physical differentiator as a guide and tracks the stiffness of a polymeric material over a range of temperatures in order to determine its Tg. The graph below plots stiffness vs. temperature and points out



"Rubber plateau"

This method is extremely accurate and sensitive, however, is also very time consuming and costly compared to the other two methods described.

Text book:

T1: Gowariker, V. R., N. V. Viswanathan and J. Sreedhar, 1986. Polymer Science, *New Age International* Private Ltd., New Delhi.

T2: Billmeyer, F.W., 2003. Text Book of Polymer Science. III Edition, John Wiley, New York.

Reference book

R1: M.S Bhatnagar,2004, " A text book of polymers". Ist Edition, S.Chand & Company.

POSSIBLE QUESTIONS

Multiple choice questions (Each carry 1 Marks)

1. The freezing point depression depends on the
   a. Number of dissolved solutes b. Average weight of solute **c. Size and nature of solute**
   d. solvent nature
2. The difference temperature between the freezing point of solute and solvent in the range of
   a. 10ºC b. 0.01ºC **c. 0.001ºC** d. 0.1ºC
3. By this method, accurately determine the molecular weights upto
   a. 10,000 b. 20,000 **c. 30,000** d. 50,000
4. The method based on observation of boiling point of a solution and solvent is known as
   a. cryoscopic **b. Ebuliometry** c. membarane Osmometry
   d. Equlibrium Osmometry
5. $\sum_{i=1}^{\alpha} N_i$ the equation belongs to
   a. **Number-average concept** b. Weight average concept c. Viscosity concept
   d. Osmostric concept
6. The weight average molecular degree of polymerisation indicates as
   a. D_p **b.** $\mathbf{(D_p)_w}$ c. $(D_p)_n$ d. D
7. A simple chemical compounds which have same molecular weight to form
   a. monodispersion b. bi dispersion c. poly dispersion d. polymer solution
8. The symbol $\bar{M}_v$ represents the
   a. Number-average molecular weight b. Weight average molecular weight
   c. Viscosity average molecular weight d. Vapour pressure molecular weight
9. A polymer contains different molecular weight compounds to form
   a. monodispersion b. bi dispersion **c. poly dispersion** d. polymer solution
10. The symbol $\bar{M}_w$ represents the
    a. Number-average molecular weight **b. Weight average molecular weight**
    c. Viscosity average molecular weight d. Vapour pressure molecular weight
11. The symbol $\bar{M}v$ represents the
    a. Number-average molecular weight b. Weight average molecular weight
    c. Viscosity average molecular weight d. Vapour pressure molecular weight
12. The phenomenon of depressing the freezing point of a liquid by the addition of solute is known as
    a. Cryoscopy b. Ebuliometry c. Osmometry d. Vapour phase Osmometry
13. The freezing point depression depends on the
    a. Number of dissolved solutes b. Average weight of solute **c. Size and nature of solute**
    d. solvent nature
14. The difference temperature between the freezing point of solute and solvent in the range of
    a. 10ºC b. 0.01ºC **c. 0.001ºC** d. 0.1ºC
15. By this method, accurately determine the molecular weights upto
    a. 10,000 b. 20,000 **c. 30,000** d. 50,000
16. The method based on observation of boiling point of a solution and solvent is known as
    a. cryoscopic **b. Ebuliometry** c. membarane Osmometry
    d. Equlibrium Osmometry

17. [η], dl/g is equal to the
    a. specific viscosity b. reduced viscosity c. inherent viscosity **d. intrinsic viscosity**
18. The intrinsic viscosity is also known as
    a. specific viscosity b. reduced viscosity c. inherent viscosity **d. Staudinger viscosity**
19. The rpm maintained for minute in the sedimentation equilibrium method is
    a. 30,000 b. 50,000 c. 15,000 **d. 65,000**
20. The error occurred in the viscometer due to the measurement of
    a. level of solute b. density c. nature **d. flow time**

Questions (Each Carry 6 Marks)

1. How to calculate the molecular weight of the polymer based on the number average method. Explain anyone of its experimental method?
2. Give an account of viscosity methods?
3. How to calculate the molecular weight of the polymer based on viscocity?
4. Give an account of light scattering method?
5. How to calculate the molecular weight of the polymer based on the weight average method. Explain anyone of its experimental method?
6. Give an account of vapour phase osmometry methods?
7. How to determine the molecular weight by osmometry?
8. Give an account of viscosity methods?
9. How to calculate the molecular weight of the polymer by Cryoscopic and Ebuliometric method?
10. What are the difference between T_g and T_m?
11. What is Glass Transition Temperature? How to determine it experimently?

Compulsory Questions (Each Carry 10 Marks)

1. What is glass transition temperature and how will you determine the T_g by experimently?
2. How to calculate the polymer weight of the polymer based on weight average method?
3. What is number average method? Explain its experimental methods to determine the molecular weight of the polymers?

16CHP305A
Karpagam Academy of Higher Education
Coimbatore-21
(For the Candidates admitted on 2016 Onwards)
III-Semester
Polymer Chemistry

Questions	**Opt-1**	**Opt-2**	**Opt-3**	**Opt-4**	**Answers**
Unit 3- Objective questions for online examination (Each carry 1 mark)					
$\sum_{i=1}^{\infty} N_i$ the equation belongs to	Number-average concept	Weight average concept	Viscosity concept	Osmostric concept	Number-average concept
The weight average molecular degree of polymerisation indicates as	D_p	$(D_p)_w$	$(D_p)_n$	D	$(D_p)_w$
A simple chemical compounds which have same molecular weight to form	monodispersion	bi dispersion	poly dispersion	polymer solution	monodispersion
A polymer contains different molecular weight compounds to form	monodispersion	bi dispersion	poly dispersion	polymer solution	poly dispersion
The symbol $\dot{M}_n$ represents the	Number-average molecular weight	Weight average molecular weight	Viscosity average molecular weight	Vapour pressure molecular weight	Number-average molecular weight
The symbol $\dot{M}_w$ represents the	Number-average molecular weight	Weight average molecular weight	Viscosity average molecular weight	Vapour pressure molecular weight	Weight average molecular weight
The symbol $\dot{M}_v$ represents the	Number-average molecular weight	Weight average molecular weight	Viscosity average molecular weight	Vapour pressure molecular weight	Viscosity average molecular weight
The experiments based on viscosity yield the	Number-average molecular weight	Weight average molecular weight	Viscosity average molecular weight	Vapour pressure molecular weight	Viscosity average molecular weight
The phenomenon of depressing the freezing point of a liquid by the addition of solute is known as	Cryoscopy	Ebuliometry	Osmometry	Vapour phase Osmometry	Cryoscopy
The freezing point depression depents on the	Number of dissolved solutes	Average weight of solute	solvent concentration	solvent nature	Number of dissolved solutes
The freezing point depression not to depents on the	size and nature of solute	nature of solvent	number of solutes	weight of solvent	size and nature of solute
Cryoscopic method is applied to determine the	Weight average molecuar weight	Number-average molecular weight	Viscosity average molecular weight	Vapour pressure molecular weight	Number-average molecular weight
The freezing point of the solvent indicates the	F	T_F	T_f	T_s	T_f
ΔT_f is the difference of	freezing point between solute and solvent	freezing point of solutes	freezing point between solvent molecules	the temperature between solute and solvent	freezing point between solute and solvent
In the cryoscopic method, the error occurred to measure the	weight of monomer	temperature	freezing point	melting point	temperature
The difference temperature between the freezing point of solute and solvent in the range of	10ºC	0.01ºC	0.001ºC	0.1ºC	0.001ºC

By this method, accurately determine the molecular weights upto	10,000	20,000	30,000	50,000	30,000
The method based on observation of boiling point of a solution and solvent is known as	cryoscopic	Ebuliometry	membarane Osmometry	Equlibrium Osmometry	Ebuliometry
The Ebuliometry is a method based on the observation of	freezing point	boiling point	meltinf point	crystalline point	boiling point
The difference in the heat of vapourisation is indicates as	ΔHv	ΔSv	ΔTv	ΔGv	ΔHv
The T_b is the symbol for	freezing point of solvent	boiling point of solvent	meltinf point of solvent	crystalline point of solvent	boiling point of solvent
The osmosis based method is known as	membrane osmometry	Ebuliometry	Cryoscopic	Viscometry	membrane osmometry
The membrane osmometry method based on	freezing point	osmotic pressure	boiling point	crystaline point	osmotic pressure
In the membrane osmometry, the pressure applied to the solution should prevent	nature of solvent	flow of solvent	nature of solute	concentration of solvent	flow of solvent
The osmotic pressure is represented as	σ	Θ	μ	π	π
The osmotic pressure is related to the	Weight average molecuar weight	Number-average molecular weight	Viscosity average molecular weight	Vapour pressure molecular weight	Number-average molecular weight
The Ebuliomrtry method, the boiling point of solution is	higher than solvent	less than solvent	same to the solvent	decrease than solvent	higher than solvent
The Ebuliometry method is applicable for	volatile solute	non-volatile solute	ionised solute	low molecular weight solute	non-volatile solute
The solution and solvent levels are measured by using	cathetometer	anometer	thermometer	osmometry	cathetometer
The cathetometer is used to measure the	height of solute and solvent	density of solute and solvent	Viscosity of solute and solvent	concentration of solute and solvent	height of solute and solvent
1 atmosphere is equal to the	1033 g wt/cm^2	1110 g wt/cm^2	1200 g wt/cm^2	1040 g wt/cm^2	1033 g wt/cm^2
The membrane osmometry is used to measure the molecular weight in the range of	30,000	30,000 to 40,000	30,000 to 1000000	50,000 to 100000	30,000 to 1000000
The vapour pressure of a solution is --- than pure solvent	more	less	same	constant	less
The total rise in temperature is proportional to the	molecular weight	mole fraction of solute	number of solutes	nature of solute	mole fraction of solute
The ratio between the functionality divided by functional group equivalent is known as	$\dot{M}_n$	$\dot{M}_w$	$\dot{M}_v$	$\dot{M}_s$	$\dot{M}_n$
The viscosity of the polymer solution is high compared to	solute	solvent	monomer	catalyst	solvent
The relative viscosity is equal to the	$\eta/\eta_0 = t/t_0 = \eta_r$	η_{sp}	η_{red}	$\ln \eta_r / C$	$\eta/\eta_0 = t/t_0 = \eta_r$
The specific viscosity is equal t the	$\eta_r - 1$	η_r	η_{red}	$\ln \eta_r / C$	$\eta_r - 1$
The reduced viscosity is equal to the	$\eta_{sp} / C = \eta_{red}$	$\eta_r - 1$	η_r	$\ln \eta_r / C$	$\eta_{sp} / C = \eta_{red}$
$\ln \eta_r / C$ is the	specific viscosity	reduced viscosity	inherent viscosity	intrinsic viscosity	inherent viscosity

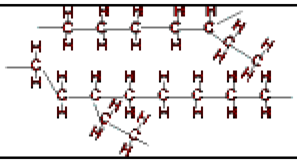
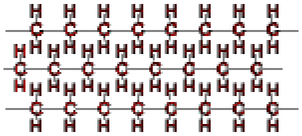
[η], dl/g is equal to the	specific viscosity	reduced viscosity	inherent viscosity	intrinsic viscosity	intrinsic viscosity
The intrinsic viscosity is also known as	specific viscosity	reduced viscosity	inherent viscosity	Staudinger viscosity	Staudinger viscosity
The limiting viscosity number known as	specific viscosity	reduced viscosity	inherent viscosity	intrinsic viscosity	intrinsic viscosity
The USLV is the	osmometer	viscometer	cathetometer	speedometer	viscometer
The viscosity highly depends on the	temperature	density	size	nature	temperature
The range of constant temperature maintained at viscometer is	0.01ºC	± 0.001ºC	± 0.1ºC	± 0.01ºC	± 0.01ºC
The error occurred in the viscometer dur to the measurement of	level of solute	density	nature	flow time	flow time
All the solutions are free from impurities, it reduces the	Number of dissolved solutes	yield	error	density	error
Which one of the following is most complex method	viscometry	osmometry	ultracentrifugation	light scattering	ultracentrifugation
In the ultracentrifugation, which force is used for polymer separation	kinetic force	magnetic force	centrifugal force	vanderwalls force	centrifugal force
The sedimentation velocity depends on the	nature of polymer	size of polymer	molecular weight	number of solute	molecular weight
The sedimentation velocity method has ----- revolution per minute	30,000	60,000	65,000	50,000	65,000
The symbol ω represents the	angular viscosity	pressure	angular moment	angular velocity	angular velocity
The sedimentation constant is denoted as	ω_0	S_0	A_0	C_0	S_0
The molecular weight distribution form a heterogenous system in the	sedimentation velocity method	sedimentation viscosity method	sedimentation equilibrium method	Osmometric method	sedimentation equilibrium method
The sedimentation equilibrium method is one of the	easy method	time consumuing	low cost	accurate	time consumuing
The rpm maintained for minute in the sedimentation equilibrium method is	30,000	50,000	15,000	65,000	15,000
The symbol $i_\Theta$is the equation $R_e = \frac{i_\theta r^2}{I_0 V}$	intensity of scattered light	intensity of incident light	intensity of solvent	intensity of both solute and solvent	intensity of scattered light
The symbol ţ is equal to the	viscosity	velosity	turbidity	density	turbidity

Unit-4

Polymer Processing

Polymer Processing: Plastics, elastomers and fibres. Compounding, processing techniques: calendering, die casting, rotational casting, film casting, injection moulding, blow moulding extrusion, moulding, thermoforming, foaming, reinforcing and fibre spinning.

Plastics- Introduction

Property	Low Density Polyethylene (LDPE)	High Density Polyethylene (HDPE)
Melting Point	~115^{o}C	~135^{o}C
Crystallinity	low crystallinity (50-60% crystalline) Main chain contains many side chains of 2-4 carbon atoms leading to irregular packing and low crystallinity (amorphous)	highly crystalline (>90% crystalline) contains less than 1 side chain per 200 carbon atoms in the main chain leading to long linear chains that result in regular packing and high crystallinity
Flexibility	more flexible than HDPE due to lower crystallinity	more rigid than LDPE due to higher crystallinity
Strength	not as strong as HDPE due to irregular packing of polymer chains	strong as a result of regular packing of polymer chains
Heat Resistance	retains toughness & pliabilty over a wide temperature range, but density drops off dramatically above room temperature.	useful above 100^{o}C
Transparency	good transparency since it is more amorphous (has non-crystalline regions) than HDPE	less transparent than LDPE because it is more crystalline
Density	0.91-0.94 g/cm^{3} lower density than HDPE	0.95-0.97 g/cm^{3} higher density than LDPE
Chemical Properties	chemically inert Insolvent at room temperature in most solvents. Good resistance to acids and alkalis. Exposure to light and oxygen results in loss of strength and loss of tear resistance.	chemically inert
Schematic diagram		
Uses	sandwich bags, cling wrap, car covers, squeeze bottles, liners for tanks and ponds, moisture barriers	freezer bags, water pipes, wire and cable insulation, extrusion coating

	in construction	

Elastomer

An **elastomer** is a polymer with viscoelasticity (having both viscosity and elasticity) and very weak inter-molecular forces, generally having low Young's modulus and high failure strain compared with other materials.[1] The term, which is derived from *elastic polymer*, is often used interchangeably with the term rubber, although the latter is preferred when referring to vulcanisates. Each of the monomers which link to form the polymer is usually made of carbon, hydrogen, oxygen or silicon. Elastomers are amorphous polymers existing above their glass transition temperature, so that considerable segmental motion is possible. At ambient temperatures, rubbers are thus relatively soft (E~3MPa) and deformable. Their primary uses are for seals, adhesives and molded flexible parts. Application areas for different types of rubber are manifold and cover segments as diverse as tires, shoe soles, and damping and insulating elements.

Rubber like solids with elastic properties are called elastomers. Polymer chains are held together in elastomers by weak intermolecular forces. These weak binding forces permit the polymers to be stretched. Natural rubber, neoprene rubber, buna-s and buna-n are elastomers.

Fibres

Fiber

A bundle of optical fibers

Fiber or **fibre** (from the Latin fibra[1]) is a natural or synthetic substance that is significantly longer than it is wide.[2] Fibers are often used in the manufacture of other materials. The strongest engineering materials often incorporate fibers, for example carbon fiber and ultra-high-molecular-weight polyethylene.

Synthetic fibers can often be produced very cheaply and in large amounts compared to natural fibers, but for clothing natural fibers can give some benefits, such as comfort, over their synthetic counterparts.

Compounding

Pharmaceutical compounding (done in **compounding pharmacies**) is the creation of a particular pharmaceutical product to fit the unique need of a patient. To do this, compounding pharmacists combine or process appropriate ingredients using various tools. This may be done for medically necessary reasons, such as to change the form of the medication from a solid pill to a liquid, to avoid a non-essential ingredient that the patient is allergic to, or to obtain the exact dose(s) needed or deemed best of particular active pharmaceutical ingredient(s). It may also be done for more optional reasons, such as adding flavors to a medication or otherwise altering taste or texture. Compounding is most routine in the case of intravenous/parenteral medication, typically by hospital pharmacists, but is also offered by privately owned compounding pharmacies and certain retail pharmacies for various forms of medication. Whether routine or rare, intravenous or oral, etc., when a given drug product is made or modified to have characteristics that are specifically prescribed for an individual patient, it is known as **"traditional" compounding**.

Due to the rising cost of compounding and the shortage of drugs, many hospitals have shown a tendency to rely more upon large-scale compounding pharmacies to meet their regular requirement, particularly of sterile-injectable medications. When compounding is done on bulk production of a given formulation rather than patient-specific production, it is known as "non-traditional" compounding (which, as discussed below, is arguably not "compounding" but rather "manufacturing"). This development raises concerns about patient safety and makes a case for proper regulatory control and monitoring.

Roles

During research and development

Pharmaceutical compounding is a branch of pharmacy that continues to play the crucial role of drug development. Compounding pharmacists and medicinal chemists develop and test combinations of active pharmaceuticals and delivery systems for new pharmaceutical formulations so that the active ingredients are effective, stable, easy to use, and acceptable to patients. However, for actual clinical trials, production of drug products is generally considered *manufacturing* because *compounding* is typically defined as being for small batch or single individual patient production only.

Patients with unique or unusual medication needs

Physicians may prescribe an individually compounded medication for a patient with an unusual health need. This allows the physician to tailor a prescription to each individual. Compounding preparations are especially prevalent for:

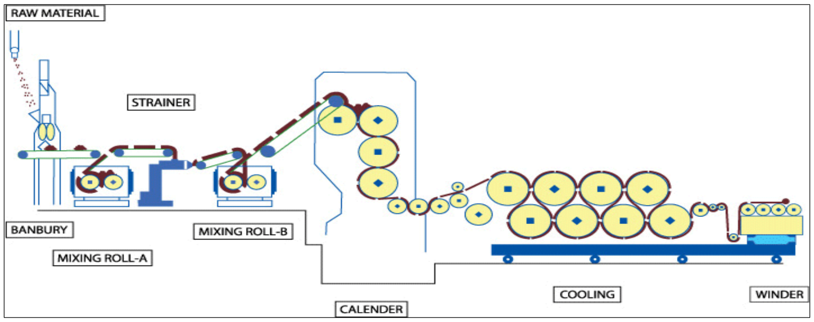
- Patients requiring an individualized compounded formulation to be developed by the pharmacist[4]
- Patients who cannot take commercially prepared prescriptions[4]
- Patients requiring limited dosage strengths, such as a very small dose for infants
- Patients requiring a different formulation, such as turning a pill into a liquid or transdermal gel for people who cannot swallow pills due to disability
- Patients requiring an allergen-free medication, such as one without gluten or colored dyes
- Patients who absorb or excrete medications abnormally[5]
- Patients who need drugs that have been discontinued by pharmaceutical manufacturers because of low profitability
- Patients facing a supply shortage of their normal drug

- Children who want flavored additives in liquid drugs, usually so that the medication tastes like candy or fruit
- Veterinary medicine, for a change in dose, change to a more easily administered form (such as from a pill to a liquid or transdermal gel), or to add a flavor more palatable to the animal. In the United States, compounded veterinary medicine must meet the standards set forth in the Animal Medicinal Drug Use Clarification Act (AMDUCA)
- Many types of bioidentical hormone replacement therapy

Polymer processing Techniques

Plastics are mainly organic polymers of high molecular mass, but they sometimes contain other substances as well. Plastics are usually synthetic, most commonly derived from petrochemicals, but many are partially natural. Plastics are usually classified by their chemical structure of the polymer's backbone and side chains. Some important groups in these classifications are the acrylics, polyesters, silicones, polyurethanes, and halogenated plastics. There are a variety of methods used to process plastic. Each method has its advantages and disadvantages and are better suited for specific applications. There are various plastic processing techniques.

1. *Calendering*



Calendering is a continuous process which works in much the same way as an old-fashioned clothes mangle. For plastics, there are usually four heated rollers of different sizes rotating at slightly different speeds. The material is fed into these rollers, heated and melted, then shaped into a sheet or film. This is then cooled and rolled up. The sheets can be mono-oriented during this process. The most commonly calendered material is PVC.

2. *Casting Process*

Casting is a manufacturing process in which a liquid material is usually poured into a mold, which contains a hollow cavity of the desired shape, and then allowed to solidify. The solidified part is also known as a *casting*, which is ejected or broken out of the mold to complete the process. Casting materials are usually metals or various *cold setting* materials that cure after mixing two or more components together; examples are epoxy, concrete, plaster and clay. Casting is most often used for making complex shapes that would be otherwise difficult or uneconomical to make by other methods.

1. **Die casting**
2. **Rotational casting**

3. **Film casting**

2.1 Die casting

Die casting is a metal casting process that is characterized by forcing molten metal under high pressure into a mold cavity. The mold cavity is created using two hardened tool steel dies which have been machined into shape and work similarly to an injection mold during the process. Most die castings are made from non-ferrous metals, specifically zinc, copper, aluminium, magnesium, lead, pewter and tin-based alloys. Depending on the type of metal being cast, a hot- or cold-chamber machine is used.

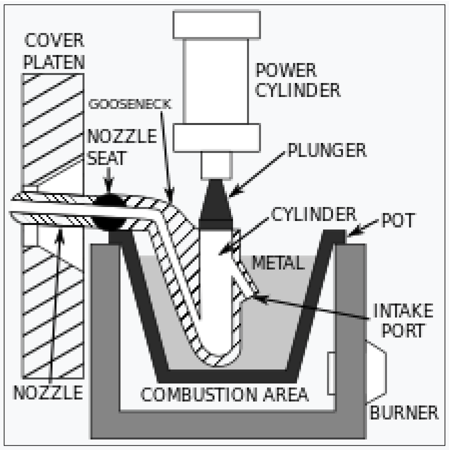
The casting equipment and the metal dies represent large capital costs and this tends to limit the process to high-volume production. Manufacture of parts using die casting is relatively simple, involving only four main steps, which keeps the incremental cost per item low. It is especially suited for a large quantity of small- to medium-sized castings, which is why die casting produces more castings than any other casting process. Die castings are characterized by a very good surface finish (by casting standards) and dimensional consistency.

Two variants are pore-free die casting, which is used to eliminate gas porosity defects; and direct injection die casting, which is used with zinc castings to reduce scrap and increase yield.

Equipment

There are two basic types of die casting machines: *hot-chamber machines* and *cold-chamber machines*. These are rated by how much clamping force they can apply. Typical ratings are between 400 and 4,000 st (2,500 and 25,400 kg).

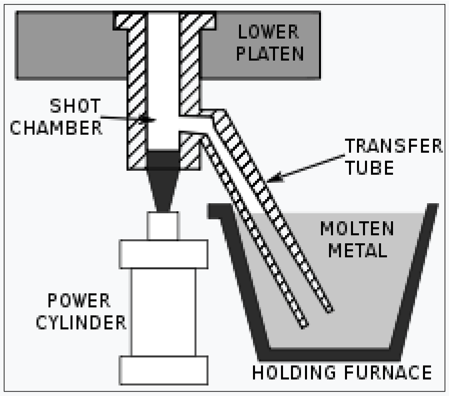
Hot-chamber die casting



Schematic of a hot-chamber machine

Hot-chamber die casting, also known as *gooseneck machines*, rely upon a pool of molten metal to feed the die. At the beginning of the cycle the piston of the machine is retracted, which allows the molten metal to fill the "gooseneck". The pneumatic- or hydraulic-powered piston then forces this metal out of the gooseneck into the die. The advantages of this system include fast cycle times (approximately 15 cycles a minute) and the convenience of melting the metal in the casting machine. The disadvantages of this system are that it is limited to use with low-melting point metals and that aluminium cannot be used because it picks up some of the iron while in the molten pool. Therefore, hot-chamber machines are primarily used with zinc-, tin-, and lead-based alloys.

Cold-chamber die casting



A schematic of a cold-chamber die casting machine.

These are used when the casting alloy cannot be used in hot-chamber machines; these include aluminium, zinc alloys with a large composition of aluminium, magnesium and copper. The process for these machines start with melting the metal in a separate furnace.[14]Then a precise amount of molten metal is transported to the cold-chamber machine where it is fed into an unheated shot chamber (or injection cylinder). This shot is then driven into the die by a hydraulic or mechanical piston. The biggest disadvantage of this system is the slower cycle time due to the need to transfer the molten metal from the furnace to the cold-chamber machine.

Advantages and disadvantages

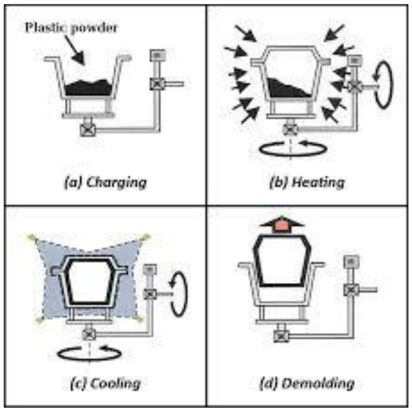
Advantages of die casting:

- Excellent dimensional accuracy (dependent on casting material, but typically 0.1 mm for the first 2.5 cm (0.005 inch for the first inch) and 0.02 mm for each additional centimeter (0.002 inch for each additional inch).
- Smooth cast surfaces (Ra 1–2.5 micrometres or 0.04–0.10 thou rms).
- Thinner walls can be cast as compared to sand and permanent mold casting (approximately 0.75 mm or 0.030 in).
- Inserts can be cast-in (such as threaded inserts, heating elements, and high strength bearing surfaces).
- Reduces or eliminates secondary machining operations.
- Rapid production rates.
- Casting tensile strength as high as 415 megapascals (60 ksi).
- Casting of low fluidity metals.

The main disadvantage to die casting is the very high capital cost. Both the casting equipment required and the dies and related components are very costly, as compared to most other casting processes. Therefore, to make die casting an economic process, a large production volume is needed. Other disadvantages are that the process is limited to high-fluidity metals, and casting weights must be between 30 grams (1 oz) and 10 kg (20 lb). In the standard die casting process the final casting will have a small amount of porosity. This prevents any heat treating or welding, because the heat causes the gas in the pores to expand, which causes micro-cracks inside the part and exfoliation of the surface. Thus a related disadvantage of die casting is that it is only for parts in which softness is acceptable. Parts needing hardening (through hardening or case hardening) and tempering are not cast in dies.

2.2 Rotational Casting

Rotational Molding (BrE **moulding**) involves a heated hollow mold which is filled with a charge or shot weight of material. It is then slowly rotated (usually around two perpendicular axes), causing the softened material to disperse and stick to the walls of the mold. In order to maintain even thickness throughout the part, the mold continues to rotate at all times during the heating phase and to avoid sagging or deformation also during the cooling phase. The process was applied to plastics in the 1940s but in the early years was little used because it was a slow process restricted to a small number of plastics. Over the past two decades, improvements in process control and developments with plastic powders have resulted in a significant increase in usage.

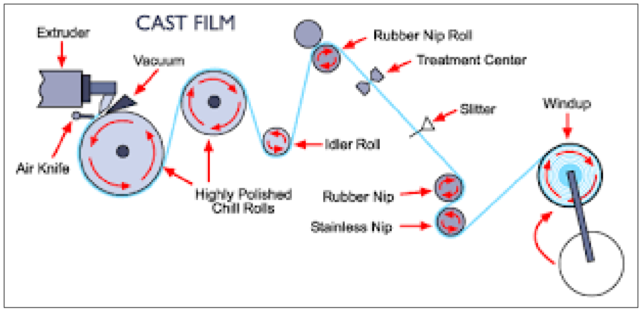


Rotocasting (also known as rotacasting), by comparison, uses self-curing resins in an unheated mould, but shares slow rotational speeds in common with rotational molding. Spin casting should not be confused with either, utilizing self-curing resins or white metal in a high-speed centrifugal casting machine.

2.3 Film Casting

Polymer solution casting is a technique that can replace film extrusion to deliver high-quality films with superior optical, mechanical and physical film properties.

In polymer solution casting, polymer is dissolved or dispersed in solution, coated onto a carrier substrate, and then the water or solvent is removed by drying to create a solid layer on the carrier. The resulting cast layer can be stripped from the carrier substrate to produce a standalone film. Before or after stripping, the cast film can be laminated with other webs or coated with other materials to create multi-layer products.



Manufacturing process advantages of polymer solution casting over traditional film extrusion methods include:

- Processing at low temperatures, which is valuable for thermally activated films or applications incorporating temperature-sensitive active ingredients.
- Ability to produce high-temperature resistant films from non-thermoplastic but soluble raw materials.

- Simplified incorporation of additives and fillers.
- Quicker changeovers for platforms with many part numbers that are differentiated based on formula.
- Single pass manufacturing of multi-layer films (*g.* the ability to cast a free film, then coat an adhesive and laminate release liner on one side, and coat a top coat on the other side).
- Wider range of material choices with casting from either aqueous or solvent-based solutions.

Advantages of the resulting film include:

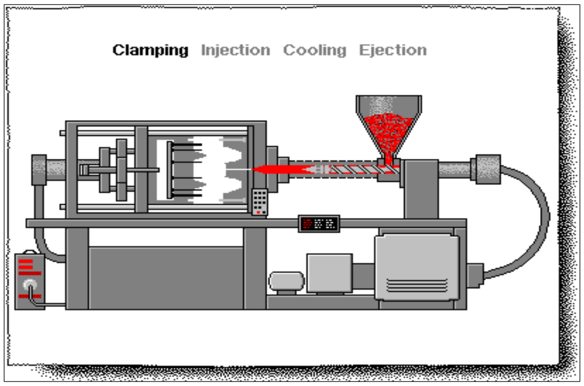
- Greater film thickness uniformity, as tight as +/-2%.
- Wider range of film thickness, from 150 microns down to less than 12 microns.
- Films that are gel and pinhole free.
- Excellent flatness and dimensional stability.
- Isotropic orientation (mechanical and optical) as film is not stretched during manufacture.
- Absence of typical extrusion process lubricants.

3. Moulding

Moulding is one of the most relavent technology to form a plastic products. They are various types. Few of them are Given below

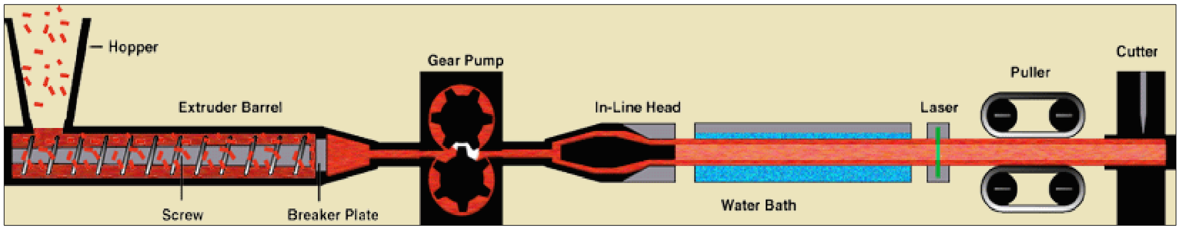
1. Injection molding
2. Extrusion
3. Blow Molding
4. Compression molding
5. Rotational molding

3.1 Injection molding



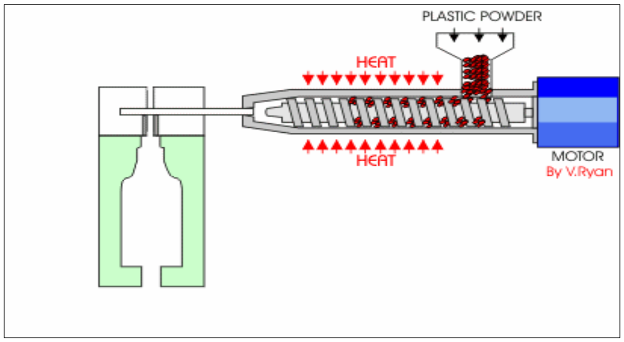
Injection molding is a manufacturing process for producing parts by injecting material into a mold. The main method used for processing plastic is injection molding. With this process, the plastic is placed into a hopper. The hopper then feeds the plastic into a heated injection unit, where it is pushed through a long chamber with a reciprocating screw. Here, it is softened to a fluid state. A nozzle is located at the end of the chamber. The fluid plastic is forced through the nozzle into a cold, closed mold. The halves of the mold are held shut with a system of clamps. When the plastic is cooled and solidified, the halves open and the finished product is ejected from the press.

3.2 Extrusion



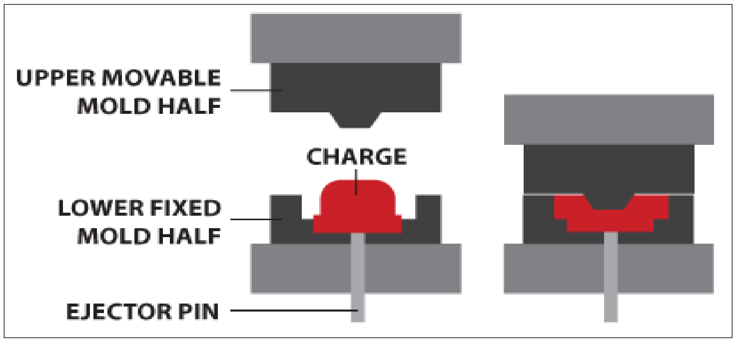
Plastics extrusion is a high volume manufacturing process in which raw plastic material is melted and formed into a continuous profile. The process of extrusion is usually used to make products such as film, continuous sheeting, tubes, profile shapes, rods, coat wire, filaments, cords, and cables. As with injection molding, dry plastic material is placed into a hopper and fed into a long heating chamber. At the end of the chamber, however, the material is forced out of a small opening or a die in the shape of the desired finished product. As the plastic exits the die, it is placed on a conveyor belt where it is allowed to cool. Blowers are sometimes used to aid in this process, or the product may be immersed in water to help it cool.

3.3 Blow Molding



Stretch Blow Molding process is mainly used when the plastic product that needs to be created should be hollow. A molten tube is created with blow molding by using compressed air, which blows up the tube and forces it to conform to the chilled mold. Variations of blow molding include injection, injection-stretch, and extrusion blow molding.

3.4 Compression molding

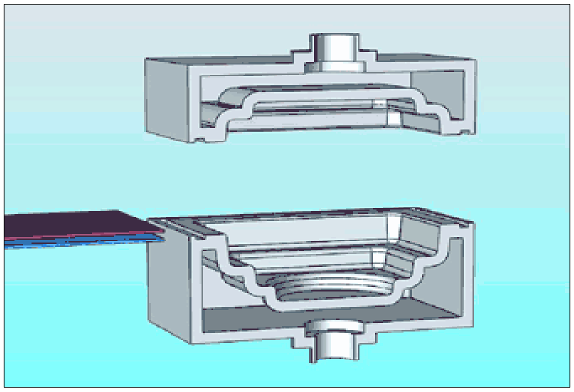


Compression molding is the most common process used with thermosetting materials and is usually not used for thermoplastics. With this process, the material is squeezed into its desired shape with the help of pressure and heat. Plastic molding powder and other materials are added to the mix in order to create special qualities or to strengthen the final product. When the mold is closed and heated, the material goes through a chemical change that causes it to harden into its desired shape. The amount temperature, amount of pressure, and length of time utilized during the process depends on the desired outcome.

3.5 Rotational molding

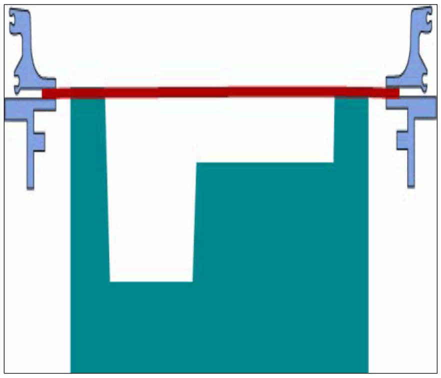
Rotational molding is an extremely popular and well-used process for producing items that are usually hollow. The mold is closed and then spun both vertically and horizontally and moved into an oven. As the powder starts to melt and the mold continues rotating, it is flung onto the walls of the mold by centrifugal force where it forms a skin. After a fixed period, the mold is removed from the oven and allowed to cool carefully to avoid the product shoring.

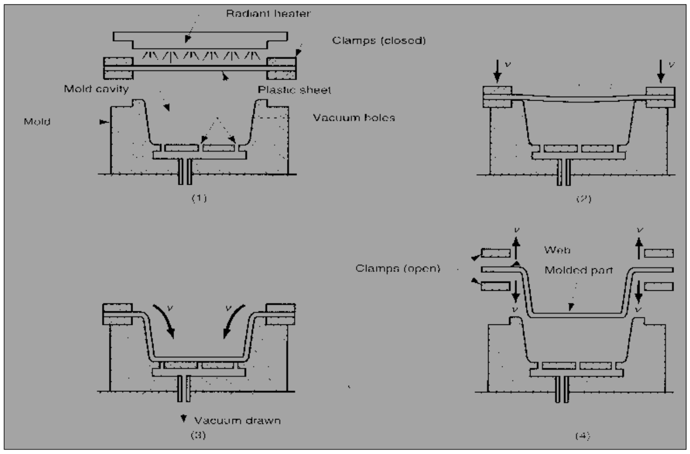
4. Thermoforming



Thermoforming is a manufacturing process where a plastic sheet is heated to a pliable forming temperature, formed to a specific part shape in a mold, and trimmed to create a usable product. The sheet, or film when referring to thinner gauges and certain material types, is heated in an oven to a high-enough temperature that it can be stretched into or onto a mold and cooled to a finished shape. The second animation shows the twin sheet thermoforming process whereby two individual components are fused together through the application of tremendous pressure which forces two molds together, thereby fusing the materials together.

4.1 Vacuum forming





Vacuum forming is a simplified version of thermoforming, whereby a sheet of plastic is heated to a forming temperature, stretched onto a convex, or into a concave, single-surface mold, and forced against the mold by a vacuum (suction of air).

5. ***Polymeric Foams***

The most of the polymeric foams are formed by a process involving nucleation and growth of gas bubbles in a polymer matrix, except in the syntactic foam where micro−beads of encapsulated gas are compounded into a polymer system or latex. According to the nucleation mechanism, the fundamental principle for the formation of polymeric foam involves three different important stages such as, bubble formation, bubble growth and bubble stability. The foam is expanded by increasing the bubble size before stabilizing the system. As the bubbles grow, the foam structure changes through number of stages.5 These are the following characteristics observed during the formation of foam. ƒInitially, small dispersed spherical bubbles are produced in a liquid polymer matrix, with a small reduction in density. The further growth of cells leads to lower foam density, which involves distortion of cells to form polyhedral structures, sometimes idealized as pentagonal dodecahedrons. ƒEffects of viscosity and surface tension subsequently cause materials to flow towards the uniform cell formation. ƒExtensive rupture before the foam is stabilized may lead to foam collapse. Cooling of closed cell foam before stabilization may lead to shrinkage, because of the reduced pressure in cells. The foaming of polymeric materials can be carried out by mechanical, chemical, or physical methods.4 Some of the most commonly used methods are; ¾Thermal decomposition of a chemical blowing agent, generating either nitrogen or carbon dioxide or both, by application of heat or as a result of the exothermic reaction during polymerization. Chemical blowing agents are either inorganic materials such as carbonates, bicarbonates, borohydrides, etc., or organic materials such as, hydrazides, azides, and nitroso compounds, etc. Copyright IIT Kharagpur Chapter 1 4 ¾Mechanical whipping (frothing) of gases into a fluid polymer system (melt, solution, or suspension), then it hardens either by catalytic action or heat or both, thus entrapping the gas bubbles in the polymeric matrix. ¾Volatilization of low−boiling liquids (fluorocarbons or methylene chloride) within the polymer mass as a result of the exothermic reaction or by application of heat. ¾Chemical blowing action via in-situ reaction during polymerization. (In this in-situ reaction water reacts with isocyanate to form carbon dioxide which is responsible for polyurethane foam formation). ¾Expansion of dissolved gas in a polymer mass upon reduction of pressure in the system. ¾Incorporation of tiny beads or microspheres into a polymer mass.

Application of Polymeric Foams

Applications of polymeric foams depend on the nature of polymer and their types. For example, the main applications of flexible foams are for cushioning, packaging, automotive safety, footwear, etc.

6. *Reinforcement*

Fibre-reinforced plastic (**FRP**) (also called **fibre-reinforced polymer**, or **fiber-reinforced plastic**) is a composite material made of a polymer matrix reinforced with fibres. The fibres are usually glass (in fibreglass), carbon, aramid, or basalt. Rarely, other fibres such as paper, wood, or asbestos have been used. The polymer is usually an epoxy, vinylester, or polyester thermosetting plastic, though phenol formaldehyde resins are still in use.
FRPs are commonly used in the aerospace, automotive, marine, and construction industries. They are commonly found in ballistic armor as well.

Process definition

A polymer is generally manufactured by step-growth polymerization or addition polymerization. When combined with various agents to enhance or in any way alter the material properties of polymers the result is referred to as a plastic. Composite plastics refer to those types of plastics that result from bonding two or more homogeneous materials with different material properties to derive a final product with certain desired material and mechanical properties. Fibre-reinforced plastics are a category of composite plastics that specifically use fibre materials to mechanically enhance the strength and elasticity of plastics.
The original plastic material without fibre reinforcement is known as the matrix or binding agent. The matrix is a tough but relatively weak plastic that is reinforced by stronger stiffer reinforcing filaments or fibres. The extent that strength and elasticity are enhanced in a fibre-reinforced plastic depends on the mechanical properties of both the fibre and matrix, their volume relative to one another, and the fibre length and orientation within the matrix.[1] Reinforcement of the matrix occurs by definition when the FRP material exhibits increased strength or elasticity relative to the strength and elasticity of the matrix alone.

Reinforcing Fibre is manufactured in both two-dimensional and three-dimensional orientations:

1. Two-dimensional fibreglass-reinforced polymer is characterized by a laminated structure in which the fibers are only aligned along the plane in x-direction, and y-direction of the material. This means that no fibers are aligned in the through-thickness or the z-direction, this lack of alignment in the through thickness can create a disadvantage in cost and processing. Costs and labor increase because conventional processing techniques used to fabricate composites, such as wet hand lay-up, autoclave and resin transfer molding, require a high amount of skilled labor to cut, stack and consolidate into a preformed component.

2. Three-dimensional fiberglass-reinforced polymer composites are materials with three-dimensional fiber structures that incorporate fibers in the x-direction, y-direction and z-direction. The development of three-dimensional orientations arose from industry's need to reduce fabrication costs, to increase through-thickness mechanical properties, and to improve impact damage tolerance; all were problems associated with two-dimensional fibre-reinforced polymers.

Material requirements

A thermoset polymer matrix material, or engineering grade thermoplastic polymer matrix material, must meet certain requirements in order to first be suitable for FRPs and ensure a successful reinforcement of itself. The matrix must be able to properly saturate, and preferably bond chemically with the fibre reinforcement for maximum adhesion within a suitable curing period. The matrix must also completely envelop the fibres to protect them from cuts and notches that would reduce their strength, and to transfer forces to the fibres. The fibres must also be kept separate from each other so that if failure occurs it is localized as much as possible, and if failure occurs the matrix must also debond from the fibre for similar reasons. Finally the matrix should be of a plastic that remains chemically and physically stable during and after the reinforcement and moulding processes. To be suitable as reinforcement material, fibre additives must increase the tensile strength and modulus of elasticity of the matrix and meet the following conditions; fibres must exceed critical fibre content; the strength and rigidity of fibres itself must exceed the strength and rigidity of the matrix alone; and there must be optimum bonding between fibres and matrix

Glass fibre

"Fibreglass reinforced plastics" or FRPs (commonly referred to simply as fibreglass) use textile grade glass fibres. These textile fibres are different from other forms of glass fibres used to deliberately trap air, for insulating applications (see glass wool). Textile glass fibres begin as varying combinations of SiO_2, Al_2O_3, B_2O_3, CaO, or MgO in powder form. These mixtures are then heated through direct melting to temperatures around 1300 degrees Celsius, after which dies are used to extrude filaments of glass fibre in diameter ranging from 9 to 17 µm. These filaments are then wound into larger threads and spun onto bobbins for transportation and further processing. Glass fibre is by far the most popular means to reinforce plastic and thus enjoys a wealth of production processes, some of which are applicable to aramid and carbon fibres as well owing to their shared fibrous qualities.

Roving is a process where filaments are spun into larger diameter threads. These threads are then commonly used for woven reinforcing glass fabrics and mats, and in spray applications.

Fibre fabrics are web-form fabric reinforcing material that has both warp and weft directions. Fibre mats are web-form non-woven mats of glass fibres. Mats are manufactured in cut dimensions with chopped fibres, or in continuous mats using continuous fibres. Chopped fibre glass is used in processes where lengths of glass threads are cut between 3 and 26 mm, threads are then used in plastics most commonly intended for moulding processes. Glass fibre short strands are short 0.2–0.3 mm strands of glass fibres that are used to reinforce thermoplastics most commonly for injection moulding.

Carbon fibre

Carbon fibres are created when polyacrylonitrile fibres (PAN), Pitch resins, or Rayon are carbonized (through oxidation and thermal pyrolysis) at high temperatures. Through further processes of graphitizing or stretching the fibres strength or elasticity can be enhanced respectively. Carbon fibres are manufactured in diameters analogous to glass fibres with diameters ranging from 4 to 17 µm. These fibres wound into larger threads for transportation and further production processes. Further production processes include weaving or braiding into carbon fabrics, cloths and mats analogous to those described for glass that can then be used in actual reinforcements.

Aramid fibre

Aramid fibres are most commonly known as Kevlar, Nomex and Technora. Aramids are generally prepared by the reaction between an amine group and a carboxylic acid halide group (aramid);[1] commonly this occurs when an aromatic polyamide is spun from a liquid concentration of sulphuric acid into a crystallized fibre. Fibres are then spun into larger threads in order to weave into large ropes or woven fabrics (Aramid). Aramid fibres are manufactured with varying grades to based on varying qualities for strength and rigidity, so that the material can be somewhat tailored to specific design needs concerns, such as cutting the tough material during manufacture.

Advantages and limitations

FRP allows the alignment of the glass fibres of thermoplastics to suit specific design programs. Specifying the orientation of reinforcing fibres can increase the strength and resistance to deformation of the polymer. Glass reinforced polymers are strongest and most resistive to deforming forces when the polymers fibres are parallel to the force being exerted, and are weakest when the fibres are perpendicular. Thus this ability is at once both an advantage or a limitation depending on the context of use. Weak spots of perpendicular fibres can be used for natural hinges and connections, but can also lead to material failure when production processes fail to properly orient the fibres parallel to expected forces. When forces are exerted perpendicular to the orientation of fibres the strength and elasticity of the polymer is less than the matrix alone. In cast resin components made of glass reinforced polymers such as UP and EP, the orientation of fibres can be oriented in two-dimensional and three-dimensional weaves. This means that when forces are possibly perpendicular to one orientation, they are parallel to another orientation; this eliminates the potential for weak spots in the polymer.

7. *Fiber Spinning*

Fiber spinning is used to make synthetic fibers for use in many industries. There are three main types of fiber spinning methods: melt, solution, and reaction spinning. In fiber spinning a liquid polymer is extruded through small holes in a spinneret to form thin filaments, as shown below. Upon leaving the spinneret the filaments solidify. After solidification, filaments can be combined to make threads and/or drawn to change the filaments' properties.

The processes governing the three types of fiber spinning differ mainly in the way the polymer is liquefied and solidified.

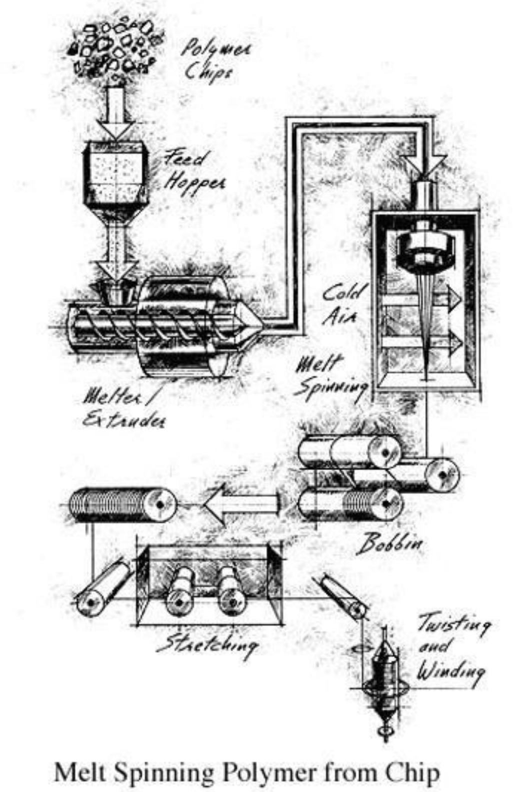
Melt Spinning

General Information

Melt spinning is the most widely used form of fiber spinning. In melt spinning either molten polymer is used or polymer pellets are melted down. Once the filaments are extruded they are cooled in a fluid medium such as air, gas, or even water.

Equipment Design

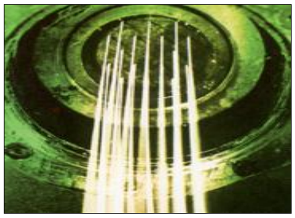
In melt spinning, as shown below , the molten or melted polymer is pushed vertically downwards through the spinneret. When the filaments emerge from the spinneret they are cooled by a gas, usually air, which flows either perpendicularly across, cocurrently , or countercurrently to the filaments.

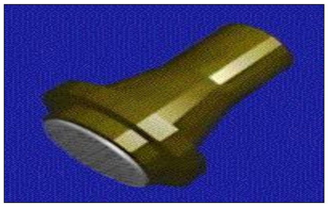


Melt Spinning Polymer from Chip

The filaments can then be brought together and/or twisted together to form a thread. Before winding the thread on the bobbin, it is often treated with water or a wetting agent and then a lubricant . Later, the wound thread may be dyed and drawn on other machines.

Spinneret design , such as those shown below, is dependent on the type of spinning and desired cross sectional shape of the filament. The cross sectional shape determines different features the filament will exhibit, such as how it will reflect light, the ability to insulate, and how easily it shows dirt.





Spin plates and spinnerets may have as many as 80,000 bores spaced less than one millimeter apart. Some spinnerets have superfine capillaries 50 micrometers in diameter. These tiny bores and capillaries are very sensitive to impurities and corrosion; this is one reason why spinnerets are often made of high-grade steel or other metals that can be easily cleaned.

Usage Examples

Some common fibers produced using melt spinning are: polypropylene, polyester, and nylon which is shown below and to the right. Nylon was the world's first synthetic fiber discovered and was initially used for tooth brush bristles before being used to produce women's stockings during the 1940's.

Advantages and Disadvantages

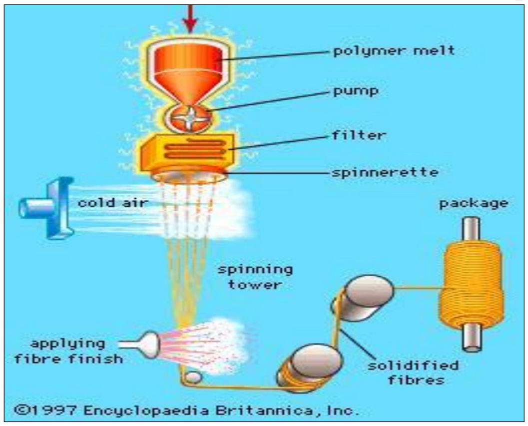
- Ablility to run at high line speeds.
- Requires no solvent that must be recovered later.
- Necessary high temperatures may damage some polymers.

Solution Spinning

Solution spinning is used when the desired polymer does not form a stable melt. These polymers are dissolved in a solution to liquefy them rather than melting them. The two main types of solution spinning are dry and wet spinning.

Dry Spinning

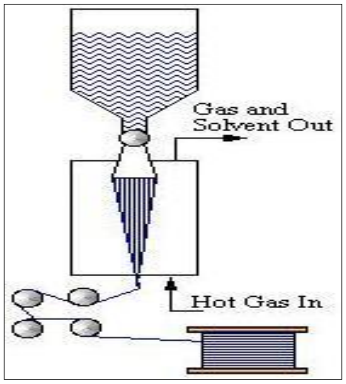
In dry spinning the polymer is dissolved in a volatile solvent. Once dissolved, the polymer solution is extruded through the spinneret which is in an enclosed drying tower. The solution goes through a drying process in this tower, where the solvent is evaporated.



Equipment Design

The spinning solution is often filtered many times to remove foreign materials that might cause thread defects or clogging in the machine . The solution is extruded into the drying tower through which hot air or other gases pass. The concentration of the polymer increases as the solvent evaporates, leaving a solid polymer filament behind. The s olvent is later recovered from the gas by condensation or absorption and is then recycled.

Solvent selection is very important, and is based on boiling point, latent heat of vaporization, thermal stability, toxicity, and inertness. Non-polar solvents are often preferred because of their low boiling points and heats of vaporization. However, non-polar solvents are prone to build-ups of electrostatic charge, which can be very dangerous.

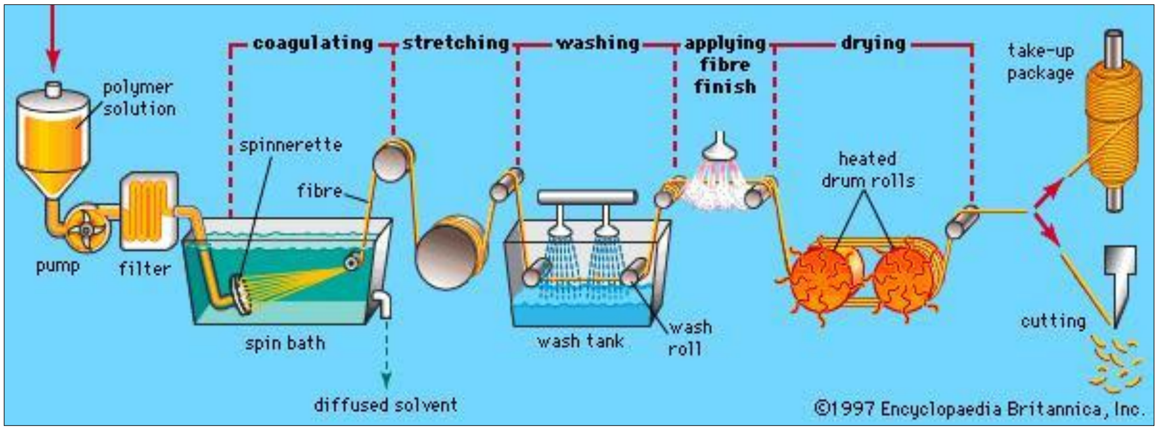


Advantages and Disadvantages

- Better than melt spinning for temperature-sensitive polymers.
- Faster production rates than melt and wet spinning.
- Solvent recovery is costly.

Wet Spinning

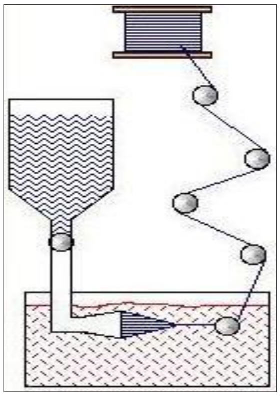
In wet spinning the polymer is dissolved in a non-volatile solvent. The spinneret is located in a coagulating bath that causes the fiber to precipitate out.



Equipment Design

The liquid in the coagulating bath is chosen so that the solvent is readily soluble in the liquid but the polymer is not. This will cause the polymer to precipitate out and form the desired solid filaments.The solvent can later be recovered by treating the wastewater in the bath.

The drag on the filament by the viscous liquid in the coagulating bath significantly reduces the production speed of the process. This makes wet spinning a slower process than melt or dry spinning.



Advantages and Disadvantages

- Better than melt and dry spinning for temperature sensitive polymers.
- Lower production rates than melt or dry spinning due to viscous drag.
- Solvent recovery is costly.

Usage Examples

The synthetic fibers produced by solution spinning are made into threads which are woven into fabric for everything from clothes and carpets to airbags and windsails. In addition, sterilized synthetic fibers are used in the medical industry as sutures, dressings, and operating room drapes, face masks, caps and overshoes. Many synthetic fibers can be cut into tiny pieces called flock . Flock is used to make velvet or suede-like materials or added to plastics or papers for a decorative finish.

Text book:

T1: Gowariker, V. R., N. V. Viswanathan and J. Sreedhar, 1986. Polymer Science, *New Age International* Private Ltd., New Delhi.

T2: Billmeyer, F.W., 2003. Text Book of Polymer Science. III Edition, John Wiley, New York.

Reference book

R1: M.S Bhatnagar,2004, " A text book of polymers". Ist Edition, S.Chand & Company.

POSSIBLE QUESTIONS

Multiple Choice Questions (Each Carry 1 Mark)

1. Which one of the following is obtained from acetaldehyde and hydrogen cyanide.
   a. Acrylonitrile monomer b. Polyamide c. Polyester d. Polyethylene terephthalte
2. Wet spinning technique is commercially used to produce filament yarn of
   a. Polypropylene b. Polyester c. Nylon 66 **d. Acrylic**
3. Too high resistivity leads to the development of static?
   a. Mechanical charges b. Positive charges c. Negative charges **d. Electrical charges**
4. Which properties of fibers are quite complex and have been subject of much experimental work?
   a. Physical **b. Mechanical** c. Chemical d. Thermal
5. In which spinning, the polymer solution is forced through a spinneret?
   a. Melt spinning **b. Dry spinning** c. Wet spinning d. Spinning
6. Birefringence of filament yarn is related to its
   Density b. Filament denier **c. Orientation** d. Crystallinity
7. In melt spinning the temperature used for melting is about ?
   29K **b. 30K** c. 31K d. 32K
8. Which one of the following is the most important fibers produced commercially?
   Nylons b. Wood **c.** Cotton d. Silk
9. In which spinning, the polymer is melted by heating and then passed through a spinneret via
   Melt spinning b. Dry spinning c. Wet spinning d. Spinning
10. Which one of the following is used for self-lubricating gears and bearings?
    Nylons b. Wood **c.** Cotton d. Silk
11. Crease resist finishing of cotton fabric does not lead to
    Reduction in tensile strength b. Increase in dimensional stability
    c. Increase in moisture regain d. Increase in bending length
12. Which property causes the fabric to cling unpleasantly and to be difficult to clean?
    a. Mechanical **b. Electrical** c. Chemical d. Thermal
13. In general, which is a difficult dye?
    a. Polyamide b. Polyester **c. Hydrophobic fiber** d. Acrylic fibre
14. In which spinning, Polymer solutions are converted into fibers by diluting a highly concentrated polymer solution in a coagulating bath?
    a. Melt spinning b. Dry spinning **c. Wet spinning** d. Spinning
15. Which is soluble only in specific solvents?
    a. Fibres **b. Polymers** c. Nylon d. Hydrophobic fibres
16. The PBNA is the standard
    a. anti-oxidant b. anti-toxin c. anti-malarial d. anti-poisionus
17. Which one of the following is used as the staining anti-oxidant
    a. DPPD **b. PBNA** c. TCS d. TMS
18. TCS is the example of the
    a. Standard anti-oxidant b. non standard anti-oxidant c. staining anti-oxidant **d. non-staining anti oxidant**
19. The rayon also known as
    a. nylon b. orelon **c. viscose** d. resin

20. The rayon polymers belongs to the
    a. silicon polymers b. epoxy polymers c. organic polymer d. rubber

6 Marks (Each Carry 6 Marks)

1. What is calendaring technique? explain it briefly?
2. Write a note on moulding techniques?
3. What are the thermoforming techniques?
4. How to produce the hollow and film products of polymers under casting technique?
5. Write a note on foaming techniques?
6. Write a note on reinforcing?
7. What is the compounding technique of polymer and fiber?
8. Write a note on injection and blow moulding?
9. What is moulding? Explain extrusion moulding in the preparation of polymers?
10. How to prepare the fiber by spinning method?

Compulsory Questions (Each Carry 10 Marks)

1. Give an account of fiber spinning technique?
2. Briefly explain the reinforcing technique?
3. What is moulding? Explain the four types of moulding?

16CHP305A
Karpagam Academy of Higher Education
Coimbatore-21
(For the Candidates admitted on 2016 Onwards)
III-Semester
Polymer Chemistry

Questions	**Opt-1**	**Opt-2**	**Opt-3**	**Opt-4**	**Answers**
Unit 4- Objective questions for online examination (Each carry 1 mark)					
The fibre that contains nitrogen and sulfur is ?	Polyester	Wool	Nylon	Kevlar	Wool
It is the class of a hair like materials that are continues filaments.	Fibre	Rubber	Wood	Glass	Fibre
Polyacrylonitrile (PAN), also known as ?	Polyvinyl cyanide	Cyanide	Polyester	Polyethylene terephthalte	Polyvinyl cyanide
Which one of the following is produced by ammonidation of propylene.	Acrylonitrile monomer	Polyamide	Polyester	Polyethylene terephthalte	Acrylonitrile monomer
Which one of the following is obtained from acetaldehyde and hydrogen cyanide.	Acrylonitrile monomer	Polyamide	Polyester	Polyethylene terephthalte	Acrylonitrile monomer
Wet spinning technique is commercially used to produce filament yarn of	Polypropylene	Polyester	Nylon 66	Acrylic	Acrylic
Too high resistivity leads to the development of static ?	Mechanical charges	Positive charges	Negative charges	Electrical charges	Electrical charges
Which properties of fibres are quite complex and have been subject of much experimental work?	Physical	Mechanical	Chemical	Thermal	Mechanical
The tenacity at break of typical fibres ranges from about 1 g/denier for ?	Synthetic	Natural	Rayons	Carbon fibres	Rayons
Which one of the following is the least satisfactory fibres from the standpoint of weather ability?	Silk	Cotton	Glass	Wood	Silk
Natural fibers are consisting of ?	Linear polymers	Nonlinear polymers	Copolymers	Chain polymers	Linear polymers
The fibre that dissolves in 59% (w/w) sulfuric acid solution is	Nylon	Viscose	Cotton	Silk	Viscose
Polyacrylonitrile is soluble in which solvent?	Dimethylformamide (DMF)	Methanol	Water	Acetone	Dimethylformamide (DMF)

In which spinning, the polymer solution is forced through a spinneret?	Melt spinning	Dry spinning	Wet spinning	Spinning	Dry spinning
In which spinning, the polymer is melted by heating and then passed through a spinneret via	Melt spinning	Dry spinning	Wet spinning	Spinning	Melt spinning
Birefringence of filament yarn is related to its	Density	Filament denier	Orientation	Crystallinity	Orientation
In melt spinning the temperature used for melting is about ?	29K	30K	31K	32K	30K
Which one of the following is the most important fibers produced commercially?	Nylons	Wood	Cotton	Silk	Nylons
Which one of the following is used for self-lubricating gears and bearings?	Nylons	Wood	Cotton	Silk	Nylons
Why does nylon make such good fibers?	Intramolecular forces	Low Molecular weight	Intermolecular forces	High Molecular weight	Intermolecular forces
During bleaching of cotton with H2O2, the stabilizer used is ?	Sodium hydroxide	Sodium silicate	Acetic acid	Sodium carbonate	Sodium silicate
The highest washing fastness in a dyed cotton fabric would be obtained if the dye-fibre bond is	Ionic	Hydrogen	Covalent	Van derWaal's force	Covalent
The melt index, is generally used to characterize which properties of polymers?	Electrical	Chemical	Mechanical	Melting	Melting
Crease resist finishing of cotton fabric does not lead to	Reduction in tensile strength	Increase in dimensional stability	Increase in moisture regain	Increase in bending length	Increase in moisture regain
Which property cause the fabric to cling unpleasantly and to be difficult to clean?	Mechanical	Electrical	Chemical	Thermal	Electrical
In general, which is difficult to dye ?	Polyamide	Polyester	Hydrophobic fibre	Acrylic fibre	Hydrophobic fibre
In which spinning, Polymer solutions are converted into fibers by diluting a highly concentrated polymer solution in a coagulating bath?	Melt spinning	Dry spinning	Wet spinning	Spinning	Wet spinning
Which is soluble only in specific solvents?	Fibres	Polymers	Nylon	Hydrophobic fibres	Polymers
Cellulose acetate, polyacrylonitrile, and polyurethane are spun by this technique?	Melt spinning	Dry spinning	Wet spinning	Spinning	Dry spinning
Nylon ends in?	Building	Ropes	Chair	Watch	Ropes
Which one of the following is a polyamide?	Terylene	Nylon 6	Cotton	Watch	Nylon 6

Synthetic fibers are consisting of ?	Linear polymers	Nonlinear polymers	Copolymers	Chain polymers	Linear polymers
The alkyd resins are condensation polymers obtained from dibasic acids and	Glycol	Phenol	Acetaldehyde	Benzaldehyde	Phenol
Nylon threads are made of	Polyester polymer	Polyamide polymer	Polyvinyl chloride	Acrylic polymer	Polyamide polymer
Acrylic resins are	Brown colour	Colourless	Gold colour	White colour	Colourless
Which one of the following can be polymerised to polythene	Ethylene	Ethyl amide	Ethyl ketone	Ethyl acetate	Ethylene
Hydrolysis of cellulose gives	D-glucose	L- glucose	D-fructose	L-fructose	D-glucose
Orlon is a polymer of	Polyamide	Polyester	Hydrophobic fibre	Acrylic fibre	Acrylic fibre
Condensation product of caprolactum is	Nylon 6	Cotton	Nylon 6,10	Nylon 66	Nylon 6
Nylon is a example of	condensation polymer	copolymer	coordination polymer	chain polymer	condensation polymer
The DPPD is the	Diphenyl phenylene diamine	Diphenyl phenylene diamide	Diphenyl phospho diamine	Diphenyl phospho diamine	Diphenyl phenylene diamine
PBNA is the	phenylα naphthyl amine	phenyl ρ naphthalene amide	phenyl β naphthyl amine	phenyl γ naphthyl amine	phenyl β naphthyl amine
The PBNA is the standard	anti-oxidant	anti-toxin	anti-malarial	anti-poisionus	anti-oxidant
Which one of the following is used as the staining anti-oxidant	DPPD	PBNA	TCS	TMS	PBNA
TCS is the example of the	Standard anti-oxidant	non standard anti-oxidant	staining anti-oxidant	non-staining anti oxidant	non-staining anti oxidant
The rayon also known as	nylon	orelon	viscose	resin	viscose
The rayon polymers belongs to the	silicon polymers	epoxy polymers	organic polymer	rubber	silicon polymers
Which one of the following should give the strength to the paper	urea-formaldehyde	phenol-formaldehyde	polysulphides	polychloroprene	urea-formaldehyde
Which one of the following is used as a core binders	urea-formaldehyde	phenol-formaldehyde	polysulphides	polychloroprene	phenol-formaldehyde
Which one of the following is used as fuel material	urea-formaldehyde	phenol-formaldehyde	polysulphides	polychloroprene	polysulphides
which one of the following is used to coating the wires and cables	urea-formaldehyde	phenol-formaldehyde	polysulphides	polychloroprene	polychloroprene
Which one of the following is used as the insulation material in electrical industry	urea-formaldehyde	phenol-formaldehyde	polybutadiene	polysulphides	polybutadiene
Which one of the following is consider as life saving substance	urea-formaldehyde	phenol-formaldehyde	polybutadiene	polyvinyl pyrrolidine	polyvinyl pyrrolidine
Which one of the following is used in the paints and surface coatings	polybutadiene	polysulphides	polyvinyl pyrrolidine	polyvinyl fluoride	polyvinyl fluoride

Which one of the following is used to form the thermoplastic material	polyvinylidene chloride	PVC	polybutadiene	polysulphides	polyvinylidene chloride
Which one of the following is the liquid resins	PPG	PVC	PEG	PABA	PPG
PEG also known as	alcowax	carbowax	hydrowax	rubber	carbowax
Which one of the following is used as the surface coating in the supersonic airgraft	polyamines	polyamides	polyimides	polyvinyls	polyimides
Which one of the following is used to making the toys	HDPE	LDPE	PPG	PEG	HDPE
Nylon is not a ?	Homo polymer	Polyamide	Caprolactum	Condensation polymer	Homo polymer

UNIT – V
Properties of Commercial Polymers

Properties of Commercial Polymers: *Polyethylene, polyvinyl chloride, polyamides, polyesters, phenolic resins, epoxy resins and silicone polymers. Functional polymers, Fire retarding polymers and electrically conducting polymers. Biomedical polymers – contact lens, dental polymers, artificial heart, kidney, skin and blood cells.*

Commercial Polymers

Synthetic polymers are human-made polymers. From the utility point of view they can be classified into four main categories: thermoplastics, thermosets, elastomers and synthetic fibers. They are found commonly in a variety of consumer products such as money, super glue, etc.
A wide variety of synthetic polymers are available with variations in main chain as well as side chains. The back bones of common synthetic polymers such as polythene, polystyrene and poly acrylates are made up of carbon-carbon bonds, whereas hetero chain polymers such as polyamides, polyesters, polyurethanes, polysulfides and polycarbonates have other elements (e.g. oxygen, sulfur, nitrogen) inserted along the backbone. Also silicon forms similar materials without the need of carbon atoms, such as silicones through siloxane linkages; these compounds are thus said to be inorganic polymers. Coordination polymers may contain a range of metals in the backbone, with non-covalent bonding present.
Some familiar household synthetic polymers include: Nylons in textiles and fabrics, Teflon in non-stick pans, Bakelite for electrical switches, polyvinyl chloride (PVC) in pipes, etc. The common PET bottles are made of a synthetic polymer, polyethylene terephthalate. The plastic kits and covers are mostly made of synthetic polymers like polythene and tires are manufactured from Buna rubbers.[1] However, due to the environmental issues created by these synthetic polymers which are mostly non-biodegradable and often synthesized from petroleum, alternatives like bioplastics are also being considered. They are however expensive when compared to the synthetic polymers.

1. Polyethylene

Polyethylene or **polythene** (abbreviated **PE**; IUPAC name **polyethene** or **poly(ethylene)**) is the most common plastic. The annual global production is around 80 million tonnes. Its primary use is in packaging (plastic bags, plastic films, geomembranes, containers including bottles, etc.). Many kinds of polyethylene are known, with most having the chemical formula $(C_2H_4)_n$. PE is usually a mixture of similar polymers of ethylene with various values of n.

Properties

The properties of polyethylene can be divided into mechanical, chemical, electrical, optical, and thermal properties.

Mechanical properties

Polyethylene is of low strength, hardness and rigidity, but has a high ductility and impact strength as well as low friction. It shows strong creep under persistent force, which can be reduced by addition of short fibers. It feels waxy when touched.

Thermal properties

The usefulness of polyethylene is limited by its melting point of 80 °C (176 °F) (HDPE, types of low crystalline softens earlier). For common commercial grades of medium- and high-density polyethylene the melting point is typically in the range 120 to 180 °C (248 to 356 °F). The melting point for average, commercial, low-density polyethylene is typically 105 to 115 °C (221 to 239 °F). These temperatures vary strongly with the type of polyethylene.

Chemical properties

Polyethylene consists of nonpolar, saturated, high molecular weight hydrocarbons. Therefore, its chemical behavior is similar to paraffin. The individual macromolecules are not covalently linked. Because of their symmetric molecular structure, they tend to crystallize; overall polyethylene is partially crystalline. Higher crystallinity increases density and mechanical and chemical stability.

Most LDPE, MDPE, and HDPE grades have excellent chemical resistance, meaning they are not attacked by strong acids or strong bases, and are resistant to gentle oxidants and reducing agents. Crystalline samples do not dissolve at room temperature. Polyethylene (other than cross-linked polyethylene) usually can be dissolved at elevated temperatures in aromatic hydrocarbons such as toluene or xylene, or in chlorinated solvents such as trichloroethane or trichlorobenzene.

Polyethylene absorbs almost no water. The gas and water vapor permeability (only polar gases) is lower than for most plastics; oxygen, carbon dioxide and flavorings on the other hand can pass it easily.

PE can become brittle when exposed to sunlight, carbon black is usually used as a UV stabilizer.

Polyethylene burns slowly with a blue flame having a yellow tip and gives off an odour of paraffin (similar to candle flame). The material continues burning on removal of the flame source and produces a drip.

Polyethylene cannot be imprinted or stuck together without pretreatment.

Electrical properties

Polyethylene is a good electrical insulator. It offers good tracking resistance; however, it becomes easily electrostatically charged (which can be reduced by additions of graphite, carbon black or antistatic agents).

Optical properties

Depending on thermal history and film thickness PE can vary between almost clear (transparent), milky-opaque (translucent) or opaque. LDPE thereby owns the greatest, LLDPE slightly less and HDPE the least transparency. Transparency is reduced by crystallites if they are larger than the wavelength of visible light

High-density polyethylene (HDPE)

HDPE pipe installation in storm drain project in Mexico

HDPE is defined by a density of greater or equal to 0.941 g/cm^3. HDPE has a low degree of branching. The mostly linear molecules pack together well, so intermolecular forces are stronger than in highly branched polymers. HDPE can be produced by chromium/silica catalysts, Ziegler-Natta catalysts or metallocene catalysts; by choosing catalysts and reaction conditions, the small amount of branching that does occur can be controlled. These catalysts prefer the formation of free radicals at the ends of the growing polyethylene molecules. They cause new ethylene monomers to add to the ends of the molecules, rather than along the middle, causing the growth of a linear chain.

HDPE has high tensile strength. It is used in products and packaging such as milk jugs, detergent bottles, butter tubs, garbage containers, and water pipes. One-third of all toys are manufactured from HDPE. In 2007, the global HDPE consumption reached a volume of more than 30 million tons.

Low-density polyethylene (LDPE)

LDPE is defined by a density range of 0.910–0.940 g/cm^3. LDPE has a high degree of short- and long-chain branching, which means that the chains do not pack into the crystal structure as well. It has, therefore, less strong intermolecular forces as the instantaneous-dipole induced-dipole attraction is less. This results in a lower tensile strength and increased ductility. LDPE is created by free-radical polymerization. The high degree of branching with long chains gives molten LDPE unique and desirable flow properties. LDPE is used for both rigid containers and plastic film applications such as plastic bags and film wrap. In 2013, the global LDPE market had a volume of almost US$33 billion.

The radical polymerization process used to make LDPE does not include a catalyst that "supervises" the radical sites on the growing PE chains. (In HDPE synthesis, the radical sites are at the ends of the PE chains, because the catalyst stabilizes their formation at the ends.) Secondary radicals (in the middle of a chain) are more stable than primary radicals (at the end of the chain), and tertiary radicals (at a branch point) are more stable yet. Each time an ethylene monomer is added, it creates a primary radical, but often these will rearrange to form more stable secondary or tertiary radicals. Addition of ethylene monomers to the secondary or tertiary sites creates branching.

Production

Production of LDPE by addition polymerization requires:

- temperature range of 100-300^{o}C
- very high pressure 1500-3000 atmospheres
- oxygen or an organic peroxide such as dibutyl peroxide, benzoyl peroxide or diethyl peroxide as initiator.
  An initiator is a substance which is added in small quantities and is decomposed by light or heat to produce a free radical ($R^{\cdot}$). A free radical is formed when a covalent bond is broken and a bonding electron is left on each part of the broken molecule. Since the O-O covalent bond is weak, free radicals are easily formed from oxygen or peroxides.
- benzene or chlorobenzene used as the solvent since both polymer (polythene) and monomer (ethene) dissolve in these compounds at the temperature and pressure used. Water or other liquids may be added to dissipate the heat of reaction as the polymerization reaction is highly exothermic.

$$\underset{\text{ethene}}{CH_2{=}CH_2} + \underset{\text{initiator}}{R^{\cdot}} \rightarrow {}^{\cdot}CH_2\text{-}CH_2\text{-}R$$

$$CH_2{=}CH_2 + {}^{\cdot}CH_2\text{-}CH_2\text{-}R \rightarrow {}^{\cdot}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}R$$

Process continues to form polythene (polyethylene) $[\text{-}CH_2\text{-}CH_2\text{-}]_n$

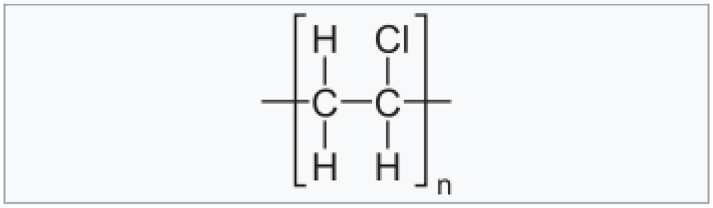
Production of HDPE

1. Production of HDPE by addition polymerization with a supported metal oxide catalyst requires:
   - temperature ~300^{o}C
   - 1 atmosphere pressure (101.3kPa)
   - aluminium-based metal oxide catalyst (metallocene catalyst)

     The catalyst can be used in a variety of operating modes including fixed-bed, moving-bed, fluid-bed or slurry processes
   - The ethene (ethylene) monomer is fed with a paraffin or cycloparaffin diluent (diluting agent).
     After polymerization the polymer (polythene) is recovered by cooling or by solvent evaporation.
2. Production of HDPE by coordination polymerization requires:
   - temperature 50-75^{o}C
   - slight pressure
   - a coordination catalyst is prepared as a colloidal suspension by reacting an aluminium alkyl and titanium chloride ($TiCl_4$) in a solvent such as heptane (C_7H_{16}).
   - The polymer (polythene) forms as a powder or granules which are insoluble in the reaction mixture. When the polymerization is completed, the catalyst is destroyed by adding water or alcohol to the reaction mixture. The polymer (polythene) is then filtered or centrifuged off, washed and dried.

2. Polyvinyl chloride

Polyvinyl chloride



Polyvinyl chloride (/ˌpɒlivaɪnəl ˈklɔːraɪd/), also known as poly vinyl or **vinyl**, commonly abbreviated **PVC**, is the world's third-most widely produced synthetic plastic polymer, after polyethylene and polypropylene.

PVC comes in two basic forms: rigid (sometimes abbreviated as RPVC) and flexible. The rigid form of PVC is used in construction for pipe and in profile applications such as doors and windows. It is also used for bottles, other non-food packaging, and cards (such as bank or membership cards). It can be made softer and more flexible by the addition of plasticizers, the most widely used being phthalates. In this form, it is also used in plumbing, electrical cable insulation, imitation leather, signage, phonograph records, inflatable products, and many applications where it replaces rubber.

Pure polyvinyl chloride is a white, brittle solid. It is insoluble in alcohol but slightly soluble in tetrahydrofuran.

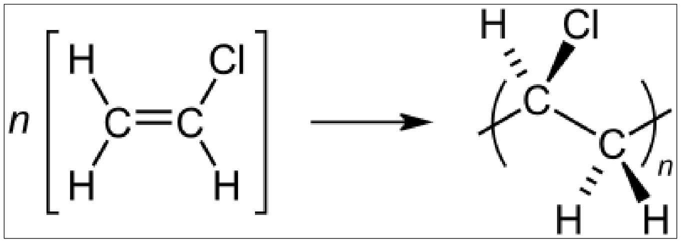
Discovery

PVC was accidentally synthesized in 1872 by German chemist Eugen Baumann. The polymer appeared as a white solid inside a flask of vinyl chloride that had been left exposed to sunlight. In the early 20th century the Russian chemist Ivan Ostromislensky and Fritz Klatte of the

German chemical company Griesheim-Elektron both attempted to use PVC in commercial products, but difficulties in processing the rigid, sometimes brittle polymer thwarted their efforts. Waldo Semon and the B.F. Goodrich Company developed a method in 1926 to plasticize PVC by blending it with various additives. The result was a more flexible and more easily processed material that soon achieved widespread commercial use.

Production

Polyvinyl chloride is produced by polymerization of the vinyl chloride monomer (VCM), as shown.



About 80% of production involves suspension polymerization. Emulsion polymerization accounts for about 12%, and bulk polymerization accounts for 8%. Suspension polymerization affords particles with average diameters of 100–180 μm, whereas emulsion polymerization gives much smaller particles of average size around 0.2 μm. VCM and water are introduced into the reactor along with a polymerization initiator and other additives. The contents of the reaction vessel are pressurized and continually mixed to maintain the suspension and ensure a uniform particle size of the PVC resin. The reaction is exothermic and thus requires cooling. As the volume is reduced during the reaction (PVC is denser than VCM), water is continually added to the mixture to maintain the suspension.

The polymerization of VCM is started by compounds called initiators that are mixed into the droplets. These compounds break down to start the radical chain reaction. Typical initiators include dioctanoyl peroxide and dicetyl peroxydicarbonate, both of which have fragile O-O bonds. Some initiators start the reaction rapidly but decay quickly, and other initiators have the opposite effect. A combination of two different initiators is often used to give a uniform rate of polymerization. After the polymer has grown by about 10 times, the short polymer precipitates inside the droplet of VCM, and polymerization continues with the precipitated, solvent-swollen particles. The weight average molecular weights of commercial polymers range from 100,000 to 200,000, and the number average molecular weights range from 45,000 to 64,000.

Once the reaction has run its course, the resulting PVC slurry is degassed and stripped to remove excess VCM, which is recycled. The polymer is then passed through a centrifuge to remove water. The slurry is further dried in a hot air bed, and the resulting powder is sieved before storage or pelletization. Normally, the resulting PVC has a VCM content of less than 1 part per million. Other production processes, such as micro-suspension polymerization and emulsion polymerization, produce PVC with smaller particle sizes (10 μm vs. 120–150 μm for suspension PVC) with slightly different properties and with somewhat different sets of applications.

Properties

PVC is a thermoplastic polymer. Its properties are usually categorized based on rigid and flexible PVCs.

Property	Rigid PVC	Flexible PVC

Density [g/cm^3]	1.3–1.45	1.1–1.35
Thermal conductivity [W/(m·K)]	0.14–0.28	0.14–0.17
Yield strength [psi]	4500–8700	1450–3600
Young's modulus [psi]	490,000	
Flexural strength (yield) [psi]	10,500	
Compression strength [psi]	9500	
Coefficient of thermal expansion (linear) [mm/(mm °C)]	5×10^{-5}	
Vicat B [°C]	65–100	Not recommended
Resistivity [Ω m]	10^{16}	10^{12}–10^{15}
Surface resistivity [Ω]	10^{13}–10^{14}	10^{11}–10^{12}

Mechanical

PVC has high hardness and mechanical properties. The mechanical properties enhance with the molecular weight increasing but decrease with the temperature increasing. The mechanical properties of rigid PVC (uPVC) are very good; the elastic modulus can reach 1500-3,000 MPa. The soft PVC (flexible PVC) elastic is 1.5–15 MPa.

Thermal and fire

The heat stability of raw PVC is very poor, so the addition of a heat stabilizer during the process is necessary in order to ensure the product's properties. PVC starts to decompose when the temperature reaches 140 °C (284 °F), with melting temperature starting around 160 °C (320 °F). The linear expansion coefficient of rigid PVC is small and has good flame retardancy, the Limiting oxygen index (LOI) being up to 45 or more. The LOI is the minimum concentration of oxygen, expressed as a percentage, that will support combustion of a polymer and noting that air has 20% content of oxygen.

Electrical

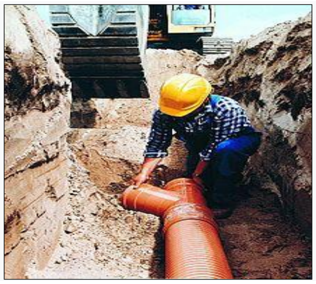
PVC is a polymer with good insulation properties, but because of its higher polar nature the electrical insulating property is inferior to non polar polymers such as polyethylene and polypropylene.

Since the dielectric constant, dielectric loss tangent value, and volume resistivity are high, the corona resistance is not very good, and it is generally suitable for medium or low voltage and low frequency insulation materials.

Chemical

PVC is chemically resistant to acids, salts, bases, fats, and alcohols; therefore, it is used in sewerage piping. It is also resistant to some solvents, mainly uPVC. Plasticized PVC, also known as PVC-P, is in some cases less resistant to solvents. For example, PVC is resistant to fuel and some paint thinners. Some solvents may only swell it or deform it but not dissolve it, but some of them, like tetrahydrofuran or acetone, may damage it.

Applications



PVC is used extensively in sewage pipe due to its low cost, chemical resistance and ease of jointing

Pipes

Roughly half of the world's polyvinyl chloride resin manufactured annually is used for producing pipes for municipal and industrial applications. In the water distribution market, it accounts for 66% of the market in the U.S., and in sanitary sewer pipe applications, it accounts for 75%. Buried PVC pipes in both water and sanitary sewer applications that are 4 inches (100 mm) in diameter and larger are typically joined by means of a gasket-sealed joint. The most common type of gasket utilized in North America is a metal reinforced elastomer, commonly referred to as a Rieber sealing system. Its light weight, low cost, and low maintenance make it attractive. However, it must be carefully installed and bedded to ensure longitudinal cracking and overbelling does not occur. Additionally, PVC pipes can be fused together using various solvent cements, or heat-fused (butt-fusion process, similar to joining HDPE pipe), creating permanent joints that are virtually impervious to leakage.

In February 2007 the California Building Standards Code was updated to approve the use of chlorinated polyvinyl chloride (CPVC) pipe for use in residential water supply piping systems. CPVC has been a nationally accepted material in the U.S. since 1982; California, however, has permitted only limited use since 2001. The Department of Housing and Community Development prepared and certified an environmental impact statement resulting in a recommendation that the commission adopt and approve the use of CPVC. The commission's vote was unanimous, and CPVC has been placed in the 2007 California Plumbing Code.

Electric cables

PVC is commonly used as the insulation on electrical cables; PVC used for this purpose needs to be plasticized. Flexible PVC coated wire and cable for electrical use has traditionally been stabilised with lead, but these are being replaced with calcium-based systems.

In a fire, PVC-coated wires can form hydrogen chloride fumes; the chlorine serves to scavenge free radicals and is the source of the material's fire retardance. While hydrogen chloride fumes can also pose a health hazard in their own right, it dissolves in moisture and breaks down onto surfaces, particularly in areas where the air is cool enough to breathe, and is not available for inhalation. Frequently in applications where smoke is a major hazard (notably in tunnels and communal areas), PVC-free cable insulation is preferred, such as low smoke zero halogen (LSZH) insulation.

Construction

"A modern Tudorbethan" house with uPVC gutters and downspouts, fascia, decorative imitation "half-timbering", windows, and doors

PVC is a common, strong but lightweight plastic used in construction. It is made softer and more flexible by the addition of plasticizers. If no plasticizers are added, it is known as uPVC (unplasticized polyvinyl chloride) or rigid PVC.

uPVC is extensively used in the building industry as a low-maintenance material, particularly in Ireland, the United Kingdom, in the United States and Canada. In the U.S. and Canada it is known as vinyl or vinyl siding. The material comes in a range of colors and finishes, including a photo-effect wood finish, and is used as a substitute for painted wood, mostly for window frames and sills when installing insulated glazing in new buildings, or to replace older single-glazed windows. Other uses include fascia, and siding or weatherboarding. This material has almost entirely replaced the use of cast iron for plumbing and drainage, being used for waste pipes, drainpipes, gutters and downspouts. uPVC is known as having strong resistance against chemicals, sunlight, and oxidation from water.

Double glazed units

Signs

Polyvinyl chloride is formed in flat sheets in a variety of thicknesses and colors. As flat sheets, PVC is often expanded to create voids in the interior of the material, providing additional thickness without additional weight and minimal extra cost (see Closed-cell PVC foamboard). Sheets are cut using saws and rotary cutting equipment. Plasticized PVC is also used to produce thin, colored, or clear, adhesive-backed films referred to simply as vinyl. These films are typically cut on a computer-controlled plotter (see Vinyl cutter) or printed in a wide-format printer. These sheets and films are used to produce a wide variety of commercial signage products, including car body stripes and stickers.

Clothing and furniture

Black PVC trousers

PVC has become widely used in clothing, to either create a leather-like material or at times simply for the effect of PVC. PVC clothing is common in Goth, Punk, clothing fetish and alternative fashions. PVC is less expensive than rubber, leather, and latex which it is used to simulate.

PVC fabric is water-resistant, so it is used in coats, skiing equipment, shoes, jackets, aprons, and bags.

Healthcare

The two main application areas for single-use medically approved PVC compounds are flexible containers and tubing: containers used for blood and blood components, for urine collection or for ostomy products and tubing used for blood taking and blood giving sets, catheters, heart-lung bypass sets, hemodialysis sets etc. In Europe the consumption of PVC for medical devices is approximately 85,000 tons each year. Almost one third of plastic-based medical devices are made from PVC. The reasons for using flexible PVC in these applications for over 50 years are numerous and based on cost effectiveness linked to transparency, light weight, softness, tear strength, kink resistance, suitability for sterilization and biocompatibility.

Flooring

Flexible PVC flooring is inexpensive and used in a variety of buildings covering the home, hospitals, offices, schools, etc. Complex and 3Ddesigns are possible, which are then protected by a clear wear layer. A middle vinyl foam layer also gives a comfortable and safe feel. The smooth, tough surface of the upper wear layer prevents the buildup of dirt, which prevents microbes from breeding in areas that need to be kept sterile, such as hospitals and clinics.

Wire rope

PVC coating placed onto wire rope and aircraft cable is used for general purpose applications. The coating process consists of a jacketing application via pressurized extrusion. The benefits of PVC coating on wire rope are for not only aesthetics, but for ergonomics, abrasion protection and visibility. It is found in a variety of industries and environments both indoor and out.

Other applications

The handles of the Victorinox Swiss Army knives are made of PVC.

PVC has been used for a host of consumer products. One of its earliest mass-market consumer applications was vinyl record production. More recent examples include wallcovering, greenhouses, home playgrounds, foam and other toys, custom truck toppers (tarpaulins), ceiling tiles and other kinds of interior cladding.

PVC piping is cheaper than metals used in musical instrument making; it is therefore a common alternative when making instruments, often for leisure or for rarer instruments such as the contrabass flute.

3. Polyamide

A **polyamide** is a macromolecule with repeating units linked by amide bonds.

Polyamides occur both naturally and artificially. Examples of naturally occurring polyamides are proteins, such as wool and silk. Artificially made polyamides can be made through step-growth polymerization or solid-phase synthesis yielding materials such as nylons, aramids, and sodium poly(aspartate). Synthetic polyamides are commonly used in textiles, automotive applications, carpets and sportswear due to their high durability and strength. The transportation manufacturing industry is the major consumer, accounting for 35% of polyamide (PA) consumption.

Classification

Polymers of amino acids are known as polypeptides or proteins.

According to the composition of their main chain, synthetic polyamides are classified as follows:

Polyamide family	**Main chain**	**Examples of polyamides**	**Examples of commercial products**
Aliphatic polyamides	Aliphatic	Nylon PA 6 and PA 66	Zytel from DuPont, Technyl from Solvay, Rilsan and Rilsamid from Arkema, Radipol from Radici Group
Polyphthalamides	Semi-	PA 6T	Trogamid T

	aromatic	= hexamethylenediamine + terephthalic acid	from Evonik Industries, Amodel from Solvay
Aramids = **ar**omatic poly**amide**s	Aromatic	Paraphenylenediamine + terephthalic acid	Kevlar and Nomex from DuPont, Teijinconex, Twaron and Technora from Teijin, Kermel from Kermel.

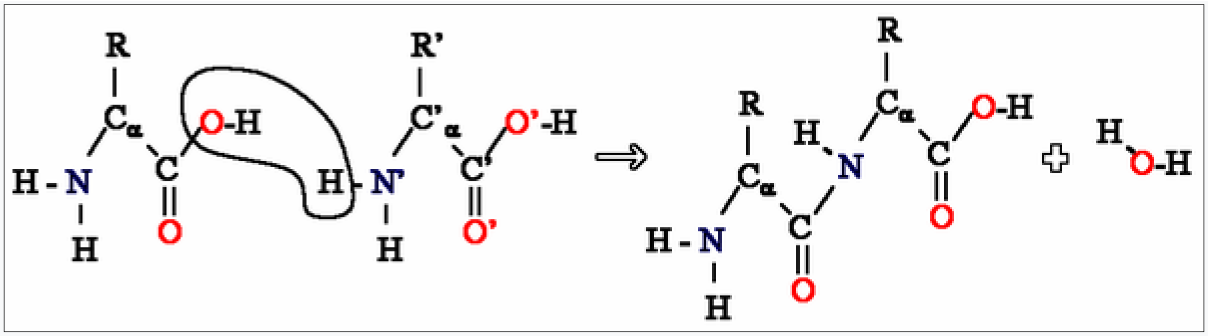
All polyamides are made by the formation of an amide function to link two molecules of monomer together. The monomers can be amides themselves (usually in the form of a cyclic lactam such as caprolactam), α,ω-amino acids or a stoichiometric mixture of a diamine and a diacid. Both these kinds of precursors give a homopolymer. Polyamides are easily copolymerized, and thus many mixtures of monomers are possible which can in turn lead to many copolymers. Additionally many nylon polymers are miscible with one another allowing the creation of blends.

Polymerization

Production of polymers requires the repeated joining of two groups to form an amide linkage. In this case this specifically involves amide bonds, and the two groups involved are an amine group, and a terminal carbonyl component of a functional group. These react to produce a carbon-nitrogen bond, creating a singular amide linkage. This process involves the elimination of other atoms previously part of the functional groups. The carbonyl-component may be part of either a carboxylic acid group or the more reactive acyl halide derivative. The amine group and the carboxylic acid group can be on the same monomer, or the polymer can be constituted of two different bifunctional monomers, one with two amine groups, the other with two carboxylic acid or acid chloride groups.

The condensation reaction is used to synthetically produce nylon polymers in industry. Nylons must specifically include an straight chain (aliphatic) monomer. The amide link is produced from an amine group (alternatively known as an amino group), and a carboxylic acid group. The hydroxyl from the carboxylic acid combines with a hydrogen from the amine, and gives rise to water, the elimination byproduct that is the namesake of the reaction.

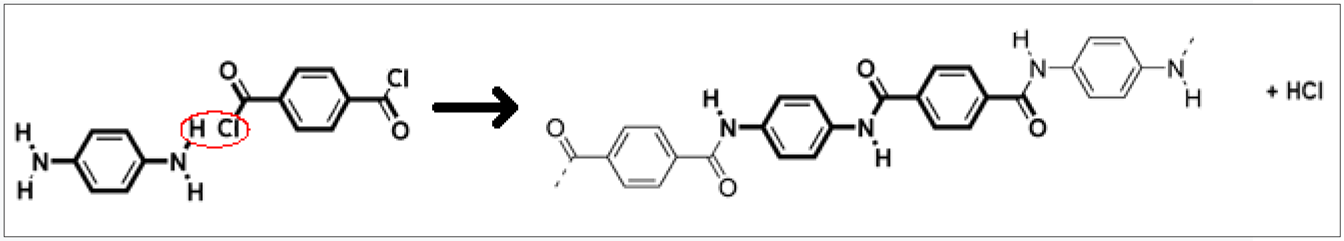
As an example of condensation reactions, consider that in living organisms, Amino acids are condensed with one another by an enzyme to form amide linkages (known as peptides). The resulting polyamides are known as proteins or polypeptides. In the diagram below, consider the amino-acids as single aliphatic monomers reacting with identical molecules to form a polyamide, focusing on solely the amine and acid groups. Ignore the substituent R groups – under the assumption the difference between the R groups are negligible:



The reaction of two amino acids. Many of these reactions produce long chain proteins

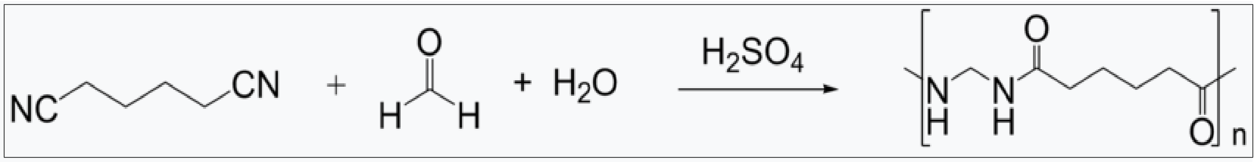
For fully aromatic polyamides or 'aramids' e.g. Kevlar, the more reactive acyl chloride is used as a monomer. The polymerization reaction with the amine group eliminates hydrogen chloride. The acid chloride route can be used as a laboratory synthesis to avoid heating and obtain an almost instantaneous reaction. The aromatic moiety itself does not participate in elimination reaction, but it does increase the rigidity and strength of the resulting material which leads to Kevlar's renowned strength.

In the diagram below, Aramid is made from two different monomers which continuously alternate to form the polymer. Aramid is an aromatic polyamide:



The reaction of 1,4-phenyl-diamine (para-phenylenediamine) and terephthaloyl chloride to produce Aramid

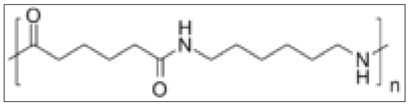
Polyamides can also be synthesized from dinitriles using acid catalysis via an application of the Ritter reaction. This method is applicable for preparation of nylon 1,6 from adiponitrile, formaldehyde and water. Additionally, polyamides can be synthesized from glycols and dinitriles using this method as well.



Synthesis of Nylon 1,6 from adiponitrile, formaldehyde, and water using sulfuric acid as a catalyst

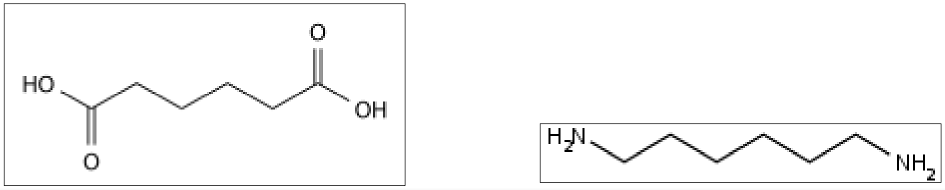
Example: Nylon 66

Nylon 66



Nylon 66 (**nylon 6-6**, **nylon 6/6** or **nylon 6,6**) is a type of polyamide or nylon. There are many types of nylon: the two most common for textile and plastics industries are nylon 6 and nylon 66. Nylon 66 is made of two monomers each containing 6 carbon atoms, hexamethylenediamine and adipic acid, which give nylon 66 its name.[1]

Synthesis and manufacturing



Hexamethylenediamine (top) and adipic acid (bottom), monomers used for polycondensation of Nylon 66.

Nylon 66 is synthesized by polycondensation of hexamethylenediamine and adipic acid. Equivalent amounts of hexamethylenediamine and adipic acid are combined with water in a reactor. This is crystallized to make nylon salt, an ammonium/carboxylate mixture. The nylon salt goes into a reaction vessel where polymerization process takes place either in batches or continuously.

$$n\ HOOC\text{-}(CH_2)_4\text{-}COOH + n\ H_2N\text{-}(CH_2)_6\text{-}NH_2 \rightarrow [\text{-}OC\text{-}(CH_2)_4\text{-}CO\text{-}NH\text{-}(CH_2)_6\text{-}NH\text{-}]_n + (2n\text{-}1)\ H_2O$$

Removing water drives the reaction toward polymerization through the formation of amide bonds from the acid and amine functions. Thus molten nylon 66 is formed. It can either be extruded and granulated at this point or directly spun into fibers by extrusion through a spinneret (a small metal plate with fine holes) and cooling to form filaments.

Applications

In 2011 worldwide production was 2 million tons. At that time fibers consumed just over half of production and engineering resins the rest. It is not used in films due to its inability to be oriented. Fiber markets represented 55% of the 2010 demand with engineering thermoplastics being the remainder.

Nylon 66 is frequently used when high mechanical strength, rigidity, good stability under heat and/or chemical resistance are required It is used in fibers for textiles and carpets and molded parts. For textiles, fibers are sold under various brands, for example Nilit brands or the Cordura brand for luggage, but it is also used in airbags, apparel, and for carpet fibres under the Ultron brand. Nylon 66 lends itself well to make 3D structural objects, mostly by injection molding finding broad use in auto application under the hood such as radiator end tanks, rocker covers, air intake manifolds, oil pans and numerous other structural parts such as ball bearing cages, electro-insulating elements, pipes, profiles, various machine parts, zip ties, conveyor belts, hoses, polymer framed weapons, and the outer layer of turnout blankets.[*clarification needed*] Nylon 66 is also a popular guitar nut material.

Nylon 66, especially glass fibre grades can be effectively fire retarded with halogen free products. Phosphorus-based flame retardant systems are used in these fire-safe polymers and are based on aluminium diethyl phosphinate and synergists. They are designed to meet UL 94flammability tests as well as Glow Wire Ignition Tests (GWIT), Glow Wire Flammability Test (GWFI) and Comparative Tracking Index (CTI). Main applications are in the electrical and electronics (E&E) industry.

The Remington Nylon 66 was a .22 rifle manufactured by Remington Arms from 1959 to 1989. It had a stock made from nylon 66.

4. **Polyester**

Close-up of a polyester shirt

Stretching polyester fabric

Polyester is a category of polymers that contain the ester functional group in their main chain. As a specific material, it most commonly refers to a type called polyethylene terephthalate (PET). Polyesters include naturally occurring chemicals, such as in the cutin of plant cuticles, as well as synthetics through step-growth polymerization such as polybutyrate. Natural polyesters and a few synthetic ones are biodegradable, but most synthetic polyesters are not. The material is used extensively in clothing.

Depending on the chemical structure, polyester can be a thermoplastic or thermoset. There are also polyester resins cured by hardeners; however, the most common polyesters are thermoplastics.

Fabrics woven or knitted from polyester thread or yarn are used extensively in apparel and home furnishings, from shirts and pants to jackets and hats, bed sheets, blankets, upholstered furniture and computer mouse mats. Industrial polyester fibers, yarns and ropes are used in car tire reinforcements, fabrics for conveyor belts, safety belts, coated fabrics and plastic reinforcements with high-energy absorption. Polyester fiber is used as cushioning and insulating material in pillows, comforters and upholstery padding. Polyester fabrics are highly stain-resistant—in fact, the only class of dyes which *can* be used to alter the color of polyester fabric are what are known as disperse dyes.

Polyester fibers are sometimes spun together with natural fibers to produce a cloth with blended properties. Cotton-polyester blends (polycotton) can be strong, wrinkle and tear-resistant, and reduce shrinking. Synthetic fibers in polyester also create materials with water, wind and environmental resistance compared to plant-derived fibers. Disadvantages of cotton and polyester blends include being less breathable than cotton and trapping more moisture while sticking to the skin. They are also less fire resistant and can melt when ignited.

Polyester blends have been renamed so as to suggest their similarity or even superiority to natural fibers (for example, China silk, which is a term in the textiles industry for a 100% polyester fiber woven to resemble the sheen and durability of insect-derived silk).

Polyesters are also used to make bottles, films, tarpaulin, canoes, liquid crystal displays, holograms, filters, dielectric film for capacitors, film insulation for wire and insulating tapes. Polyesters are widely used as a finish on high-quality wood products such as guitars, pianos and vehicle/yacht interiors. Thixotropic properties of spray-applicable polyesters make them ideal for use on open-grain timbers, as they can quickly fill wood grain, with a high-build film thickness per coat. Cured polyesters can be sanded and polished to a high-gloss, durable finish.

Liquid crystalline polyesters are among the first industrially used liquid crystal polymers. They are used for their mechanical properties and heat-resistance. These traits are also important in their application as an abradable seal in jet engines.

Synthesis

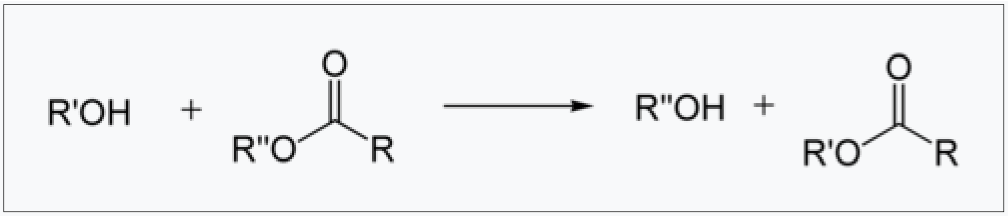
Synthesis of polyesters is generally achieved by a polycondensation reaction. See "condensation reactions in polymer chemistry". The general equation for the reaction of a diol with a diacid is :

$$(n+1)\ R(OH)_2 + n\ R'(COOH)_2 \rightarrow HO[ROOCR'COO]_nROH + 2n\ H_2O$$

Azeotrope esterification

In this classical method, an alcohol and a carboxylic acid react to form a carboxylic ester. To assemble a polymer, the water formed by the reaction must be continually removed by azeotrope distillation.

Alcoholic transesterification



Transesterification: An alcohol-terminated oligomer and an ester-terminated oligomer condense to form an ester linkage, with loss of an alcohol. R and R' are the two oligomer chains, R" is a sacrificial unit such as a methyl group (methanol is the byproduct of the esterification reaction).

Acylation (HCl method)

The acid begins as an acid chloride, and thus the polycondensation proceeds with emission of hydrochloric acid (HCl) instead of water. This method can be carried out in solution or as an enamel.

Silyl method

In this variant of the HCl method, the carboxylic acid chloride is converted with the trimethyl silyl ether of the alcohol component and production of trimethyl silyl chloride is obtained

Acetate method (esterification)

Silyl acetate method

Ring-opening polymerization

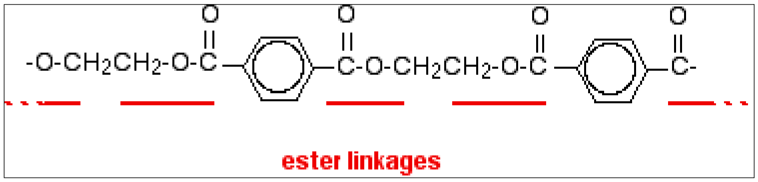
Aliphatic polyesters can be assembled from lactones under very mild conditions, catalyzed anionically, cationically or metallorganically. A number of catalytic methods for the copolymerization of epoxides with cyclic anhydrides have also recently been shown to provide a wide array of functionalized polyesters, both saturated and unsaturated.

Cross-linking

Unsaturated polyesters are thermosetting resins. They are generally copolymers prepared by polymerizing one or more diol with saturated and unsaturated dicarboxylic acids (maleic acid, fumaric acid...) or their anhydrides. The double bond of unsaturated polyesters reacts with a vinyl monomer, usually styrene, resulting in a 3-D cross-linked structure. This structure acts as a thermoset. The exothermic cross-linking reaction is initiated through a catalyst, usually an organic peroxide such as methyl ethyl ketone peroxide or benzoyl peroxide.

Example: Poly(ethylene terephthalate)

A polyester is a polymer (a chain of repeating units) where the individual units are held together by ester linkages.



The diagram shows a very small bit of the polymer chain and looks pretty complicated. But it isn't very difficult to work out - and that's the best thing to do: work it out, not try to remember it. You will see how to do that in a moment.

The usual name of this common polyester is poly(ethylene terephthalate). The everyday name depends on whether it is being used as a fibre or as a material for making things like bottles for soft drinks.

When it is being used as a fibre to make clothes, it is often just called *polyester*. It may sometimes be known by a brand name like *Terylene*.

When it is being used to make bottles, for example, it is usually called *PET*.

Making polyesters as an example of condensation polymerisation

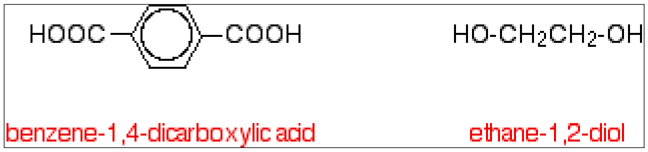
In condensation polymerisation, when the monomers join together a small molecule gets lost. That's different from addition polymerisation which produces polymers like poly(ethene) - in that case, nothing is lost when the monomers join together.

A polyester is made by a reaction involving an acid with two -COOH groups, and an alcohol with two -OH groups.

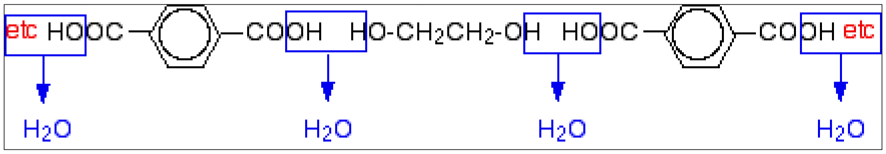
In the common polyester drawn above:

The acid is benzene-1,4-dicarboxylic acid (old name: terephthalic acid).

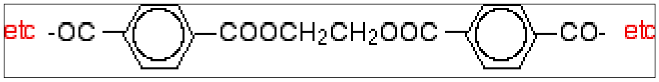
The alcohol is ethane-1,2-diol (old name: ethylene glycol).



Now imagine lining these up alternately and making esters with each acid group and each alcohol group, losing a molecule of water every time an ester linkage is made.



That would produce the chain shown above (although this time written without separating out the carbon-oxygen double bond - write it whichever way you like).



Hydrolysis of polyesters

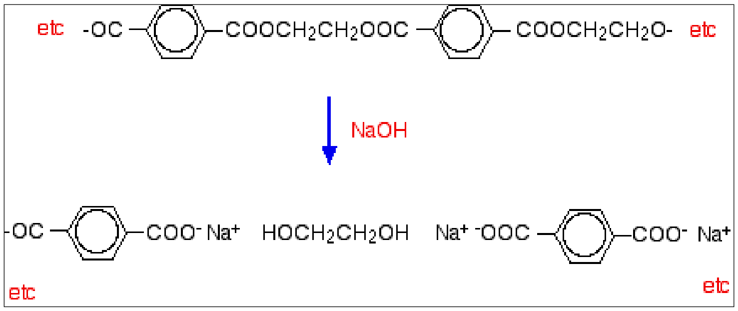
Simple esters are easily hydrolysed by reaction with dilute acids or alkalis.

Polyesters are attacked readily by alkalis, but much more slowly by dilute acids. Hydrolysis by water alone is so slow as to be completely unimportant. (You wouldn't expect your polyester fleece to fall to pieces if you went out in the rain!)

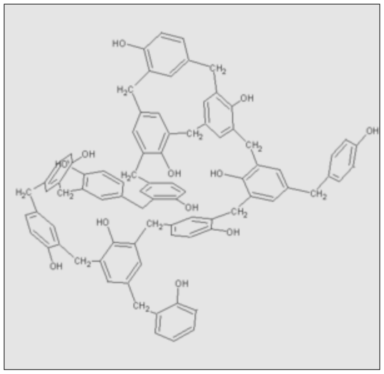
If you spill dilute alkali on a fabric made from polyester, the ester linkages are broken. Ethane-1,2-diol is formed together with the salt of the carboxylic acid.

Because you produce small molecules rather than the original polymer, the fibres are destroyed, and you end up with a hole!

For example, if you react the polyester with sodium hydroxide solution:



5. Phenol formaldehyde resin



Phenol formaldehyde resins (PF) or **phenolic resins** are synthetic polymers obtained by the reaction of phenol or substituted phenol with formaldehyde. Used as the basis for Bakelite, PFs were the first commercial synthetic resins (plastics). They have been widely used for the production of molded products including billiard balls, laboratory countertops, and as coatings and adhesives. They were at one time the primary material used for the production of circuit boards but have been largely replaced with epoxy resins and fiberglass cloth, as with fire-resistant FR-4 circuit board materials.

There are two main production methods. One reacts phenol and formaldehyde directly to produce a thermosetting network polymer, while the other restricts the formaldehyde to produce a prepolymer known as **novolac** which can be moulded and then cured with the addition of more formaldehyde and heat. There are many variations in both production and input materials that are used to produce a wide variety of resins for special purposes.

Formation and structure

Phenol-formaldehyde resins, as a group, are formed by a step-growth polymerization reaction that can be either acid- or base-catalysed. Since formaldehyde exists predominantly in solution as a dynamic equilibrium of methylene glycol oligomers, the concentration of the *reactive* form of formaldehyde depends on temperature and pH.

Phenol reacts with formaldehyde at the ortho and para sites (sites 2, 4 and 6) allowing up to 3 units of formaldehyde to attach to the ring. The initial reaction in all cases involves the formation of a hydroxymethyl phenol:

$$HOC_6H_5 + CH_2O \rightarrow HOC_6H_4CH_2OH$$

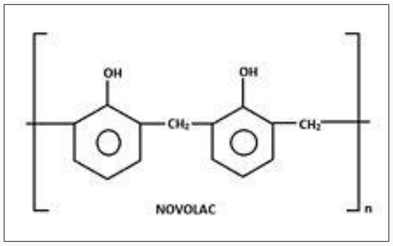
The hydroxymethyl group is capable of reacting with either another free ortho or para site, or with another hydroxymethyl group. The first reaction gives a methylene bridge, and the second forms an ether bridge:

$$HOC_6H_4CH_2OH + HOC_6H_5 \rightarrow (HOC_6H_4)_2CH_2 + H_2O$$

$$2\ HOC_6H_4CH_2OH \rightarrow (HOC_6H_4CH_2)_2O + H_2O$$

The diphenol $(HOC_6H_4)_2CH_2$ (sometimes called a "dimer") is called bisphenol F, which is an important monomer in the production of epoxy resins. Bisphenol-F can further link generating tri- and tetra-and higher phenol oligomers.

Novolacs



Novolac

Novolacs are phenol-formaldehyde resins with a formaldehyde to phenol molar ratio of less than one. The polymerization is brought to completion using acid-catalysis such as oxalic acid, hydrochloric acid or sulfonate acids. The phenol units are mainly linked by methylene and/or ether groups. Novolacs are commonly used as photoresists. See also photolithography. The molecular weights are in the low thousands, corresponding to about 10–20 phenol units.

Hexamethylenetetramine or "hexamine" is a hardener added to crosslink novolac. At a temperature >90 °C, it forms methylene and dimethylene amino bridges.

Applications

Phenolic resins are found in a myriad of industrial products. Phenolic laminates are made by impregnating one or more layers of a base material such as paper, fiberglass or cotton with phenolic resin and laminating the resin-saturated base material under heat and pressure. The resin fully polymerizes (cures) during this process forming the thermoset polymer matrix. The base material choice depends on the intended application of the finished product. Paper phenolics are used in manufacturing electrical components such as punch-through boards, in household laminates, and in paper composite panels. Glass phenolics are particularly well suited for use in the high speed bearing market. Phenolic micro-balloons are used for density control. Snooker balls as well as balls from many table-based ball games are also made from phenol formaldehyde resin. The binding agent in normal (organic) brake pads, brake shoes and clutch disks are phenolic resin. Synthetic resin bonded paper, made from phenolic resin and paper, is used to make countertops.

Phenolic resins are also used for making exterior plywood commonly known as WBP (Weather & boil proof) Plywood because phenolic resins have no melting point but only a decomposing point in the temperature zone of 220 °C (428 °F) and above.

Phenolic resin is used as a binder in loudspeaker driver suspension components which are made of cloth.

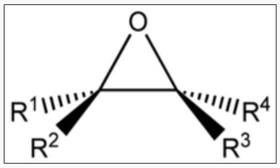
Billiard balls are made from solid Phenolic resin.

Sometimes people select phenolic resin parts because their coefficient of thermal expansion closely matches that of the aluminium used for other parts of a system, as in early computer systems and Duramold.

6. <u>Epoxy</u>

This article is about the thermoset plastic materials. For the chemical group, see epoxide.

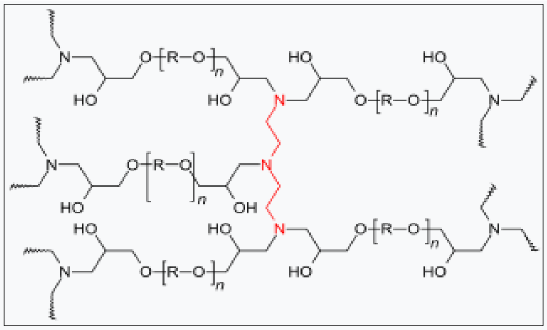
A syringe of "5-minute" epoxy glue, containing separate compartments for the epoxy resin and the hardener.



Structure of the highly reactive epoxide group present in all epoxy resins.

Epoxy is either any of the basic components or the cured end products of **epoxy resins**, as well as a colloquial name for the epoxidefunctional group.[1] Epoxy resins, also known as **polyepoxides**, are a class of reactive prepolymers and polymers which contain epoxide groups. Epoxy resins may be reacted (cross-linked) either with themselves through catalytic homopolymerisation, or with a wide range of co-reactants including polyfunctional amines, acids (and acid anhydrides), phenols, alcohols and thiols. These co-reactants are often referred to as hardeners or curatives, and the cross-linking reaction is commonly referred to as curing. Reaction of polyepoxides with themselves or with polyfunctional hardeners forms a thermosetting polymer, often with high mechanical properties, temperature and chemical resistance. Epoxy has a wide range of applications, including metal coatings, use in electronics / electrical components/LED, high tension electrical insulators, paint brush manufacturing, fiber-reinforced plastic materials and structural adhesives.

Epoxy resin



Structure of a cured epoxy glue. The triamine hardener is shown in red, the resin in black. The resin's epoxide groups have reacted with the hardener and are not present anymore. The material is highly crosslinkedand contains many OH groups, which confer adhesive properties.

Epoxy resins are low molecular weight pre-polymers or higher molecular weight polymers which normally contain at least two epoxide groups. The epoxide group is also sometimes referred to as a glycidyl or oxirane group.

A wide range of epoxy resins are produced industrially. The raw materials for epoxy resin production are today largely petroleum derived, although some plant derived sources are now becoming commercially available (e.g. plant derived glycerol used to make epichlorohydrin).

Epoxy resins are polymeric or semi-polymeric materials, and as such rarely exist as pure substances, since variable chain length results from the polymerisation reaction used to produce them. High purity grades can be produced for certain applications, e.g. using a distillation purification process. One downside of high purity liquid grades is their tendency to form crystalline solids due to their highly regular structure, which require melting to enable processing.

An important criterion for epoxy resins is the epoxide content. This is commonly expressed as the **epoxy equivalent weight**, which is the number of epoxide equivalents in 1 kg of resin (Eq./kg), or as the **equivalent weight**, which is the weight in grammes of resin containing 1 mole equivalent of epoxide (g/mol). One measure may be simply converted to another:

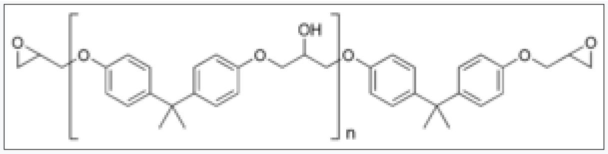
Equivalent weight (g/mol) = 1000 / epoxide number (Eq./kg)

The equivalent weight or epoxide number is used to calculate the amount of co-reactant (hardener) to use when curing epoxy resins. Epoxies are typically cured with stoichiometric or near-stoichiometric quantities of curative to achieve maximum physical properties.

As with other classes of thermoset polymer materials, blending different grades of epoxy resin, as well as use of additives, plasticizers or fillers is common to achieve the desired processing or final properties, or to reduce cost. Use of blending, additives and fillers is often referred to as **formulating**.

Examples: Bisphenol A epoxy resin

Important epoxy resins are produced from combining epichlorohydrin and bisphenol A to give bisphenol A diglycidyl ethers.



Structure of bisphenol-A diglycidyl ether epoxy resin: *n* denotes the number of polymerized subunits and is typically in the range from 0 to 25

Increasing the ratio of bisphenol A to epichlorohydrin during manufacture produces higher molecular weight linear polyethers with glycidyl end groups, which are semi-solid to hard crystalline materials at room temperature depending on the molecular weight achieved. As the molecular weight of the resin increases, the epoxide content reduces and the material behaves more and more like a thermoplastic. Very high molecular weight polycondensates (ca. 30 000 – 70 000 g/mol) form a class known as phenoxy resins and contain virtually no epoxide groups (since the terminal epoxy groups are insignificant compared to the total size of the molecule). These resins do however contain hydroxyl groups throughout the backbone, which may also undergo other cross-linking reactions, e.g. with aminoplasts, phenoplasts and isocyanates.

Bisphenol F epoxy resin

Bisphenol F may also undergo epoxidation in a similar fashion to bisphenol A. Compared to DGEBA, bisphenol F epoxy resins have lower viscosity and a higher mean epoxy content per gramme, which (once cured) gives them increased chemical resistance.

Applications

The applications for epoxy-based materials are extensive and include coatings, adhesives and composite materials such as those using carbon fiber and fiberglass reinforcements (although polyester, vinyl ester, and other thermosetting resins are also used for glass-reinforced plastic). The chemistry of epoxies and the range of commercially available variations allows cure polymers to be produced with a very broad range of properties. In general, epoxies are known for their excellent adhesion, chemical and heat resistance, good-to-excellent mechanical properties and very good electrical insulating properties. Many properties of epoxies can be modified (for example silver-filled epoxies with good electrical conductivity are available, although epoxies are typically electrically insulating). Variations offering high thermal insulation, or thermal conductivity combined with high electrical resistance for electronics applications, are available.[6]

Paints and coatings

Two part epoxy coatings were developed for heavy duty service on metal substrates and use less energy than heat-cured powder coatings. These systems provide a tough, protective coating with excellent hardness. Some epoxy coatings are formulated as an emulsion in water, and can be cleaned up without solvents. Epoxy coatings are often used in industrial and automotive applications since they are more heat resistant than latex-based and alkyd-based paints. Epoxy paints tend to deteriorate, known as "chalking out", due to UV exposure.[7]

Polyester epoxies are used as powder coatings for washers, driers and other "white goods". Fusion Bonded Epoxy Powder Coatings (FBE) are extensively used for corrosion protection of steel pipes and fittings used in the oil and gas industry, potable water transmission pipelines (steel), and concrete reinforcing rebar. Epoxy coatings are also widely used as primers to improve the adhesion of automotive and marine paints especially on metal surfaces where corrosion (rusting) resistance is important. Metal cans and containers are often coated with epoxy to prevent rusting, especially for foods like tomatoes that are acidic. Epoxy resins are also used for decorative flooring applications such as terrazzo flooring, chip flooring, and colored aggregate flooring. Epoxies were modified in a variety of ways, Reacted with fatty acids derived from oils to yield epoxy esters, which were cured the same way as alkyds .

Adhesives

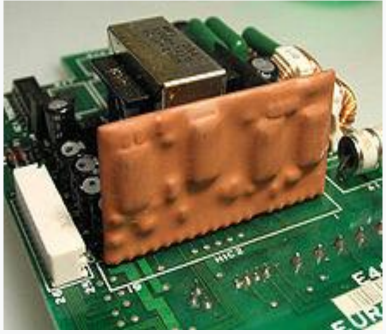
Special epoxy is strong enough to withstand the forces between a surfboard fin and the fin mount. This epoxy is waterproof and capable of curing underwater. The blue-coloured epoxy on the left is still undergoing curing.

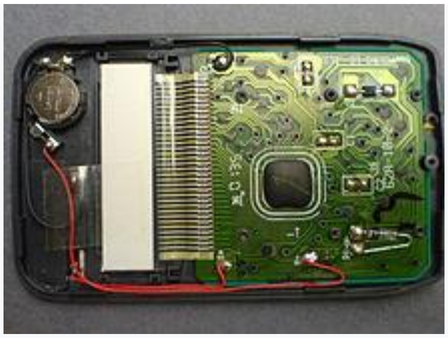
Epoxy adhesives are a major part of the class of adhesives called "structural adhesives" or "engineering adhesives" (that includes polyurethane, acrylic, cyanoacrylate, and other chemistries.) These high-performance adhesives are used in the construction of aircraft, automobiles, bicycles, boats, golf clubs, skis, snowboards, and other applications where high strength bonds are required. Epoxy adhesives can be developed to suit almost any application. They can be used as adhesives for wood, metal, glass, stone, and some plastics. They can be made flexible or rigid, transparent or opaque/colored, fast setting or slow setting. Epoxy adhesives are better in heat and chemical resistance than other common adhesives. Some epoxies are cured by exposure to ultraviolet light. Such epoxies are commonly used in optics, fiber optics, and optoelectronics.

Industrial tooling and composites

Epoxy systems are used in industrial tooling applications to produce molds, master models, laminates, castings, fixtures, and other industrial production aids. This "plastic tooling" replaces metal, wood and other traditional materials, and generally improves the efficiency and either lowers the overall cost or shortens the lead-time for many industrial processes. Epoxies are also used in producing fiber-reinforced or composite parts. They are more expensive than polyester resins and vinyl ester resins, but usually produce stronger and more temperature-resistant thermoset polymer matrix composite parts.

Electrical systems and electronics





An epoxy encapsulated hybrid circuit on a printed circuit board.

The interior of a pocket calculator. The dark lump of epoxy in the center covers the processor chip

Epoxy resin formulations are important in the electronics industry, and are employed in motors, generators, transformers, switchgear, bushings, and insulators. Epoxy resins are excellent electrical insulators and protect electrical components from short circuiting, dust and moisture. In the electronics industry epoxy resins are the primary resin used in overmolding integrated circuits, transistors and hybrid circuits, and making printed circuit boards. The largest volume type of circuit board—an "FR-4 board"—is a sandwich of layers of glass cloth bonded into a composite by an epoxy resin. Epoxy resins are used to bond copper foil to circuit board substrates, and are a component of the solder mask on many circuit boards.

Petroleum & petrochemical

Epoxies can be used to plug selective layers in a reservoir which are producing excessive brine. The technique is named "water shut-off treatment".[2]

Consumer and marine applications

Epoxies are sold in hardware stores, typically as a pack containing separate resin and hardener, which must be mixed immediately before use. They are also sold in boat shops as repair resins for marine applications. Epoxies typically are not used in the outer layer of a boat because they deteriorate by exposure to UV light. They are often used during boat repair and assembly, and then over-coated with conventional or two-part polyurethane paint or marine-varnishes that provide UV protection.

There are two main areas of marine use. Because of the better mechanical properties relative to the more common polyester resins, epoxies are used for commercial manufacture of components where a high strength/weight ratio is required. The second area is that their strength, gap filling properties and excellent adhesion to many materials including timber have created a boom in amateur building projects including aircraft and boats.

Epoxy materials tend to harden somewhat more gradually, while polyester materials tend to harden quickly, particularly if a lot of catalyst is used.[9] The chemical reactions in both cases are exothermic. Large quantities of mix will generate their own heat and greatly speed the reaction, so it is usual to mix small amounts which can be used quickly.

As adhesives, epoxies bond in three ways: a) Mechanically, because the bonding surfaces are roughened; b) By proximity, because the cured resins are physically so close to the bonding surfaces that they are hard to separate; c) Ionically, because the epoxy resins form ionic bonds at an atomic level with the bonding surfaces. This last is substantially the strongest of the three. By contrast, polyester resins can only bond using the first two of these, which greatly reduces their utility as adhesives and in marine repair.

Aerospace applications

In the aerospace industry, epoxy is used as a structural matrix material which is then reinforced by fiber. Typical fiber reinforcements include glass, carbon, Kevlar, and boron. Epoxies are also used as a structural glue. Materials like wood, and others that are 'low-tech' are glued with epoxy resin.

Biology

Water-soluble epoxies such as Durcupan are commonly used for embedding electron microscope samples in plastic so they may be sectioned (sliced thin) with a microtomeand then imaged.

Art

Epoxy resin, mixed with pigment, may be used as a painting medium, by pouring layers on top of each other to form a complete picture.

Industry

These commodity epoxy manufacturers mentioned above typically do not sell epoxy resins in a form usable to smaller end users, so there is another group of companies that purchase epoxy raw materials from the major producers and then compounds (blends, modifies, or otherwise customizes) epoxy systems from these raw materials. These companies are known as "formulators". The majority of the epoxy systems sold are produced by these formulators and they comprise over 60% of the dollar value of the epoxy market. There are hundreds of ways that these formulators can modify epoxies—by adding mineral fillers (talc, silica, alumina, etc.), by adding flexibilizers, viscosity reducers, colorants, thickeners, accelerators, adhesion promoters, etc. These modifications are made to reduce costs, to improve performance, and to improve processing convenience. As a result, a typical formulator sells dozens or even thousands of formulations—each tailored to the requirements of a particular application or market.

7. Silicone

Silicone caulk can be used as a basic sealant against water and air penetration.

Silicones, also known as **polysiloxanes**, are polymers that include any inert, synthetic compound made up of repeating units of siloxane, which is a chain of alternating silicon atoms and oxygen atoms, frequently combined with carbon and/or hydrogen. They are typically heat-resistant and rubber-like, and are used in sealants, adhesives, lubricants, medicine, cooking utensils, and thermal and electrical insulation. Some common forms include silicone oil, silicone grease, silicone rubber, silicone resin, and silicone caulk. Silicones are of three types: 1. straight chain silicones; 2. cyclic silicones; 3. crosslinked silicones.

Synthesis

Most common are materials based on polydimethylsiloxane, which is derived by hydrolysis of dimethyldichlorosilane. This dichloride reacts with water as follows:

$$n\,\mathrm{Si(CH_3)_2Cl_2} + n\,\mathrm{H_2O} \rightarrow [\mathrm{Si(CH_3)_2O}]_n + 2n\,\mathrm{HCl}$$

The polymerization typically produces linear chains capped with Si-Cl or Si-OH (silanol) groups. Under different conditions the polymer is a cyclic, not a chain.

For consumer applications such as caulks silyl acetates are used instead of silyl chlorides. The hydrolysis of the acetates produce the less dangerous acetic acid (the acid found in vinegar) as the reaction product of a much slower curing process. This chemistry is used in many consumer applications, such as silicone caulk and adhesives.

Branches or cross-links in the polymer chain can be introduced by using organosilicone precursors with fewer alkyl groups, such as methyltrichlorosilane and methyltrimethoxysilane. Ideally, each molecule of such a compound becomes a branch point. This process can be used to produce hard silicone resins. Similarly, precursors with three methyl groups can be used to limit molecular weight, since each such molecule has only one reactive site and so forms the end of a siloxane chain.

Combustion

When silicone is burned in air or oxygen, it forms solid silica (silicon dioxide)(SiO_2) as a white powder, char, and various gases. The readily dispersed powder is sometimes called silica fume.

Properties

Silicones exhibit many useful characteristics, including:[1]

- Low thermal conductivity
- Low chemical reactivity
- Low toxicity
- Thermal stability (constancy of properties over a wide temperature range of −100 to 250 °C).
- The ability to repel water and form watertight seals.
- Does not stick to many substrates, but adheres very well to others, e.g. glass.
- Does not support microbiological growth.
- Resistance to oxygen, ozone, and ultraviolet (UV) light. This property has led to widespread use of silicones in the construction industry (e.g. coatings, fire protection, glazing seals) and the automotive industry (external gaskets, external trim).
- Electrical insulation properties. Because silicone can be formulated to be electrically insulative or conductive, it is suitable for a wide range of electrical applications.
- High gas permeability: at room temperature (25 °C), the permeability of silicone rubber for such gases as oxygen is approximately 400 times[*citation needed*] that of butyl rubber, making silicone useful for medical applications in which increased aeration is desired. Conversely, silicone rubbers cannot be used where gas-tight seals are necessary.

Uses

Silicones are used in many products. Ullmann's Encyclopedia of Industrial Chemistry lists the following major categories of application: Electrical (e.g., insulation), electronics (e.g., coatings), household (e.g., sealants for cooking apparatus), automobile (e.g., gaskets), aeroplane (e.g., seals), office machines (e.g., keyboard pads), medicine/dentistry (e.g., teeth impression molds), textiles/paper (e.g., coatings). For these applications, an estimated 400,000 tons of silicones were produced in 1991. Specific examples, both large and small are presented below.

Automotive

In the automotive field, silicone grease is typically used as a lubricant for brake components since it is stable at high temperatures, is not water-soluble, and is far less likely than other lubricants to foul. It is also used as DOT 5 brake fluid.

Automotive spark plug wires are insulated by multiple layers of silicone to prevent sparks from jumping to adjacent wires, causing misfires. Silicone tubing is sometimes used in automotive intake systems (especially for engines with forced induction).

Sheet silicone is used to manufacture gaskets used in automotive engines, transmissions, and other applications.

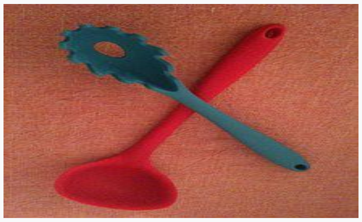
Automotive body manufacturing plants and paint shops avoid silicones, as they may cause "fish eyes", small, circular craters in the finish.

Coatings

Silicone films can be applied to such silica-based substrates as glass to form a covalently bonded hydrophobic coating.

Many fabrics can be coated or impregnated with silicone to form a strong, waterproof composite such as silnylon.

Cookware



Soup ladle and pasta ladle made of silicone.

A silicone food steamer to be placed inside a pot of boiling water.

Ice cube trays made of silicone.

- As a low-taint, non-toxic material, silicone can be used where contact with food is required. Silicone is becoming an important product in the cookware industry, particularly bakeware and kitchen utensils.
- Silicone is used as an insulator in heat-resistant potholders and similar items; however, it is more conductive of heat than similar less dense fiber-based products. Silicone oven mitts are able to withstand temperatures up to 260 °C (500 °F), allowing reaching into boiling water.
- Molds for chocolate, ice, cookies, muffins and various other foods.
- Non-stick bakeware and reusable mats used on baking sheets.
- Other products such as steamers, egg boilers or poachers, cookware lids, pot holders, trivets, and kitchen mats.

Defoaming

Silicones are used as active compound in defoamers due to their low water solubility and good spreading properties.

Dry cleaning

Liquid silicone can be used as a dry cleaning solvent, providing an alternative to the traditional chlorine-containing perchloroethylene (perc)solvent. Use of silicones in dry cleaning reduces the environmental impact of a typically high-polluting industry.

Electronics

Electronic components are sometimes encased in silicone to increase stability against mechanical and electrical shock, radiation and vibration, a process called "potting".

Silicones are used where durability and high performance are demanded of components under hard conditions, such as in space (satellite technology). They are selected over polyurethane or epoxy encapsulation when a wide operating temperature range is required (−65 to 315 °C). Silicones also have the advantage of little exothermic heat rise during cure, low toxicity, good electrical properties and high purity.

The use of silicones in electronics is not without problems, however. Silicones are relatively expensive and can be attacked by solvents. Silicone easily migrates as either a liquid or vapor onto other components.

Silicone contamination of electrical switch contacts can lead to failures by causing an increase in contact resistance, often late in the life of the contact, well after any testing is completed. Use of silicone-based spray products in electronic devices during maintenance or repairs can cause later failures.

Firestops

Silicone foam has been used in North American buildings in an attempt to firestop openings within fire-resistance-rated wall and floor assemblies to prevent the spread of flames and smoke from one room to another. When properly installed, silicone-foam firestops can be fabricated for building code compliance. Advantages include flexibility and high dielectric strength. Disadvantages include combustibility (hard to extinguish) and significant smoke development.

Silicone-foam firestops have been the subject of controversy and press attention due to smoke development from pyrolysis of combustible components within the foam, hydrogen gas escape, shrinkage, and cracking. These problems have led to reportable events among licensees (operators of nuclear power plants) of the Nuclear Regulatory Commission (NRC).

Silicone firestops are also used in aircraft.

8. Functional polymers

Functional polymers are polymers with advanced optic and/or electronic properties. Advantages of functional polymers are low cost, ease of processing and a range of attractive mechanical characteristics for functional organic molecules. One can adjust properties while keeping material usage low. This opens interesting environmental perspectives. Polymer bound substances can spread their activity without endangering people or the environment. The new REACH (Registration, Evaluation and Authorisation of Chemicals) legislation will require chemical industry to come up with safe chemicals. Functional polymers can help achieve this goal.

Examples of functional polymers are;

- Semiconducting Conjugated Polymers
- Stimuli-Responsive Polymers (these allow for responsive drug delivery systems and smart surfaces for cell culture and regenerative medicine.)
- Biomimetic Materials
- Supramolecular Metallopolymers

9. Fire-safe polymers

Fire-safe polymers are polymers that are resistant to degradation at high temperatures. There is need for fire-resistant polymers in the construction of small, enclosed spaces such as skyscrapers, boats, and airplane cabins. In these tight spaces, ability to escape in the event of a fire is compromised, increasing fire risk. In fact, some studies report that about 20% of victims of airplane crashes are killed not by the crash itself but by ensuing fires. Fire-safe polymers also find application as adhesives in aerospace materials, insulationfor electronics, and in military materials such as canvas tenting.

Some fire-safe polymers naturally exhibit an intrinsic resistance to decomposition, while others are synthesized by incorporating fire-resistant additives and fillers. Current research in developing fire-safe polymers is focused on modifying various properties of the polymers such as ease of ignition, rate of heat release, and the evolution of smoke and toxic gases.[1]Standard methods for testing polymer flammability vary among countries; in the United States common fire tests include the UL 94 small-flame test, the ASTM E 84 Steiner Tunnel, and the ASTM E 622 National Institute of Standards and Technology (NIST) smoke chamber.[1] Research on developing fire-safe polymers with more desirable properties is concentrated at the University of Massachusetts Amherst and at the Federal Aviation Administration where a long-term research program on developing fire-safe polymers was begun in 1995. The Center for UMass/Industry Research on Polymers (CUMIRP) was established in 1980 in Amherst, MA as a concentrated cluster of scientists from both academia and industry for the purpose of polymer science and engineering research.

Purpose and methods of fire-retardant systems

The purpose is to control heat below the critical level. To achieve this, one can create an endothermic environment, produce non-combustible products, or add chemicals that would remove fire-propagating radicals (H and OH), to name a few. These specific chemicals can be added into the polymer molecules permanently (see Intrinsically Fire-Resistant Polymers) or as additives and fillers (see Flame-Retardant Additives and Fillers).

Role of oxygen

Oxygen catalyzes the pyrolysis of polymers at low concentration and initiates oxidation at high concentration. Transition concentrations are different for different polymers. (e.g., polypropylene, between 5% and 15%). Additionally, polymers exhibit a structural-dependent relationship with oxygen. Some structures are intrinsically more sensitive to decomposition upon reaction with oxygen. The amount of access that oxygen has to the surface of the polymer also plays a role in polymer combustion. Oxygen is better able to interact with the polymer before a flame has actually been ignited.

Role of heating rate

In most cases, results from a typical heating rate (e.g. 10℃/min for mechanical thermal degradation studies) do not differ significantly from those obtained at higher heating rates. The extent of reaction can, however, be influenced by the heating rate. For example, some reactions may not occur with a low heating rate due to evaporation of the products.

Role of pressure

Volatile products are removed more efficiently under low pressure, which means the stability of the polymer might have been compromised. Decreased pressure also slows down decomposition of high boiling products.

Intrinsically fire-resistant polymers

The polymers that are most efficient at resisting combustion are those that are synthesized as intrinsically fire-resistant. However, these types of polymers can be difficult as well as costly to synthesize. Modifying different properties of the polymers can increase their intrinsic fire-resistance; increasing rigidity or stiffness, the use of polar monomers, and/or hydrogen bonding between the polymer chains can all enhance fire-resistance.

Linear, single-stranded polymers with cyclic aromatic components

Most intrinsically fire-resistant polymers are made by incorporation of aromatic cycles or heterocycles, which lend rigidity and stability to the polymers. Polyimides, polybenzoxazoles (PBOs), polybenzimidazoles, and polybenzthiazoles (PBTs) are examples of polymers made with aromatic heterocycles (Figure).

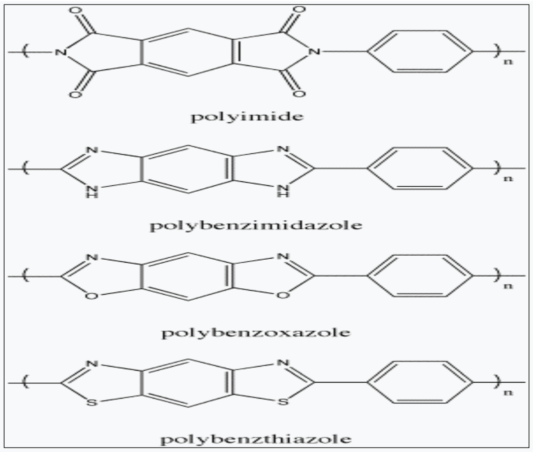


Figure: Different fire-resistant polymers made with aromatic heterocycles.

Polymers made with aromatic monomers have a tendency to condense into chars upon combustion, decreasing the amount of flammable gas that is released. Syntheses of these types of polymers generally employ prepolymers which are further reacted to form the fire-resistant polymers.

Ladder polymers

Ladder polymers are a subclass of polymers made with aromatic cycles or heterocycles. Ladder polymers generally have one of two types of general structures, as shown in Figure 3.

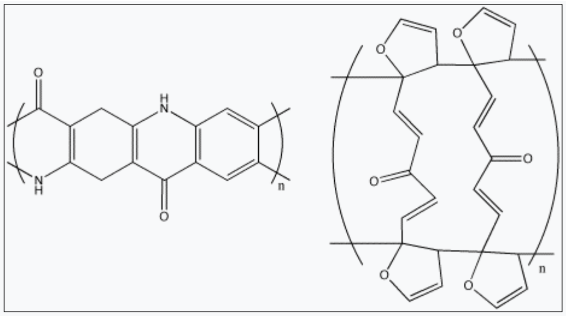


Figure: Two representative structures of different types of ladder polymers.

One type of ladder polymer links two polymer chains with periodic covalent bonds. In another type, the ladder polymer consists of a single chain that is double-stranded. Both types of ladder polymers exhibit good resistance to decomposition from heat because the chains do not necessarily fall apart if one covalent bond is broken. However, this makes the processing of ladder polymers difficult because they are not easily melted. These difficulties are compounded because ladder polymers are often highly insoluble.

Inorganic and semiorganic polymers

Inorganic and semiorganic polymers often employ silicon-nitrogen, boron-nitrogen, and phosphorus-nitrogen monomers. The non-burning characteristics of the inorganic components of these polymers contribute to their controlled flammability. For example, instead of forming toxic, flammable gasses in abundance, polymers prepared with incorporation of cyclotriphosphazene rings give a high char yield upon combustion. Polysialates (polymers containing frameworks of aluminum, oxygen, and silicon) are another type of inorganicpolymer that can be thermally stable up to temperatures of 1300-1400 °C.

Flame-retardant additives and fillers

Additives are divided into two basic types depending on the interaction of the additive and polymer. Reactive flame retardants are compounds that are chemically built into the polymer. They usually contain heteroatoms. Additive flame retardants, on the other hand, are compounds that are not covalently bound to the polymer; the flame retardant and the polymer are just physically mixed together. Only a few elements are being widely used in this field: aluminum, phosphorus, nitrogen, antimony, chlorine, bromine, and in specific applications magnesium, zinc and carbon. One prominent advantage of the flame retardants (FRs) derived from these elements is that they are relatively easy to manufacture. They are used in important quantities: in 2013, the world consumption of FRs amounted to around 1.8/2.1 Mio t for 2013 with sales of 4.9/5.2 billion USD. Market studies estimate FRs demand to rise between 5/7 % pa to 2.4/2.6 Mio t until 2016/2018 with estimated sales of 6.1/7.1 billion USD.

The most important flame retardants systems used act either in the gas phase where they remove the high energy radicals H and OH from the flame or in the solid phase, where they shield the polymer by forming a charred layer and thus protect the polymer from being attacked by oxygen and heat.[14] Flame retardants based on bromine or chlorine, as well as a number of phosphorus compounds act chemically in the gas phase and are very efficient. Others only act in the condensed phase such as metal hydroxides (aluminum trihydrate, or ATH, magnesium hydroxide, or MDH, and boehmite), metal oxides and salts (zinc borate and zinc oxide, zinc hydroxystannate), as well as expandable graphite and some nanocomposites (see below). Phosphorus and nitrogen compounds are also effective in the condensed phase, and as they also may act in the gas phase, they are quite efficient flame retardants. Overviews of the main flame retardants families, their mode of action and applications are given in.[15][16] Further handbooks on these topics are [17][18] A good example for a very efficient phosphorus-based flame retardant system acting in the gas and condensed phases is aluminium diethyl phosphinate in conjunction with synergists such as melamine polyphosphate (MPP) and others. These phosphinates are mainly used to flame retard polyamides (PA) and polybutylene terephthalate (PBT) for flame retarded applications in electrical engineering/electronics (E&E).

Natural fiber-containing composites

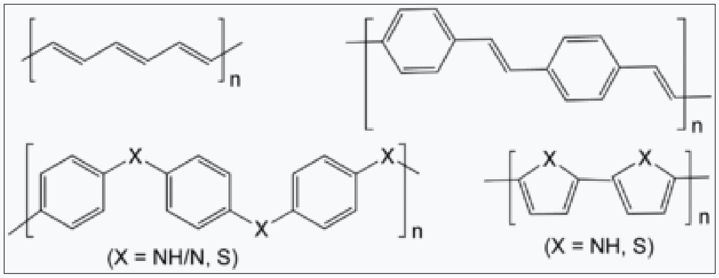
Besides providing satisfactory mechanical properties and renewability, natural fibers are easier to obtain and much cheaper than man-made materials. Moreover, they are more environmentally friendly. Recent research focuses on application of different types of fire retardants during the manufacturing process as well as applications of fire retardants(especially intumescent coatings) at the finishing stage.

Nanocomposites

Nanocomposites have become a hotspot in the research of fire-safe polymers because of their relatively low cost and high flexibility for multifunctional properties. Gilman and colleagues did the pioneering work by demonstrating the improvement of fire-retardancy by having nanodispersed montmorillonite clay in the polymer matrix. Later, organomodified clays, TiO_2 nanoparticles, silica nanoparticles, layered double hydroxides, carbon nanotubes and polyhedral silsesquioxanes were proved to work as well. Recent research has suggested that combining nanoparticles with traditional fire retardants (e.g., intumescents) or with surface treatment (e.g., plasma treatment) effectively decreases flammability.

10. Conductive polymer

This article is about bulk applications of conductive polymers. For single-molecule electronics, see Molecular scale electronics.



Chemical structures of some conductive polymers. From top left clockwise: polyacetylene; polyphenylene vinylene; polypyrrole (X = NH) and polythiophene (X = S); and polyaniline (X = NH/N) and polyphenylene sulfide (X = S).

Conductive polymers or, more precisely, **intrinsically conducting polymers** (ICPs) are organic polymers that conduct electricity. Such compounds may have metallic conductivity or can be semiconductors. The biggest advantage of conductive polymers is their processability, mainly by dispersion. Conductive polymers are generally not thermoplastics, *i.e.*, they are not thermoformable. But, like insulating polymers, they are organic materials. They can offer high electrical conductivity but do not show similar mechanical properties to other commercially available polymers. The electrical properties can be fine-tuned using the methods of organic synthesis[2] and by advanced dispersion techniques.

Types

Linear-backbone "polymer blacks" (polyacetylene, polypyrrole, and polyaniline) and their copolymers are the main class of conductive polymers. Poly(p-phenylene vinylene) (PPV) and its soluble derivatives have emerged as the prototypical electroluminescent semiconducting polymers. Today, poly (3-alkylthiophenes) are the archetypical materials for solar cellsand transistors.

The following table presents some organic conductive polymers according to their composition. **The well-studied classes are written in bold** and *the less well studied ones are in italic*.

The main chain contains	**Heteroatoms present**		
	No heteroatom	**Nitrogen-containing**	**Sulfur-containing**
Aromatic cycles	- *Poly(fluorene)s* - *polyphenylenes* - *polypyrenes* - *polyazulenes* - *polynaphthalenes*	The N is in the aromatic cycle: - **poly(pyrrole)s (PPY)** - *polycarbazoles* - *polyindoles* - *polyazepines* The N is outside the aromatic cycle: - **polyanilines (PANI)**	The S is in the aromatic cycle: - **poly(thiophene)s (PT)** - **poly(3,4-ethylenedioxythiophene) (PEDOT)** The S is outside the aromatic cycle: - **poly(p-phenylene sulfide) (PPS)**
Double bonds	- **Poly(acetylene)s (PAC)**		
Aromatic cycles and	- **Poly(p-phenylene vinylene) (PPV)**		

double bonds			

Synthesis

Conductive polymers are prepared by many methods. Most conductive polymers are prepared by oxidative coupling of monocyclic precursors. Such reactions entail dehydrogenation:

$$n\ H–[X]–H \rightarrow H–[X]_n–H + 2(n–1)\ H^+ + 2(n–1)\ e^-$$

The low solubility of most polymers presents challenges. Some researchers have addressed this through the formation of nanostructures and surfactant-stabilized conducting polymer dispersions in water. These include polyaniline nanofibers and PEDOT: PSS. These materials have lower molecular weights than that of some materials previously explored in the literature. However, in some cases, the molecular weight need not be high to achieve the desired properties.

Molecular basis of electrical conductivity

The conductivity of such polymers is the result of several processes. For example, in traditional polymers such as polyethylenes, the valence electrons are bound in sp^3 hybridized covalent bonds. Such "sigma-bonding electrons" have low mobility and do not contribute to the electrical conductivity of the material. However, in conjugated materials, the situation is completely different. Conducting polymers have backbones of contiguous sp^2 hybridized carbon centers. One valence electron on each center resides in a p_z orbital, which is orthogonal to the other three sigma-bonds. All the p_z orbitals combine with each other to a molecule wide delocalized set of orbitals. The electrons in these delocalized orbitals have high mobility when the material is "doped" by oxidation, which removes some of these delocalized electrons. Thus, the conjugated p-orbitals form a one-dimensional electronic band, and the electrons within this band become mobile when it is partially emptied. The band structures of conductive polymers can easily be calculated with a tight binding model. In principle, these same materials can be doped by reduction, which adds electrons to an otherwise unfilled band. In practice, most organic conductors are doped oxidatively to give p-type materials. The redox doping of organic conductors is analogous to the doping of silicon semiconductors, whereby a small fraction silicon atoms are replaced by electron-rich, *e.g.*, phosphorus, or electron-poor, *e.g.*, boron, atoms to create n-type and p-type semiconductors, respectively.

Although typically "doping" conductive polymers involves oxidizing or reducing the material, conductive organic polymers associated with a protic solvent may also be "self-doped."

Undoped conjugated polymers state are semiconductors or insulators. In such compounds, the energy gap can be > 2 eV, which is too great for thermally activated conduction. Therefore, undoped conjugated polymers, such as polythiophenes, polyacetylenes only have a low electrical conductivity of around 10^{-10} to 10^{-8} S/cm. Even at a very low level of doping (< 1%), electrical conductivity increases several orders of magnitude up to values of around 0.1 S/cm. Subsequent doping of the conducting polymers will result in a saturation of the conductivity at values around 0.1–10 kS/cm for different polymers. Highest values reported up to now are for the conductivity of stretch oriented polyacetylene with confirmed values of about 80 kS/cm. Although the pi-electrons in polyactetylene are delocalized along the chain, pristine polyacetylene is not a metal. Polyacetylene has alternating single and double bonds which have lengths of 1.44 and 1.36 Å, respectively. Upon doping, the bond alteration is diminished in conductivity increases. Non-doping increases in conductivity can also be accomplished in a field effect transistor (organic FET or OFET) and by irradiation. Some materials also exhibit negative differential resistanceand voltage-controlled "switching" analogous to that seen in inorganic amorphous semiconductors.

Despite intensive research, the relationship between morphology, chain structure and conductivity is still poorly understood.[19] Generally, it is assumed that conductivity should be higher for the higher degree of crystallinity and better alignment of the chains, however this could not be confirmed for polyaniline and was only recently confirmed for PEDOT, which are largely amorphous.

Properties and applications

Due to their poor processability, conductive polymers have few large-scale applications. They have promise in antistatic materials and they have been incorporated into commercial displays and batteries, but there have been limitations due to the manufacturing costs, material inconsistencies, toxicity, poor solubility in solvents, and inability to directly melt process. Literature suggests they are also promising in organic solar cells, printing electronic circuits, organic light-emitting diodes, actuators, electrochromism, supercapacitors, chemical sensors and biosensors, flexible transparent displays, electromagnetic shielding and possibly replacement for the popular transparent conductor indium tin oxide. Another use is for microwave-absorbent coatings, particularly radar-absorptive coatings on stealth aircraft. Conducting polymers are rapidly gaining attraction in new applications with increasingly processable materials with better electrical and physical properties and lower costs. The new nanostructured forms of conducting polymers particularly, augment this field with their higher surface area and better dispersability.

With the availability of stable and reproducible dispersions, PEDOT and polyaniline have gained some large scale applications. While PEDOT (poly(3,4-ethylenedioxythiophene)) is mainly used in antistatic applications and as a transparent conductive layer in form of PEDOT:PSS dispersions (PSS=polystyrene sulfonic acid), polyaniline is widely used for printed circuit board manufacturing – in the final finish, for protecting copper from corrosion and preventing its solderability.

Electroluminescence

Electroluminescence is light emission stimulated by electric current. In organic compounds, electroluminescence has been known since the early 1950s, when Bernanose and coworkers first produced electroluminescence in crystalline thin films of acridine orange and quinacrine. In 1960, researchers at Dow Chemical developed AC-driven electroluminescent cells using doping. In some cases, similar light emission is observed when a voltage is applied to a thin layer of a conductive organic polymer film. While electroluminescence was originally mostly of academic interest, the increased conductivity of modern conductive polymers means enough power can be put through the device at low voltages to generate practical amounts of light. This property has led to the development of flat panel displays using organic LEDs, solar panels, and optical amplifiers.

Barriers to applications

Since most conductive polymers require oxidative doping, the properties of the resulting state are crucial. Such materials are salt-like (polymer salt), which diminishes their solubility in organic solvents and water and hence their processability. Furthermore, the charged organic backbone is often unstable towards atmospheric moisture. The poor processability for many polymers requires the introduction of solubilizing or substituents, which can further complicate the synthesis.

Experimental and theoretical thermodynamical evidence suggests that conductive polymers may even be completely and principally insoluble so that they can only be processed by dispersion.

Trends

Most recent emphasis is on organic light emitting diodes and organic polymer solar cells. The Organic Electronics Association is an international platform to promote applications of organic semiconductors. Conductive polymer products with embedded and improved electromagnetic interference (EMI) and electrostatic discharge (ESD) protection have led to both prototypes and products. For example, Polymer Electronics Research Center at University of Auckland is developing a range of novel DNA sensor technologies based on conducting polymers, photoluminescent polymers and inorganic nanocrystals (quantum dots) for simple, rapid and sensitive gene detection. Typical conductive polymers must be "doped" to produce high conductivity. As of 2001, there remains to be discovered an organic polymer that is *intrinsically* electrically conducting.

11. Biodegradable polymer

Example of cutlery made from biodegradable plastic

Biodegradable polymers are a specific type of polymer that breaks down after its intended purpose to result in natural byproducts such as gases (CO_2, N_2), water, biomass, and inorganic salts.[1][2] These polymers are found both naturally and synthetically made, and largely consist of ester, amide, and ether functional groups. Their properties and breakdown mechanism are determined by their exact structure. These polymers are often synthesized by condensation reactions, ring opening polymerization, and metal catalysts. There are vast examples and applications of biodegradable polymers.

Bio-based packaging materials have been introduced as a green alternative in the past decades,among which, edible films have gained more attention due to their environmentally-friendly characteristics, vast variety and avail-ability, non-toxicity, and low-cost.

Properties

Even though biodegradable polymers have numerous applications, there are properties that tend to be common among them. All biodegradable polymers should be stable and durable enough for use in their particular application, but upon disposal they should easily break down.[7] Polymers, specifically biodegradable polymers, have extremely strong carbon backbones that are difficult to break, such that degradation often starts from the end-groups. Since the degradation begins at the end, a high surface area is common as it allows easy access for either the chemical, light, or organism. Biodegradable polymers also tend to have minimal chain branching as this cross linking often decreases the number of end groups per unit weight. Crystallinity is often low as it also inhibits access to end groups. A low degree of polymerization is normally seen, as hinted at above, as doing so allows for more accessible end groups for reaction with the degradation initiator. Another commonality of these polymers is their hydrophillicity. Hydrophobicpolymers and end groups will prevent an enzyme from easily interacting if the water-soluble enzyme cannot easily get in contact with the polymer.

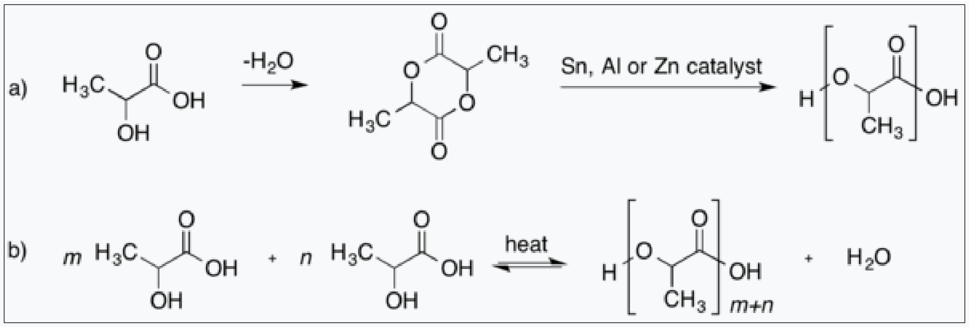
Other properties of biodegradable polymers that are common among those used for medicinal usages include

1. non-toxic,
2. capable of maintaining good mechanical integrity until degraded, and
3. capable of controlled rates of degradation.

A goal is not to elicit the immune response, and the products of degradation also need not to be toxic. These are important as biodegradable polymers are used for drug delivery where it is critical to slowly release the drug into the body over time instead of all at once and that the pill is stable in the bottle until ready to be taken. Factors controlling the rate of degradation include: 1) percent crystallinity, 2) molecular weight, and 3) hydrophobicity. The degradation rate depends on the location in the body, which influences the environment surrounding the polymer such as pH, enzymes concentration, and amount of water among others. These are rapidly decomposed.

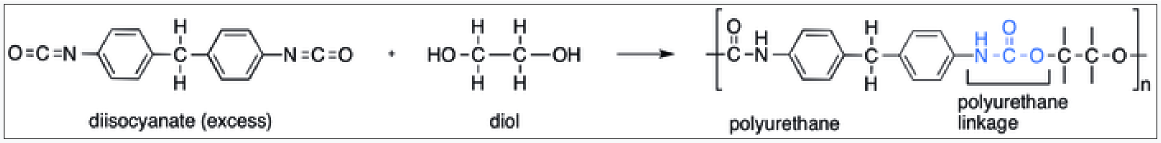
Synthesis

One of the most important and most studied groups of biodegradable polymers are polyesters. Polyesters can be synthesized in a number of ways including direct condensation of alcohols and acids, ring opening polymerizations (ROP), and metal-catalyzed polymerization reactions.[11] A great disadvantage of the step-wise polymerization via condensation of an acid and an alcohol is the need to continuously remove water from this system in order to drive the equilibrium of the reaction forward.[12] This can necessitate harsh reaction conditions and long reaction times, resulting in a wide dispersity. A wide variety of starting materials can be used to synthesize polyesters, and each monomer type endows the final polymer chain with different characteristics and properties. The ROP of cyclic dimeric glycolic or lactic acid forms α-hydroxy acids which then polymerize into poly-(α-esters).[12] A variety of organometallic initiators can be used to start the polymerization of polyesters, including tin, zinc, and aluminum complexes. The most common is tin(II)octanoate and has been approved as a food additive by the U.S. FDA, but there are still concerns about using the tin catalysts in the synthesis of biodegradable polymers for biomedical uses.[11] The synthesis of poly(β-esters) and poly(γ-esters) can be carried out by similar ROP or condensation methods as with poly(γ-esters). Development of metal-free process that involve the use of bacterial or enzymatic catalysis in polyester formation is also being explored.[13][14] These reactions have the benefit of generally being regioselective and stereospecific but suffer from the high cost of bacteria and enzymes, long reaction times, and products of low molecular weight.



Example of routes to polyester formation using lactic acid. a) Condensation of lactic acid into dimeric lactide followed by ring-opening polymerization of to form poly(lactic acid); b) Direct condensation of lactic acid, demonstrating the need to continuously remove water from the system in order to drive the reaction forward.

While polyesters dominate both the research and industrial focus on synthetic biodegradable polymers, other classes of polymers are also of interest. Polyanhydrides are an active area of research in drug delivery because they only degrade from the surface and so are able to release the drug they carry at a constant rate. Polyanhydrides can be made via a variety of methods also used in the synthesis of other polymers, including condensation, dehydrochlorination, dehydrative coupling, and ROP. Polyurethanes and poly(ester amide)s are used in biomaterials.[16] Polyurethanes were initially used for their biocompatibility, durability, resilience, but are more recently being investigated for their biodegradability. Polyurethanes are typically synthesized using a diisocyanate, a diol, and a polymer chain extender.[11] The initial reaction is carried out between the diisocyanate and the diol, with the diisocyanate in excess to ensure that the ends of the new polymer chain are isocyanate groups. This polymer can then be reacted with either a diol or a diamine to form urethane or urethane-urea end groups, respectively. The choice of terminal groups affects the properties of the resulting polymer. Additionally, the use of vegetable oil and biomass in the formation of polyurethanes, as well as the conversion of polyurethanes to polyols, is an active area of research.



Synthesis of polyurethane from a diisocyanate and a diol. To cap this polymer, chain extenders of either diols or diamines can be added in order to tailor the properties.

Application

The widespread use of synthetic polymers in technology and in every day life is an accepted feature of modern civilization .There exists one important area in which the use of synthetic polymers has generally been cautious and limited, that is field of medicine has become one of the principal challenges facing the polymer scientists .The types of synthetic polymers needed for biodmedical applications can be grouped roughly into three categories. Polymers that are sufficiently biostable to allow their long-term use in artificial organs ie , In Blood Pumps , Blood

Vessel Prosthesis , Heart Valves , Skeletal Joints , Kidney Prosthesis and so on . Polymers that are bioerodable-materials that will serve a short-term purpose in the body and decompose to small molecules that can be metabolized or excreted , sometimes with the concurrent release of drug molecules . Polymers that are water soluble and that form part of plasma or whole blood substitute solutions or which function as macromolecular drugs . A polymer must fulfill certain critical requirements if it is to be used in an artificial organ .It must be physiologically inert , the polymer itself should be stable , it must be strong and resistant to impact , it should be chemically and thermally stable.

Cardiovascular Applications Heart Valves & Vascular Prosthesis: Polymers have been used extensively to correct cardiovascular disorders . Defective heart valves can be replaced by mechanical valves based on various designs .In one design, a ball of silicone rubber is retained inside a stainless steel cage. {Starr-Edwards ball-type heart valves constructed from a silicone rubber ball, a chrome-cobalt cage, and a Teflon ring for suturing to the heart tissue.} The silicone rubber is used because of it`s inertness, elasticity, and low capacity to cause blood clotting .Valves of this type are still being used . A more recent design makes use of a small, circular plates as a flap valve,with the flap made from pyrolytic carbon or poly(oxymethylene). Another surgical practice is to implant modified(cross-linked)tissue heart valves from pigs("porcine valves"). Devices fabricated from synthetic hydrogels may eventually replace porcine valves. Aneurisms(balloon-like expansions of the arterial wall)can be repaired by reinforcement of the artery with a tube of woven polyester or PTFE fabric.Completely blocked arterial sections are removed and replaced by a tube of porous PTFE. The polymer is relatively noninteractive with blood from the polymer.

The Artificial Heart: For patients with irreversibly damaged heart, the functions of the damaged heart may be taken over permanently or temporarily by an artificial pump. Synthetic elastomers and rigid polymers have been used extensively for the conuction of these devices. Unfortunarely, most synthetic polymers accelerate the clotting of blood. Avoidance of the clotting process is depends on the design of the pump and presence or absence of turbulence as well as on the materials used for construction.

Heart Pump Designs: The Auxiliary blood pumps to bypass or supplement the of a damaged heart until it can repair itself. Many of the booster pumps have used a rigid housing, often made of reinforcfed epoxy resin, with an internal tube of silicone rubber Compressed air applied inside the rigid casing compresses the silicon or PU rubber inner tube which is connected to the aorta and this forces blood from the pump. Valves may be used to prevent back flow, or the compression cycle may be synchronized with the pumping motion of the heart. A related device is the intraaortic balloon, a 25cm*2cm polyurethane ballooninserted in to the aorta which expands as compressed helium or carbon dioxide is pulsed in or out. Other devices use hemisphere of titanium,polycarbonate,or PMMA containing a PU diaphragm . Pulses of compressed air or carbon dioxide actuate the diaphragm and cause the pumping of the blood. The total artifical heart pumps that can completely replace the living organ.They resembles the general structure of a human heart by which are actuated by compressed gas or oil.

Polymers For Heart Pumps: A wide variety of polymers such as Silicone rubber, Polyurethane rubber, Dacron polyester, Teflon, Polycarbonate, PMMA, PVC, and Pyrolytic carbon. Most of these material cause blood clotting, destruction of red cells, or alteration of the blood proteins, although some are markedly better than others. Polyurethanes are among the most commonly used flexible biomaterials. They have excellent flexing strength. The diaphragm in a heart pump would have to withstand about 90 million flexing motions without breaking over a 10 year period. Calcification of PU membranes is a problem during long-term use. Silicone rubber is an ideal biomaterial. Its chemical inertness is impressive, and it is soft and flexible. However, it can promote blood clotting if the blood is flowing slowly, and it can fail after continuous flexing. Another problem is the tendency of silicone rubber to absorb fats from the blood, to swell, and eventually to weaken. Fluoroalkylsiloxane polymers or polyphosphazenes may prove to be more suitable for artificial heart applications. The ability of a synthetic polymer to initiate the clotting of blood depends on the nature of the surface (smooth surfaces are better than rough) and on the chemical and physical properties of the polymer. Because the inside lining of blood vessels is negatively charged, it has also been speculated that polymers with a surface charge might be more effective than neutral polymers .

Tissue Adhesives And Artificial Skin: A group of polymers based on the poly(alpha-cyanoacrylate)structure have proved to be effective to glue tissues together. Alpha-cyanoacrylates have the general formula, Where group R can be methyl, butyl, octyl, and so on. CN These monomers polymerize by an anionic mechanism | in the presence of water. Higher alkyl derivatives $CH2=C$ polymerize more rapidly on biological substrates and | are less irritating to tissues than are the lower alkyl $C=O$ derivatives . In addition to their use as skin adhesives, | they have been tested as adhesives in corneal and O retinal surgery , and as an adjunct to suturing in | internal surgery. R Synthetic poly(amino acid) films are used as synthetic skin to cover large burns.Velours of nylon fiber have also been tested for this use, as have films of poly(alpha-cyanoacrylates).

Bones,Joints And Teeth: Bone fractures are occasionally repaired with the use of polyurethanes, epoxy resins and rapid-curing vinyl resins. Silicone rubber rods and closed-cell sponges have been used as replacement finger and wrist joints, and vinyl polymers and nylon have been investigated as replacement wrist bones or elbow joints. Further more, cellophane and more recently, silicone rubber have been used in knee joints to prevent fusion of the bones. In hip-joint surgery with the use of stainless steel or polyethylene ball joints attached to the femur by means of a PMMA filler and binder. Teflon fabric and silicone rubber have been used to make synthetic ligaments and tendons. Synthetic polymers have been utilized for the fabrication of dentures. PMMA is the principal polymer used both for acrylic teeth and for the base material. Acrylic resins are also used for dental crowns, and epoxy resins are sometimes employed to cement crowns to the tooth post. More recent work and anticipated developments include the use of polymeric coatings or paint to prevent the decay of teeth and the development of thermo or photo-setting polymers to replace silver amalgam or gold as tooth-filling materials.

Contact Lenses And Intraocular Lenses: Rigid polymers such as PMMA have traditionally been used for ‘hard’ contact lenses ,the modern tendency is toward flexible or ‘soft’ contact lenses. A soft contact lens is made from a lightly cross linked, water-soluble polymer. Such polymers swell in aqueous media but do not dissolve. Instead they form soft hydrogels , the expanded shape of which is defined at the point of cross linking. The design of hydrogels for intraocular lenses (ie, for lenses to replace the natural lens following eye injury or removal of catatact-damaged lenses) is a special challenge since the replacement lens must be folded without damage into a small volume before insertion through a small incision into the eye.

Artificialkidney And Hemodialysis MateriALS: Cellophane (regenerated cellulose) has been used for semi permeable dialysis membranes in conventional kidney machines. For miniaturization of machine bundles of hollow fibers are used as a dialysis cell. In one particular development, a bundle of 2000 to 11,000 hollow fibers of modified PAN (17 cm long and 300micro meter dia:)are used. The polymer is "heparinized" to prevent blood clotting. Hollow rayon fibers or polycarbonate or cellulose acetate fibers have also been used for the same purpose.

Oxygen-Transport Membranes: Surgical work on the heart frequently requires the use of a heart-lung machine to circulate and oxygenate the blood. Many of such machines make use of a membrane through which oxygen and carbon dioxide must pass. Poly(dimethylsiloxane) membranes are highly efficient gas transporters. They are made by dip-coating a Dacron or Teflon screen in a xylene dispersion of silicone rubber. When dried, a film of .075 mm or more in thickens can be obtained, and this can be incorporated into the oxygenator . silicone rubber membranes have also been tested in "artificial gills" for under water breathing.

Bioeodable Polymers Three medical applications exists for polymers of this type .
a*) surgical sutures*: Catgut used for all sutures recently is relatively inert and post operative procedure were usually necessary for the removal of the suture after the normal 15-days healing of the tissue. A replacement for catgut is synthetic poly(glycolic acid) or condensation copolymers of glycolic acid with lactic acid. Poly(glycolic acid) has a high tensil strength and is compatible with human tissue. However, it differs from catgut in being totally absorbable by many parients within 15 days, thus removing the need for a suture-removal operation. The polymer degrades by hydrolysis to nontoxic glycolic acid.
b) tissue ingrowth polymers : Polymers like polyurethans degrade slowly as they are colonized and replaced by living cells of the host. They are clear advantages to the use of biomaterials of this type, since the long-range biocompatibility problems become less important. Polyanhydrides have the right properties to be utilized in this way. A group of amino acid ester-substituted polyphosphazenes, such as, $NHCH_2COOC_2H_5$ | -(N=P)-n | $NHCH_2COOC_2H_5$ Which degrades slowly to amino acid, phosphate, and ethanol, which are metabolized, and traces of ammonia , which are exerted.
c) controlled release of drugs: Three approaches are there to use polymers to effect a slow release of drugs. They are, (1) Diffusion-controlling Membranes Or Matrices: Many chemotherapeutic drugs are relatively small molecules that can diffuse slowly through polymer membranes. Thus, if an aqueous solution of a drug is enclosed by a polymer membrane, the drug will escape through the membrane at a rate that can be controlled by membrane thickness and composition. A device that employs this principle is in use for the slow controlled release of the antiglaucoma drug, pilocarpine, from a polymer capsule placed beneath the eyelid. The same principle applies if a film, rod or bead of a of polymer is impregnated with a drug and it is then implanted in the body at a site where the drug can have the maximum beneficial effect. One important medical advantage in controlled-release devices of this kind is that the drug delivery system can be removed at any time when the therapy is no longer needed. (2) Solid Biodegradable Matrices: An excellent way to achieve the slow, controlled release of a drug from

a solid matrix is to use a biodegradable polymer as the matrix. As the polymer degrades slowly (usually by hydrolysis), the chemotherapeutic molecules are released. An important requirement is that the hydrolysis products from the polymer should be nontoxic and readily excreted. A second requirement is that rate of release should follow a predetermined protocol. For example for treatment of some diseases a burst of drug in high local concentration might be followed by no release, with the cycle repeated at precise intervals. Alternatively (and more usually),a so called “Zero Order” protocol may be preferred in which the rate of release of the drug remains constant over a period of days, weeks or months. These requirements provides many opportunities for ingenuity in both the design of the matrix polymer and shape of the device. A number of polymers, polyglycolic acid , poly(amino acid ester phosphazenes) such as polyphosphazenes with imidazolyl sugar or glyceryl residues as side groups, and aliphatic polyanhydrides are all of interest for this application. (3)Water Soluble Polymer Bound Drugs: Water soluble biodegradable polymers are of interest for two types of applications. First , water soluble polymers that are bound to drug molecules could bring about a marked improvement in the behavior of most pharmaceuticals. Second there is the prospect that such polymers can be used in synthetic blood substitutes as viscosity enhancers or as oxygen transport macromolecules. Water soluble polymers diffuse only slowly through the tissues and more over, will not be excreted as rapidly as small molecules because macromolecules can not normally pass through semi permeable membranes. Thus a polymer bound drug should offer considerable advantages over a small molecule drug.

Three possibilities exist, (1) The drug could be linked to a relatively stable molecule, in which case the activity of the drug and its entry in to the cell may be modified by the presence of the polymer . (2) If the polymer degrades in the body and concurrently release the drug, the chemotherapeutic activity of the drug will be unchanged. (3) The water soluble polymer itself is bioactive. It will be clear that the design and synthesis of polymers that have the correct water solubility, lack of toxicity and an appropriate rate of hydrolytic decomposition at body temperature is one of the most demanding challenges faced by the polymer chemists.

Polymeric Blood Substitutes: Synthetic polymers have been investigated for use in plasma substitutes and as volume expanders to reduce the amount of whole blood needed, for example during the use of a heart- lung machine. Furthermore, the transmission of hepatitis and other diseases through the use of pooled plasma provides a continuing incentive for the development of a synthetic substitute for this fluid. Poly(Vinyl Pyrolidone) was used extensively as a colloidal plasma substitute for the treatment of casualties. Its disadvantages for this applications are connected with its poor biodegradability. Hence, there is a serious need for the development of a water soluble polymer that is nontoxic and biodegradable. Some water soluble Poly Phosphazenes may be of value for this application.

Text book:

T1: Gowariker, V. R., N. V. Viswanathan and J. Sreedhar, 1986. Polymer Science, *New Age International* Private Ltd., New Delhi.

T2: Billmeyer, F.W., 2003. Text Book of Polymer Science. III Edition, John Wiley, New York

Reference book

R1: M.S Bhatnagar,2004, “ A text book of polymers”. Ist Edition, S.Chand & Company.

Web Address:

W$_1$: https://en.wikipedia.org/wiki/Fire-safe polymers or Functional or Electrically conducting polymers
W$_2$: https://biomedical polymers/applications.

POSSIBLE QUESTIONS

Multiple choice questions (Each Carry 1 Mark)

1. Limited compatibility with the polymers are?
a. Primary plasticizers **b. Secondary plasticizers** c. Antioxidants d. Colourants

2. Inhibiting the oxidation of polymers is usually filled by a substance which itself is readily oxidized.
a. Antioxidants b. Flame retardants c. Colourents d. Mgo

3. In polymer industry 2-hydroxybenzophones are used as
a. Light stabilizers b. Antioxidants c. Polymer initiators d. Fillers

4. Any of a group of substances that are used in plastics or other materials to impart viscosity, flexibility, softness or other properties to the finished product
a. Plasticizers b. Antioxidants c. Polymer initiators d. Fillers

5.The addition of polyethylene glycol in dielectric property significantly improves?
a. Electrolytic conductivity b. Dielectric conductivity c. Electric conductivity
d. Ionic conductivity

6. Melamine is
a. White crystaline solid b. Gas c. Colourless liquid d. Yellow liquid

7. Plastics are?
a. Hydrocarbons b. Aldehyde c. Ester d. Amide

8. Which one is an inorganic pigment?
a. Barium sulfate b. Perylenes c. Pyrroles d. Arylamides

9. Poly vinyl chloride is?
a. An allotrope polymer of vinyl chloride **b. An addition product of vinyl chloride**
c. An isomer of vinyl chloride d. A polymer of hydrated vinyl chloride

10. Which one is more active flame retardant?
a. Aluminum hydroxide **b. Antimony oxychloride** c. Phosphorous
d. Halogen compounds

11. Which one of the following flame retardant forms a gas shield layer?
a. Calcium b. Phosphorous c. Ammonium **d. Aluminium oxide**

12. Melting Point of Low Density Polyethylene (LDPE) is?
a. ~115^{o}C b. ~116 ^{o}C **c. ~135^{o}C** d. ~148 ^{o}C

13. The most useful material imparting flame retardance to plastics is?
a. Antimony trioxide b. Aluminum hydroxide c. Halogen compounds
d. Antimony oxychloride

14. Which one of the following flame-retardant breaks down endothermic reaction?
a. Phosphorous b. Ammonium c. Aluminium oxide **d. Aluminum Hydroxide**

15. Styrene (butadiene rubber) was commercially introduced during the year
a. 1943 **b. 1930** c. 1936 d. 1947

16. Polyvinyl acetate is insoluble in which solvent?
    a. Alcohols b. Aromatic solvents c. Esters **d. Water**
17. Polythene was first synthesied in ?
    a. 1877 b. 1853 c. 1890 **d. 1898**
18. Polythene was first produced in ?
    a. German **b. England** c. India d. USA
19. Polyethylene was first synthesized by?
    a**. Pechmann** b. Fawcett c. Karl Ziegler d. Walter
20. Which one of the compound is used in the manufacture of terylene?
    a. Vinyl chloride **b. Ethylene glycol** c. Vinyl alcohol d. Ethylene

Questions (Each Carry 6 Marks)

1. Explain in brief i. polyvinyl chloride
   ii. polyamides
2. Write about the silicon polymers?
3. Explain in brief i. phenolic resin
   ii. Epoxy resin?
4. Write about the biopolymers?
5. Explain in brief about functional polymer?
6. Write about the polyethylene and PVC?
7. Explain in brief i. polyesters
   ii. polyamides?
8. How the bio polymers used in dental treatment and artificial heart?
9. Explain in brief i. PVC
   ii. phenolic resins?
10. Write about the silicon polymers?

Compulsory Questions (Each Carry 10 Marks)

1. What is biopolymers and explain its pharmaceutical applications?
2. Explain briefly the preparation, properties and uses of PVC and Polyethylene?
3. Give an account of Phenolic resins and Silicon polymers?
4. Briefly explain the preparation and uses of phenolic and epoxy resins?

16CHP305A
Karpagam Academy of Higher Education
Coimbatore-21
(For the Candidates admitted on 2016 Onwards)
III-Semester
Polymer Chemistry

Questions	Opt-1	Opt-2	Opt-3	Opt-4	Answers
Unit 5- Objective questions for online examination (Each carry 1 mark)					
Which is more flexible than HDPE due to lower crystallinity?	Polyethylene	Low Density Polyethylene	Polyamide	Low density polyamide	Low Density Polyethylene
80-90% of all plasticizers used with?	DOP	DIOP	PVC	Colourants	PVC
It must not exude from the plastic material?	Primary plasticizers	Secondary plasticizers	Antioxidents	Colourants	Primary plasticizers
Limited compatibility with the polymers are?	Primary plasticizers	Secondary plasticizers	Antioxidents	Colourants	Secondary plasticizers
Inhibiting the oxidation of polymers is usually filled by a substance which itself is readily oxidized.	Antioxidants	Flame retardants	Colourants	Mgo	Antioxidants
In polymer industry 2-hydroxybenzophones are used as	Light stabilizers	Antioxidants	Polymer initiators	Fillers	Light stabilizers
Any of a group of substances that are used in plastics or other materials to impart viscosity, flexibility, softness or other properties to the finished product	Plasticizers	Antioxidants	Polymer initiators	Fillers	Plasticizers
It often added to semicrystalline polymer to lower the value of Tg below room temperature.	Light stabilizers	Colouarants	Plasticizers	Flame retardents	Plasticizers
The basic requirement that must be met by a plasticizer are	Compatibility	Prevent oxidation	Retard flame	Impart a colour	Compatibility
Porosity increased as plasticizers content?	Increased	Decreased	Suddenly decreased	Never change	Increased
The substances which weaken the intermolecular forces between the polymer chains and decrease Tg.	Plasticizers	Antioxidants	Polymer initiators	Fillers	Plasticizers
Which content did not have a significant effect on the rate of erosion?	Light stabilizers	Colouarants	Plasticizers	Flame retardents	Plasticizers
Which type of compound is not used as a flame retardant in polymers	Aluminum Hydroxide	Halogen compounds	Phosphorous compounds	Ferrocene	Ferrocene
Chemical compounds capable of interfering with the physical and chemical processes of UV light-induced degradation .	Plasticizers	Antioxidants	Polymer initiators	Light stabilizer	Light stabilizer
which one of the following polymers is the product of a condensation polymerisation reaction?	Polypropylene	Polytetrafluoroethene	Polyacetic acid	PVC	Polyacetic acid
The phenol-formaldehyde resins are formed by polymerisation of phenol and formaldehyde by	Addition polymerisation	Cationic polymerisation	Condensation polymerisation	Anionic polymerisation	Condensation polymerisation
The addition of polyethylene glycol in dielectric property significantly improves?	Electrolytic conductivity	Dielectric conductivity	Electric conductivity	Ionic conductivity	Ionic conductivity
Melamine is	White crystaline solid	Gas	Colourless liquid	Yellow liquid	White crystaline solid

Plastics are ?	Hydrocarbons	Aldehyde	Ester	Amide	Hydrocarbons
Which one is an inorganic pigment?	Barium sulfate	Perylenes	Pyrroles	Arylamides	Barium sulfate
Poly vinyl chloride is?	An allotrope polymer of vinyl chloride	An addition product of vinyl chloride	An isomer of vinyl chloride	A polymer of hydrated vinyl chloride	An addition product of vinyl chloride
Which one is more active flame retardant?	Aluminum hydroxide	Antimony oxychloride	Phosphorous	Halogen compounds	Antimony oxychloride
The most useful material imparting flame retardance to plastics is?	Antimony trioxide	Aluminum hydroxide	Halogen compounds	Antimony oxychloride	Antimony trioxide
Which one of the following flame retardant forms a gas shield layer?	Calcium	Phosphorous	Ammonium	Aluminium oxide	Phosphorous
Which one of the following flame retardant breaks down endothermic reaction?	Phosphorous	Ammonium	Aluminium oxide	Aluminum Hydroxide	Aluminum Hydroxide
Melting Point of Low Density Polyethylene (LDPE) is?	~115^{o}C	~116 ^{o}C	~135^{o}C	~148 ^{o}C	~135^{o}C
Which one is a synthetic polymer?	Cellulose	Cotton	Polyamide	Fibers	Polyamide
Polymethyl methacrylate is a colourless and transparent ?	Plastic	Rubber	Cotton	Nylon	Plastic
Polymethyl methacrylate can be prepared by using acetone cyanohydrin and	Nitric acid	Acetic acid	Sulphuric acid	Hydrochloric acid	Sulphuric acid
Silicones was commercially introduced in ?	1943	1930	1936	1947	1943
Polyvinyl chloride was commercially introduced in ?	1943	1930	1936	1947	1936
Polyvinyl acetate monomer is prepared by the reaction of acetic anhydride with ?	Benzaldehyde	Acetaldehyde	Acetic acid	Sodium acetate	Acetaldehyde
Polyvinyl acetate is used for the manufacture of ?	Polyvinyl chloride	Polyvinyl alcohol	Poly methyl methacrylate	Polyvinyl acetate	Polyvinyl alcohol
Styrene(butadiene rubber) was commercially introduced during the year	1943	1930	1936	1947	1930
Polyvinyl acetate is insoluble in which solvent?	Alcohols	Aromatic solvents	Esters	Water	Water
Polythene was first synthesied in ?	1877	1853	1890	1898	1898
Polythene was first produced in ?	German	England	India	USA	England c
Polyethylene was first synthesized by ?	Pechmann	Fawcett	Karl ziegler	Walter	Pechmann
Which one of the compound is used in the manufacture of terylene ?	Vinyl chloride	Ethylene glycol	Vinyl alcohol	Ethylene	Ethylene glycol
Which one of the following is an example of condensation polymer?	Terylene	PVC	Vinyl alcohol	Ethylene	Terylene
The synthetic polymer which resembles natural rubber is ?	Cotton	Nylon	Chloroprene	Neoprene	Neoprene
Which one is prepared by the melt polycondensation between dicarboxylic acids and diamides.	Polyamides	Polyester	Acrylic fibre	Polyethylene	Polyamides
Aliphatic polyamides are generally known as ?	Cotton	Nylon	Polyamide	Polyester	Nylon
Which one of the following is obtained from dibasic acids and diamides.	Cotton	Nylon	Polyamide	Polyester	Nylon
The ring opening polymerization of lactometated is represented only by ?	Single number	Double number	Triple number	No number	Single number

It has good tensile strength and abrasion resistance	Polyamides	Polyester	Acrylic fibre	Polyethylene	Polyamides
It is used as a plastic as well as a fibre	Polyamides	Polyester	Acrylic fibre	Polyethylene	Polyamides
Which one is used in tires and ropes?	Cotton	Nylon	Polyamide	Polyester	Nylon
Which is used in clothes, belts and accessories?	Cotton	Nylon	Polyamide	Polyester	Nylon
It is prepared by polycondesation reaction between a dicarboxylic acid and a diol.	Polyamides	Polyester	Acrylic fibre	Polyethylene	Polyester
Which polymers contains ester groups in the main chain of the polymer itself.	Polyamides	Polyester	Acrylic fibre	Polyethylene	Polyester
The molecular weight of cellulose varies between	20000 to 500000	10000 to 20000	10000 to 12000	1000 to 2000	20000 to 500000
Condensation polymerization is not used to produce	Polyester	Nylon 6	Nylon 66	Polypropylene	Polypropylene
Polyethylene terephthalte (PETP) has a high melting point because of the presence of ?	Aliphatic chain	Aromatic ring	Nitrogen bond	CN bond	Aromatic ring
Which one of the following is resistant to heat and moisture.	Polyamides	Polyester	Acrylic fibre	Polyethylene	Polyester
PETP melts at ?	275□C	266□C	267□C	265□C	265□C
Which one of the following is used in the manufacturing of magnetic recording tapes, aluminished sheets for certain special applications?	Polyethylene terephthalte	Polyester	Acrylic fibre	Polyethylene	Polyethylene terephthalte
The polymer made from acrylenitrile ?	Polyacrylic fibres	Polyethylene	Polyester	Polyethylene terephthalte	Polyacrylic fibres
Polymer which contains between 35-65% of acrylonitrile are known as?	Orlon	Modaerylics	Acrilan	Verel	Modaerylics
Polymers which contain 85% or more acrylenitrile is?	Orlon	Modaerylics	Vinyl acetate	Verel	Orlon

Reg. No. : ---------------------------- [16CHP305A]

KARPAGAM UNIVERSITY
(Karpagam Academy Of Higher Education)
COIMBATORE-641021
DEPARTMENT OF CHEMISTRY
III – SEMESTER
II- M.Sc., Chemistry
1st Internal Test
Polymer Chemistry (Elective-III)

Time: 2 Hours Maximum: 50 marks
Date:

Section-A 20X1=20

1. Which is obtained from the reaction of diamines with diacids?
   (a) Polyamides (b) polyester (c) Acrylicfibre (d) Poly vinyl chloride
2. In step polymerization the reactivity of a functional group depends on?
   (a) The collision frequency of the group (b) diffusion rate of the whole molecule
   © Nature of the functional group (d) Size of the group
3. The alkyl resins are condensation polymers obtained from dibasic acids and
   (a) Phenol (b) formaldehyde (c) Acetaldehyde (d) Glycol
4. Reactivity of a functional group depends on the ------ ?
   (a) Collision frequency (b) diffusion rate (c) Size (d) Molecular weight
5. In a polymer chain the functional group has appreciable mobility due to
   (a) the conformational rearrangements (b) different stereochemical forms
   © Tautomeric arrangements (d) Optical activity
6. The first step in the reaction of the diol and diacid monomer is to form ?
   (a) Dimer (b) trimer (c) Pentamer (d) Tetramer
7. The rate of a step polymerization is conveniently expressed in terms of the
   (a) Concentrations of the reacting functional groups.
   (b) Concentration of the monomeric
   (c) Concentration of monomer and the solvent
   (d) Concentration of the functional groups and monomers
8. A dimer reacts with a monomer to give
   (a) Trimer (b) Dimer (c) Pentamer (d) Tetramer
9. In thermal catalyzed polymerizations the most widely used mode of generating radicals to initiate polymerization?
   (a) Homolytic dissociation of initiators (b) Heterolytic dissociation of initiators
   © Decomposition of the initiator (d) Association of the initiator
10. The Polyesterification of a diol and a diacid will illustrate the general kinetics of a typical ?
    (a) Step polymerization (b) Ionic polymerization (c) Radical polymerization
    (d) Self catalysted polymerization
11. The catalyst used for the Ziegler–Natta polymerizations?
    (a) $TiCl_3$ with $Al(C_2H_5)_2Cl$ (b) BCl_3 with $Al(C_2H_5)_2Cl$
    © $TiCl_3$ with $Fe(C_2H_5)_2Cl$ (d) TiF_3 with $Al(C_2H_5)_2F$
12. In the acid hydrolysis of cellulose there is no effect of?
    (a) Frequency (b) Molecular weight (c)Density (d) Molecular size
13. Isotactic polymerization depends intimately on the?
    (a) Crystal structure of the initiator surface (b) Surface area of the initiator
    © Volume of the initiator (d) Concentration of the initiator
14. In isotactic polymerization the polymerization occurs at active sites found on the ?
    (a) Edges (surfaces) of elementary sheets of the crystal
    (b) Edges of the basal planes
    (c) Corners of the basal planes
    (d) Inside the pores of the catalyst
15. Which find extensive use as radical sources?
    (a) Peroxides (b) Epoxides (c) Nitrenes (d) Carbenes
16. The enantiomorphic site control model attributes stereo control in which of the following polymerization?
    (a) Isoselective polymerization (b) Isotactic polymerization
    © Free radical polymerization (d) Ionic polymerization
17. The C–N bond dissociation energy is?
    (a) ~ 190 kJ mol -1 (b) ~ 390 kJ mol -1 (c) ~ 290 kJ mol -1 (d) ~ 360 kJ mol -1

18. The various initiators are used at different temperatures depending on their rates of

(a) Reaction (b) Decomposition (c) Composition (d) Entropy

19. The azobis-isobutyronitrile (AIBN) is commonly used at?

(a) 60-70°C (b) 50–70°C (c) 80-90°C (d) 40-50°C

20. Teflon is a polymer of the monomer or Teflon is obtained by the polymerisation of?

(a) Monofluroethene (b) Difluroethene (c)Trifluroethene

(d) Tetrafluroethene

Section B

3x2 = 6

21. Define monomer and repeat unit?

22. Write a note on co-ordination polymerization?

23. What is Polydispersion?

Section C

3x8 = 24

24. Write a note on mechanism of step-growth polymerization?

(Or)

Explain the addition polymerization and its types?

25. What is Zeigler-Natta Catalyst? Explain its mechanism?

(Or)

Explain brief reactivity ration of co-polymerization?

26. Briefly explain the average molecular weight concept?

(Or)

How to measure the molecular weight of polymer by viscosity method?

Reg. No. : ----------------------------- [16CHP305A]

KARPAGAM ACADEMY OF HIGHER EDUCATION

COIMBATORE-641021

DEPARTMENT OF CHEMISTRY

III – SEMESTER

II- M.Sc., Chemistry

Ist Internal Test

Polymer Chemistry (Elective-III)

Time: 2 Hours Maximum: 50 marks

Answer Key

Section-A 20x 1 = 20

1. (a) Polyamides
2. (a) The collision frequency of the group
3. (a) Phenol
4. (a) Collision frequency
5. (a) The conformational rearrangement
6. (a) Dimer
7. (d) Concentration of the functional groups and monomers
8. (a) Trimer
9. (a) Homolytic dissociation of initiators
10. (a) Step polymerization
11. (a) $TiCl_3$ and $Al(C_2H_5)_2Cl$
12. (d) Molecular size
13. (a) Crystal structure of the initiator surface
14. (a) Edges(surfaces) of elementary sheets of the crystal
15. (a) Peroxides
16. (a) Isoelective polymerization
17. © ~ 290KJ mol^{-1}
18. (b) Decomposition
19. (b) 50-70°C
20. (d) Tetrafluroethene

Section- B 3x 2 = 6

21. Monomer

A **monomer** is a molecule that, as a unit, binds chemically or supramolecularly to other molecules to form a supramolecularpolymer. Large numbers of monomer units combine to form polymers in a process called polymerization. It is a small molecule of an organic substance. A double bond exist between the individual molecule which is weak.

Repeat unit

A **repeat unit** or **repeating unit** is a part of a polymer whose repetition would produce the complete polymer chain (except for the end-groups) by linking the repeat units together successively along the chain, like the beads of a necklace.

22. Co-ordination polymerization

Coordination polymerisation is a form of addition polymerization in which monomer adds to a growing macromolecule through an organometallic active center. The development of this polymerization technique started in the 1950s with heterogeneous Ziegler-Natta catalysts based on titanium tetrachloride and an aluminium co-catalyst such as methylaluminoxane. Coordination polymerization has a great impact on the physical properties of vinyl polymers such as polyethylene and polypropylene compared to the same polymers prepared by other techniques such as free-radical polymerization.

23. Polydispersion

In physical and organic chemistry, the **dispersity** is a measure of the heterogeneity of sizes of molecules or particles in a mixture. A collection of objects is called **uniform** if the objects have the same size, shape, or mass. A sample of objects that have an inconsistent size, shape and mass distribution is called **non-uniform**.

Section-C 3x 8 = 24

24. (a) Mechanism of step-growth polymerization

Stepwise polymerization

A number of different chemical reactions may be used to synthesize polymeric materials by step polymerization. These include esterification, amidation, the formation of urethanes, aromatic substitution, and others. Polymerization usually proceeds by the reactions between two different functional groups, for example, hydroxyl and carboxyl groups, or isocyanate and hydroxyl groups.All step polymerizations fall into two groups depending on the type of monomer(s)employed. The first involves two different bifunctional and/or polyfunctional monomers in which each monomer possesses only one type of functional group. (A polyfunctional monomer is a monomer with more than one functional group per molecule. A bifunctional monomeris one with two functional groups per molecule.) The second involves a single monomer containing both types of functional groups. The synthesis of polyamides illustrates both groups of polymerization reactions. Thus polyamides can be obtained from the reaction of diamines with diacids.

$$nH_2N\text{-}R\text{-}NH_2 + nHO_2C\text{-}R'\text{-}CO_2H \rightarrow \text{-(-}NH\text{-}R\text{-}NHCO\text{-}R'\text{-}CO\text{-)-}_nOH + (2n-1)H_2O$$

or from the reaction of amino acids with themselves:

$$nH_2N\text{-}R\text{-}CO_2H \rightarrow H\text{-(-}NH\text{-}R\text{-}CO\text{-)-}_nOH + (n-1)H_2O$$

The two groups of reaction can be represented in a general manner by the equations

$$nA\text{-}A + nB\text{-}B \rightarrow \text{-(-}A\text{-}AB\text{-}B\text{-)-}_n$$

$$nA\text{-}B \rightarrow \text{-(-}A\text{-}B\text{-)-}_n$$

where A and B are the two different types of functional groups. The characteristics of these two polymerization reactions are very similar. The successful synthesis of high polymers (i.e., polymer of sufficiently high molecular weight to be useful from the practical viewpoint) using any step polymerization reaction generally is more difficult than the corresponding small molecule reaction, since high polymers can be achieved only at very high conversions (>98–99%). A conversion of 90%, which would be considered excellent for the synthesis of ethyl acetate or methyl benzamide, is a disaster for the synthesis of the corresponding polyester or polyamide. The need for very high conversions to synthesize high polymer places several stringent requirements on any reaction to be used for polymerization—a favorable equilibrium and the absence of cyclization and other side reactions. These stringent requirements are met by a relatively small fraction of the reactions familiar to and used by chemists to synthesize small molecules. An additional requirement for achieving high molecular weights is the need for the A and B functional groups to be present at very close to stoichiometric amounts.

(b) Addition polymerization and its types

Addition polymerization

Polymers are long chain giant organic molecules are assembled from many smaller molecules called **monomers**. **Polymers** consist of many repeating monomer units in long chains. A polymer is analogous to a necklace made from many small beads (monomers). Many monomers are alkenes or other molecules with double bonds which react by **addition** to their unsaturated double bonds.

The electrons in the double bond are used to bond two monomer molecules together. This is represented by the red arrows moving from one molecule to the space between two molecules where a new bond is to form. The formation of polyethylene from ethylene (ethene) may be illustrated in the graphic on the left as follows. In the complete polymer, all of the double bonds have been turned into single bonds. No atoms have been lost and you can see that the monomers have just been joined in the process of addition. A simple representation is -[A-A-A-A-A]-. Polyethylene is used in plastic bags, bottles, toys, and electrical insulation.

Cationic polymerization

Cationic polymerization is a type of chain growth polymerization in which a cationic initiator transfers charge to a monomer which then becomes reactive. This reactive monomer goes on to react similarly with other monomers to form a polymer. The types of monomers necessary for cationic polymerization are limited to olefins with electron-donating substituents and heterocycles. Similar to anionic polymerization reactions, cationic polymerization reactions are very sensitive to the type of solvent used. Specifically, the ability of a solvent to form free ions will dictate the reactivity of the propagating cationic chain. Cationic polymerization is used in the production of polyisobutylene (used in inner tubes) and poly(N-vinylcarbazole) (PVK).

Anionic addition polymerization

Anionic addition polymerization is a form of chain-growth polymerization or addition polymerization that involves the polymerization of vinyl monomers with strong electronegative groups. This polymerization is carried out through a carbanion active species. Like all chain-growth polymerizations, it takes place in three steps: chain initiation, chain propagation, and chain termination. Living polymerizations, which lack a formal termination pathway, occur in many anionic addition polymerizations. The advantage of living anionic addition polymerizations is that they allow for the control of structure and composition.

Anionic polymerizations are used in the production of polydiene synthetic rubbers, solution styrene/butadiene rubbers (SBR), and styrenic thermoplastic elastomers.

25. (a) Zeigler-Natta Catalyst

The major interest will be on the titanium–aluminum systems for isoselective polymerization, more specifically, $TiCl_3$ with $Al(C_2H\ 5)_2Cl$ and $TiCl_4$ with $Al(C_2H\ 5)_3$—probably the most widely studied systems, and certainly the most important systems for industrial polymerizations. Before proceeding with the mechanistic consideration it is useful to review the evolution of the Ti-Al initiator system for industrial applications. The original initiator used by Ziegler for ethylene polymerization was obtained in situ as a precipitate on mixing the components $TiCl_4$ and $Al(C_2H\ 5)_3$ in a hydrocarbon solvent. The mixture was used directly for initiating polymerization. Natta, recognizing that the major product of the reaction was b-$TiCl_3$ (brown in color), explored various methods of preforming it outside the polymerization system, for example, by reduction of TiCl4 with hydrogen, aluminum, and various alkylaluminum compounds. The stereoselectivity of these early initiator systems was low with isotactic indices of only 20–40% for polypropene. The isotactic index, a measure of the isotactic content of a polymer, is the percentage of the sample insoluble in a hydrocarbon solvent such as boiling n-heptane. This is not as informative a technique as high-resolution NMR since insoluble molecules may contain some syndiotactic and atactic sequences and soluble molecules may contain some isotactic sequences. It does, however, give a simple measure of isotacticity that is usually within about 10% of the value obtained from NMR,
especially for highly isotactic samples.
There was a dramatic increase in stereoselectivity when the α-, δ-,or γ-crystalline form of $TiCl_3$ (all violet in color) was used directly. The early generations of industrial processes used $TiCl_3$ together with $Al(C_2H\ 5)_3$ and/or $Al(C_2H\ 5)_2Cl$. Over a two decade period starting in the late 1950s, the isotactic indices for polypropene increased to the low 90 percentile range. The initiator activity was enhanced by various ball milling and heat treatments of the initiator components before and after mixing. Ball milling involves mechanical grinding and not only increases surface area but also facilitiates reactions between the initiator components.
However, the activities were too low to allow the polymer products to be used without purification (by treatment with base or acid) to remove the residual metals, a process referred to as deashing. Also, optimization of the physical properties of the product often required removal of the atactic fraction. The initiator systems were inefficient with less than 1% of the Ti being active in polymerization. The later generations of initiators, starting in the late 1970s, increased initiator efficiency and activity without sacrificing stereoselectivity [Bohm, 2001; Busico and Cipullo, 2001; Cecchin et al., 2001; Chadwick, 2001; Chadwick et al., 2001; Chien et al., 1982; Hu and Chien, 1988]. The effective surface area of the active component of the initiator system was increased by close to 2 orders of magnitude by using $MgCl_2$ as a solid support in which $TiCl_4$ is finely dispersed. Stereoselectivity was kept high and actually increased by the addition of electron-donor additives.

A typical recipe for a present-day superactive or high-mileage initiator system involve ball milling of $MgCl_2$ (or the alkoxide) and TiCl4 followed by the addition of $Al(C_2H\ 5)_3$ with an electron donor (such as dialkyl phthalate and alkoxysilane) usually added in each step of preparation. Activity is 50–200 kg polymer per gram of initiator system. Typically, the initiator system is no more than 2–4% Ti, which makes the activity about 1500–6000 kg polymer per gram of Ti. The high activity not only minimizes initiator and production costs but also avoids the costly task of initiator removal from the polymer product (except possibly for food- and medical-grade products). Isotactic indices for polypropene have been increased to 98% or higher with (mmmm) pentad fractions up to 98% and higher. This not only improves the product's physical properties but also avoids the need to remove the a tactic fraction.

Chemical Nature of Propagating Species

Some early polymerizations reported as Ziegler–Natta polymerizations were conventional free-radical, cationic, or anionic polymerizations proceeding with low stereoselectivity.Some Ziegler–Natta initiators contain components that are capable of initiating conventional ionic polymerizations of certain monomers, such as anionic polymerization of methacrylates by alkyllithium and cationic polymerization of vinyl ethers by $TiCl_4$. Most Ziegler–Natta components participate in a complex set of reactions involving alkylation and reduction of the transition-metal component by the group I–III component as shown below for $TiCl_4 + AlR_3$:

$TiCl_4 + AlR_3 \longrightarrow TiCl_3\,R + AlR_2\,Cl$

$TiCl_4 + AlR2Cl \longrightarrow TiCl_3R + AlRCl_2$

$TiCl3R + AlR_3 \longrightarrow TiCl_2\,R_2 + AlRCl_2$

$TiCl_3\,R \longrightarrow TiCl_3 + R\bullet$

$TiCl_3 + AlR_3 \longrightarrow TiCl_2\,R + AlR_2\,Cl$
$R\bullet \longrightarrow$ combination + disproportionation

Radicals produced in Eq. 8-31 are capable of initiating radical polymerizations with some monomers, for example, vinyl chloride.The mechanism for the tereoselective polymerization of a-olefins and other nonpolar alkenes is a p-complexation of monomer and transition metal (utilizing the latter's d-orbitals) followed by a four-center anionic coordination insertion process in which monomer is inserted into a metal–carbon bond as described in Fig. 8-10. Support for the initial p-complexation has come from ESR, NMR, and IR studies [Burfield, 1984]. The insertion reaction has both cationic and anionic features. There is a concerted nucleophilic attack by the incipient carbanion polymer chain end on the a-carbon of the double bond together with an electrophilic attack by the cationic counterion on the alkene p-electrons.The anionic character of the polymerization is consistent with the polymerization rate decreasing in the order ethylene > propene > 1-butene [Bier, 1961; Boor, 1967].

The reverse order is expected for a polymerization involving the conversion of a monomer into the corresponding carbocation. For addition of a carbanion to the monomers, attack occurs at the a-carbon to form the less substituted (and more stable) carbanion. Further, a-substituents sterically hinder the approach of a carbanion and/or counterion with the result that reactivity decreases with increasing substituent size. Evidence for the anionic nature of propagation also comes from studies in which labeled methanol is used to terminate chain growth. The terminated polymer is radioactive when CH_3 O_3 H is used, while termination by $^{14}CH_3$ OH yields a nonradioactive polymer.

(b) Reactivity ratio of co-polymerization

Copolymer Composition

Terminal Model; Monomer Reactivity Ratios

The instantaneous copolymer composition—the composition of the copolymer formed at very low conversions (about <5%)—is usually different from the composition of the comonomer feed from which the copolymer is produced, because different monomers have differing tendencies to undergo copolymerization. It was observed early that the relative copolymerization tendencies of monomers often bore little resemblance to their relative rates of homopolymerization [Staudinger and Schneiders, 1939]. Some monomers are more reactive in copolymerization than indicated by their rates of homopolymerization; other monomers are less reactive. Further, and most dramatically, a few monomers, such as maleic anhydride and stilbene undergo facile copolymerization with radical initiation, although they have very little or no tendency to undergo homopolymerization.

The composition of a copolymer thus cannot be determined simply from a knowledge of the homopolymerization rates of the two monomers. The determinants of copolymerization composition have been elucidated by several workers by assuming the chemical reactivity of the propagating chain (which may be a free radical, carbocation, or carbanion) in a copolymerization is dependent only on the identity of the monomer unit at the growing end and independent of the chain composition preceding the last monomer unit [Alfrey and Goldfinger, 1944; Mayo and Lewis, 1944; Wall, 1944; Walling, 1957]. This is referred to as the firstorder Markov or terminal model of copolymerization. Consider the case for the copolymerization of the two monomers M_1 and M_2.

Q–e Scheme

Various attempts have been made to place the radical–monomer reaction on a quantitative basis in terms of correlating structure with reactivity. Success in this area would give a better understanding of copolymerization behavior and allow the prediction of the monomer reactivity ratios for comonomer pairs that have not yet been copolymerized. A useful correlation is the Q – e scheme of Alfrey and Price [1947], who proposed that the rate constant for a radical–monomer reaction, for example, for the reaction of M_1**.** radical with M_2 monomer, be written as

$$K_{12} = P_1Q_2 \exp(-e_1e_2) \qquad 15$$

where P_1 represents the intrinsic reactivity of $M_1\bullet$ radical, Q_2 represents the intrinsic reactivity of M_2 monomer, e_1 represents the polarity of $M_1\bullet$ radical, and e_2 represents the polarity of M_2 monomer. By assuming that the same e value applies to both a monomer and its corresponding radical (i.e., e_1 defines the polarities of M_1 and M_1**.**, while e_2 defines the polarities of M_2 and

$M_2\bullet$), one can write expressions for k_{11}, k_{22}, k_{21} analogous to Eq. 15. These can be appropriately combined to yield the monomer reactivity ratios in the forms

$$r_1 = Q_1/ Q_2 \exp[-e_1(e_1 - e_2)] \qquad 16$$

$$r_2 = Q_2/ Q_1 \exp[-e_2(e_2 - e_1)] \qquad 17$$

which correlate monomer–radical reactivity with the parameters Q_1, Q_2, e_1, and e_2. The basis of the Q–e scheme (Eqs. 15 to 17) is the theoretically unsatisfactory suggestion that the alternating tendency is due to ground-state electrostatic interactions between permanent charges in the monomer and radical [Price, 1948].

Although there have been attempts to place it on a solid theoretical basis [Colthup, 1982; O'Driscoll and Yonezawa, 1966], the Q–e scheme is best considered as an empirical approach to placing monomer reactivity on a quantitative basis. Monomer reactivity is separated into the parameter Q, which describes the resonance factor (and to a slight extent the steric factor) present in the monomer, and the parameter e, which describes the polar factor.

Consider now the use of the Q–e shceme to predict monomer reactivity ratios. Values of Q and e have been assigned to monomers on the basis of their r values and the arbitrarily chosen reference values of Q = 1 and e = - 80 for styrene [Greenley, 1989b, 1999]. Table 6-7 shows the average Q and e values for some common monomers. The practical success of the Q–e scheme in predicting the r_1 and r_2 values for comonomer pairs not previously copolymerized has been limited in its quantitative aspects. The reason for this is that the Q and e values for a monomer are not unique values for both experimental and theoretical reasons. The precision of the calculated Q and e values is often poor as a result of inaccuracies in the experimentally determined r values. Further, the Q and e values for a monomer vary considerably depending on the monomer with which it is copolymerized as a result of inherent deficiencies of the Q–e scheme. It does not explicitly take into account steric factors that may affect monomer reactivity ratios for certain radical–monomer combinations. The assumption of the same e value for a monomer and its corresponding radical is also inadequate. Attempts to refine the Q–e scheme by using separate e values for monomer and radical have not been successful.

In spite of these deficiencies the Q–e scheme is a reasonable qualitative and even semi quantitative approach to the effect of structure on monomer reactivity. It can be used to give a general idea of the behavior to be expected from a comonomer pair that has not been studied. The Q–e values can be used to more quantitatively discuss reactivity data such as those in Table 6-4 and 6-6. The monomers are lined up in Table 6-6 in order of their e values. This order defines the polarities of the various monomers. The relative importance of resonance and polar factors in determining monomer reactivity can be discussed by considering the data in Table 6-4 in terms of the Q and e values of the monomers.

The various reference radicals can be divided into two groups: one composed of the relatively unreactive radicals and the other composed of reactive radicals. For the reactive radicals, such as vinyl chloride and vinyl acetate, monomer reactivity depends on Q with k_{12} increasing with increasing Q and polar effects are too subtle to discern. The unreactive radicals from styrene and, 3-butadiene show the same trends except that one can discern the polar effects. There is enhanced reactivity of these radicals (processing negative e values) toward a onomer such as acrylonitrile with relatively high positive e values. The resonance factor is, however, more important than the polar factor; the former determines the magnitude of monomer reactivity. Thus monomer reactivities toward the 1,3-butadiene and styrene radicals fall into two groups—one group of monomers with high Q values and high reactivities and another group with low Q values and low reactivities.

A number of useful generalizations are possible regarding which pairs of monomers will copolymerize and the behavior to be expected. Copolymerization proceeds poorly with monomers whose Q values are very different, since copolymer formation would require the energetically unfavorable conversion of a resonance-stabilized radical to a less stabilized radical and vice versa . Thus vinyl chloride and vinyl acetate do not copolymerize well with styrene or 1,3-butadiene. Copolymerization is more suitable between monomers of similar Q values, preferably high Q values, for example, styrene and 1,3-butadiene. Ideal copolymerization occurs between two monomers having similar Q and e values, for example, styrene–1,3-butadiene, vinyl chloride–vinyl acetate, and acrylonitrile–methyl acrylate. The tendency toward alternation is greatest for monomers having the same Q values with high e values of opposite sign.

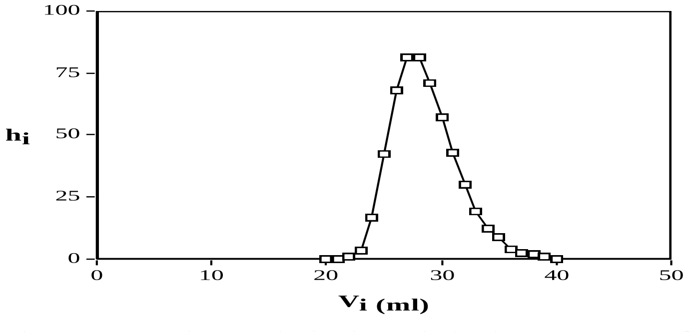
TABLE: Q and e Values for Monomersa; a Data from Greenley [1989b, 1999].

Monomer	**Q**	**e**
Ethyl vinyl ether	0.018	-1.80
Propene	0.009	-1.69
N-Vinylpyrrolidone	0.088	-1.62
n-Butyl vinyl ether	0.038	-1.50

26. <u>(a) Average molecular weight concept</u>

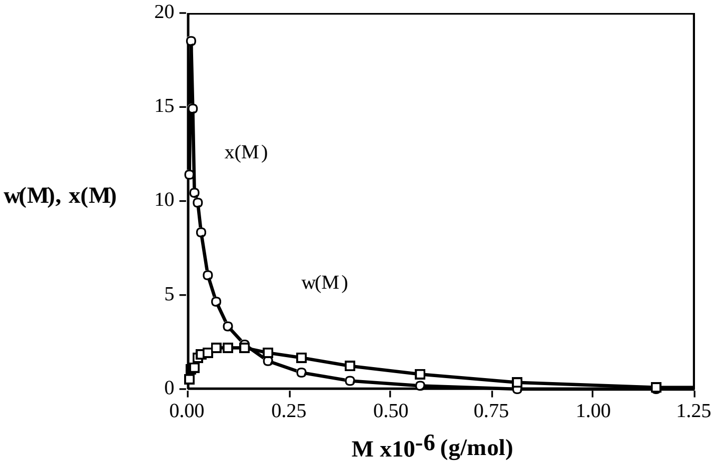
Molecular Weight Distributions -

Consider ways that this molecular weight distribution might be graphically presented. Most commonly, the distribution is shown as the raw GPC trace, which is given next. A single, well-defined molecular weight peak is noted. [To define the molecular weight distribution better, there should be more data points spread over the peak; I didn't want to do more hand calculations, so the table has only enough data to illustrate trends clearly.]



Despite this sample's large PDI, the peak looks relatively narrow. This trace, termed the chromatogram, is by itself is pretty meaningless, since we don't know how M_i and $V_i$are related: the poorer the molecular weight separation, for example, the narrower is the chromatogram peak. Notwithstanding this trivial fact, raw GPC traces are frequently cited when arguing for low polydispersity.

In this instance, the relationship between M_i and V_i is known by a calibration with polystyrene standards, so we can do much better than the chromatogram. Given below are the weight and number fraction distributions derived above.



These bear no resemblance to the raw trace, and the significant polydispersity of the sample is amply evident. Indeed, the x(M) curve shows that the most common polymer species has a molecular weight of 7,200 g/mol even though M_n and M_w both exceed 100,000 g/mol. Approximately 10% of the molecules by weight have molecular weights in excess of 800,000 g/mol, while 10% by weight have molecular weights less than 50,000 g/mol. The value of M_n falls slightly above the maximum of w(M), whereas the value of M_w lies well above this maximum, a fact commonly mentioned in introductory polymer texts. The difference between x(M) and w(M) simply manifests that it takes many small chains to balance the mass of a few larger chains. By number, the short chains dominate, while by weight, the converse is true. Surveying a whole year of Macromolecules, one is likely to never see a x(M) curve and just a handful of w(M) curves.

(b) Measure the molecular weight of polymers by viscosity method

Viscosity Method

Polymers are, in general, less soluble than their corresponding monomers. Dissolving polymers in solvents leads to an increase in viscosity; the longer the average chain length of the polymer molecules, the more the viscosity changes (known as positive viscosity). The viscosity of a solution can be easily measured; therefore, viscosity measurements are widely used in determining the average DP of cellulose.

In 1930, Hermann Staudinger was the first to recognize an empirical relationship between the relative magnitude of the increase in viscosity and the molecular weight of the polymer [27]. The simplest method for determining the viscosity of a polymer solution is by capillary viscometry, using the Ubbelohde U-tube viscometer. Here, the flow time t of the polymer solution and of pure solvent $t_0$are recorded. The ratio of the flow time of a polymer solution t to that of pure solvent is equal to the ratio of their viscosities ($\eta/\eta 0$) if their densities are equal. This is only feasible for dilute solutions (in which density differences level out). Because unity is the lower limit of the relative viscosity ηr, the specific viscosity $\eta sp$is more useful, as it depicts the relative increase brought about by the dissolved polymer.

Relating the specific viscosity to concentration gives the reduced viscosity. The intrinsic viscosity is expressed as the limit of the reduced viscosity at zero concentrations. The inherent viscosity is given as the natural logarithm of the relative viscosity divided by the concentration. At concentration zero the inherent viscosity becomes equal to the intrinsic viscosity. Thus, either the extrapolation of the reducedviscosity or the inherent viscosity gives the intrinsic viscosity:

$$\begin{gathered}
\text{Relative Viscosity: } \eta_r = \frac{\eta}{\eta_0} \\
\text{Specific Viscosity: } \eta_{sp} = \frac{\eta - \eta_0}{\eta_0} = \eta_r - 1 \\
\text{Reduced Viscosity: } \eta_{red} = \frac{\eta_{sp}}{c} \\
\text{Intrinsic Viscosity: } [\eta] = \lim_{c \to 0} \frac{\eta_{red}}{c} \\
\text{Inherent Viscosity: } \eta_{inh} = \frac{\ln \eta_r}{c}
\end{gathered}$$

For a given polymer-solvent pair the intrinsic viscosity is a unique function of molecular mass. The Mark-Houwink (or Kuhn-Mark-Houwink-Sakurada) equation then relates the molecular weight of the polymer plus solvent at a specified temperature to the intrinsic viscosity

$$\boxed{[\eta] = K_v M^v}$$

Kv(or sometimes KM) and v (sometimes notated a) must be established by calibrating with polymers of known molecular weights. Once this has been performed, only [η] will give the molecular weight for an unknown molecule, which is normally done by plotting log [η] against log M and subsequent interpolation.

For a theta solvent, $v = 0.5$, and as the solvent becomes thermodynamically better, v increases. For most practical systems, these values can be found in data handbooks. The extrapolation factors for cellulose to zero concentration are also listed. Under these assumptions, it is possible to calculate the intrinsic viscosity by measuring only one concentration of the sample. Molecular weights derived via the

Mark-Houwink equation and viscometry yield the viscosity average molar mass [Mv], which is given by:

$$\boxed{M_v = \left[\frac{\sum n_i M_i^{1+v}}{\sum n_i M_i}\right]^{1/v}}$$

where$ni$is the number of molecules of molar mass $Mi$and the exponent v is the exponent of the Mark-Houwink equation. It should be noted that the viscosity average is not an absolute average and depends on solvent and/or temperature; therefore, viscosity measurements yield relative values. $Mv$is not a fixed quantity—it depends on v. If v becomes unity, viscosity and weight average are equal; Mvlies therefore, in between Mn and Mw in magnitude but will be usually closer to Mw.

Reg. No. : ------------------------------ [16CHP305A]

KARPAGAM UNIVERSITY
KARPAGAM ACADEMY OF HIGHER EDUCATION
COIMBATORE-641021
(For the candidates admitted from 2017 & onwards)
DEPARTMENT OF CHEMISTRY
II- M.Sc., Chemistry (III – Semester)
IInd Internal Test
Polymer Chemistry (Elective-III)

Time: 2 Hours Maximum: 50 marks

Date:

Section-A **20X1=20**

Answer all the questions

1. The freezing point depression not to depends on the
   (a) size and nature of solute (b) nature of solvent (c) number of solutes
   (d) weight of solvent
2. Cryoscopic method is applied to determine the
   (a) Weight average molecular weight (b) Number-average molecular weight
   © Viscosity average molecular weight (d) Vapor pressure molecular weight
3. The term ln η_r /C is the
   (a) specific viscosity (b) reduced viscosity (c) inherent viscosity (d) intrinsic viscosity
4. In the ultracentrifugation, which force is used for polymer separation
   (a) kinetic force (b) magnetic force (c) centrifugal force
   (d) Vander walls force
5. Wet spinning technique is commercially used to produce filament yarn of
   (a) Polypropylene (b) Polyester (c) Nylon 66 (d) Acrylic
6. Too high resistivity leads to the development of static?
   (a) Mechanical charges (b) Positive charges (c) Negative charges
   (d) Electrical charges
7. Which properties of fiber are quite complex and have been subject of much experimental work?
   (a) Physical (b) Mechanical (c) Chemical (d) Thermal
8. The tenacity at break of typical fibers ranges from about 1 g/denier for?
   (a) Synthetic (b) Natural (c) Rayons (d) Carbon fibres
9. Which one of the following is the least satisfactory fibers from the standpoint of weather ability?
   (a) Silk (b) Cotton (c) Glass (d) Wood

No 31 [illegible]

10. Natural fibers are consisting of?
    (a) Linear polymers (b) Nonlinear polymers (c) Copolymers (d) Chain polymers
11. In which spinning, the polymer is melted by heating and then passed through a spinneret via
    (a) Melt spinning (b) Dry spinning (c) Wet spinning (d) Spinning
12. Birefringence of filament yarn is related to its
    (a) Density (b) Filament denier (c) Orientation (d) Crystallinity
13. Which is more flexible than HDPE due to lower crystalline?
    (a) Polyethylene (b) Low Density Polyethylene (c) Polyamide
    (d) Low density polyamide
14. 80-90% of all plasticizers used with?
    (a) DOP (b) DIOP (c) PVC (d) Colorants
15. It must not exude from the plastic material?
    (a) Primary plasticizers (b) Secondary plasticizers (c) Antioxidants
    (d) Colorants
16. Porosity increased as plasticizers content?
    (a) Increased (b) Decreased (c) Suddenly decreased (d) Never change
17. The substances which weaken the intermolecular forces between the polymer chains and decrease T_g.
    (a) Plasticizers (b) Antioxidants (c) Polymer initiators (d) Fillers
18. Which type of the compound is not used as a flame retardant in polymers
    (a) Aluminum Hydroxide (b) Halogen compounds
    © Phosphorous compounds (d) Ferrocene
19. Which one of the following polymers is the product of a condensation polymerisation reaction?
    (a) Polypropylene (b) Polytetrafluoroethene (c) Poly acetic acid
    (d) PVC
20. Melamine is
    (a) White crystalline solid (b) Gas (c) Colorless liquid (d) Yellow liquid

Section B 3x2 = 6

Answer all the questions

21. What is the principle of Ebuliometry method?

22. Define compounding?

23. Write any four uses of PVC?

Section C

3x8 = 24

Answer all the questions

24. (a) Explain in brief about the method to determine the molecular weight of the polymer based on osmosis?

(or)

(b) Write a note on (i) Compounding technique

(ii) Calendaring technique?

25. (a) Give an account of casting method and its types?

(or)

(b) What is fiber spinning? & explain its various types?

26. (a) Explain the preparation, properties and uses of polyethylene and polyester?

(or)

(b) Discuss about Epoxy resins and Silicone polymers?

Reg. No. : ----------------------------- [16CHP305A]

KARPAGAM ACADEMY OF HIGHER EDUCATION

COIMBATORE-641021

DEPARTMENT OF CHEMISTRY

III – SEMESTER

II- M.Sc., Chemistry

II^nd^ Internal Test

Polymer Chemistry (Elective-III)

Time: 2 Hours Maximum: 50 marks

Answer Key

Section-A **20x 1 =20**

1. (a) Size and Nature of solute
2. (b) Number Average molecular weight
3. © Inherent viscosity
4. © Centrifugal force
5. (d) Acry;ic
6. (d) Electrical charges
7. (b) Mechanical
8. © Rayons
9. (a) Silk
10. (a) Linear polymers
11. (b) Dry spinning
12. © Orientation
13. (b) Low Density Polyethylene
14. © PVC
15. (a) Primary plasticizers
16. (a) Increased
17. (a) Plasticizers
18. (d) Ferrocene
19. © Poly acetic acid
20. (a) White crystalline solid

Section- B **2x 3 = 6**

21. Principles of Ebuliometry

It is one of the molecular weight determination method by using the variation in the boiling point of the polymers. It is based on osmometric method.

Ebuliometer is used for measure the boiling points of the monomers and various concentration and time.

22. Compounding

Pharmaceutical compounding (done in **compounding pharmacies**) is the creation of a particular pharmaceutical product to fit the unique need of a patient. To do this, compounding pharmacists combine or process appropriate ingredients using various tools. This may be done for medically necessary reasons, such as to change the form of the medication from a solid pill to a liquid, to avoid a non-essential ingredient that the patient is allergic to, or to obtain the exact dose(s) needed or deemed best of particular active pharmaceutical ingredient(s). It may also be done for more optional reasons, such as adding flavors to a medication or otherwise altering taste or texture.

23. Uses of PVC

- **Pipes**

Roughly half of the world's polyvinyl chloride resin manufactured annually is used for producing pipes for municipal and industrial applications.

- **Electric cables**

PVC is commonly used as the insulation on electrical cables; PVC used for this purpose needs to be plasticized.

- PVC has become widely used in clothing, to either create a leather-like material or at times simply for the effect of PVC. PVC clothing is common in Goth, Punk, clothing fetish and alternative fashions.
- **Healthcare**

The two main application areas for single-use medically approved PVC compounds are flexible containers and tubing: containers used for blood and blood components, for urine collection or for ostomy products and tubing used for blood taking and blood giving sets, catheters, heart-lung bypass sets, hemodialysis sets etc.

24. Determination of molecular weight of polymer based on osmosis

End Group Method

The molecular weight of polymers which have an end group amenable to analysis could be principally analyzed by an end-group assay [42]. The biggest drawback of this method is the decrease in sensitivitywith an increased chain length. The first measurements with this method were performed by Staudinger and Eder and gave determination limits of about 15,000 g·mol−1. Weber and Husemann treated cellulose with an alkaline copper sulfate solution to oxidize aldehydes to aldonic acids. Afterwards, they determined the so-called "*Monosezahl*" (number of glucose units per carboxyl group). With this method, they were able to determine molecular weights up to 200,000 g·mol^{-1}. However, due to processing, cellulose usually already contains oxidized end groups and additional carbonyl groups. Hence, a direct relationship between carboxyl groups (aldonic acid) and molecular weight determined with a high rate of accuracy.

Osmotic Pressure

Osmometry is among the methods for determining molecular mass which rely on colligative properties (from the Latin word *colligere*for "collect"), meaning that only the number of dissolved molecules influences the properties of a solution [46]. In addition, the osmotic pressure, boiling point elevation, vapor pressure reduction, and the freezing point depression are based on colligative properties. Out of the four colligative methods, only membrane osmometry (MO) is of interest for cellulosic samples.

However, vapor pressure osmometry (VPO) is superior for analyzing samples with Mn < 20,000 g·mol^{-1}. This is because the diffusion of low molecular weight molecules through the membrane limits the utility of membrane osmometry for this especially low molecular weight region. Only a few publications address the use of VPO experiments on directly-dissolved cellulose and these will be discussed at the end of this chapter.

Since the osmotic pressure of a solution depends on molecular weight and concentration *c*, the following equation can be used to determine the number average of the molecular weight

$$\boxed{\frac{\Pi}{c} = RT\left(\frac{1}{M_n} + A_2 c + A_3 c^2 + \cdots\right)}$$

whereΠ is the osmotic pressure, c is the solute concentration, R is the ideal gas constant, T the temperature, Mn is the number average, and $A2$ and $A3$ are the second and third virial coefficients. The most common method of osmometry is membrane osmometry. In membrane osmometry, the osmotic pressure is measured directly using a semi-permeable membrane [42]. In experiments, the osmotic pressure must be measured at several different concentrations. By extrapolating the Π/c versus c plot to zero, the intercept gives the molecular weight, whereas slope yields $A2$. Note, that $A2$ is an empirical constant for a given solute/solvent system and it depends on the temperature. It represents the interaction of a single molecule with the solvent. For the fundamental theory of osmometry.

Using osmometry for cellulose molecular weight determination creates a few problems. First, the osmotic pressure is inversely proportional to molecular weight, so molecules with a high molecularweight contribute very little. Therefore, the sample must be free of low molecular compounds when applying osmometry. This is especially true for salts and, therefore, for aqueous cellulose solutions. This is the main reason that osmometry is ordinarily used with cellulose derivatives in organic solvents.

In most cases, cellulose-based membranes such as cellophane or bacterial cellulose are used for membrane osmometry. However, these membranes are not completely resistant against solvents used for cellulose. Hence, the usual cellophane membrane gels which are used in an osmometer would dissolve in, for example, cuen solutions.

Working with those membranes, they measured the molecular weights of two cellulose samples directly. Since cellulose in cuen behaves as a polyelectrolyte, they faced another problem beyond membrane instability. However, by proper conditioning of the membranes, the polyelectrolyte character of the solution can be compensated and allow for a valid measurement. Immergut's paper is one of the few dealing with the direct osmometry of pure cellulose.

This method continues to play a minor role today, even for derivatized cellulose.

It is worth noting that osmometry was originally used to determine the relationship between intrinsic viscosity and molecular weight. It has been shown that under mild conditions, the degradation during cellulose nitration is negligible. In his pioneering work, Staudinger used the osmometry of cellulose nitrates in acetone to determine the constant $Kcm$of the Staudinger Equation:

$$\boxed{\log \eta_r = K_{cm} * M * c}$$

where$\eta r$is the relative viscosity (see Chapter 2.4), M is the molecular weight, and $Kcm$is the molecular weight-concentration constant. The Staudinger equation was later the basis for the Mark-Houwinkequation (see Chapter 2.4).

Using VPO instruments with increased sensitivity, Kamide*et al*. detected an upper limit of 1 × 105 g·mol^{-1}. Compared with the results for cellulose acetate obtained by MO and SEC, VPO values differed by only a small percentage.

(b)i) Compounding technique

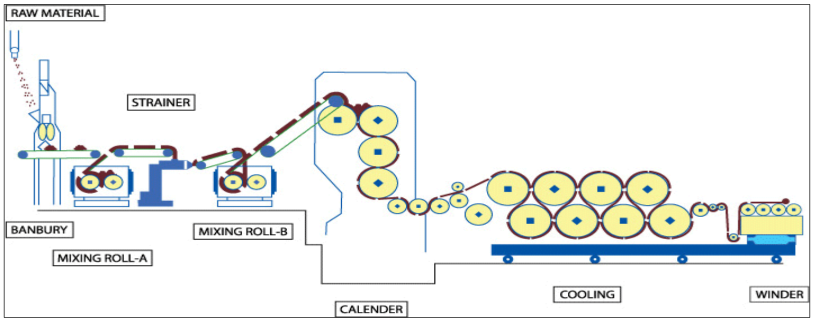
Compounding

Pharmaceutical compounding (done in **compounding pharmacies**) is the creation of a particular pharmaceutical product to fit the unique need of a patient. To do this, compounding pharmacists combine or process appropriate ingredients using various tools. This may be done for medically necessary reasons, such as to change the form of the medication from a solid pill to a liquid, to avoid a non-essential ingredient that the patient is allergic to, or to obtain the exact dose(s) needed or deemed best of particular active pharmaceutical ingredient(s). It may also be done for more optional reasons, such as adding flavors to a medication or otherwise altering taste or texture. Compounding is most routine in the case of intravenous/parenteral medication, typically by hospital pharmacists, but is also offered by privately owned compounding pharmacies and certain retail pharmacies for various forms of medication. Whether routine or rare, intravenous or oral, etc., when a given drug product is made or modified to have characteristics that are specifically prescribed for an individual patient, it is known as **"traditional" compounding**.

Due to the rising cost of compounding and the shortage of drugs, many hospitals have shown a tendency to rely more upon large-scale compounding pharmacies to meet their regular requirement, particularly of sterile-injectable medications. When compounding is done on bulk production of a given formulation rather than patient-specific production, it is known as "non-traditional" compounding (which, as discussed below, is arguably not "compounding" but rather "manufacturing"). This development raises concerns about patient safety and makes a case for proper regulatory control and monitoring.

ii) Calendering technique

1. *Calendering*



Calendering is a continuous process which works in much the same way as an old-fashioned clothes mangle. For plastics, there are usually four heated rollers of different sizes rotating at slightly different speeds. The material is fed into these rollers, heated and melted, then shaped into a sheet or film. This is then cooled and rolled up. The sheets can be mono-oriented during this process. The most commonly calendered material is PVC.

25. (a) Casting method and Types

2. *Casting Process*

Casting is a manufacturing process in which a liquid material is usually poured into a mold, which contains a hollow cavity of the desired shape, and then allowed to solidify. The solidified part is also known as a *casting*, which is ejected or broken out of the mold to complete the process. Casting materials are usually metals or various *cold setting* materials that cure after mixing two or more components together; examples are epoxy, concrete, plaster and clay. Casting is most often used for making complex shapes that would be otherwise difficult or uneconomical to make by other methods.

1. **Die casting**
2. **Rotational casting**
3. **Film casting**

2.1 Die casting

Die casting is a metal casting process that is characterized by forcing molten metal under high pressure into a mold cavity. The mold cavity is created using two hardened tool steel dies which have been machined into shape and work similarly to an injection mold during the process. Most die castings are made from non-ferrous metals, specifically zinc, copper, aluminium, magnesium, lead, pewter and tin-based alloys. Depending on the type of metal being cast, a hot- or cold-chamber machine is used.

The casting equipment and the metal dies represent large capital costs and this tends to limit the process to high-volume production. Manufacture of parts using die casting is relatively simple, involving only four main steps, which keeps the incremental cost per item low. It is especially suited for a large quantity of small- to medium-sized castings, which is why die casting produces more castings than any other casting process. Die castings are characterized by a very good surface finish (by casting standards) and dimensional consistency.

Two variants are pore-free die casting, which is used to eliminate gas porosity defects; and direct injection die casting, which is used with zinc castings to reduce scrap and increase yield.

Equipment

There are two basic types of die casting machines: *hot-chamber machines* and *cold-chamber machines*. These are rated by how much clamping force they can apply. Typical ratings are between 400 and 4,000 st (2,500 and 25,400 kg).

Advantages and disadvantages

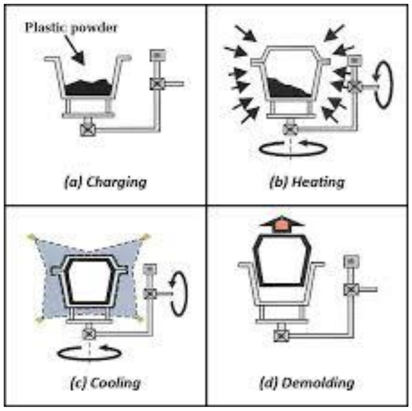
Advantages of die casting:

- Excellent dimensional accuracy (dependent on casting material, but typically 0.1 mm for the first 2.5 cm (0.005 inch for the first inch) and 0.02 mm for each additional centimeter (0.002 inch for each additional inch).
- Smooth cast surfaces (Ra 1–2.5 micrometres or 0.04–0.10 thou rms).
- Thinner walls can be cast as compared to sand and permanent mold casting (approximately 0.75 mm or 0.030 in).
- Inserts can be cast-in (such as threaded inserts, heating elements, and high strength bearing surfaces).
- Reduces or eliminates secondary machining operations.
- Rapid production rates.
- Casting tensile strength as high as 415 megapascals (60 ksi).
- Casting of low fluidity metals.

The main disadvantage to die casting is the very high capital cost. Both the casting equipment required and the dies and related components are very costly, as compared to most other casting processes. Therefore, to make die casting an economic process, a large production volume is needed. Other disadvantages are that the process is limited to high-fluidity metals, and casting weights must be between 30 grams (1 oz) and 10 kg (20 lb). In the standard die casting process the final casting will have a small amount of porosity. This prevents any heat treating or welding, because the heat causes the gas in the pores to expand, which causes micro-cracks inside the part and exfoliation of the surface. Thus a related disadvantage of die casting is that it is only for parts in which softness is acceptable. Parts needing hardening (through hardening or case hardening) and tempering are not cast in dies.

2.2 Rotational Casting

Rotational Molding (BrE **moulding**) involves a heated hollow mold which is filled with a charge or shot weight of material. It is then slowly rotated (usually around two perpendicular axes), causing the softened material to disperse and stick to the walls of the mold. In order to maintain even thickness throughout the part, the mold continues to rotate at all times during the heating phase and to avoid sagging or deformation also during the cooling phase. The process was applied to plastics in the 1940s but in the early years was little used because it was a slow process restricted to a small number of plastics. Over the past two decades, improvements in process control and developments with plastic powders have resulted in a significant increase in usage.

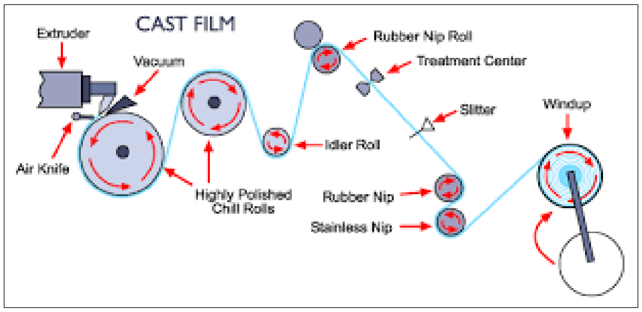


Rotocasting (also known as rotacasting), by comparison, uses self-curing resins in an unheated mould, but shares slow rotational speeds in common with rotational molding. Spin casting should not be confused with either, utilizing self-curing resins or white metal in a high-speed centrifugal casting machine.

2.3 Film Casting

Polymer solution casting is a technique that can replace film extrusion to deliver high-quality films with superior optical, mechanical and physical film properties.

In polymer solution casting, polymer is dissolved or dispersed in solution, coated onto a carrier substrate, and then the water or solvent is removed by drying to create a solid layer on the carrier. The resulting cast layer can be stripped from the carrier substrate to produce a standalone film. Before or after stripping, the cast film can be laminated with other webs or coated with other materials to create multi-layer products.



Manufacturing process advantages of polymer solution casting over traditional film extrusion methods include:

- Processing at low temperatures, which is valuable for thermally activated films or applications incorporating temperature-sensitive active ingredients.
- Ability to produce high-temperature resistant films from non-thermoplastic but soluble raw materials.
- Simplified incorporation of additives and fillers.
- Quicker changeovers for platforms with many part numbers that are differentiated based on formula.
- Single pass manufacturing of multi-layer films (*g.* the ability to cast a free film, then coat an adhesive and laminate release liner on one side, and coat a top coat on the other side).
- Wider range of material choices with casting from either aqueous or solvent-based solutions.

Advantages of the resulting film include:

- Greater film thickness uniformity, as tight as +/-2%.
- Wider range of film thickness, from 150 microns down to less than 12 microns.
- Films that are gel and pinhole free.
- Excellent flatness and dimensional stability.
- Isotropic orientation (mechanical and optical) as film is not stretched during manufacture.
- Absence of typical extrusion process lubricants.

(b) Fiber Spinning and its types

3. Fiber Spinning

Fiber spinning is used to make synthetic fibers for use in many industries. There are three main types of fiber spinning methods: melt, solution, and reaction spinning. In fiber spinning a liquid polymer is extruded through small holes in a spinneret to form thin filaments, as shown below. Upon leaving the spinneret the filaments solidify. After solidification, filaments can be combined to make threads and/or drawn to change the filaments' properties.

The processes governing the three types of fiber spinning differ mainly in the way the polymer is liquefied and solidified.

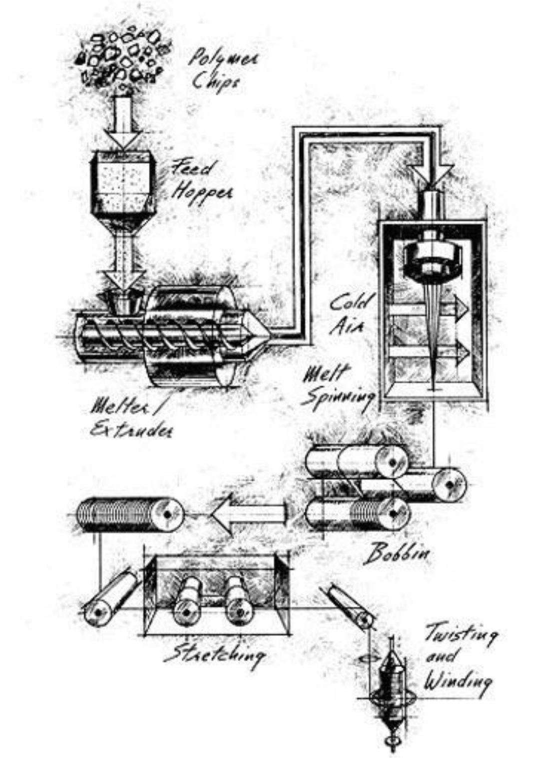
1. Melt Spinning

General Information

Melt spinning is the most widely used form of fiber spinning. In melt spinning either molten polymer is used or polymer pellets are melted down. Once the filaments are extruded they are cooled in a fluid medium such as air, gas, or even water.

Equipment Design

In melt spinning, as shown below , the molten or melted polymer is pushed vertically downwards through the spinneret. When the filaments emerge from the spinneret they are cooled by a gas, usually air, which flows either perpendicularly across, cocurrently , or countercurrently to the filaments.



Melt Spinning Polymer from Chip

The filaments can then be brought together and/or twisted together to form a thread. Before winding the thread on the bobbin, it is often treated with water or a wetting agent and then a lubricant . Later, the wound thread may be dyed and drawn on other machines.

Spinneret design , such as those shown below, is dependent on the type of spinning and desired cross sectional shape of the filament. The cross sectional shape determines different features the filament will exhibit, such as how it will reflect light, the ability to insulate, and how easily it shows dirt.

Spin plates and spinnerets may have as many as 80,000 bores spaced less than one millimeter apart. Some spinnerets have superfine capillaries 50 micrometers in diameter. These tiny bores and capillaries are very sensitive to impurities and corrosion; this is one reason why spinnerets are often made of high-grade steel or other metals that can be easily cleaned.

Usage Examples

Some common fibers produced using melt spinning are: polypropylene, polyester, and nylon which is shown below and to the right. Nylon was the world's first synthetic fiber discovered and was initially used for tooth brush bristles before being used to produce women's stockings during the 1940's.

Advantages and Disadvantages

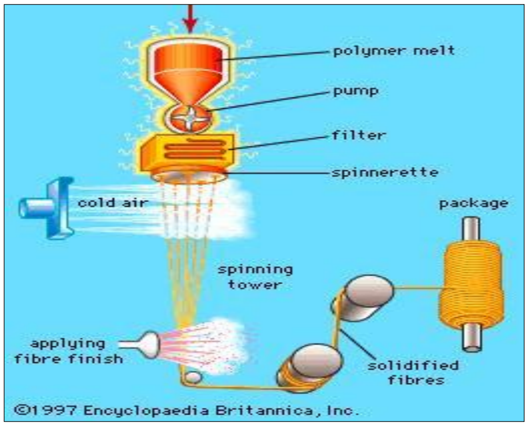
- Ablility to run at high line speeds.
- Requires no solvent that must be recovered later.
- Necessary high temperatures may damage some polymers.

Solution Spinning

Solution spinning is used when the desired polymer does not form a stable melt. These polymers are dissolved in a solution to liquefy them rather than melting them. The two main types of solution spinning are dry and wet spinning.

2. Dry Spinning

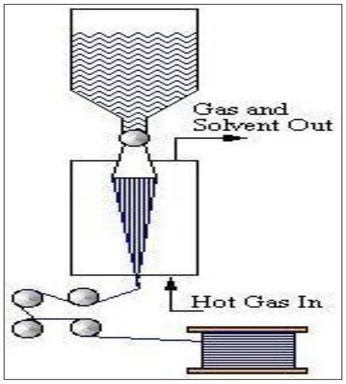
In dry spinning the polymer is dissolved in a volatile solvent. Once dissolved, the polymer solution is extruded through the spinneret which is in an enclosed drying tower. The solution goes through a drying process in this tower, where the solvent is evaporated.



Equipment Design

The spinning solution is often filtered many times to remove foreign materials that might cause thread defects or clogging in the machine . The solution is extruded into the drying tower through which hot air or other gases pass. The concentration of the polymer increases as the solvent evaporates, leaving a solid polymer filament behind. The s olvent is later recovered from the gas by condensation or absorption and is then recycled.

Solvent selection is very important, and is based on boiling point, latent heat of vaporization, thermal stability, toxicity, and inertness. Non-polar solvents are often preferred because of their low boiling points and heats of vaporization. However, non-polar solvents are prone to build-ups of electrostatic charge, which can be very dangerous.

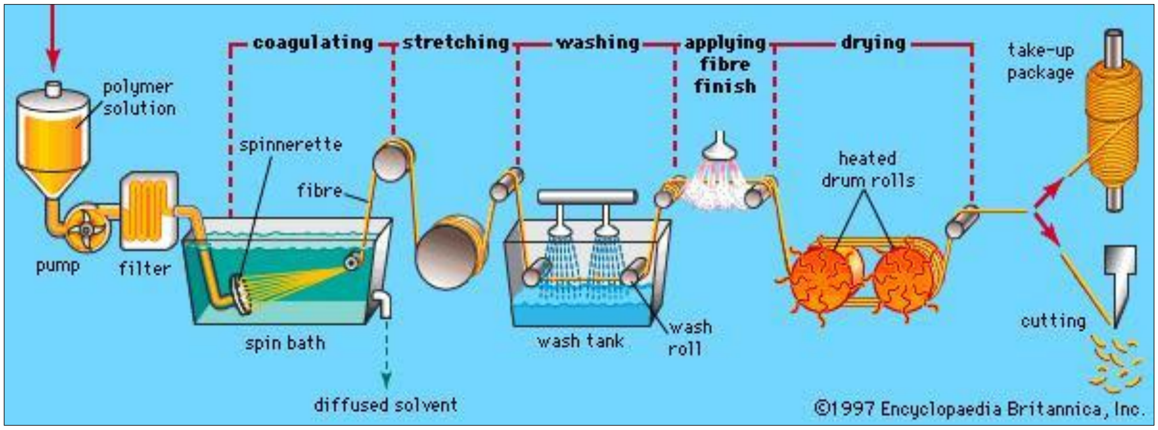


Advantages and Disadvantages

- Better than melt spinning for temperature-sensitive polymers.
- Faster production rates than melt and wet spinning.
- Solvent recovery is costly.

3. Wet Spinning

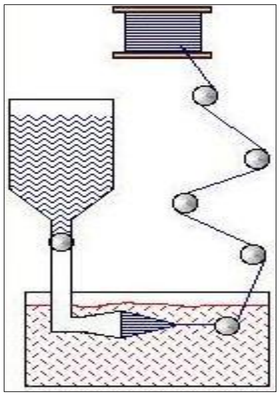
In wet spinning the polymer is dissolved in a non-volatile solvent. The spinneret is located in a coagulating bath that causes the fiber to precipitate out.



Equipment Design

The liquid in the coagulating bath is chosen so that the solvent is readily soluble in the liquid but the polymer is not. This will cause the polymer to precipitate out and form the desired solid filaments.The solvent can later be recovered by treating the wastewater in the bath.

The drag on the filament by the viscous liquid in the coagulating bath significantly reduces the production speed of the process. This makes wet spinning a slower process than melt or dry spinning.



Advantages and Disadvantages

- Better than melt and dry spinning for temperature sensitive polymers.
- Lower production rates than melt or dry spinning due to viscous drag.
- Solvent recovery is costly.

Usage Examples

The synthetic fibers produced by solution spinning are made into threads which are woven into fabric for everything from clothes and carpets to airbags and windsails. In addition, sterilized synthetic fibers are used in the medical industry as sutures, dressings, and operating room drapes, face masks, caps and overshoes. Many synthetic fibers can be cut into tiny pieces called flock . Flock is used to make velvet or suede-like materials or added to plastics or papers for a decorative finish.

26. (a) Poly ethylene and poly ester

1. *Polyethylene*

Polyethylene or **polythene** (abbreviated **PE**; IUPAC name **polyethene** or **poly(ethylene)**) is the most common plastic. The annual global production is around 80 million tonnes. Its primary use is in packaging (plastic bags, plastic films, geomembranes, containers including bottles, etc.). Many kinds of polyethylene are known, with most having the chemical formula $(C_2H_4)_n$. PE is usually a mixture of similar polymers of ethylene with various values of n.

Properties

1. *Chemical properties*

Polyethylene consists of nonpolar, saturated, high molecular weight hydrocarbons. Therefore, its chemical behavior is similar to paraffin. The individual macromolecules are not covalently linked. Because of their symmetric molecular structure, they tend to crystallize; overall polyethylene is partially crystalline. Higher crystallinity increases density and mechanical and chemical stability.

Most LDPE, MDPE, and HDPE grades have excellent chemical resistance, meaning they are not attacked by strong acids or strong bases, and are resistant to gentle oxidants and reducing agents. Crystalline samples do not dissolve at room temperature.

2. *Electrical properties*

Polyethylene is a good electrical insulator. It offers good tracking resistance; however, it becomes easily electrostatically charged (which can be reduced by additions of graphite, carbon black or antistatic agents).

3. *Optical properties*

Depending on thermal history and film thickness PE can vary between almost clear (transparent), milky-opaque (translucent) or opaque. LDPE thereby owns the greatest, LLDPE slightly less and HDPE the least transparency. Transparency is reduced by crystallites if they are larger than the wavelength of visible light

Production

1. Production of LDPE by addition polymerization requires:

- temperature range of 100-300°C
- very high pressure 1500-3000 atmospheres
- oxygen or an organic peroxide such as dibutyl peroxide, benzoyl peroxide or diethyl peroxide as initiator.
  An initiator is a substance which is added in small quantities and is decomposed by light or heat to produce a free radical ($R^{\cdot}$). A free radical is formed when a covalent bond is broken and a bonding electron is left on each part of the broken molecule. Since the O-O covalent bond is weak, free radicals are easily formed from oxygen or peroxides.
- benzene or chlorobenzene used as the solvent since both polymer (polythene) and monomer (ethene) dissolve in these compounds at the temperature and pressure used. Water or other liquids may be added to dissipate the heat of reaction as the polymerization reaction is highly exothermic.

$$\underset{\text{ethane}}{CH_2{=}CH_2} + \underset{\text{initiator}}{R^{\cdot}} \rightarrow {}^{\cdot}CH_2\text{-}CH_2\text{-}R$$

$$CH_2{=}CH_2 + {}^{\cdot}CH_2\text{-}CH_2\text{-}R \rightarrow {}^{\cdot}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}R$$

Process continues to form polythene (polyethylene) $[\text{-}CH_2\text{-}CH_2\text{-}]_n$

2. Production of HDPE

1. Production of HDPE by addition polymerization with a supported metal oxide catalyst requires:
   - temperature ~300°C
   - 1 atmosphere pressure (101.3kPa)
   - aluminium-based metal oxide catalyst (metallocene catalyst)

   The catalyst can be used in a variety of operating modes including fixed-bed, moving-bed, fluid-bed or slurry processes

The ethene (ethylene) monomer is fed with a paraffin or cycloparaffin diluent (diluting agent).

Uses

HDPE is defined by a density of greater or equal to 0.941 g/cm^3. HDPE has a low degree of branching. The mostly linear molecules pack together well, so intermolecular forces are stronger than in highly branched polymers

LDPE is used for both rigid containers and plastic film applications such as plastic bags and film wrap

2. Polyester

Polyester is a category of polymers that contain the ester functional group in their main chain. As a specific material, it most commonly refers to a type called polyethylene terephthalate (PET). Polyesters include naturally occurring chemicals, such as in the cutin of plant cuticles, as well as synthetics through step-growth polymerization such as polybutyrate.

Synthesis

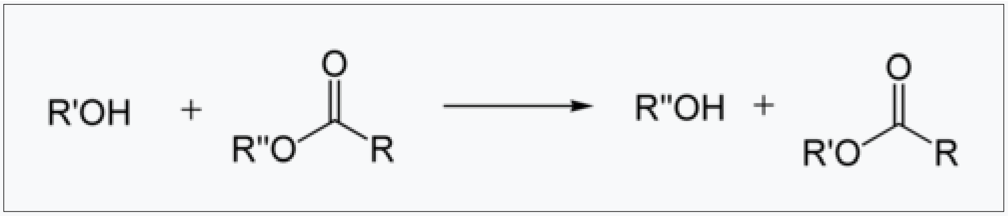
1. Synthesis of polyesters is generally achieved by a polycondensation reaction. See "condensation reactions in polymer chemistry". The general equation for the reaction of a diol with a diacid is :

   $(n+1)\ R(OH)_2 + n\ R'(COOH)_2 \rightarrow HO[ROOCR'COO]_nROH + 2n\ H_2O$

2. **Azeotrope esterification**

In this classical method, an alcohol and a carboxylic acid react to form a carboxylic ester. To assemble a polymer, the water formed by the reaction must be continually removed by azeotrope distillation.

3. **Alcoholic transesterification**



4. **Transesterification**: An alcohol-terminated oligomer and an ester-terminated oligomer condense to form an ester linkage, with loss of an alcohol. R and R' are the two oligomer chains, R" is a sacrificial unit such as a methyl group (methanol is the byproduct of the esterification reaction).

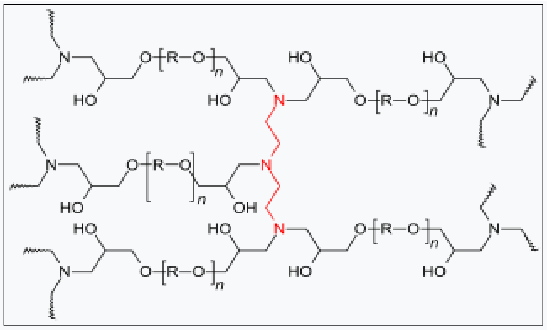
Uses

Polyesters are widely used as a finish on high-quality wood products such as guitars, pianos and vehicle/yacht interiors. Thixotropic properties of spray-applicable polyesters make them ideal for use on open-grain timbers, as they can quickly fill wood grain, with a high-build film thickness per coat. Cured polyesters can be sanded and polished to a high-gloss, durable finish.

Liquid crystalline polyesters are among the first industrially used liquid crystal polymers. They are used for their mechanical properties and heat-resistance. These traits are also important in their application as an abradable seal in jet engines.

(b) Silicone and Epoxy Polymers

Epoxy resin



Structure of a cured epoxy glue. The triamine hardener is shown in red, the resin in black. The resin's epoxide groups have reacted with the hardener and are not present anymore. The material is highly crosslinkedand contains many OH groups, which confer adhesive properties.

Epoxy resins are low molecular weight pre-polymers or higher molecular weight polymers which normally contain at least two epoxide groups. The epoxide group is also sometimes referred to as a glycidyl or oxirane group.

A wide range of epoxy resins are produced industrially. The raw materials for epoxy resin production are today largely petroleum derived, although some plant derived sources are now becoming commercially available (e.g. plant derived glycerol used to make epichlorohydrin).

Epoxy resins are polymeric or semi-polymeric materials, and as such rarely exist as pure substances, since variable chain length results from the polymerisation reaction used to produce them. High purity grades can be produced for certain applications, e.g. using a distillation purification process. One downside of high purity liquid grades is their tendency to form crystalline solids due to their highly regular structure, which require melting to enable processing.

Applications

The applications for epoxy-based materials are extensive and include coatings, adhesives and composite materials such as those using carbon fiber and fiberglass reinforcements (although polyester, vinyl ester, and other thermosetting resins are also used for glass-reinforced plastic).

Silicone

Silicones, also known as **polysiloxanes**, are polymers that include any inert, synthetic compound made up of repeating units of siloxane, which is a chain of alternating silicon atoms and oxygen atoms, frequently combined with carbon and/or hydrogen. They are typically heat-resistant and rubber-like, and are used in sealants, adhesives, lubricants, medicine, cooking utensils, and thermal and electrical insulation. Some common forms include silicone oil, silicone grease, silicone rubber, silicone resin, and silicone caulk. Silicones are of three types: 1. straight chain silicones; 2. cyclic silicones; 3. crosslinked silicones.

Synthesis

4. Most common are materials based on polydimethylsiloxane, which is derived by hydrolysis of dimethyldichlorosilane. This dichloride reacts with water as follows:

$$n\ \mathrm{Si(CH_3)_2Cl_2} + n\ \mathrm{H_2O} \rightarrow [\mathrm{Si(CH_3)_2O}]_n + 2n\ \mathrm{HCl}$$

The polymerization typically produces linear chains capped with Si-Cl or Si-OH (silanol) groups. Under different conditions the polymer is a cyclic, not a chain.

For consumer applications such as caulks silyl acetates are used instead of silyl chlorides. The hydrolysis of the acetates produce the less dangerous acetic acid (the acid found in vinegar) as the reaction product of a much slower curing process. This chemistry is used in many consumer applications, such as silicone caulk and adhesives.

Branches or cross-links in the polymer chain can be introduced by using organosilicone precursors with fewer alkyl groups, such as methyltrichlorosilane and methyltrimethoxysilane. Ideally, each molecule of such a compound becomes a branch point. This process can be used to produce hard silicone resins. Similarly, precursors with three methyl groups can be used to limit molecular weight, since each such molecule has only one reactive site and so forms the end of a siloxane chain.

5. ***Combustion***

When silicone is burned in air or oxygen, it forms solid silica (silicon dioxide)(SiO_2) as a white powder, char, and various gases. The readily dispersed powder is sometimes called silica fume.

Properties

Silicones exhibit many useful characteristics, including:[1]

- Low thermal conductivity
- Low chemical reactivity
- Low toxicity
- Thermal stability (constancy of properties over a wide temperature range of −100 to 250 °C).

Uses

Silicones are used in many products. Ullmann's Encyclopedia of Industrial Chemistry lists the following major categories of application: Electrical (e.g., insulation), electronics (e.g., coatings), household (e.g., sealants for cooking apparatus), automobile (e.g., gaskets), aeroplane (e.g., seals), office machines (e.g., keyboard pads), medicine/dentistry (e.g., teeth impression molds), textiles/paper (e.g., coatings).