KARPAGAM ACADEMY OF HIGHER EDUCATION

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

Coimbatore – 641 021.

SYLLABUS
DEPARTMENT OF CHEMISTRY
B.Sc CHEMISTRY

Class	:	B.Sc Chemistry
Subject	:	Polymer Chemistry
Subject Code	:	16CHU502A
Semester / Year	:	V / III

Semester-V

16CHU502A POLYMER CHEMISTRY 4H 4C

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

Scope

The course deals with the polymeric materials, functionality and its importance of the monomers, kinetics of polymerization, crystallinity, characterisation of polymers and their properties.

Methodology

Blackboard teaching, Powerpoint presentation and group discussion.

Programme outcome

This course enable the student to

1. Understand the history of polymeric materials
2. Understand the criteria for polymerisation
3. Understand the kinetics of polymerisation
4. Understand the characterisation of polymerisation
5. Understand the properties of polymers

Programme Learning Outcome

1. The students understood the history and classification of polymeric materials.
2. They gain the knowledge about the criteria for polymerisation.
3. They understood the mechanism and kinetics of polymerisation reactions.
4. They learned about the properties and applications of polymers.

UNIT I

Introduction and history of polymeric materials:
Different schemes of classification of polymers, Polymer nomenclature, Molecular forces and chemical bonding in polymers, Texture of Polymers.

Functionality and its importance:
Criteria for synthetic polymer formation, classification of polymerization processes, Relationships between functionality, extent of reaction and degree of polymerization. Bifunctional systems, Poly-functional systems.

UNIT II

Kinetics of Polymerization:
Mechanism and kinetics of step growth, radical chain growth, ionic chain (both cationic and anionic) and coordination polymerizations, Mechanism and kinetics of copolymerization, polymerization techniques.

Crystallization and crystallinity:
Determination of crystalline melting point and degree of crystallinity, Morphology of crystalline polymers, Factors affecting crystalline melting point.

UNIT III

Nature and structure of polymers-Structure Property relationships.
Determination of molecular weight of polymers (*Mn*, *Mw*, etc) by end group analysis, viscometry, light scattering and osmotic pressure methods. Molecular weight distribution and its significance. Polydispersity index.

UNIT IV

Glass transition temperature (Tg) and determination of Tg, Free volume theory, WLF equation, Factors affecting glass transition temperature (Tg).

Polymer Solution – Criteria for polymer solubility, Solubility parameter, Thermodynamics of polymer solutions, entropy, enthalpy, and free energy change of mixing of polymers solutions, Flory- Huggins theory, Lower and Upper critical solution temperatures.

UNIT V

Properties of Polymers (Physical, thermal, Flow & Mechanical Properties).
Brief introduction to preparation, structure, properties and application of the following polymers: polyolefins, polystyrene and styrene copolymers, poly(vinyl chloride) and related polymers, poly(vinyl acetate) and related polymers, acrylic polymers, fluoro polymers, polyamides and related polymers. Phenol formaldehyde resins (Bakelite, Novalac), polyurethanes, silicone polymers, polydienes, Polycarbonates, Conducting Polymers, [polyacetylene, polyaniline, poly(p-phenylene sulphide polypyrrole, polythiophene)].

Suggested Readings

Text Books:

1. *Seymour's Polymer Chemistry.* Marcel Dekker, Inc.
2. G. Odian. *Principles of Polymerization*. John Wiley.
3. F.W. Billmeyer. *Text Book of Polymer Science*. John Wiley.
4. P. Ghosh. *Polymer Science & Technology*. Tata Mcgraw-Hill.

Reference Book

1. R.W. Lenz. *Organic Chemistry of Synthetic High Polymers.*
2. *V.R.Gowariker, N.V.Viswanathan and Jayadev sreedhar, polymer science, (2014),* New Age International publishers, New Delhi.

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LESSION PLAN
DEPARTMENT OF CHEMISTRY
B.Sc CHEMISTRY

STAFF NAME : Dr. M.MAKESWARI
SUBJECT NAME : POLYMER CHEMISRY
SUB. CODE : 16CHU502A
SEMESTER : V
CLASS : III- B. Sc-CHEMISTRY

S.No	Lecture Duration Period	Topics to be Covered	Support Material/Page Nos
		UNIT-I	
1	1	classification of polymers	**R1:** 12
2	1	Polymer nomenclature	**W1**
3	1	Molecular forces and chemical bonding in polymers,	**T1:** 11
4	1	Texture of Polymers.	**T1:** 6
5	1	Functionality and its importance:-Criteria for synthetic polymer formation,	**T1:** 10
6	1	classification of polymerization processes	**T1:** 4
7	1	Relationships between functionality, extent of reaction and degree of polymerization.	**T1:** 60
8	1	Bifunctional systems	**T1:** 61
9	1	Poly-functional systems	**T1:** 62
10	1	Recapitulation and Discussion of important questions	
	Total No of Hours Planned For Unit 1=10		
1	1	Mechanism and kinetics of step growth polymerization	**T1:** 25
2	1	Radical chain growth polymerization	**T1:** 49
3	1	Ionic chain polymerizations	**T1:** 82

4	1	Coordination polymerizations	**T1:** 91
5	1	Copolymerisation	**T1:** 101
6	1	Polymerization techniques	**T1:** 71
7	1	Determination of crystalline melting point and degree of crystallinity	**T1:** 331
8	1	Morphology of crystalline polymers, Factors affecting crystalline melting point.	**T1:** 261
9	1	Recapitulation and Discussion of important questions	
	Total No of Hours Planned For Unit II=9		
		UNIT-III	
1	1	**Nature and structure of polymers**-Structure Property relationships.	**T1: 340**
2	1	**Determination of molecular weight of polymers**	**R1:** 86
3	1	**Determination of molecular weight of polymers** by end group analysis,	**T1:** 186
4	1	Viscometry, light scattering method	**T1:** 187
5	1	Osmotic pressure methods.	**T1:** 188
6	1	Molecular weight distribution and its significance.	**T1:** 96
7	1	Polydispersity index.	**T1:** 93
8	1	Recapitulation and Discussion of important questions	
	Total No of Hours Planned For Unit III=8		
		UNIT-IV	
1	1	Glass transition temperature (Tg) and determination of Tg	**R1:** 150
2	1	Free volume theory, WLF equation	**R1:** 169
3	1	Factors affecting glass transition temperature (Tg).	**R1:** 163
4	1	Polymer Solution – Criteria for polymer solubility	**T1:** 151
5	1	Thermodynamics of polymer solutions- entropy, enthalpy	**T1:** 159
6	1	Free energy change of mixing of polymer solutions,	**T1:** 159
7	1	Flory- Huggins theory,	**R1:** 344
8	1	Lower and Upper critical solution temperatures	**T1:** 242
9	1	Recapitulation and Discussion of important questions	

	Total No of Hours Planned For Unit IV= 9		
		UNIT-V	
1	1	Properties of Polymers	**R1:** 330, 340
2	1	preparation, structure, properties and application of polyolefins	**R1:** 244
3	1	preparation, structure, properties and application of polystyrene and styrene copolymers	**R1:** 218
4	1	preparation, structure, properties and application of PVC and related polymers,	**R1:** 236
5	1	preparation, structure, properties and application of PVA and related polymers,	**R1:** 232
6	1	preparation, structure, properties and application of acrylic polymers, fluoro polymers,	**R1:** 229, 238
7	1	polyamides and related polymers, Phenol formaldehyde resins	**R1:** 227, 248
8	1	polyurethanes, silicone polymers,	**R1:** 229, 255
9	1	Conducting Polymers	W2
10	1	Recapitulation and Discussion of important questions	
11	1	End semester question paper discussion	
12	1	End semester question paper discussion	
	Total No of Hours Planned for unit V=12		
Total Planned Hours	**48**		

TEXT BOOK

T1: F.W. Billmeyer.(1972). *Text Book of Polymer Science*. 1984, ^{3d} Edition, John Wiley and sons, Delhi.

REFERENCE BOOK

R1: *V.R.Gowariker, N.V.Viswanathan and Jayadev sreedhar, polymer science, (2014),* New Age international publishers, New Delhi.

WEB SITE

W1: WW.rsc.org/polymer/,https://en.wikipedia.org/wiki/IUPAC_polymer_nomenclature
W2: https://en.wikipedia.org/wiki/

UNIT-I

SYLLABUS

Introduction and history of polymeric materials:

Different schemes of classification of polymers, Polymer nomenclature, Molecular forces and chemical bonding in polymers, Texture of Polymers.

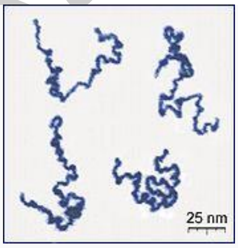
Functionality and its importance:

Criteria for synthetic polymer formation, classification of polymerization processes,Relationships between functionality, extent of reaction and degree of polymerization. Bifunctional systems, Poly-functional systems.

LECTURE NOTES

Polymer

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.



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.

Introduction to polymeric materials

Polymers form a very important class of materials without which the life seems very difficult. They are all around us in everyday use; in rubber, in plastic, in resins, and in adhesives and adhesives tapes. The word polymer is derived from greek words, poly= many and mers= parts or units of high molecular mass each molecule of which consist of a very large number of single structural units joined together in a regular manner. In other words polymers are giant molecules of high molecular weight, called macromolecules, which are build up by linking together of a large number of small molecules, called monomers. The reaction by which the monomers combine to form polymer is known as polymerization. The polymerization is a chemical reaction in which two or more substances combine together with or without evolution of anything like water, heat or any other solvents to form a molecule of high molecular weight. The product is called polymer and the starting material is called monomer.

History of Polymers

Polymers have existed in natural form since life began and those such as DNA, RNA, proteins and polysaccharides play crucial roles in plant and animal life. From the earliest times, man has exploited naturally-occurring polymers as materials for providing clothing, decoration, shelter, tools, weapons, writing materials and other requirements. However, the origin of today's polymer industry is commonly accepted as being the nineteenth century when important discoveries were made concerning the modification of certain natural polymers. In eighteenth century, Thomas Hancock gave an idea of modification of natural rubber through blending with ceatrain additives. Later on, Charles Goodyear improved the properties of natural rubber through vulcanization process with sulfur. The Bakelite was the first synthetic polymer produced in 1909 and was soon followed by the synthetic fiber, rayon, which was developed in 1911. The systematic study of polymer science started only about a centurybackwiththepioneeringworkofHermanStaudinger.Staudingerhasgivenanew definition of polymer. He in1919 first published this concept that high molecular mass compounds were composed of long covalently bonded molecules.

Classification ofPolymers

Polymer is a generic name given to a vast number of materials of high molecular weight. These materials exist in countless form and numbers because of very large number and type of atoms present in their molecule. Polymer can have different chemical structure, physical properties, mechanical behavior, thermal characteristics, etc., and on the basis of these properties polymer can be classified in different ways, which are summarized in Table 1., whereas, important and broad classification of polymers are described in the next section.

Table.1. Classification of polymers

BasisofClassification	Polymer Type
Origin	Natural, Semi synthetic,Synthetic
ThermalResponse	Thermoplastic,Thermosetting
Modeof formation	Addition,Condensation
Linestructure	Linear, Branched, Cross-linked Application and Physical
Properties	Rubber, Plastic,Fibers
Tacticity	Isotactic, Syndiotactic,Atactic
Crystallinity -	Crystalline, Non crystalline(amorphous), Semi-crystalline,
Polarity	Polar, Nonpolar
Chain	Hetro,Homo-chain

1.On the basis of their occurrence in nature, polymers have been classified in three types:-

Natural polymer:- The polymers, which occur in nature are called natural polymer also known as biopolymers. Examples of such polymers are natural rubber, natural silk, cellulose, starch, proteins,etc..

Semi synthetic polymer:- They are the chemically modified natural polymers such as hydrogenated, natural rubber, cellulosic, cellulose nitrate, methyl cellulose, etc.

Synthetic polymer:- The polymer which has been synthesized in the laboratory is known as synthetic polymer. These are also known as manmade polymers. Examples of such polymers are polyvinyl alcohol, polyethylene, polystyrene, polysulfone,etc..

2. Thermal Response

On the basis of thermal response, polymers can be classified into two groups,

Thermoplastic polymers:- They can be softened or plasticized repeatedly on application of thermal energy, without much change in properties if treated with certain precautions. Example of such polymers are Polyolefins, nylons, linear polyesters and polyethers, PVC, sealing waxetc..

Thermosetting polymers:- Some polymers undergo certain chemical changes on heating and convert themselves into an infusible mass. The curing or setting process involves chemical reaction leading to further growth and cross linking of the polymer chain molecules and producing giant molecules. For example, Phenolic, resins, urea, epoxy resins, diene rubbers,etc.

3.Mode ofFormation

On the basis of mode of formation, polymers can be classified as

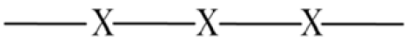
Addition polymers:- They are formed from olefinic, diolefnic, vinyl and related monomers. They are formed from simple addition of monomer molecules to each other in a quick succession by a chain mechanism. This process is called addition polymerization. Examples of such polymers are polyethylene, polypropylene, polystyrene.

Condensationpolymer:-Theyareformedfromintermolecularreactionsbetween bifunctional or polyfunctional monomer molecules having groups reactive functional such as –OH, -COOH, -NH_2, -NCO, etc..

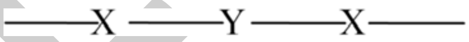
4. LineStructure

On the basis of structure, polymers are of three types.

Linear polymer:- If the monomer units are joined in a linear fashion, polymer is said to be linearpolymer.

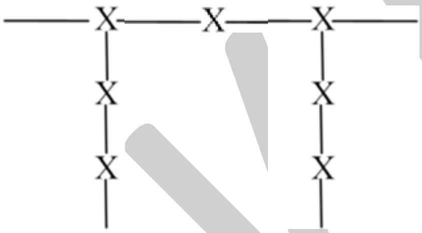


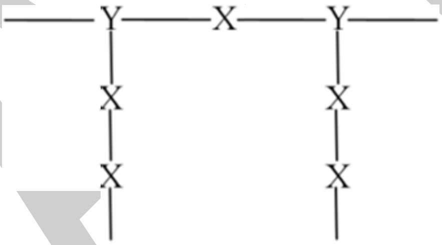
Linear Homopolymer



Linear Copolymer

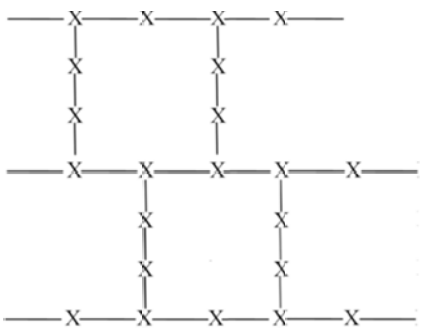
Branched polymer:-monomer units are joined in branched manner, it isWhen called branchedpolymer.



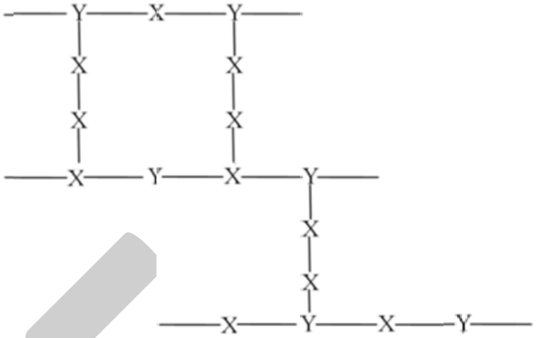


Branched Homopolymer Branched Copolymer

Cross linked polymer:- A polymer is said to be a cross linked polymer, if the monomer units are joined together in a chain fashion.



Crosslinked Homopolymer



Cross linked Copolymer

5. Application and PhysicalProperties

Depending on its ultimate form and use a polymer can be classified as

Rubber(Elastomers):- Rubber is high molecular weightpolymer with longflexible chains and weak intermolecular forces. They exhibits tensile strength in the range of 300-3000 psi and elongation at break ranging between 300-1000% . Examples are natural and syntheticrubber.

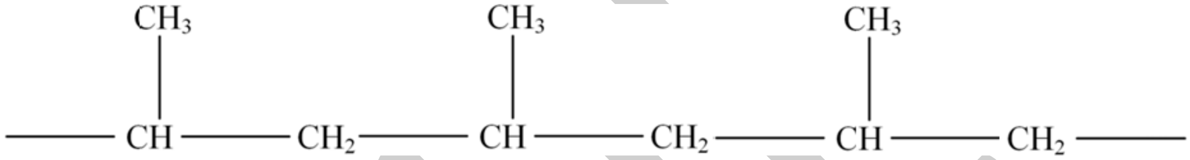
Plastics:- Plastics are relatively tough substances with high molecular weight that can be molded with (or without) the application of heat. These are usually much stronger than rubbers. They exhibit tensile strength ranging between 4000-15000 psi and elongation at break ranging usually from 20 to 200% or even higher. The examples of plastics are, polyethylene, polypropylene, PVC, polystyrene,etc.

Fibers:-Fibers are long- chain polymers characterized by highly crystalline regions resulting mainly from secondary forces. They have a much lower elasticity than plastics and elastomers. They also have high tensile strength ranging between 20,000- 150,000 psi., are light weight and possess moisture absorption properties.

Tacticity:-

It may be defined as the geometric arrangement (orientation)of the characteristic group of monomer unit with respect to th main chain (backbone) of the polymers. On the basis of structure, polymer may be classified into three groups:-

Isotactic polymer:-

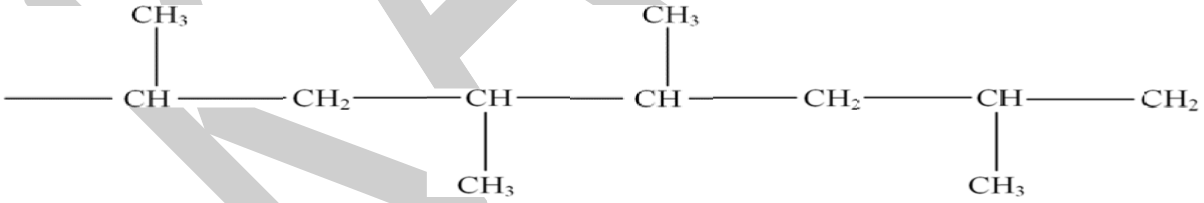


$$-\overset{CH_3}{\overset{|}{CH}}-CH_2-\overset{CH_3}{\overset{|}{CH}}-CH_2-\overset{CH_3}{\overset{|}{CH}}-CH_2-$$

It is the type of polymer in which the characteristic group are arranged on the same side of the mainchain.

Isotactic Polypropene

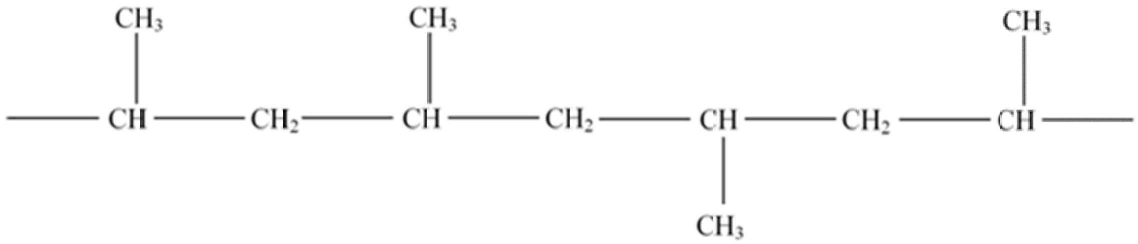
Syndiotactic polymer:- A polymer is said to be syndiotactic if the side group (characteristic group) are arranged in an alternate fashion.



$$-\overset{CH_3}{\overset{|}{CH}}-CH_2-\underset{CH_3}{\underset{|}{CH}}-\overset{CH_3}{\overset{|}{CH}}-CH_2-\underset{CH_3}{\underset{|}{CH}}-CH_2$$

Syndiotatic Polypropene

Atactic polymer:- A polymer is said to be atactic, if the characteristic groups (side group) are arranged in irregular fashion (randomness) around the main chain. It has proper strength and moreelasticity.



Atactic Polypropene

Polymer Nomenclature

The universal adoption of an agreed nomenclature has never been more important for the description of chemical structures in publishing and on-line searching. The International Union of Pure and Applied Chemistry (IUPAC)and Chemical Abstracts Service (CAS)make similar recommendations. The main points are shown here with hyperlinks to original documents. Further details can be found in the IUPAC PurpleBook.

The terms polymer and macromolecule do not mean the same thing. A polymer is a substance composed of macromolecules. The latter usually have a range of molar masses (unit g mol^{-1}), the distributions of which are indicated by dispersity ($Đ$). It is defined as the ratio of the mass-average molar mass (M_m) to the number-average molar mass (M_n) i.e. $Đ = M_m/M_n$.Symbols for physical quantities or variables are in italic font but those representing units or labels are in romanfont.

Polymer nomenclature usually applies to idealised representations; minor structural irregularities are ignored. A polymer can be named in one of two ways. Source-based nomenclature can be used when the monomer can be identified. Alternatively, more explicit structure-based nomenclature can be used when the polymer structure is proven. Where there is no confusion, some traditional names are alsoacceptable.

Whatever method is used, all polymer names have the prefix poly, followed by enclosing marks around the rest of the name. The marks are used in the order:

{[( )]}. Locants indicate the position of structural features, e.g., poly(4-chlorostyrene).Ifasource-basednameisonewordandhasnolocants,thenthe enclosing marks are not essential, but they should be used when there might be confusion, e.g., poly(chlorostyrene) is a polymer whereas polychlorostyrene might be a small, multi-substituted molecule. End-groups are described with α, βand γ-, e.g., α-chloro-γ-hydroxy-polystyrene.

Source based Nomenclature

Homopolymers

A homopolymer is named using the name of the real or assumed monomer (the 'source') from which it is derived, e.g., poly(methyl methacrylate). Monomers can be named using IUPAC recommendations, or well-established traditional names. Should ambiguity arise, class names can be added.For example, the source-based name poly(vinyloxirane) could correspond to either ofthe structures shown below. To clarify the polymer is named usingthe polymer class name followed by a colon and the name of the monomer, i.e., class name:monomer name. Thus on the left and right, respectively, are polyalkylene:vinyloxirane and polyether:vinyloxirane.

Copolymers

The structure of a copolymer can be described using the most appropriate of the connectives shown in Table 1. These are written in italic font.

Non-linearpolymers

Non-linear polymers and copolymers, and polymer assemblies are named using the italicized qualifiers in Table 2. The qualifier, such as *branch*, is used as a prefix (P) when naming a (co)polymer, or as a connective (C), e.g., *comb*, between two polymer names.

Table 1 – Qualifiers for copolymers.

Copolymer	Qualifier	Example
unspecified	*co* (C)	poly(styrene-*co*-isoprene)
statistical	*stat* (C)	poly[isoprene-*stat*-(methyl methacrylate)]
random	*ran* (C)	poly[(methyl methacrylate)-*ran*-(butyl acrylate)]
alternating	*alt* (C)	poly[styrene-*alt*-(maleic anhydride)]
periodic	*per* (C)	poly[styrene-*per*-isoprene-*per*-(4-vinylpyridine)]
block	*Block* (C)	poly(buta-1,3-diene)-*block*-poly(ethene-*co*-propene)
graft[*a*]	*Graft* (C)	polystyrene-*graft*-poly(ethylene oxide)

Table 2 – Qualifiers for non-linear (co)polymers and polymer assemblies.[5]

(Co)polymer	Qualifier	Example
blend	*blend* (C)	poly(3-hexylthiophene)-*blend*-polystyrene
comb	*comb* (C)	polystyrene-*comb*-polyisoprene
complex	*compl* (C)	poly(2,3-dihydrothieno[3,4-*b*][1,4]dioxine)-*compl*-poly(vinylbenzenesulfonic acid)[a]
cyclic	*cyclo* (P)	*cyclo*-polystyrene-*graft*-polyethylene
branch	*branch* (P)	*branch*-poly[(1,4-divinylbenzene)- *stat*-styrene]
network	*net* (C orP)	*net*-poly(phenol-*co*-formaldehyde)

interpenetrating network	*ipn*	(C)	(*net*-polystyrene)-*ipn*-[*net*- poly(methyl acrylate)]
semi-interpenetrating network	*sipn*	(C)	(*net*-polystyrene)-*sipn*-polyisoprene
star	*star*	(P)	*star*-polyisoprene

In accordance with IUPAC organic nomenclature, square brackets enclose locants that refer to the numbering of the components of the fusedring.

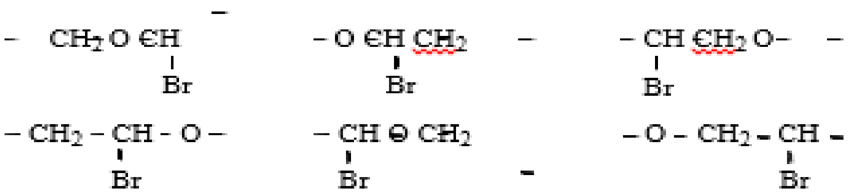
Structure based Nomenclature

Regular single-strand organic polymers

In place of the monomer name used in source-based nomenclature, structure- based nomenclature uses that of the preferred constitutional repeating unit (CRU). It can be determined as follows: (i) a large enough part of the polymer chain is drawn to show the structural repetition,

$$-\underset{\displaystyle Br}{\underset{|}{CH}}-CH_2-O-\underset{\displaystyle Br}{\underset{|}{CH}}-CH_2-O-\underset{\displaystyle Br}{\underset{|}{CH}}-CH_2-O-$$

(ii) the smallest repeating portion is a CRU, so all such possibilities are identified. In this case:



$$-CH_2-O-\underset{\displaystyle Br}{\underset{|}{CH}}- \qquad -O-\underset{\displaystyle Br}{\underset{|}{CH}}-CH_2- \qquad -\underset{\displaystyle Br}{\underset{|}{CH}}-CH_2-O-$$

$$-CH_2-\underset{\displaystyle Br}{\underset{|}{CH}}-O- \qquad -\underset{\displaystyle Br}{\underset{|}{CH}}-O-CH_2- \qquad -O-CH_2-\underset{\displaystyle Br}{\underset{|}{CH}}-$$

Molecular Forces in Polymers

Depending upon the inter-molecular forces between monomer molecules, the polymers have been classified into four types:

- Elastomers

- Fibers
- Thermoplastics
- Thermosetting

Elastomers

In case of elastomers, the polymer chains are held together by weak van der waals forces. Due to weak forces, the polymers can be easily stretched on applying small stress and they regain their original shape when the stress is removed. This is due to the presence of few cross links between the chains, which help the polymer to retract to its original position after the force is removed, as in vulcanized rubber.

The most important example of elastomer is natural rubber.

Fibres

These are the polymers which have strong inter-molecular forces between the chains. These forces are either hydrogen bonds or dipole-dipole interactions. Because of the strong forces, the chains are closely packed, giving them high tensile strength and less elasticity. These polymers can be drawn into long, thin and thread like fibres and therefore can be woven into fabrics. The common examples are nylon-66, dacron, and silk.

Thermoplastics

These are linear polymers with very few cross linkages or no cross linkages at all. The polymeric chains are held by weak van der waals forces and slide over one another. Due to lack of cross linkages these polymers soften on heating and harden or become rigid on cooling. Thus they can be moulded to any shape. Polythene, PVC, polystyrene are addition type thermoplastics and Terylene, nylon are condensation type thermoplastics.

Plasticizers:

Certain plastics do not soften much on heating. These can be easily softened by the addition of some organic compounds which are called plasticizers. For example, polyvinyl chloride (PVC) is very stiff and hard but is made soft by adding di-n-butylphthalate (a plasticizer). Some other common plasticizers are dialkyl phthalates and cresyl phthalate.

Thermosetting Polymers

Usually thermosetting polymer can be heated only once when it permanently sets into a solid which can not be remelted and re-moulded. Thermosetting polymers are produced from relatively low molecular mass semi fluid polymers (called polymers) which on heating develop extensive cross-linking by themselves or by adding some cross-linking agents and become infusible and insoluble hard mass. The cross links hold the molecules in place so that heating does not allow them to move freely. Therefore, a thermosetting plastic is cross linked and is permanently rigid. The common examples are bakelite melamine and formaldehyde resin.

The intermolecular forces for polymers are the same as for small molecules. Because polymer molecules are so large, though, the magnitude of their intermolecular forces can vastly exceed those between small molecules.

The presence of strong intermolecular forces is one of the main factors leading to the unique physical properties of polymers.

Dispersion Forces

Dispersion forces are due to instantaneous dipoles that form as the charge clouds in the molecules fluctuate. Dispersion forces, the weakest of the intermolecular forces, are present in all polymers. They are the only forces possible for nonpolar polymers such as polyethylene.

Dispersion forces depend on the polarizability of a molecule. Larger molecules generally are more polarizable, so large polymers with high molecular weights can have significant dispersion forces. Ultra high molecular weight polyethylene (UHMWPE), which has a molecular weight in excess of 3,000,000 g/mole, is used to make bulletproof vests.

Dipole-Dipole Forces

Dipole-dipole forces result from the attraction between polar groups, such as those in polyesters and vinyl polymers with chlorine pendant groups.

Hydrogen Bonding

Hydrogen bonding can take place when the polymer molecule contains -OH or -NH groups. Hydrogen bonding is the strongest of the intermolecular forces. Polymers such as poly(vinyl alcohol) and polyamides are hydrogen bonded.

Functionality of polymers

In chemistry, **functionality** is the presence of functional groups in a molecule. In organic chemistry (and other fields of chemistry) functionality of a molecule has a decisive influence on its reactivity.

In polymer chemistry the functionality of a monomer means its number of polymerizable groups, and affects the formation and the degree of crosslinking of polymers. A monofunctional molecule possesses one function, a difunctional two, a trifunctional three

Monomers need to contain two or more bonding sites in order to form a polymer chain or a network. A **monomer** with a functionality of 2, i.e. a **bifunctional monomer**, can react with two other **monomers** and if this process is repeated many times it will lead to the formation of a linear chain.

Monomers are the building block of polymeric materials. The number of bonding sites in a chemical compound, *i.e.* its **functionality**, determines the reactivity of the chemical unit.

Monomers need to contain two or more bonding sites in order to form a polymer chain or a network.

A monomer with a functionality of 2, *i.e.* a **bifunctional** monomer, can react with two other monomers and if this process is repeated many times it will lead to the formation of a linear chain. **Bifunctional** monomers give rise to linear polymer chains. A three-dimensional network may be obtained if the functionality is greater than two.

For example, consider the reaction between two bifunctional monomers such as a *diacid*and a *diol* (a di-alcohol). The condensation reaction between these two monomers is an esterification

$$HOOC–R_1–COOH + HO–R_2–OH \longrightarrow$$

$$HOOC–R_1–COO–R_2–OH + H_2O$$

and leads to the formation of an ester product with two **unreacted** end groups. The **dimer**that is formed is also **bifunctional** and can react further with other monomers or dimers. As the reaction proceeds longer chains are formed.

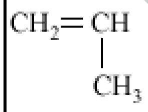
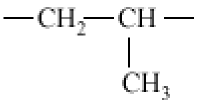
The two functional groups in the monomer may be the same (as in the example given above) or two different groups may be attached at the two ends. For example, a hydroxy carboxylic acid is a bifunctional monomer with -OH and -COOH groups. This molecule may react with similar monomers to produce a linear polyester:

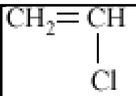
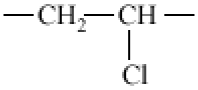
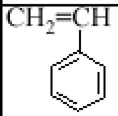
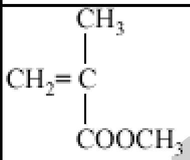
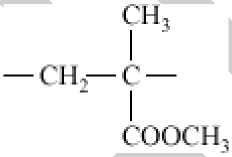
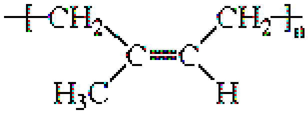
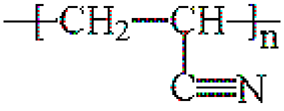
$$n\ \mathrm{HOOC{-}R{-}OH} \longrightarrow \mathrm{H[{-}O{-}R{-}CO{-}]}_n\mathrm{OH} + (n - 1)\ \mathrm{H_2O}$$

Monomers do not necessarily contain functional groups. Unsaturated compounds such as*vinyl monomers* (CH_2CHX) do not contain functional groups but behave as bifunctional monomers, capable of forming polymer chains. In the presence of a suitable initiator, the opening of the double bond in a monomer leads to its bonding to two other monomers. Sequential addition of monomers takes place:

$$n\ \mathrm{CH_2CHX} \longrightarrow$$

where X represents a substituent such as hydrogen, a halogen, alkyl or aryl group. A number of common unsaturated monomers and their corresponding polymers are listed below.

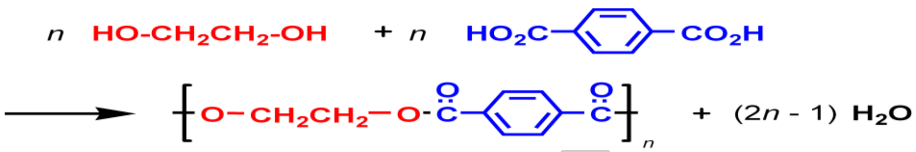
Source Name	**Monomer**	**Repeat Unit**	**Properties**	**Uses**
Polyethylene *low density* (*LDPE*)	$CH_2 = CH_2$ ethylene	$—CH_2—CH_2—$	soft, waxy solid	film wrap, plastic bags
Polyethylene *high density* (*HDPE*)	$CH_2 = CH_2$ ethylene	$—CH_2—CH_2—$	rigid, translucent solid	electrical insulation bottles, toys
Polypropylene (*PP*)	 $CH_2{=}\underset{\displaystyle CH_3}{\underset{\vert}{CH}}$ propylene	 $—CH_2—\underset{\displaystyle CH_3}{\underset{\vert}{CH}}—$	<u>atactic</u>: soft, elastic <u>isotactic</u>: hard, strong	as LDPE carpet, upholstery

Poly(vinyl chloride) (*PVC*)	 $CH_2{=}\underset{\displaystyle Cl}{CH}$ vinyl chloride	 $-CH_2-\underset{\displaystyle Cl}{CH}-$	strong rigid solid	pipes, house siding, and eaves
Polystyrene (*PS*)	 styrene		hard, rigid, clear solid	toys, packaging (foamed)
Poly(methyl methacrylate) (*PMMA, Lucite, Plexiglas*)	 $CH_2{=}\overset{\displaystyle CH_3}{\underset{\displaystyle COOCH_3}{C}}$ methyl methacrylate	 $-CH_2-\overset{\displaystyle CH_3}{\underset{\displaystyle COOCH_3}{C}}-$	hard, transparent solid	lighting covers, signs skylights
cis-Polyisoprene natural rubber	$CH_2=CH-C(CH_3)=CH_2$ isoprene		soft, sticky solid	requires vulcanisation for practical use
Polyacrylonitrile (*PAN, Orlon, Acrilan*)	$CH_2=CHCN$ acrylonitrile	 $-[CH_2-\underset{\displaystyle C\equiv N}{CH}]_n-$	high-melting solid	rugs, blankets clothing

Polymers were first classified by **Carothers** in 1929 as **addition** and **condensation**polymers, depending on the composition of the monomers and the corresponding polymer.

Condensation polymers are those prepared from *condensation reactions* such as those between a *diacid* and a *dialcohol* to produce a *polyester*.

For example, the polymer prepared from **ethylene glycol** and **terephthalic acid**, *i.e.* poly(ethylene terephthalate), is a **condensation polymer**.



As with condensation reactions occurring between low molecular weight compounds, a small molecule (in this case water) is eliminated. Hence, the chemical composition of the repeat unit differs from that of the reacting monomers.

Addition polymers are prepared by addition or chain-reaction polymerisations without loss of a small molecule. As a consequence, the repeat unit contains the same atoms as the monomers.

For example, the polymer which is prepared from vinyl chloride:

$n\ CH_2{=}CHCl \longrightarrow [–CH_2CHCl–]_n$

i.e. poly(vinyl chloride) (PVC) has the same chemical composition as its monomer.

However, the original classification by Carothers was found to be inadequate and confusing. For example, although polyurethanes are structurally similar to condensation polymers, according to Carothers' classification, they should be incorrectly regarded as addition polymers. As shown below, the formation of polyurethanes from the reaction of diols and diisocyanates does not involve elimination of a small molecule as it is expected for a condensation polymer:

$$n\ HO–R_1–OH + OCN–R_2–NCO \longrightarrow$$

$$[–O–R_1–OCONH–R_2–NHCO–]_n$$

The classification that is now preferred is based on the type of chain growth mechanism that leads to the formation of the polymer chain.

REFERENCE BOOK

R1: Gowariker, V. R., N. V. Viswanathan and J. Sreedhar, 1986. Polymer Science, *New Age International* Private Ltd., New Delhi.

TEXT BOOK:

T1: Billmeyer, F.W., 2003. Text Book of Polymer Science. III Edition, John Wiley, New York.

WEB SITE

W1: WW.rsc.org/polymer/,https://en.wikipedia.org/wiki/IUPAC_polymer_nomenclature

POSSIBLE QUESTIONS

UNIT-I

PART-A (20 MARKS)

(Q.NO 1 To 20 Online Examination)

PART-B (2 MARKS)

1. Define degree of polymerization.
2. Define functionality of a polymer.
3. What are bifunctional monomers? Give 2 examples.
4. What are thermoplastics?
5. What do you mean by the term addition polymers?
6. Define polymerization.

PART-C (6 MARKS)

(Either or type question)

1. How will you classify polymers on the basis of their physical properties?
2. Based on structure, how polymers are classified?
3. On the basis of physical and chemical properties, how polymers are classified?
4. Define polymer. How will you classify polymers on the basis of their (i) Thermal behavior

and (ii) Tacticity.

5. Write a note on the history of polymers.

6. Write a note on the molecular forces and chemical bonding in polymers.

KARPAGAM ACADEMY OF HIGHER EDUCATION

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Coimbatore – 641 021.

UNIT-I- MULTIPLE CHOICE QUESTIONS

DEPARTMENT OF CHEMISTRY
B.Sc CHEMISTRY

STAFF NAME : Dr. M.MAKESWARI
SUBJECT NAME : POLYMER CHEMISRY
SUB. CODE : 16CHU502A
SEMESTER : V
CLASS : III- B. Sc-CHEMISTRY

S.No	Questions	Option 1	Option 2	Option 3	Option 4	Answer
1	Monomers show high selectivity towards?	Cationic initiators	Cationic and anionic initiators	Ionic initiators	Anionic initiators	Ionic initiators
2	These polymers consist of coil-like polymer chains: Elastomers	Thermoplasts	Thermosets	Elastomers	Fibres	Elastomers
3	Strong covalent bonds exist between polymer chains in __________.	Thermoplasts	Thermosets	Elastomers	Fibres	Thermosets

4	Polymers are?	Large molecule	Small molecule	Small chain molecule	Large chain molecule	Large chain molecule
5	The word 'polymer' meant for material made from _______________.	Single entity	Two entities	Multiple entities	Any entity	Multiple entities
6	One of the characteristic properties of polymer material is	High temperature stability	High mechanical strength	High elongation	Low hardness	High temperature stability
7	These polymers can not be recycled:	Thermoplasts	Thermosets	Elastomers	Resins	Thermosets
8	Which of the following is an example of bifunctional monomer	methyl isonate	acetylene	malic acid	glycine	glycine
9	Polythene was first synthesized in?	1877	1853	1890	1898	1898
10	Which of the following is the functionality of Gallic Acid?	monofunctional	bifunctional	tetrafunctional	trifunctional	tetrafunctional
11	Which of the following is an example of condensation polymer?	PVC	polyamide	Terylene	Polyester	Terylene
12	Kevlar is a commercial name for _____.	Glass fibers	Carbon fibers	Aramid fibers	Cermets	Aramid fibers
13	In general, strongest polymer group is _________.	Thermoplasts	Thermosets	Elastomers	Resins	Thermosets
14	Polyvinyl chloride was commercially introduced in?	1943	1930	1936	1947	1936
15	Elastic deformation in polymers is due to ______________.	Slight adjust of molecular chains	Slippage of molecular chains	Straightening of molecular chains	Severe of Covalent bonds	Slight adjust of molecular chains
16	Following is the unique to polymeric materials is known as	Elasticity	Viscoelasticity	Plasticity	Thermal Stability	Viscoelasticity

17	Styrene(butadiene rubber) was commercially introduced during the year	1943	1930	1936	1947	1930
18	Polyethylene was first synthesized by?	Pechmann	Fawcett	Karl ziegler	Walter	Pechmann
19	What is the range of tensile strength, exhibited by fibres?	300-3,000	4,000-15,000	20,000-150,000	5,000-10,000	20,000-150,000
20	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
21	Which is more flexible than HDPE due to lower crystallinity?	Polyethylene	Low Density Polyethylene	Polyamide	Low density polyamide	Low Density Polyethylene
22	Which one is a natural polymer?	Polyamide	Polyester	Cellulose	PVC	Cellulose
23	Synthetic fiber is?	Rayon	Boron filaments	Glass fibre	Polyvinylalcohol	polyvinylalcohol
24	Silicones was commercially introduced in?	1943	1930	1936	1947	1943
25	Natural fibers are consisting of?	Linear polymers	Nonlinear polymers	Copolymers	Chain polymers	Linear polymers
26	A high molecular weight molecule built from a large number of simple molecules is called a	Monomer	Isomer	Polymer	Tautomer	Polymer
27	Which of the following is not a biopolymer?	Proteins	Nucleic	Cellulose	Neoprene	Neoprene
28	Natural rubber is a polymer of	Butadiene	Ethyne	Stryene	Isoprene	Isoprene
29	Terylene is a condensation polymer of ethylene glycol and	Benzoic acid	Phthalic acid	Sakucylic acid	Terephthalic acid	Terephthalic acid
30	Ebonite is	Natural rubber	Synthetic rubber	Higly vulcanized rubber	Polypropene	Polypropene
31	Artificial silk is	nylon-6	rayon	Nylon 66	nylon6,10	Rayon
32	Natural silk is a	polypeptide	polyacrylate	polyester	polysaccharide	polypeptide

33	The process of vulcanization of rubber was introduced by	Zeigler	MRF	Charles goodyear	Wohler	Charles goodyear
34	Which one is a synthetic polymer?	Starch	Silk	Protein	Neoprene	Neoprene
35	Natural rubber is	polyisoprene	polyvinyl chloride	polychloroprene	polyfluoroethylene	polyisoprene
36	Which of the following is a natural polymer?	Bakellite	Cellulose	PVC	Nylon	Cellulose
37	Which is a protein?	Nylon	Rayon	Natural silk	Terylene	Natural silk
38	Natural rubber is which type of polymer	condensation of polymer	co-ordination polymer	Addition polymer	co-polymer	co-ordination polymer
39	Cellulose acetate is a	natural polymer	Semi- synthetic polymer	synthetic polymer	Plasticizer	Semi- synthetic polymer
40	Which of the following is a polyamide molecule?	Terylene	Rayon	Nylon-6	Polystrene	Nylon-6
41	Soft drinks and baby feeding bottles are generally made up of	polyester	Polyurethane	polyester	polyester	Polyamide
42	The process involving heating of rubber with sulphur is called	Galvanisation	Vulcanization	Bessemerisation	Sulphonation	Vulcanization
43	Starch is the condenstion polymer of	α-Glucose	β-Glucose	α-Fructose	β-Fructose	α-Glucose
44	The repeating structural unit in neoprene	Chloroprene	Chloroethene	Chloropicrin	Chlorotrifluoroethylene	Chloroprene
45	Which of the following is a linear polymer?	Nylon	Bakelite	Alkyl resin	Melamine-formaldehyde polymer.	Nylon
46	Amongst the following, the branched chain polymer is	PVC	Polyester	Low density polythene	Nylon-66	Low density polythene

47	Intermolecular forces present in nylon 66 are	Hydrogen bonding	Vander walls forces	Dipole-Dipole interactions	Polarity	Hydrogen bonding
48	Which interparticle forces between linear chains in nylon 66 are	H-Bonding	Covalent bonds	Dacron	Glyptol	H-Bonding
49	Among the following polymer, the strongest intermolecular forces of attraction are present in	Elastomers	Thermoplastics	Fibres	Thermosetting polymers	Fibres
50	Among the following the weakest interparticle forces of attraction present in	Thermosetting polymers	Thermoplastics polymers	Fibers	Elastomers	Elastomers
51	Among the following which is an mono functional monomer	Methyl acetate	Malonic acid	Glycerol	Adipic acid	Methyl acetate
52	Among the following which is an bi functional monomer	Methyl acetate	Malonic acid	Glycerol	Adipic acid	Adipic acid
53	Among the following which is an tri functional monomer	Methyl acetate	Malonic acid	Glycerol	Adipic acid	Glycerol
54	Which type of polymer is formed if the functionality of a monomer is 2?	Linear polymer	Branched polymer	Cross-linked polymer	Branched Chain polymer	Linear polymer
55	Which type of polymer is formed if the functionality of a monomer is ≥ 3	Linear polymer	Branched polymer	Cross-linked polymer	Branched Chain polymer	Branched polymer
56	The number average degree of polymerization is represented by the symbol of	X_n	X_w	Dn	Dw	X_n
57	The weight average degree of polymerization is represented by the symbol of	X_n	X_w	Dn	Dw	X_w
58	Degree of polymerization is represented by the symbol of	Dp	Dn	Dw	Pd	Dp
59	The degree of polymerization is the number of ------------in the polymers	Monomers	Chemical bonds	Initiators	Free radicals formed	monomers

60	The number of monomeric units in a polymer is known as	Degree of polymerization	Tacticity	Viscosity	Molecular weight	Degree of polymerization

UNIT-II

SYLLABUS

Kinetics of Polymerization:

Mechanism and kinetics of step growth, radical chain growth, ionic chain (both cationic and anionic) and coordination polymerizations, Mechanism and kinetics of copolymerization, polymerization techniques.

Crystallization and crystallinity:

Determination of crystalline melting point and degree of crystallinity, Morphology of crystalline polymers, Factors affecting crystalline melting point.

STEP POLIMERISATION

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.

REACTIVITY OF FUNCTIONAL GROUPS

Basis for Analysis of Polymerization kinetics:

The kinetics of polymerization are of prime interest from two viewpoints. The practical synthesis of high polymers requires a knowledge of the kinetics of the polymerization reaction. From the theoretical viewpoint the significant differences between step and chain polymerizations reside in large part in their respective kinetic features.Step polymerization proceeds by a relatively slow increase in molecular weight of the polymer. Consider the synthesis of a polyester from a diol and a diacid. The first step is the reaction of the diol and diacid monomers to form dimer:

HO-R-OH + HO_2C-R'-CO_2H → HO-R-OCO-R'-CO_2H + H_2O

The dimer then forms trimer by reaction with diol monomer

HO-R-OCO-R'-CO_2H + HO-R-OH → HO-R-OCO-R'-COO-R-OH + H_2O

and also with diacid monomer:

HO-R-OCO-R'-CO_2H + HO_2C-R'-CO_2H →HO_2C-R'-COO-R-OCO-R'-CO_2H +H_2O

Dimer reacts with itself to form tetramer:

2HO-R-OCO-R'-CO_2H → HO-R-OCO-R'-COO-R-OCO-R'-CO_2H + H_2O

The tetramer and trimer proceed to react with themselves, with each other, and with monomer and dimer. The polymerization proceeds in this stepwise manner with the molecular weight of the polymer continuously increasing with time (conversion). Step polymerizations are characterized by the disappearance of monomer early in the reaction far before the production of any polymer of sufficiently high molecular weight (approximately >5000–10,000) to be of practical utility. Thus for most step polymerizations there is less than 1% of the original monomer remaining at a point where the average polymer chain contains only ˜10 monomer units. As will be seen in Chap. 3, the situation is quite different in the case of chain polymerization.

The rate of a step polymerization is, therefore, the sum of the rates of reaction between molecules of various sizes, that is, the sum of the rates for reactions such as

Monomer + monomer → dimer

Dimer + monomer→ trimer

Dimer + dimer→ tetramer

Trimer + monomer →tetramer

Trimer + dimer→ pentamer

Trimer + trimer→ hexamer

Tetramer + monomer→ pentamer

Tetramer + dimer→ hexamer

Tetramer + trimer→ heptamer

Tetramer + tetramer→ octamer

Pentamer + trimer →octamer

Pentamer + tetramer→ nonamer

which can be expressed as the general reaction

n-mer + m-mer → (n + m)-mer

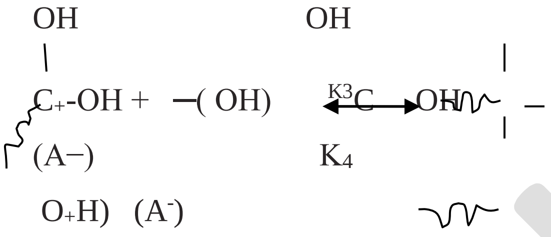
The reaction mixture at any instance consists of various-sized diol, diacid, and hydroxy acid molecules. Any HO-containing molecule can react with any COOH-containing molecule.This is a general characteristic of step polymerization.The kinetics of such a situation with innumerable separate reactions would normally be difficult to analyze. However, kinetic analysis is greatly simplified if one assumes that the reactivities of both functional groups of a bifunctional monomer (e.g., both hydroxyls of a diol) are the same, the reactivity of one functional group of a bifunctional reactant is the same irrespective of whether the other functional group has reacted, and the reactivity of a functional group is independent of the size of the molecule to which it is attached (i.e., independent of the values of n and m). These simplifying assumptions, often referred to as the concept of equal reactivity of functional groups, make the kinetics of step polymerization identical to those for the analogous small molecule reaction. As will be seen shortly, the kinetics of a polyesterification, for example, become essentially the same as that for the esterification of acetic acid with ethanol.

KINETICS OF STEP 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,

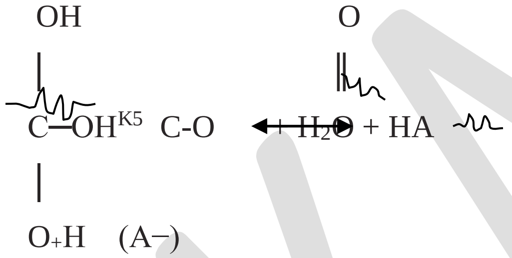
$$(C\text{-}OH) + HA \underset{K_2}{\overset{K_1}{\rightleftharpoons}} (HO\text{-}C_{+}\text{-}OH(A^{-})) \qquad 2.12$$

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



$$\overset{OH}{\underset{(A^-)}{C_{+}\text{-}OH}} + \text{—}(OH) \underset{K_4}{\overset{K_3}{\rightleftharpoons}} \overset{OH}{\underset{O_{+}H)\ (A^-)}{C\text{—}OH}} \qquad 2.13$$

II



$$\overset{OH}{\underset{O_{+}H\ \ (A^-)}{C\text{—}OH}} \overset{K_5}{\rightleftharpoons} \overset{O}{\overset{\|}{C}}\text{-O} + H_2O + HA \qquad 2.14$$

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. 2-14).

Under these conditions the kinetics of polymerization can be handled by considering the reactions in Eqs. 2-13 and 2-14 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. 2-13 and 2-14 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

$$R = -d[COOH]/dt = k_3[C^+(OH)_2][OH] \qquad 2.15$$

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 2-15 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

$$K = k_1/k_2 = [C^+(OH)_2] / [COOH][HA] \qquad 2.16$$

for the protonation reaction (Eq. 2-12). Combination of Eqs. 2-15 and 2-16 yields

$$-d[COOH]/dt = k_3K[COOH][OH][HA] \qquad 2\text{-}17$$

Two quite different kinetic situations arise from Eq. 2-17 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. 2-17 can be written in the usual form [Flory, 1953]

$$-d[COOH]/dt = k[COOH]^2\,[OH] \qquad 2\text{-}18$$

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. 2-18 can be written as

$$-d[M]/dt = k[M]^3 \qquad 2\text{-}19a$$

Or

$$-d[M]/[M]^3 = kdt \qquad 2\text{-}19b$$

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

Integration ofEq. 2-19b yields

$$2kt = 1/[M]^2 - 1/[M_0]^2 \qquad 2\text{-}20$$

where $[M_0]$ is the initial (at t = 0) concentration of hydroxyl or carboxyl groups. It is convenient at this point to write Eq. 2-20 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

$[M]=[M_0]-[M_0]p =[M_0](1-p)$ 2-21

Combination of Eqs. 2-20 and 2-21 yields

$1/(1- p)^2 =2[M_0]^2kt+1$ 2-22

Experimental Observations

Equation 2-22 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, 1967,1972]. 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

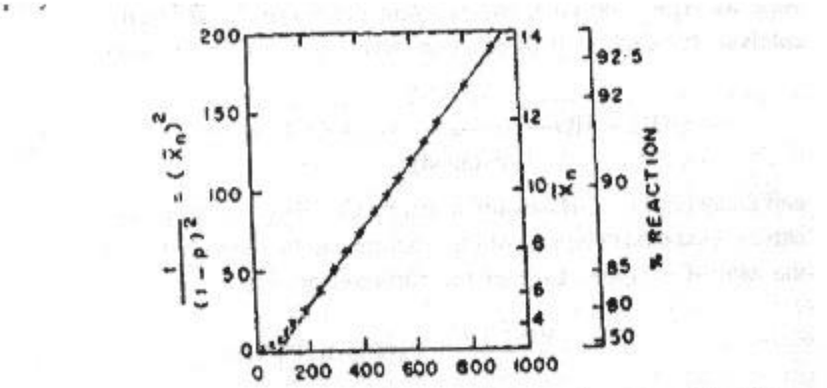


Fig. 2. Plot showing $1/(1 - p)^2$ or ($\overline{X}_n$) vs time for self catalyzed polyesterification of diethylene glycol with adipic acid at 166°C.

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

$-d[COOH]/dt = k[COOH][OH]$ 2-23a

And

$-d[COOH]/dt = k[COOH]^{3/2}[OH]$ 2-23b

However, a critical evaluation shows that both kinetic possibilities leave much to bedesired. The experimental rate data fits Eq. 2-23a well only in the region between 50 and86% conversion with an excessively poor fit above 86% conversion. On the other hand, aplot according to Eq. 2-23b fits reasonably well up to about 80% conversion but deviatesbadly above that point. Neither of the two alternate kinetic plots comes close to being asuseful as the third-order plot in Fig. 2-1. The third-order plot fits the experimental datamuch better than does either of the others at the higher conversions. The fit of the data tothe third-order plot is reasonably good over a much greater range of the higher conversionregion. The region of high conversion is of prime importance, since, as will be shown in Sec.2-2a-3, high-molecular-weight polymer is obtained only at high conversions. From the practicalviewpoint, 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,

$-d[M]/dt=K' [M]^2$ 2-31

where the various constant terms in Eq. 2-17 have been collected into the experimentally determinable rate constant K′. Equation 2-31 applies to reactions between stoichiometric concentrations of the diol and diacid. Integration of Eq. 2-31 yields

$K't = 1/[M] - 1/[M_0]$ 2-32

Combining Eqs. 2-32 and 2-21 yields the dependence of the degree of polymerization on reaction time as

$[M_o]k't = 1/(1 - p) - 1$ 2-33a

Or

$\bar{X}_n = 1 + [M_o]k't$ 2-33b

Data for the polymerization of diethylene glycol with adipic acid catalyzed by p-toluenesulfonic acid are shown in Fig. 2-2. The plot follows Eq. 2-33 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.

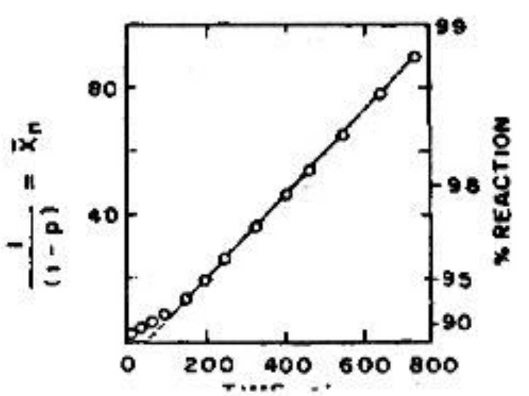


Fig. 3. Plot showing $1/(1-p)$ or $\overline{X}_n$ vs time for polycondensation of diethylene glycol and adipic acid at 109 °C using 0.4 mole, % p-toluene sulphonic acid as the catalyst[4,5].

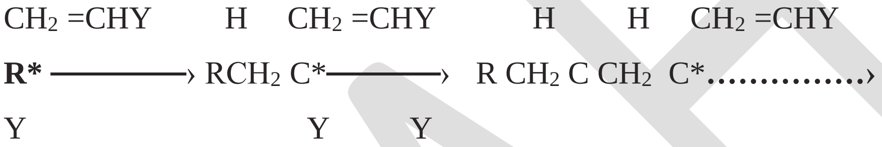
Fig 2.2 continues its second-order behavior at least up to a degree of polymerization of 90 corresponding to a molecular weight of _10,000. There is no change in the reactivities of the hydroxyl and carboxyl groups in spite of the large increase in molecular size (and the accompanying large viscosity 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.

RADICAL CHAIN POLYMERIZATION

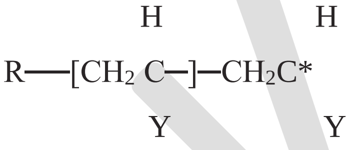
In the previous chapter, the synthesis of polymers by step polymerization was considered. Polymerization of unsaturated monomers by chain polymerization will be discussed in this and several of the subsequent chapters. Chain polymerization is initiated by a reactive species R* produced from some compound I termed an initiator:

$I \rightarrow \rightarrow R^*$ 3-1

The reactive species, which may be a free radical, cation, or anion, adds to a monomer molecule by opening the p-bond to form a new radical, cation, or anion center, as the case may be. The process is repeated as many more monomer molecules are successively added to continuously propagate the reactive center:



$$R^* \xrightarrow{CH_2=CHY} RCH_2\overset{H}{\underset{Y}{C^*}} \xrightarrow{CH_2=CHY} RCH_2\overset{H}{\underset{Y}{C}}CH_2\overset{H}{\underset{Y}{C^*}} \xrightarrow{CH_2=CHY} \ldots$$



$$R-[CH_2\overset{H}{\underset{Y}{C}}-]-CH_2\overset{H}{\underset{Y}{C^*}}$$

3.2

Polymer growth is terminated at some point by destruction of the reactive center by an appropriate reaction depending on the type of reactive center and the particular reaction conditions.

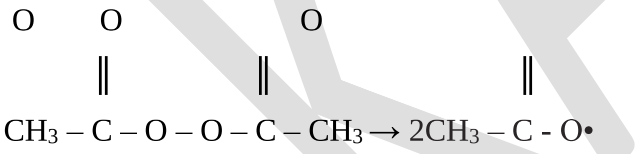
INITIATION

The derivation of Eq. 3-25 is general in that the reaction for the production of radicals (Eq. 3-13) is not specified and the initiation rate is simply shown asRi. Avariety of initiator systemscan be used to bring about the polymerization. (The term catalyst is often used synonomouslywith initiator, but it is incorrect in the classical sense, since the initiator is consumed.The use of the term catalyst may be condoned since very large numbers of monomer moleculesare converted to polymer for each initiator molecule that is consumed.) Radicals can beproduced by a variety of thermal,

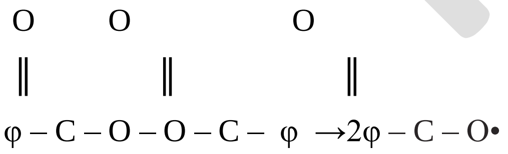
photochemical, and redox methods [Bamford, 1988;Denisova et al., 2003; Eastmond, 1976a,b,c; Moad et al., 2002]. In order to function as auseful source of radicals an initiator system should be readily available, stable under ambientor refrigerated conditions, and possess a practical rate of radical generation at temperatures
which are not excessive (approximately <150_C).

Types of Initiators

The thermal, homolytic dissociation of initiators is the most widely used mode of generatingradicals to initiate polymerization–for both commercial polymerizations and theoretical studies.Polymerizations initiated in this manner are often referred to as thermal initiated orthermal catalyzed polymerizations. The number of different types of compounds that can beused as thermal initiators is rather limited. One is usually limited to compounds with bonddissociation energies in the range 100–170 kJ mol^{-1}. Compounds with higher or lower dissociationenergies will dissociate too slowly or too rapidly. Only a few classes of compounds—including those with O─O, S─S, or N─O bonds–possess the desired range ofdissociation energies. However, it is the peroxides which find extensive use as radicalsources. The other classes of compounds are usually either not readily available or not stableenough. Several different types of peroxy compounds are widely used [Sheppard, 1988].These are acyl peroxides such as acetyl and benzoyl peroxides

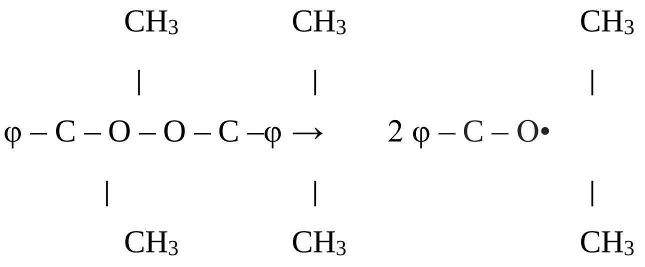


$$CH_3 - \overset{O}{\overset{\|}{C}} - O - O - \overset{O}{\overset{\|}{C}} - CH_3 \rightarrow 2CH_3 - \overset{O}{\overset{\|}{C}} - O\bullet \qquad 3.26a$$

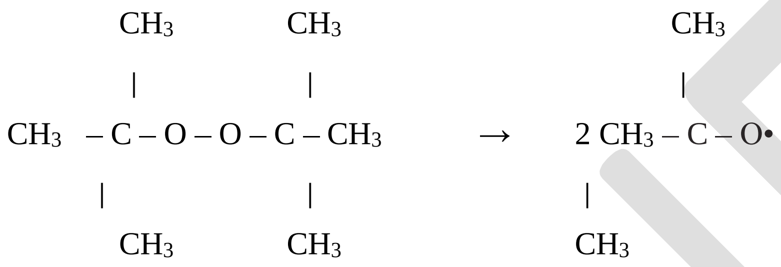


$$\varphi - \overset{O}{\overset{\|}{C}} - O - O - \overset{O}{\overset{\|}{C}} - \varphi \rightarrow 2\varphi - \overset{O}{\overset{\|}{C}} - O\bullet \qquad 3.26b$$

alkyl peroxides such as cumyl and t-butyl peroxides

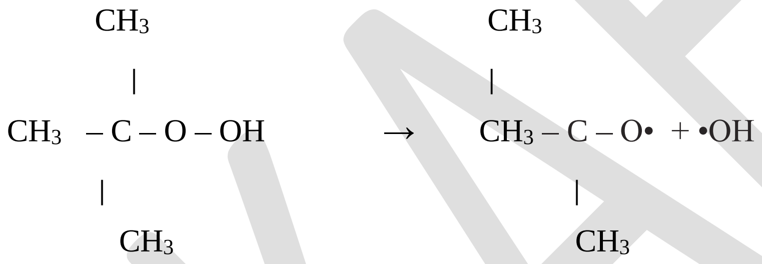
 3.26c

$$\varphi - \overset{CH_3}{\underset{CH_3}{C}} - O - O - \overset{CH_3}{\underset{CH_3}{C}} - \varphi \rightarrow 2\ \varphi - \overset{CH_3}{\underset{CH_3}{C}} - O\bullet$$

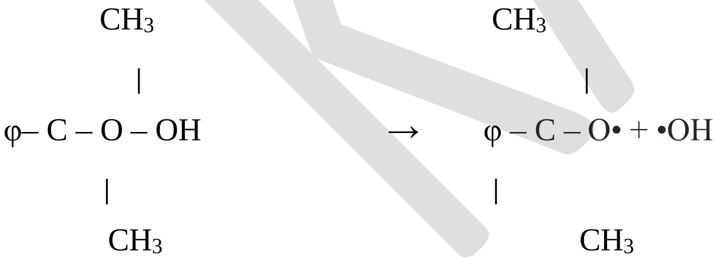
 3.26d

$$CH_3 - \overset{CH_3}{\underset{CH_3}{C}} - O - O - \overset{CH_3}{\underset{CH_3}{C}} - CH_3 \rightarrow 2\ CH_3 - \overset{CH_3}{\underset{CH_3}{C}} - O\bullet$$

hydroperoxides such as t-butyl and cumyl hydroperoxides

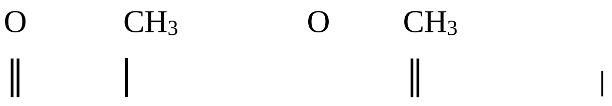
 3.26e

$$CH_3 - \overset{CH_3}{\underset{CH_3}{C}} - O - OH \rightarrow CH_3 - \overset{CH_3}{\underset{CH_3}{C}} - O\bullet + \bullet OH$$

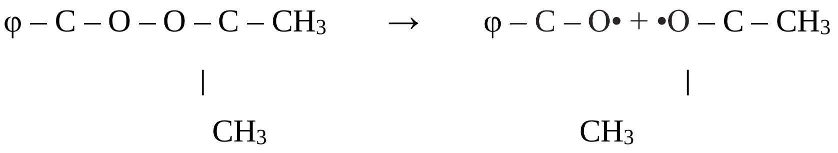
 3.26f

$$\varphi - \overset{CH_3}{\underset{CH_3}{C}} - O - OH \rightarrow \varphi - \overset{CH_3}{\underset{CH_3}{C}} - O\bullet + \bullet OH$$

and peresters such as t-butyl perbenzoate:



$$\overset{O}{\|} \quad \overset{CH_3}{|} \qquad \overset{O}{\|} \quad \overset{CH_3}{|}$$



$$\varphi - C - O - O - \underset{\underset{CH_3}{|}}{C} - CH_3 \rightarrow \varphi - C - O\bullet + \bullet O - \underset{\underset{CH_3}{|}}{C} - CH_3$$

3.26g

Other peroxides used to initiate polymerization are acyl alkylsulfonyl peroxides (Va), dialkylperoxydicarbonates (Vb), diperoxyketals (Vc), and ketone peroxides (Vd).

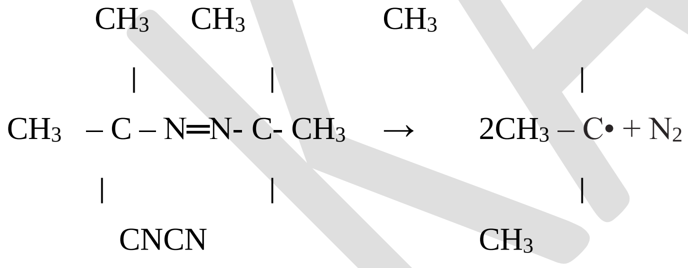
$R-SO_2-OO-CO-R'$ $RO-CO-OO-CO-OR$

Va **Vb**

$(ROO)_2C(R')_2$ $RR'C(OOH)_2$

Vc **Vd**

Aside from the various peroxy compounds, the main other class of compound used extensivelyas initiators are the azo compounds. 2,20-Azobisisobutyronitrile (AIBN) is themost important member of this class of initiators, although other azo compounds such as



$$CH_3 - \underset{\underset{CN}{|}}{\overset{\overset{CH_3}{|}}{C}} - N{=}N - \underset{\underset{CN}{|}}{\overset{\overset{CH_3}{|}}{C}} - CH_3 \rightarrow 2CH_3 - \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}\bullet + N_2$$

3.26h

2,2′-azobis(2,4-dimethylpentanenitrile), 4,40-azobis(4-cyanovaleric acid), and 1,10-azobis(cylohexanecarbonitrile)are also used [Sheppard, 1985]. The facile dissociation of azo compoundsis not due to the presence of a weak bond as is the case for the peroxycompounds. The C─N bond dissociation energy is high (~ 290 kJ mol $^{-1}$), but the drivingforce for homolysis is the formation of the highly stable nitrogen molecule.

Among other initiators that have been studied are disulfides

$RS-SR \longrightarrow 2RS\bullet$ 3-26i

and tetrazenes

$R_2N-N=N-NR_2 \longrightarrow 2R_2N\bullet + N_2$ 3-26j

[Oda et al., 1978; Sato et al., 1979a,b].

The various initiators are used at different temperatures depending on their rates ofdecomposition. Thus azobisisobutyronitrile (AIBN) is commonly used at 50–70^{O}C, acetylperoxide at 70–90^{O}C, benzoyl peroxide at 80–95^{O}C, and dicumyl or di-t-butyl peroxide at120–140^{O}C. The value of the decomposition rate constant kd varies in the range10^{-4}-10^{-9} s^{-1},depending on the initiator and temperature [Eastmond, 1976a,b,c]. Mostinitiators are used at temperatures where kd is usually 10^{-4}–$10^{-6s-1,}$ The great utilityof peroxide and azo compounds results from the availability in stable form of many differentcompounds with a range of use temperatures.The differences in the rates of decomposition of the various initiators are related to differencesin the structures of the initiators and of the radicals produced. The effects of structureon initiator reactivity have been discussed elsewhere [Bamford, 1988; Eastmond,1976a,b,c; Sheppard, 1985, 1988]. For example, *kd*is larger for acyl peroxides than for alkylperoxides since the RCOO•radical is more stable than the RO•radical and for R-N=N-R,
kd increases in the order R =allyl, benzyl >tertiary >secondary >primary [Koenig, 1973].
The differences in the decomposition rates of various initiators can be convenientlyexpressed in terms of the initiator half-life t(1/2) defined as the time for the concentration ofI to decrease to one half its original value. The rate of initiatordisappearance by Eq. 3-13 is

$-d[I]/dt=K_d[I]$ 3-27

which on integration yields

$[I] = [I]_O e^{-Kd\ t}$ 3-28a

or

$\ln([I]_o/[I]) = K_d t$ 3-28b

where $[I]_0$ is the initiator concentration at the start of polymerization. T(1/2) is obtained as

$t1/2 = 0:693/ k_d$ 3-29

by setting$[I] =[I]_0 /2$.

Half-Lives of Initiators[a,b] ; atvarious temp,

	Half-Life at					
Initiator	50°C	70°C	85°C	100°C	130°C	175°C
Azobisisobutyronitrile	74 h	4.8 h	-	7.2 min	-	-
Benzoyl peroxide	-	7.3 h	1.4 h	20 min	-	-
Acetyl peroxide	158h	8.1 h	1.1 h	-	-	-
t-Butyl peracetate	-	-	88h	13 h	18 min	-
Cumyl peroxide	-	-	-	-	1.7 h	-
t-Butyl peroxide	-	-	-	218 h	6.4 h	-
t-Butyl hydroperoxide	-	-	-	338 h	-	4.81 h

a Data from Brandrup and Immergut [1989], Brandrup et al. [1999], and Huyser [1970].

b Half-life t (1/2) values are for benzene or toluene solutions of the initiators.

Kinetics of Initiation and Polymerization

The rate of producing primary radicals by thermal homolysis of an initiator Rd (Eqs. 3-13 and3-26) is given by

R_d=2fk_d [I] 3-30

where [I] is the concentration of the initiator and f is the initiator efficiency. The initiator efficiency is defined as the fraction of the radicals produced in the homolysis reaction thatinitiate polymer chains. The value of f is usually less than unity due to wastage reactions. Thefactor of 2 in Eq. 3-30 follows the convention previously discussed for Eq. 3-23.The initiation reaction in polymerization is composed of two steps (Eqs. 3-13 and 3-14) asdiscussed previously. In most polymerizations, the second step (the addition of the primaryradical to monomer) is much faster than the first step. The homolysis of the initiator is therate-determining step in the initiation sequence, and the rate of initiation is then given by

Ri =2fk_d [I] 3-31

Substitution of Eq. 3-31 into Eq. 3-25 yields

R_p= k_p[M] (fk_d[I] / kt)$^{1/2}$ 3-32

Dependence of Polymerization Rate on Initiator

Equation 3-32 describes the most common case of radical chain polymerization. It shows thepolymerization rate to be dependent on the square root of the initiator concentration.The dependence has been abundantly confirmed for many different monomer–initiator combinationsover wide ranges of monomer and initiator concentrations [Eastmond, 1976a,b,c;Kamachi et al., 1978; Santee et al., 1964; Schulz and Blaschke, 1942; Vrancken and Smets,1959]. Figure 3-1 shows typical data illustrating the square-root dependence on [I]. Deviationsfrom this behavior are found under certain conditions.The order of dependence ofRpon [I] may be observed to be less than one-half at very high initiator concentrations. However,such an effect is not truly a deviation from Eq. 3-32. It may be due to a decrease in fwith increasing initiator concentration (Sec. 3-4g-2).

Alternately, the termination mode may change from the normal bimolecular termination between propagating radicals to primary termination, which involves propagating radicals reacting with primary radicals [Berger et al., 1977; David et al., 2001; Ito, 1980]:

$$Mn\bullet + R\bullet \xrightarrow{K_{tp}} Mn\text{—}R \qquad \text{3-33a}$$

This occurs if primary radicals are produced at too high a concentration and/or in the presence of too low a monomer concentration to be completely and rapidly scavenged by monomer (by Eq. 3-14a). If termination occurs exclusively by primary termination, the polymerization rate is given by

$$Rp = k_p\, k_i\, [M]^2 / k_{tp} \qquad \text{3-33b}$$

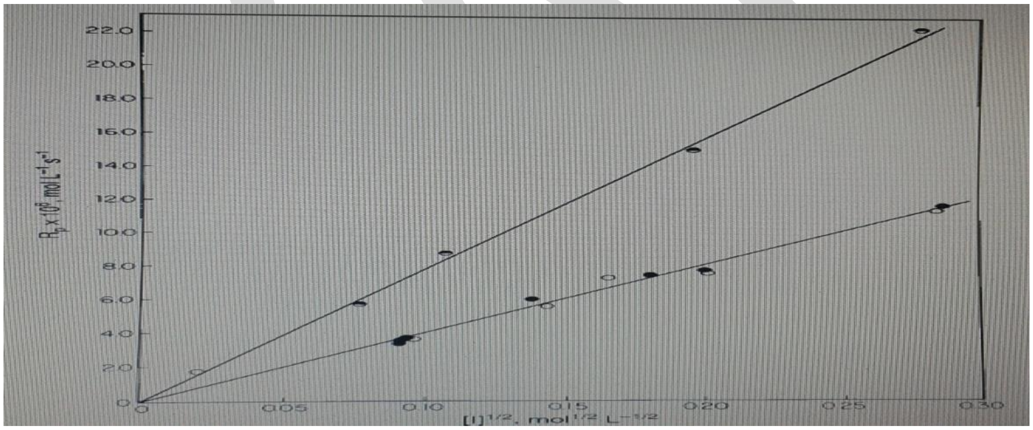


Fig. 3-1 Square root dependence of the polymerization rate Rp on the initiator concentration [I].♦=Methyl methacrylate, benzoyl peroxide, 50°C. After Schulz and Blaschke [1942] (by permission ofAkademische Verlagsgesellschaft, Geest and Portig K.-G., Leipzig). o,•=Vinyl

benzoate,azobisisobutyronitrile, 60°C. After Santee et al. [1964] and Vrancken and Smets [1959] (by permissionof Huthig and Wepf Verlag, Basel and Wiley-VCH, Weinheim).

Eq. 3-33b, derived by combining the rate expressions for Eqs. 3-14a, 3-15d, and 3-33a, howsthat the polymerization rate becomes independent of the initiator concentration (but not ki)and second-order in monomer concentration.Primary termination and the accompanying change in the order of dependence of Rp on [I]may also be found in the Trommsdorff polymerization region (Sec. 3-10).

Situations alsoarise where the order of dependence of R_P on [I] will be greater than one-half. This behaviormay be observed in the Trommsdorff region if the polymer radicals do not undergo terminationor under certain conditions of chain transfer or inhibition (Sec. 3-7).

Lower than one-half order dependence of $R_P$on Ri is also expected if one of the two primaryradicals formed by initiator decomposition has low reactivity for initiation, but is stillactive in termination of propagating radicals. Modeling this situation indicates that thedependence of $R_P$on Ri becomes one-third order in the extreme of this situation whereone of the primary radicals has no reactivity toward initiation, but still active for termination

Radical versus Ionic Chain Polymerizations

Whether a particular monomer can be converted to polymer depends on both thermodynamicand kinetic considerations. The polymerization will be impossible under any and all reactionconditions if it does not pass the test of thermodynamic feasibility. Polymerization is possibleonly if the free-energy difference -G between monomer and polymer is negative (Sec. 3-9b).A negative -G does not, however, mean that olymerization will be observed under a particularset of reaction conditions (type of initiation, temperature, etc.). The ability to carry outa thermodynamically feasible polymerization depends on its kinetic feasibility—on whetherthe process proceeds at a reasonable rate under a proposed set of reaction conditions. Thus,whereas the polymerization of a wide variety of unsaturated monomers is thermodynamicallyfeasible, very specific reaction conditions are often required to achieve kinetic feasibility inorder to accomplish a particular polymerization.

Although radical, cationic, and anionic initiators are used in chain polymerizations, thecannot be used indiscriminately, since all three types of initiation do not work for all monomers.Monomers show varying degrees of selectivity with regard to the type of reactive centerthat will cause their polymerization. Most monomers will undergo polymerization with aradical initiator, although at varying rates. However, monomers show high selectivity towardionic initiators. Some monomers may not polymerize with cationic initiators, while othersmay not polymerize with anionic initiators. The variety of behaviors can be seen inTable 3-1. The types of initiation that bring about the polymerization of various monomersto high-molecular-weight polymer are indicated. Thus, although the polymerization of all themonomers in Table 3-1 is thermodynamically feasible, kinetic feasibility is achieved in manycases only with a specific type of initiation

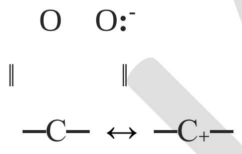
TABLE 3-1 Types of Chain Polymerization Undergone by Various Unsaturated Monomers

	Type of Initiation		
Monomers	Radical	Cationic	Anionic
Ethylene	+	-	+
1-Alkyl alkenes (a-olefins)	-	-	+
1,1-Dialkyl alkenes	-	+	-
1,3-Dienes	+	+	+
Styrene, a-methyl styrene	+	+	+
Halogenated alkenes	+	-	-
Vinyl esters (CH2-CHOCOR)	+	-	-
Acrylates, methacrylates	+	-	+

Acrylonitrile, methacrylonitrile	+	-	+
Acrylamide, methacrylamide	+	-	+
Vinyl ethers	-	+	-
N-Vinyl carbazole	+	+	-
N-Vinyl pyrrolidone	+	+	-
Aldehydes, ketones	-	+	+

The carbon–carbon double bond in vinyl monomers and the carbon–oxygen double bond in aldehydes and ketones are the two main types of linkages that undergo chainpolymerization. The polymerization of the carbon–carbon double bond is by far the most

important of the two types of monomers. The carbonyl group is not prone to polymerization by radical initiators because of its polarized nature:



$$-\overset{\overset{O}{\|}}{C}- \leftrightarrow -\overset{\overset{O:^{-}}{\|}}{C_{+}}- \qquad 3\text{-}3$$

CHAIN COPOLYMERIZATION

For most step polymerizations, for example, in the synthesis ofpoly(hexa -methylene adipamide)or poly(ethylene terephthalate), two reactants or monomers are used in the process,and the polymer obtained contains two different kinds of structures in the chain. This isnot the case for chain polymerizations, where only one monomer need be used to producea polymer. However, chain polymerizations can be carried out with mixtures of two monomersto form polymeric products with two different structures in the polymer chain. This typeof chain polymerization process in which two monomers are simultaneously polymerized istermed a copolymerization, and the product is a copolymer. It is important to stress that thecopolymer is not an alloy of two homopolymers but contains units of both monomersincorporated into each copolymer molecule. The process can be depicted as

$M_1 + M2 \longrightarrow$ ─[$M_1M_2M_2M_1M_2M_2M_2M_1M_1M_2M_2M_1M1M_2M_1M_1M_1M_2M_2M_1M_1$]─6-1

The two monomers enter into the copolymer in overall amounts determined by their relativeconcentrations and reactivities. The simultaneous chain polymerization of different monomerscan also be carried out with mixtures of three or more monomers. such polymerizationsare generally referred to as multicomponent copolymerizations; the term terpolymerization isspecifically used for systems of three monomers.Copolymerization is also important in step polymerization. Relatively few studies on stepcopolymerization have been carried out, although there are considerable commercialapplications. Unlike the situation in chain copolymerization, the overall composition of thecopolymer obtained in a step copolymerization is usually the same as the feed compositionsince step reactions must be carried out to close to 100% conversion for the synthesis ofhigh-molecular-weight polymers. Further, most step polymerizations are equilibriumreactions and the initially formed copolymer composition is rapidly changed by equilibration.

Types of Copolymers

The copolymer described by Eq. 6-1, referred to as a statistical copolymer, has a distributionof the two monomer units along the copolymer chain that follows some statistical law, forexample, Bernoullian (zero-order Markov) or first- or second-order Markov. Copolymersformed via Bernoullian processes have the two monomer units distributed randomly andare referred to as random copolymers. The reader is cautioned that the distinction betweenthe terms statistical and random, recommended by IUPAC [IUPAC, 1991, in press], has oftennot been followed in the literature. Most references use the term random copolymer independentof the type of statistical process involved in synthesizing the copolymer. There are threeother types of copolymer structures—alternating, block, and graft. The alternating copolymer
contains the two monomer units in equimolar amounts in a regular alternating distribution:

$$—[M_1M_2M_1M_2M_1M_2M_1M_2M_1M_2M1M_2M1M_2M_1M_2M_1M_2M_1M_2M_1]—$$

I

Alternating, statistical, and random copolymers are named by following the prefix poly withthe names of the two repeating units. The specific type of copolymer is noted by inserting-alt-, -stat-, or -ran- in between the names of the two repeating units with -—co- used when thetype of copolymer is not specified, for example, poly(styrene-alt-acrylonitrile), poly(styrenestat-acrylonitrile), poly(styrene-ran-acrylonitrile), and poly(styrene-co-acrylonitrile) [Wilks,2000].Block and graft copolymers differ from the other copolymers in that there are longsequences of each monomer in the copolymer chain. A block copolymer is a linear copolymerwith one or more long uninterrupted sequences of each polymeric species,

$$—[M_1M_1M_1M_1M_1M_1M_1M_1M_1M_2M_2M_2M_2M_2M_2M_2M_2M_2M_2M_2M_2M_2]—$$

II

while a graft copolymer is a branched copolymer with a backbone of one monomer to whichare attached one or more side chains of another monomer,

$$\begin{array}{l} —[\ M_1M_1M_1M_1M_1M_1M_1M_1M_1M_1M_1M_1M_1M_1M_1M_1M_1M_1M_1M_1M_1M_1M_1M_1M_1M_1]— \\ \qquad\qquad\qquad\quad | \\ M_2M_2M_2M_2M_2M_2M_2M_2M_2M_2M_2M_2M_2M_2M_2M_2M_2M_2]— \end{array}$$

III

This chapter is concerned primarily with the simultaneous polymerization of two monomersto produce statistical and alternating copolymers. The different monomers compete witheach other to add to propagating centers, which can be radical or ionic. Graft and blockcopolymers are not synthesized by the simultaneous and competititive polymerization oftwo monomers. Each monomer undergoes polymerization alone. A sequence of separate,noncompetitive polymerizations is used to incorporate the different monomers into one polymerchain.

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 ofhomopolymerization [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.

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 propagatingspecies—one with M_1 at the propagating end and the other with M_2. These can be representedby M_1^* and M_2^* where the asterisk represents either a radical, a carbocation, or acarbanion as the propagating species depending on the particular case. If it is assumedthat the reactivity of the propagating species is dependent only on the monomer unit atthe end of the chain (referred to as the end or ultimate unit), four propagation reactionsare then possible. Monomers M_1 and M_2 can each add either to a propagating chain endingin M_1 or to one ending in M_2, that is,

$M_1* + M_1 \xrightarrow{K11} M_1*$6-2

$M_1* + M_2 \xrightarrow{k12} M_2*$ 6-3

$M_2* + M_1 \xrightarrow{k21} M_1*$ 6-4

$M_2* + M_2 \xrightarrow{K22} M_2*$ 6-5

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. Thepropagation of a reactive center by addition of the same monomer (i.e., Reactions 6-2 and6-5) is often referred to as homopropagation or self-propagation; propagation of a reactivecenter by addition of the other monomer (Reactions 6-3 and 6-4) is referred to as crosspropagationor a crossover reaction. All propagation reactions are assumed to be irreversible.

Monomer M_1 disappears by Reactions 6-2 and 6-4, while monomer M_2 disappearsby Reactions 6-3 and 6-5. The rates of disappearance of the two monomers, which aresynonymous with their rates of entry into the copolymer, are given by

$-d[M_1]/dt = k_{11}[M_1*][M_1] + k_{21}[M_2*][M_1]$ 6-6

$-d[M_2]/dt = k_{12}[M_1 *][M_2] + k_{22}[M_2*][M_2]$ 6-7

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

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

6-8

In order to remove the concentration terms in M1* and M2* from Eq. 6-8, a steady-stateconcentration is assumed for each of the reactive species M1* and M2* separately. For the concentrationsof M1* and M2* ro remain constant, their rates of interconversion must be equal. Inother words, the rates of Reactions 6-3 and 6-4 must be equal:

$K_{21}[M_2*][M_1*] = k_{12}[M_1*][M_2]$ 6-9

Equation 6-9 can be rearranged and combined with Eq. 6-8 to yield

$d[M_1]/d[M_2]=((k_{11}k_{21}[M_2*][M_1]^2/k_{12}[M_2])+k_{21}[M_2*][M_1])/k_{22}[M_2*][M_2] + k_{21}[M2*][M_1]$ 6-10

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

$r_1=k_{11}/k_{12}$ and$r_2=k_{22} / k_{21}$ 6-11

one finally obtains

$d[M_1] / d[M_2] = [M_1] (r_1[M_1] + [M_2]) / [M_2] ([M_1] + r_2 [M_2])$ 6-12

Equation 6-12 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 monomerunits in the copolymer. $d[M_1] = d[M_2]$ is expressed by Eq. 6-12 as being related to the concentrationsof the two monomers in the feed, $[M_1]$ and $[M_2]$, and the parameters r_1 and r_2. Theparameters r_1 and $r_2$are termed the monomer reactivity ratios. Each **r**as defined above inEq. 6-11 is the ratio of the rate constant for a reactive propagating species adding tis own typeof monomer to the rate constant for its additon of the other monomer.The tendency of twomonomers to copolymerize is noted by r values between zero and unity. An r_1 value greaterthan unity means that M_1* preferentially adds M_1 instead of M_2, while an r_1 value less thanunity means that M_1* preferentially adds M_2. An r_1 value of zero would mean that M_1 isincapable of undergoing homopolymerization.

The copolymerization equation can also be expressed in terms of mole fractions instead ofconcentrations. 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

$$f_1 = 1 - f_2 = [M_1] / ([M_1] + [M_2]) \qquad 6\text{-}13$$

and

$$F_1 = 1 - F_2 = d[M_1] / (d[M_1] + d[M_2]) \qquad 6\text{-}14$$

Combining Eqs. 6-13 and 6-14 with Eq. 6-12 yields

$$F_1 = (r_1 f_1^2 + f_1 f_2) / (r_1 f_1^2 + 2 f_1 f_2 + r_2 f_2^2) \qquad 6\text{-}15a$$

or

$$f_1/f_2 = f_1(r_1 f_1 + f_2) / f_2 (r_2 f_2 + f_1) \qquad 6\text{-}15b$$

Equation 6-15 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 (Eq. 6-12) ofthe copolymerization equation.

Q–e Scheme

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

$K_{12} = P_1Q_2 \exp(-e_1e_2)$ 6-57

where P_1 represents the intrinsic reactivity of M_1•radical, Q_2 represents the intrinsic reactivityof M_2 monomer, e_1 represents the polarity of M_1•radical, and e_2 represents the polarityof M_2 monomer. By assuming that the same e value applies to both a monomer andits corresponding radical (i.e., e_1 defines the polarities of M_1 and M_1•, while e_2 definesthe polarities of M_2 and M_2•), one can write expressions for k_{11}, k_{22}, k_{21} analogous toEq. 6-57. These can be appropriately combined to yield the monomer reactivity ratios inthe forms

$r_1 = Q_1/Q_2 \exp[-e_1(e_1 - e_2)]$ 6-58

$r_2 = Q_2/Q_1 \exp[-e_2(e_2 - e_1)]$ 6-59

which correlate monomer–radical reactivity with the parameters Q_1, Q_2, e_1, and e_2. The basisof the Q–e scheme (Eqs. 6-57 to 6-59) is the theoretically unsatisfactory suggestion that thealternating tendency is due to ground-state electrostatic interactions between permanentcharges in the monomer and radical [Price, 1948].

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

Consider now the use of the Q–e shceme to predict monomer reactivity ratios. Values of Qand e have been assigned to monomers on the basis of their r values and the arbitrarily chosenreference values of Q =1 and e = - 80 for styrene [Greenley, 1989b, 1999]. Table 6-7shows the average Q and e values for some common monomers. The practical success of theQ–e scheme in predicting the r_1 and r_2 values for comonomer pairs not previously copolymerizedhas been limited in its quantitative aspects. The reason for this is that the Q and evalues 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 theexperimentally determined r values. Further, the Q and e values for a monomer vary considerablydepending on the monomer with which it is copolymerized as a result of inherent deficienciesof the Q–e scheme. It does not explicitly take into account steric factors that mayaffect monomer reactivity ratios for certain radical–monomer combinations. The assumptionof the same e value for a monomer and its corresponding radical is also inadequate. Attemptsto refine the Q–e scheme by using separate e values for monomer and radical have not beensuccessful.

In spite of these deficiencies the Q–e scheme is a reasonable qualitative and even semiquantitativeapproach to the effect of structure on monomer reactivity. It can be used to give ageneral 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 inTable 6-4 and 6-6. The monomers are lined up in Table 6-6 in order of their e values. Thisorder defines the polarities of the various monomers. The relative importance of resonanceand polar factors in determining monomer reactivity can be discussed by considering the datain Table 6-4 in terms of the Q and e values of the monomers.

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

A number of useful generalizations are possible regarding which pairs of monomers willcopolymerize and the behavior to be expected. Copolymerization proceeds poorly withmonomers whose Q values are very different, since copolymer formation would requirethe energetically unfavorable conversion of a resonance-stabilized radical to a less stabilizedradical and vice versa (Fig. 6-11). Thus vinyl chloride and vinyl acetate do not copolymerizewell with styrene or 1,3-butadiene. Copolymerization is more suitable between monomers ofsimilar Q values, preferably high Q values, for example, styrene and 1,3-butadiene. Idealcopolymerization occurs between two monomers having similar Q and e values, forexample, styrene–1,3-butadiene, vinyl chloride–vinyl acetate, and acrylonitrile–methyl acrylate.The tendency toward alternation is greatest for monomers having the same Q valueswith high e values of opposite sign.

TABLE 6-7;;; 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

POSSIBLE QUESTIONS

UNIT-I

PART-A (20 MARKS)

(Q.NO 1 To 20 Online Examination)

PART-B (2 MARKS)

1. What are the steps involved in the free radical chain polymerization?
2. Give an example for free radical polymerization, write its mechanism.
3. Give one examples each for cationic and anionic polymerization process.
4. Define crystalline melting point.
5. What are the factors affecting crystalline melting point?
6. What is coploymerisation?

PART-C (6 MARKS)

(Either or type questions)

1. Explain the kinetics of step growth polymerisation?
2. Write a note on condensation polymerization?
3. Write the mechanism and kinetics of cationic polymerization.
4. Explain the mechanism of anionic polymerization?
5. Write a note on co polymerization mechanism?
6. Write a note on linear, branched and crosslinked polymers ?
7. Explain the polymerization in homogenous and heterogenous systems ?
8. Write a note on conditions of polymerization?
9. Explain the morphology of crystalline polymers.
10. Explain the crystalline melting point of polymers.

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UNIT-II- MULTIPLE CHOICE QUESTIONS

DEPARTMENT OF CHEMISTRY
B.Sc CHEMISTRY

STAFF NAME : Dr. M.MAKESWARI
SUBJECT NAME : POLYMER CHEMISRY
SUB. CODE : 16CHU502A
SEMESTER : V
CLASS : III- B. Sc-CHEMISTRY

S.No	Questions	Option 1	Option 2	Option 3	Option 4	Answer
1	Which is obtained from the reaction of diamines with diacids?	Polyamides	polyester	Acrylicfibre	poly vinyl chloride	Polyamides
2	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
3	The alkyl resins are condensation polymers obtained from dibasic acids and	phenol	formaldehyde	Acetaldehyde	Glycol	Phenol

4	Reactivity of a functional group depends on?	Collision frequency	diffusion rate	Size	Molecular weight	Collision frequency
5	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
6	The first step in the reaction of the diol and diacid monomer is to form?	dimer	trimer	Pentamer	Tetramer	Dimer
7	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
8	A dimer reacts with a monomer to give	Trimer	Dimer	Pentamer	Tetramer	Trimer
9	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
10	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
11	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
12	The polyesterification becomes a much more economically feasible reaction when it is catalyzed by an?	Base	Acid	Alkali	Neutral	Acid
13	Example for radical sources for the polymerization reactions?	Peroxides	Epoxides	Nitrenes	Carbenes	Peroxides
14	A titanium atom at the surface is bonded by?	Five chlorines	Six chlorines	Three chlorines	Two chlorines	Five chlorines

15	In free radical vinyl polymerization	The electrons in the pi bond split up	The electrons in the sigma bond split up	Nonbonding electrons are used	Electrons from the functional group splits.	The electrons in the pi bond split up
16	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
17	In the acid hydrolysis of cellulose there is no effect of?	Frequency	Molecular wight	Density	Molecular size	Molecular size
18	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
19	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
20	Which find extensive use as radical sources?	Peroxides	Epoxides	Nitrenes	Carbenes	Peroxides
21	The enantiomorphic site control model attributes stereo control in?	Isoselective polymerization	Isotactic polymerization	Free radical polymerization	Ionic polymerization	Isoselective polymerization
22	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}
23	The various initiators are used at different temperatures depending on their rates of	Reaction	Decomposition	Composition	Entropy	Decomposition
24	The azobisisobutyronitrile (AIBN) is commonly used at?	60-70 OC	50–70OC	80-90 OC	40-50 OC	50–70^{O}C

25	Teflon is a polymer of the monomer or Teflon is obtained by the polymerisation of?	Monofloroethene	Difloroethene	Trifloroethene	Tetrafloroethene	Tetrafloroethene
26	Which of the following is an example of condensation polymer?	PVC	Polyamide	Terylene	Polyester	Terylene
27	Monomer concentration decreases steadily throughout reaction in?	Step polymerization	Ionic polymerization	Radical polymerization	Self catalysted polymerization	Ionic polymerization
28	Polymer molecular weight rises steadily throughout reaction in ?	Step polymerization	Ionic polymerization	Radical polymerization	Self catalysted polymerization	Step polymerization
29	In which step of cationic polymerization follows the first order kinetics	Initiation	propagation	termination	transfermation	termination
30	A simple termination or chain transfer depending to	chain growth	degree of polymerization	kinetics	polymer deformation	degree of polymerization
31	The temperature would decreases the	molecular weight of polymer	chain formation	initiator	monomer	molecular weight of polymer
32	In the radical polymerization, the propagation rate depends on	monomer	concentration of monomer radical	concentration of catalyst	reaction rate	concentration of monomer radical
33	In Cationic vinyl polymerization electron flow is?	Same direction	Same and opposite direction	Opposite direction	Same or opposite direction	Opposite direction
34	Ionic polymerization necessarily carry along a?	Counter ion	Cation	Anion	Cation or anion	Counter ion
35	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

36	A dimer react with another dimer to form a	Trimer	Dimer	Pentamer	Tetramer	Tetramer
37	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
38	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
39	Monomers show high selectivity towards?	Cationic initiators	Cationic and anionic initiators	Ionic initiators	Anionic initiators	Ionic initiators
40	Most monomers will undergo polymerization with a radical initiator, although at?	Varying rates	Reliable rates	Stable rates	Positive rates	Varying rates
41	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
42	The property of fabric which influences drape the most is?	Tensile	Compressional	Shear	Surface	Shear
43	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
44	3, 4-Difluorophenylamine is a weaker base than ?	Phenylamine	Phenylacetate	Phenol	Henepthyl alcohol	Phenylamine
45	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
46	Suspension free radical polymerization of styrene would be preferred over bulk polymerization to overcome the problem	Branching	Cross-linking	Stereo-isomerism	Polymeric impurities	Branching

	of?					
47	Crystallinity of polymer was determined by using	X-ray diffraction technique	SEM	TEM	EPS	X-ray diffraction technique
48	X-ray crystallography was used to determine which of the polymer	Size	Shape	Volume	Crystallinity	Crystallinity
49	The degree of polymerisation can be determined from which of the following	measuring the density of a polymer	measuring monomer concentration in a polymer	measuring kinetic chain length of the polymer	measuring viscosity of a polymer	measuring the density of a polymer
50	Crystallinity of a polymer is defined as	the fraction of the samples which is crystalline	the concentration of the initiator	the concentration of the monomer	fraction of the samples which is amorphous	the fraction of the samples which is crystalline
51	The fraction of the samples which is crystalline in a polymer is known as	crystallinity of a polymer	Kinetic chain length	degree of polymerisation	rate constant of a polymer	crystallinity of a polymer
52	The X-ray diffraction pattern of most polymers contain	Sharp band	broad band	very brand band only	sharp and broad band	sharp and broad band
53	Crystallisability of a polymer is defined as	the maximum crystallinity of a polymer can achieve at a particular temperature	the maximum crystallinity of a polymer can achieve at a particular pressure	the maximum crystallinity of a polymer can achieve at a particular time	the maximum crystallinity of a polymer can achieve at a certain monomer concentration	the maximum crystallinity of a polymer can achieve at a particular temperature
54	the maximum crystallinity of a polymer can achieve at a particular temperature is known as	crystallinity of a polymer	Crystallisability of a polymer	degree of polymerisation	Rate of polymerisation	Crystallisability of a polymer
55	What happens when a polymer melt when it is cooled? It will be	solidified	amorphous	crystallined	powdered	solidified
56	The factor which affect the crystallinity	polarity	molecular	hydrogen	structural	polarity

	of a polymer		forces between the monomer	bonding between the monomer	regularity	
57	Among the following which factor affect the crystallinty of a polymer	structural regularity	molecular forces between the monomer	hydrogen bonding between the monomer	polarity	structural regularity
58	The helical structure of DNA was determined by	Watson and Crick	Walden	Einstein	Nobel	Watson and Crick
59	Who won the noble prize for the determination of helical structure in DNA	Watson and Crick	Walden	Einstein	Nobel	Watson and Crick
60	For a standard polymer, the lamellar thickness is around	200 Å	300 Å	400 Å	100 Å	100 Å

UNIT-III

SYLLABUS

Nature and structure of polymers-Structure Property relationships.

Determination of molecular weight of polymers (*Mn*, *Mw*, etc) by end group analysis, viscometry, light scattering and osmotic pressure methods. Molecular weight distribution and its significance. Polydispersity index.

LECTURE NOTES

Polymer structure

Polymer structure 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 x-ray 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.

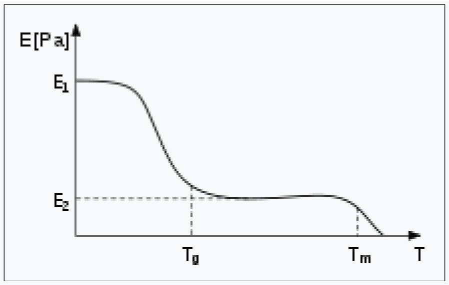
Hard plastics like polystyrene and poly(methyl methacrylate) are used well below their glass transition temperatures,that is in their glassy state. Their T_g values are well above room temperature, both at around 100 °C (212 °F). Rubber elastomers like polyisoprene and polyisobutylene are used above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

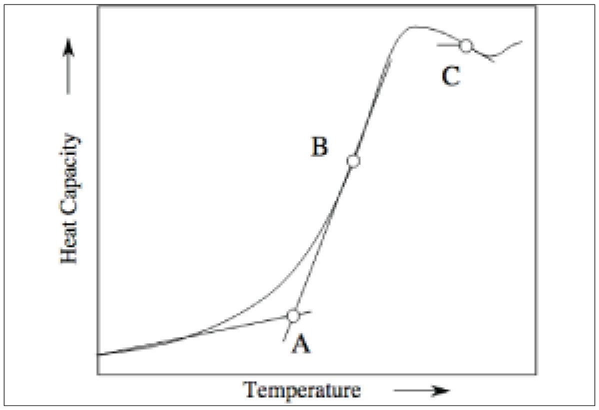
Determination of T_g

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)

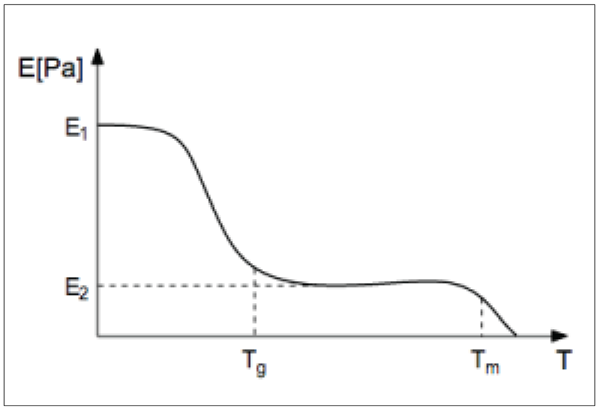
TMA estimates the glass transition temperature of a material by tracking its coefficient of thermal expansion (CTE). In many cases the CTE of a polymer material will increase 3-5x as it transitions from the glassy to the rubbery state.

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



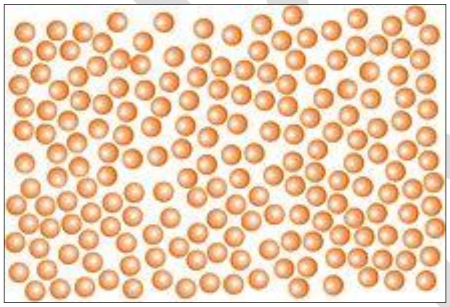
"Rubber plateau"

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

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) collectionA 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),

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

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,

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

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.

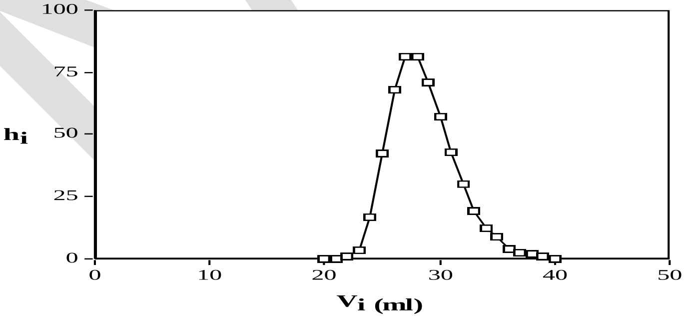
K is typically obtained by measuring the refractive index increment dn/dc as polymer is added to solvent, and as a consequence, I would prefer the light scattering method instead be termed the light scattering-refractive index method. The standard formula for K is written,

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

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 [$\sim(dn/dc)^2$], 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 -

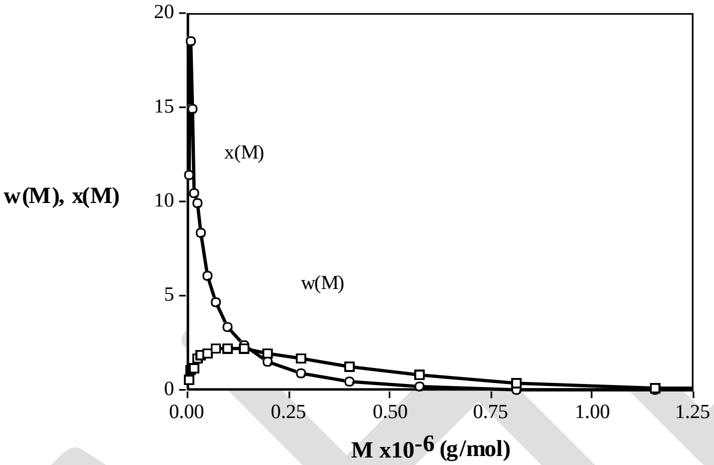
Consider ways that this molecular weight distribution might be graphically presented. Most commonly, the distribution is shown as the raw GPC trace, which is given next. A single, well-defined molecular weight peak is noted. [To define the molecular weight distribution better, there should be more data 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,

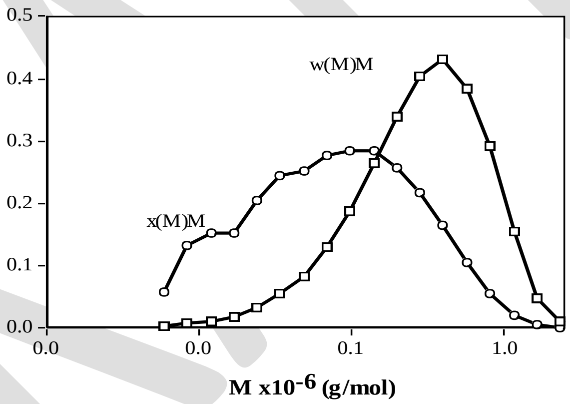
$$y\,dx = y'\,d\log(x)$$

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

$$\boxed{\frac{\Pi}{c} = RT\left(\frac{1}{M_n} + A_2c + A_3c^2 + \cdots\right)}$$

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 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:

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

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

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

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

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

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.

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

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

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.

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:

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

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:

$$\boxed{\frac{K^*c}{R(\theta,c)} = \frac{1}{M_w P(\theta)} + 2A_2c}$$

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:

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

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 M_w, 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.

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R1: Gowariker, V. R., N. V. Viswanathan and J. Sreedhar, 1986. Polymer Science, *New Age International* Private Ltd., New Delhi.

TEXT BOOK:

T1: Billmeyer, F.W., 2003. Text Book of Polymer Science. III Edition, John Wiley, New York.

UNIT-III-POSSIBLE QUESTIONS

PART-A (20 MARKS)

(Q.NO 1 To 20 Online Examination)

PART-B (2 MARKS)

1. Define number average molecular weight.
2. Define weight average molecular weight.
3. What is Glass Transition Temperature?
4. What is mean by crystalisability?
5. What is polydispercity index?

PART –C(6 MARKS)

Either or type questions

6. How to calculate the molecular weight of the polymer based on the number average method. Explain anyone of its experimental method?
7. Give an account of viscosity methods?
8. How to calculate the molecular weight of the polymer based on viscocity?
9. Give an account of light scattering method?
10. How to calculate the molecular weight of the polymer based on the weight average method. Explain anyone of its experimental method?
11. Give an account of vapour phase osmometry methods?
12. How to determine the molecular weight by osmometry?
13. Give an account of viscosity methods?
14. How to calculate the molecular weight of the polymer by Cryoscopic and Ebuliometric method?

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UNIT-III- MULTIPLE CHOICE QUESTIONS

DEPARTMENT OF CHEMISTRY
B.Sc CHEMISTRY

STAFF NAME : **Dr. M.MAKESWARI**
SUBJECT NAME : **POLYMER CHEMISRY**
SUB. CODE : **16CHU502A**
SEMESTER : **V**
CLASS : **III- B. Sc-CHEMISTRY**

S.No	Questions	Option 1	Option 2	Option 3	Option 4	Answer
1	The weight average molecular degree of polymerization indicated as	D_p	$(D_p)_w$	$(D_p)_n$	D	$(D_p)_w$
2	A simple chemical compounds which have same molecular weight to form	monodispersion	bi dispersion	poly dispersion	polymer solution	monodispersion
3	A polymer contains different molecular weight compounds to form	monodispersion	bi dispersion	poly dispersion	polymer solution	poly dispersion
4	The symbol $\dot{M}_n$ represents the	Number-average	Weight average	Viscosity average	Vapour pressure molecular weight	Number-average molecular weight

		molecular weight	molecular weight	molecular weight		
5	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
6	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
7	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
8	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
9	The freezing point depression depents on the	Number of dissolved solutes	Average weight of solute	solvent concentration	solvent nature	Number of dissolved solutes
10	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
11	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
12	The freezing point of the solvent indicates the	F	T_F	T_f	T_s	T_f
13	ΔT_f is the difference of	freezing point between solute	freezing point of solutes	freezing point between solvent	the temperature between solute	freezing point between solute and

		and solvent		molecules	and solvent	solvent
14	In the cryoscopic method, the error occurred to measure the	weight of monomer	temperature	freezing point	melting point	temperature
15	The difference temperature between the freezing point of solute and solvent in the range of	10ºC	0.01ºC	0.001ºC	0.1ºC	0.001ºC
16	By this method, accurately determine the molecular weights upto	10,000	20,000	30,000	50,000	30,000
17	The method based on observation of boiling point of a solution and solvent is known as	cryoscopic	Ebuliometry	membarane Osmometry	Equlibrium Osmometry	Ebuliometry
18	The Ebuliometry is a method based on the observation of	freezing point	boiling point	meltinf point	crystalline point	boiling point
19	The difference in the heat of vapourisation is indicates as	ΔHv	ΔSv	ΔTv	ΔGv	ΔHv
20	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
21	The osmosis based method is known as	membrane osmometry	Ebuliometry	Cryoscopic	Viscometry	membrane osmometry
22	The membrane osmometry method based on	freezing point	osmotic pressure	boiling point	crystaline point	osmotic pressure
23	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
24	The osmotic pressure is represented as	σ	ϴ	μ	π	π
25	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

26	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
27	The Ebuliometry method is applicable for	volatile solute	non-volatile solute	ionised solute	low molecular weight solute	non-volatile solute
28	The solution and solvent levels are measured by using	cathetometer	anometer	thermometer	osmometry	cathetometer
29	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
30	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
31	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
32	The vapour pressure of a solution is --- than pure solvent	more	less	same	constant	less
33	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
34	The ratio between the functionality divided by functional group equivalent is known as	$\dot{M}_n$	$\dot{M}_w$	$\dot{M}_v$	$\dot{M}_s$	$\dot{M}_n$
35	The viscosity of the polymer solution is high compared to	solute	solvent	monomer	catalyst	solvent
36	The relative viscosity is equal to the	$\eta/\eta_0 = t/t_0 = \eta_r$	η_{sp}	η_{red}	ln η_r /C	$\eta/\eta_0 = t/t_0 = \eta_r$
37	The specific viscosity is equal t the	η_r - 1	η_r	η_{red}	ln η_r /C	η_r - 1
38	The reduced viscosity is equal to the	η_{sp} /C = η_{red}	η_r - 1	η_r	ln η_r /C	η_{sp} /C = η_{red}
39	ln η_r /C is the	specific viscosity	reduced viscosity	inherent viscosity	intrinsic viscosity	inherent viscosity
40	[η], dl/g is equal to the	specific	reduced	inherent	intrinsic viscosity	intrinsic viscosity

		viscosity	viscosity	viscosity		
41	The intrinsic viscosity is also known as	specific viscosity	reduced viscosity	inherent viscosity	Staudinger viscosity	Staudinger viscosity
42	The limiting viscosity number known as	specific viscosity	reduced viscosity	inherent viscosity	intrinsic viscosity	intrinsic viscosity
43	The USLV is the	osmometer	viscometer	cathetometer	speedometer	viscometer
44	The viscosity highly depends on the	temperature	density	size	nature	temperature
45	The range of constant temperature maintained at viscometer is	0.01ºC	± 0.001ºC	± 0.1ºC	± 0.01ºC	± 0.01ºC
46	The error occurred in the viscometer dur to the measurement of	level of solute	density	nature	flow time	flow time
47	All the solutions are free from impurities, it reduces the	Number of dissolved solutes	yield	error	density	error
48	Which one of the following is most complex method	viscometry	osmometry	ultracentrifugation	light scattering	ultracentrifugation
49	In the ultracentrifugation, which force is used for polymer separation	kinetic force	magnetic force	centrifugal force	vanderwalls force	centrifugal force
50	Viscosity of a polymer solution is determined by	viscometry	osmometry	ultracentrifugation	light scattering	viscometry
51	Molecular weight of a polymer solution is determined by which method	viscometry	osmometry	ultracentrifugation	light scattering	viscometry
52	Degree of polymerisation of a polymer is determined by using which of the following method	viscometry	osmometry	ultracentrifugation	light scattering	viscometry
53	Viscometry is used to find out which of the following of a polymer	kinetic force	magnetic force	centrifugal force	molecular weight	molecular weight
54	Light scattering method is used to determine the ________ of the polymer	Molecular weight	kinetic force	magnetic force	centrifugal force	molecular weight

55	The molecular weight of a polymer is determined by which method	ultracentrifugation	magnetic force	kinetic force	osmotic pressure method	osmotic pressure method
56	Intermolecular forces present in nylon 66 are	Hydrogen bonding	Vander walls forces	Dipole-Dipole interactions	Polarity	Hydrogen bonding
57	Which interparticle forces between linear chains in nylon 66 are	H-Bonding	Covalent bonds	Dacron	Glyptol	H-Bonding
58	Which of the following is not an example of addition polymer?	polystyrene	polypropylene	Dacron	Polyethylene	Dacron
59	Copolymer is	Nylon-6	Nylon -66	PMMA	Dacron	PMMA
60	Polyacrylonitrile is an example of	Addition polymer	Condensation polymer	Natural polymer	Thermoplastic polymer	Addition polymer

UNIT-IV

SYLLABUS

Glass transition temperature (Tg) and determination of Tg, Free volume theory, WLF equation, Factors affecting glass transition temperature (Tg).

Polymer Solution – Criteria for polymer solubility, Solubility parameter, Thermodynamics of polymer solutions, entropy, enthalpy, and free energy change of mixing of polymers solutions, Flory- Huggins theory, Lower and Upper critical solution temperatures.

LECTURE NOTES

GLASS-TRANSITION TEMPERATURE

Definition

The glass–liquid transition, or glass transition, is the gradual and reversible transition in amorphous materials (or in amorphous regions within semi crystalline 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.

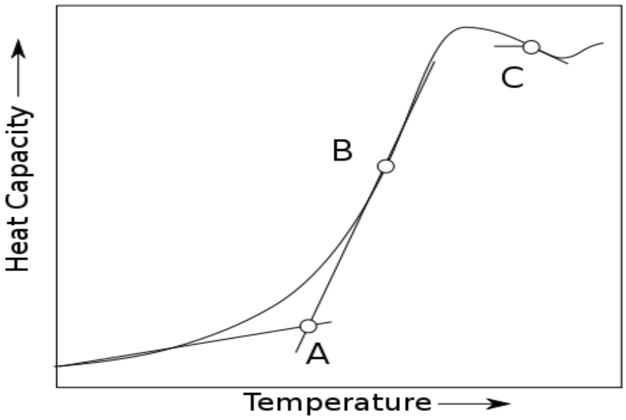
Hard plastics like polystyrene and poly(methyl methacrylate) are used well below their glass transition temperatures, that is in their glassy state. Their T_g values are well above room temperature, both at around 100 °C (212 °F). Rubber elastomers like polyisoprene and polyisobutylene are used above 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. The question of whether some phase transition underlies the glass transition is a matter of continuing research.

Explanation

The glass transition of a liquid to a solid-like state may occur with either cooling or compression. The transition comprises a smooth increase in the viscosity of a material by as much as 17 orders of magnitude within a temperature range of 500 K without any pronounced change in material structure. The consequence of this dramatic increase is a glass exhibiting solid-like mechanical properties on the timescale of practical observation. This transition is in contrast to the freezing or crystallization transition, which is a first-order phase transition in the Ehrenfest classification and involves discontinuities in thermodynamic and dynamic properties such as volume, energy, and viscosity. In many materials that normally undergo a freezing transition, rapid cooling will avoid this phase transition and instead result in a glass transition at some lower temperature. Other materials, such as many polymers, lack a well defined crystalline state and easily form glasses, even upon very slow cooling or compression. The tendency for a material to form a glass while quenched is called glass forming ability. This ability depends on the composition of the material and can be predicted by the rigidity theory.

Below the transition temperature range, the glassy structure does not relax in accordance with the cooling rate used. The expansion coefficient for the glassy state is roughly equivalent to that of the crystalline solid. If slower cooling rates are used, the increased time for structural relaxation (or intermolecular rearrangement) to occur may result in a higher density glass product. Similarly, by annealing (and thus allowing for slow structural relaxation) the glass structure in time approaches an equilibrium density corresponding to the supercooled liquid at this same temperature. T_g is located at the intersection between the cooling curve (volume versus temperature) for the glassy state and the supercooled liquid.

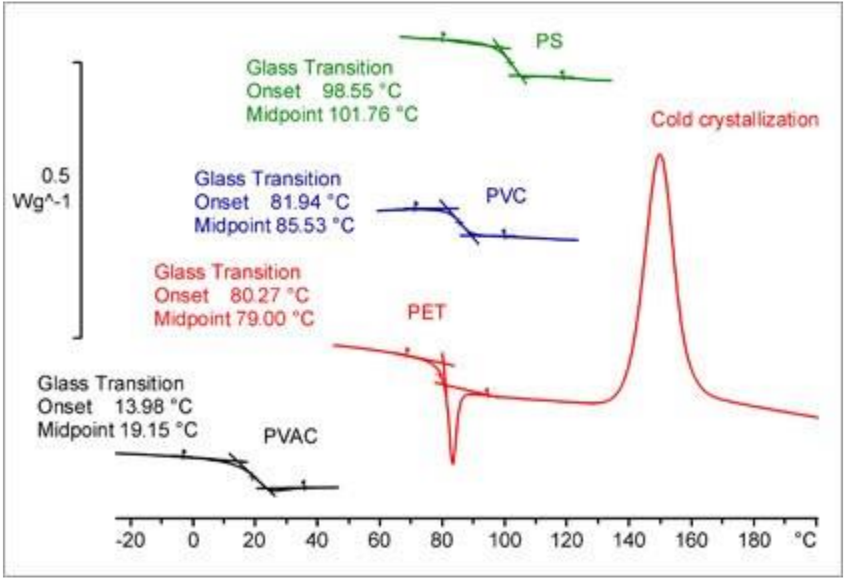


The configuration of the glass in this temperature range changes slowly with time towards the equilibrium structure. The principle of the minimization of the Gibbs free energy provides the thermodynamic driving force necessary for the eventual change. It should be noted here that at somewhat higher temperatures than T_g, the structure corresponding to equilibrium at any temperature is achieved quite rapidly. In contrast, at considerably lower temperatures, the configuration of the glass remains sensibly stable over increasingly extended periods of time.

Thus, the liquid-glass transition is not a transition between states of thermodynamic equilibrium. It is widely believed that the true equilibrium state is always crystalline. Glass is believed to exist in a kinetically locked state, and its entropy, density, and so on, depend on the thermal history. Therefore, the glass transition is primarily a dynamic phenomenon. Time and temperature are interchangeable quantities (to some extent) when dealing with glasses, a fact often expressed in the time–temperature superposition principle. On cooling a liquid, internal degrees of freedom successively fall out of equilibrium. However, there is a longstanding debate whether there is an underlying second-order phase transition in the hypothetical limit of infinitely long relaxation times.

Determination of Glass Transition Temperature

A comprehensive coverage of TA techniques for the determination of glass transition temperature



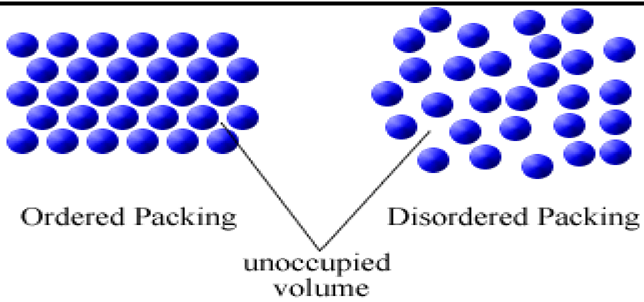
The determination of glass transition temperature (Tg) is critical for understanding a material's properties. It indicates the temperature at which a substance transforms from a glassy state to a rubbery state or vice versa. The formation of such amorphous glasses is a universal phenomenon observed in practically all materials.

For practical applications, it is important to realize that the properties of glasses differ significantly from those of other solids. For example, the solubility of glasses is higher than for crystals; this influences the biological activity of pharmaceutical substances.

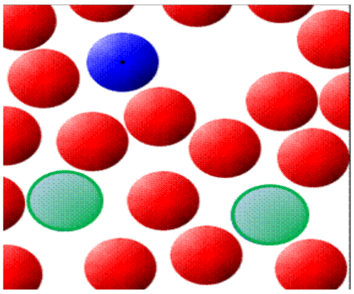
FREE VOLUME – THEORY

In the previous section, we have introduced the word "free volume" to explain the decrease in T_g that takes place with increasing size of flexible side-chains attached to a polymer backbone. Although free volume cannot be easily measured experimentally, it provides a useful concept to understand how T_g varies with addition of plasticizers, with increasing polymer molar mass, etc.

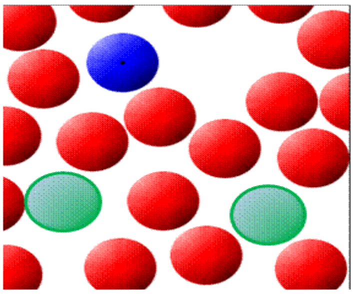
The free volume, V_f, is defined as the space in a solid or liquid that is not occupied by the molecules *i.e.* the empty space. As shown below, amorphous solids present a relatively large amount of free volume compared to ordered materials due to inefficient packing.



The transition from a liquid to a glass can be explained in terms of changes in free volume as this is identified with the unoccupied space which is available to a polymer to undergo rotational and translational motion.

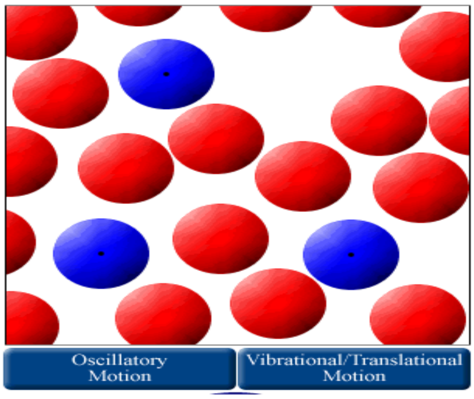


Oscillatory motion (vibrations): Occurs within a "cage" formed by nearest neighbours. This is "solid-like" motion and is associated with small free volume.

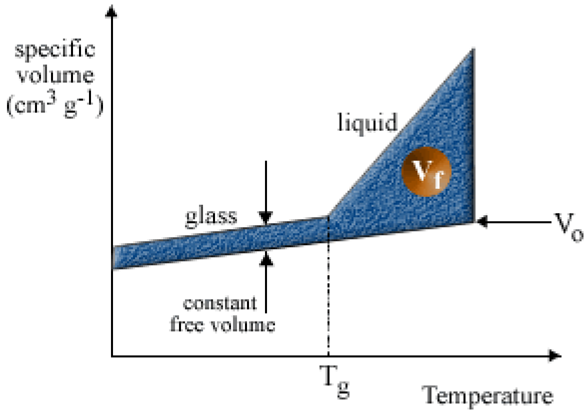


Translational motion (diffusion): Molecules jumps to new positions. This is "liquid-like" motion and is associated with large free volume.

The animation below shows how vibrational and and translational motions can be related to free volume.



According to this definition, free volume is high in the liquid state where molecular motion can take place relatively easily. With decreasing temperature, there is a reduction in free volume until, at some temperature on cooling, there will not be enough empty space to allow molecules to move relative to one other *i.e.* there is not enough free volume for large scale conformational changes. The glass transition, T_g corresponds to the temperature when a critical value of free volume V_f is reached so that the polymer chains can be considered as "frozen" in fixed positions.



As shown above, the free volume, V_f, is constant below T_g and increases above the glass transition (shaded area). The free volume fraction, V_f/V, in the glassy state is constant (2.5 % of the total volume for most polymers).

WLF THEORY

Polymers exhibit behavior during flow and deformation which depends on both temperature and time (frequency), that is, the viscoelastic response of a polymer will depend on the shear history. Only for Newtonian liquids, and in a first approximation for low molecular weight polymers, is the viscosity independent of the shear history. In this case, the temperature dependence of the viscosity may be decribed by an Arrhenius equation of the form

$$\eta = A\, e^{E/RT}$$

where T is the absolute temperature, R the universal gas constant, A a material constant, and E the activation energy. Knowledge of the two material-dependent parameters E and A allows for the prediction of the viscosity for any temperature. The two parameters are usually determined from a plot of log η against $1/T$ which yields a straight line:

$$\log \eta = \log A + E / RT$$

For most polymer melts a straight line can only be drawn over a fairly small temperature range of about 50°C. In general, the lower the shear rate and the molecular weight the better the agreement.

Doolittle provided another equation that is much more accurate for entangled polymer systems. He postulated that the viscosity is an exponential function of the reciprocal of the fractional free volume *f*:

$$\eta = A\, e^{B/f(T)}$$

or

$$\log \eta = \log A + B / f(T)$$

where *A* and *B* are constants and *f* is the free volume fraction,

$$f = v_f / v = (v - v_{hc}) / v$$

v_{hc} is the inaccessible volume and v the measured (molar) volume. Similar to the (molar) polymer volume, it can be assumed that the fractional free volume *f* increases linearly with temperature. Choosing the free volume at the glass transition temperature *Tg* as the reference state, the free volume as a function of temperature may be written as

$$f = f_g + \alpha_f (T - T_g)$$

where f_g is the fractional free volume at *Tg* and α_f is the thermal expansion coefficient. It has been suggested that the two parameters have the univerals values

$$f_g \approx 0.025$$
$$\alpha_f \approx 4.8 \times 10^{-4}\ K^{-1}$$

Williams, Landel and Ferry (1955) have suggested that the viscosity η at a temperature *T* may be related to the viscosity η_g at the glass transition temperature:

$$\log a_T = \log \eta(T) - \log \eta_g = B \left\{ \frac{1}{f(T)} - \frac{1}{f_g} \right\}$$

or

$$\log_{10} a_T = \log_{10}\frac{\eta(T)}{\eta(T_g)} = \frac{B}{2.303 f_g}\left\{\frac{-\alpha(T - T_g)}{f_g + \alpha(T - T_g)}\right\}$$

where a_T is the so called WLF shift factor. Using the universal values of f_g and α_f yields two new constants:

$$C_1 = B / f_g \approx 17.44$$

$$C_2 = f_g / \alpha_f = 51.6\ K$$

The two constants are not universal at all. Only polymers with isoviscose behavior will obey the WLF equation. For all other polymers, the two parameters might be very different.

Many polymers have melt viscosities of about 10^{13} poise at their glass transition temperature. Lets assume a polymer has a glass transition temperature of about 373 K then the viscosity at 423 K is:

$$\log_{10} a_T = \log_{10}\frac{\eta(T)}{\eta(T_g)} = -\frac{17.44\,(T - T_g)}{51.6 + T - T_g}$$

$$\log_{10} \eta(423\ K) = 13 - \frac{17.44\,(423 - 373)}{51.6 + 423 - 373} = 4.42$$

or $\eta = 2.61 \times 10^4$ Poise.

FACTORS AFFECTING GLASS TRANSITION TEMPERATURE

For synthetic polymers, T_g values vary between 150 K to 500 K. This section deals with the relationship between T_g and chemical structure.

We can understand why polymers have different glass transition temperatures if we consider what happens to a chain as the sample is heated across T_g. In the glassy state, the chains are frozen into rigid conformations and only local motion can take place such as vibrations and side group rotations. As temperature increases so does the probability of rotation about the single bonds. When the average thermal energy becomes higher than the potential energy barrier between conformational states, then the local bonds will rapidly interchange among different conformations. The conformational transitions that take place at T_g are not isolated and localised but involve movement of neighbouring segments. It is this co-ordinated movement that is responsible for the change in physical appearance of the material at T_g. This is usually summarised by saying that the transition from glass to rubbery state marks the onset of long range, coordinated molecular motion.

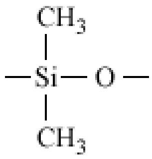
Because T_g is associated with molecular motion and internal rotations about chemical bonds, it is expected that whatever restricts rotational freedom should increase the glass transition temperature. Both intra- and inter- molecular parameters affect T_g:

- intramolecular parameters : chain stiffness, steric effects
- intermolecular parameters : specific interactions between chains

We will see that, for low molar mass polymers, T_g varies with M_n and can be altered by addition of plasticisers and through random copolymerisation.

Effect of chain stiffness on Tg

As Tg depends on the ability of a chain to undergo internal rotations, we expect chain flexibility to be associated with low glass transitions. Poly(dimethyl siloxane) is an extremely flexible polymer due to the large separation between the methyl substituted silicon atoms

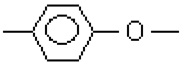
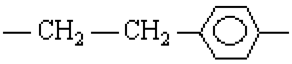
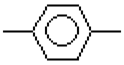


$$-Si(CH_3)_2-O-$$

Compared to other polymeric materials, poly(dimethyl siloxane) has the lowest glass transition temperature (Tg = 150 K).

As shown in Table 1, polymers that contain −CH2 −CH2 − sequences and ether linkages in the main-chain have relatively easy internal rotations and therefore low Tg values. Substitution of ethylene groups with p-phenylene units leads to increased chain rigidity and high glass transition temperature

Table 1 – Effect of Chain Stiffness

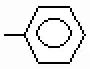
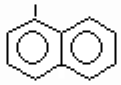
Repeat unit	***name***	***T_g***
$—CH_2—CH_2—$	*polyethylene*	180 K
$—CH_2—CH_2—O—$	*poly(oxyethylene)*	206 K
	*poly(phenylene oxide)*	363 K
	*poly(p-xylylene)*	353 K
	*poly(p-phenylene)*	rigid, intractable structure

Steric effects on Tg

The presence of bulky side groups hinders rotation of the backbone atoms due to steric hindrance , and therefore results in an increase in T_g. The magnitude of this effectdepends on the size of the side groups and it is possible to establish a correlation between the molar volume of the side group and T_g. This is illustrated in Table 2 for vinyl polymers having the general structure

$$— [CH_2 — CHX] —$$

Table 2 – Steric Effects

X=	—H	*polyethylene*	T_g=	180 K	V_X = 3.7 $cm^3 mol^{-1}$
	$—CH_3$	*polypropylene*		253 K	25.9 $cm^3 mol^{-1}$
		*polystyrene*		373 K	92 $cm^3 mol^{-1}$
		*poly(α–vinylnaphthalene)*		408 K	144 $cm^3 mol^{-1}$

An increase of ca. 120 K is observed with increasing the size of the side group.

For polymers of type

$$—[CH_2 — CYX] —$$

steric hindrance effects are even more pronounced. As shown in Table 3, compared to poly(methyl acrylate), the glass transition of poly(methyl methacrylate) is 100 K higher.

Table 3 – Steric Effects

$X = —COOCH_3$	$Y = —H$	*poly(methyl acrylate)*	$T_g =$	279 K
$—COOCH_3$	$—CH_3$	*poly(methyl methacrylate)*		383 K

Effect of Intermolecular Forces

The presence of polar side groups leads to strong intermolecular attractive interactions between chains which hinders molecular motion thus causing an increase in T_g. This effect is illustrated for the polymers of type

$$- [CH_2 - CHX] -$$

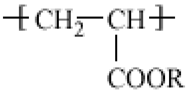
reported in Table 4. The three substituents *i.e.* methyl, Cl and OH groups have comparable size and therefore hinder bond rotation to the same extent. However, the non-polar polypropylene has a T_g that is 100 K below that of polar poly(vinyl cloride) and poly(vinyl alcohol).

Table 4 – Effect of Intermolecular Forces

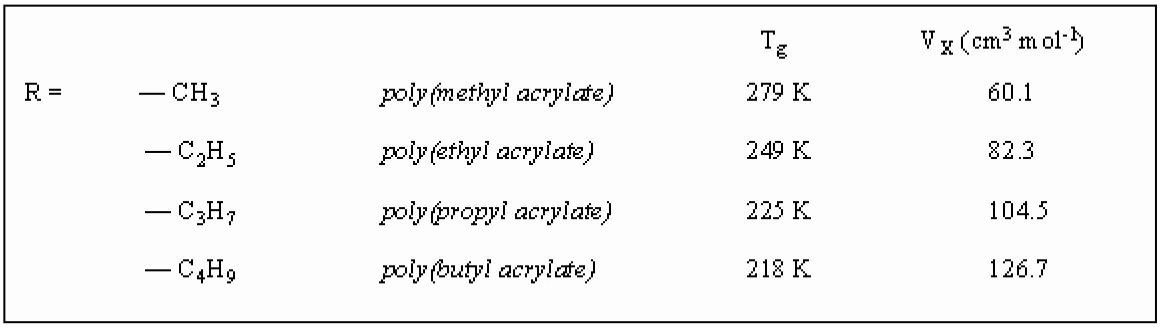
X =	$—CH_3$	*polypropylene*	$T_g =$	253 K
	$—Cl$	*poly(vinyl chloride)*		354 K
	$—OH$	*poly(vinyl alcohol)*		358 K

Flexible Alkyl chain and Internal Plasticisation

We have seen that, due to steric hindrance, the presence of bulky side groups causes an increase in T_g. However, this is only true if the side groups are rigid. Flexible alkyl chains cause a decrease in the glass transition temperature. This effect is illustrated below for the acrylate series: the glass transition decreases as the size of the side group increases.



$$-\!\!\!\left[CH_2 - \underset{\displaystyle COOR}{\underset{|}{CH}} \right]\!\!\!-$$



			T_g	V_X (cm^3 mol^{-1})
R =	$-CH_3$	*poly(methyl acrylate)*	279 K	60.1
	$-C_2H_5$	*poly(ethyl acrylate)*	249 K	82.3
	$-C_3H_7$	*poly(propyl acrylate)*	225 K	104.5
	$-C_4H_9$	*poly(butyl acrylate)*	218 K	126.7

The effect is similar to the decrease in T_g that is observed due to addition of low molar mass compounds (*i.e.* plasticizers) and is therefore referred to as "internal plasticization". It is explained by considering that only the first units of the side group, *i.e.* $-COO$ and $-CH_2-$ groups which are closest to the chain provide steric hindrance to internal rotation. The additional flexible CH_2 units do affect the motion of the backbone atoms as they are flexible and can undergo rotations about side-chain bonds. As it will be evident from the discussion in the following section, the flexible side-chains, with their motion, produce an increase in free volume and this makes the motion of the backbone atoms less hindered. As a consequence the glass transition decreases.

POLYMER SOLUTIONS

Definition

Polymer solutions are solutions containing dissolved polymers. These may be liquid solutions (e.g. in aqueous solution), or solid solutions (e.g. a substance which has been plasticized).

The introduction into the polymer of small amounts of a solvent (plasticizer) reduces the temperature of glass transition, the yield temperature, and the viscosity of a melt. [3] An understanding of the thermodynamics of a polymer solution is critical to prediction of its behavior in manufacturing processes — for example, its shrinkage or expansion in injection molding processes, or whether pigments and solvents will mix evenly with a polymer in the manufacture of paints and coatings.

General rules foe polymer solubility:

- Like dissolve like;
- Polar polymers- polar solvents
- Nonpolar polymer-nonpolar solvent (e.g.)- poly(vinyl alcohol), Polystyrene
- Solubility will decrease with increasing molecular weight at const. temp.
- Crystallinity decreases solubility.
- Crosslinking eliminates solubility.
- The rate of solubility increases with short branches, allowing the solvent molecules to penetrate more easily.
- The rate of solubility decreases with longer branches, because the entanglement makes it harder for individual molecules to separate.

The thermodynamic basis

$\Delta G_m = \Delta H_m - T\Delta S_m < 0$

Where ΔG_m = the change in Gibbs free energy in the process

ΔH_m = the change in enthalpy in the process

ΔS_m = the change in entropy in the process

Only if ΔG_m is negative will the solution process be feasible.

A positive ΔH – solvent and polymer “prefer their own company”, 즉, the pure materials are in a lower energy state.

A negative ΔH – the solution is in the lower energy state, specific interactions are formed between the solvents and polymer molecules.

(b) Fig. Lattice model of solubility.

Solvent, open circles ; solute, filled circles.

(a) Low-molecular-weight solute (b) polymeric solute.

-for(a): non polymer liquids:

free energy of dilution of a solution

Polymer solubility parameter

Solubility parameters were initially developed to guide solvent selection in the paint and coatings industry. Today, they are widely used in in many other fields to predict miscibility and solubility of polymers, chemical resistance, and permeation rates.

One of the most important application of solubility parameters is the prediction of polymer solubility in solvents. The closer the solubility parameters of the solute and the solvent are, the more likely the solubility of the solute in the given solvent. In the case of polymers, there are several rules of thumb for selecting suitable solvents:

Using Hildebrand solubility parameters, if the polymer (p) and the solvent (s) have similar polar and hydrogen bonding parameter, following simple rule applies:

$$|\delta_s - \delta_p| \leq 3.6 \text{ MPa}^{1/2}$$

Using Hansen solubility parameters, an approximate spherical "volume" of solubility with radius *R* can be drawn up for each solute. Only solvents that have Hansen solubility parameters within this volume are likely to dissolve the polymer in question:

$$[4(\delta_{d2} - \delta_{d1})^2 + (\delta_{p2} - \delta_{p1})^2 + (\delta_{h2} - \delta_{h1})^2]^{1/2} \leq R$$

The interaction radius, *R*, depends on the type of polymer. The *R* values are usually in the range of 4 to 15 $\text{MPa}^{1/2}$.

It is important to note that the higher the molecular weight of a polymer, the closer the solubility parameter of the solvent and polymer need to be to dissolve the polymer in the solvent. For linear and branched polymers, a plot of solubility versus solubility parameter for a range of solvents will peak when the (Hansen / Hildebrand) solubility parameters of the solute and solvent match. In the case of a cross-linked polymer, the swell volume, i.e. the solvent uptake, will peak when the solubility parameters of the solvent match those of the polymer.

As a general rule, the solubility parameters of polymers do not change much with temperature, whereas those of low molecular weight compounds often decrease noticeably with increasing temperature. In some cases, a solvent passes through soluble conditions to once more to become a non-solvent as the temperature increases.

For regular solutions[1] in which intermolecular (specific) attractions are minimal and the solution diverges only moderately from the ideal solution*, the enthalpy of mixing can be estimated from the solubility parameters as proposed by Hildebrand and Scott:[2]

$$\Delta H_{1,2} \approx \Delta U_{1,2} = \varphi_1\,\varphi_2\,(\delta_1 - \delta_2)^2$$

where $\Delta U_{1,2}$ is the internal energy change of mixing per unit volume and φ_1 and $\varphi_2$are the volume fractions of the solvent and the polymer in the mixture.

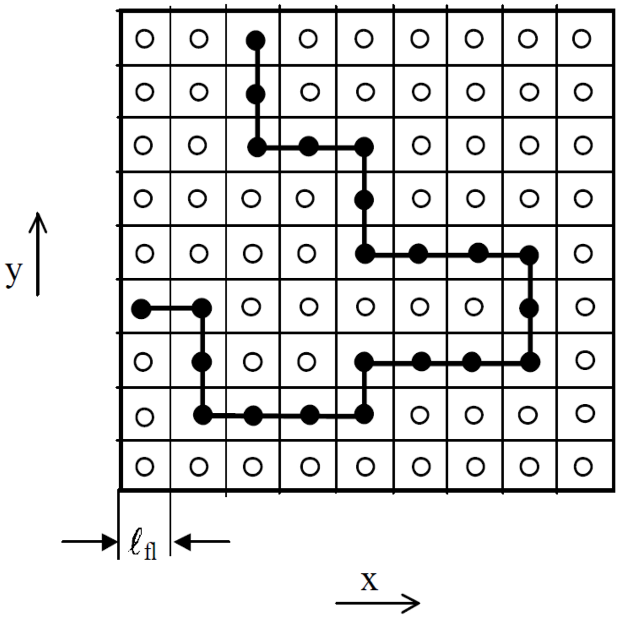
Florry- Huggins theory

The thermodynamics of (binary) regular polymer solutions[1] were first investigated by Paul Flory[2] and Maurice Huggins[3] independently in the early 1940s. They assumed a rigid lattice frame, that is, the molecules in the pure liquids and in their solution / mixture are considered to be distributed over N_0 lattice sites, as illustrated in the figure below. The total number of lattice sites, N_0, is assumed to be equal to the number of solvent molecules, N_s, and polymer repeat units, $N_p r$:

$$N_0 = N_s + N_p r$$

where N_p is the number of polymer molecules each consisting of r repeat units.

TWO-DIMENSIONAL LATTICE



The model has been described in great detail by Flory in his famous book "*Principles of Polymer Chemistry*" (1953).[4] Following the standard theory of mixing for small molecules of similar size and using Stirling's approximation $\ln M! = M \ln M - M$, Flory and Huggins obtained following expression for the entropy of mixing:

$$\Delta S_{mix} \approx -k\,(N_p \ln \varphi_p + N_s \ln \varphi_s)$$

Alternately, the entropy of mixing can be written as

$$\Delta s_{mix} = \Delta S_{mix} / N_0 \approx -k\,\{\varphi_p / (r \cdot v_r) \cdot \ln \varphi_p + \varphi_s / v_s \cdot \ln \varphi_s\}$$

where φ_s and φ_p are the volume fractions of the solvent and polymer,

$$\varphi_s = N_s v_s / (N_s v_s + N_p r v_r), \quad \varphi_p = N_p r v_r / (N_s v_s + N_p r v_r)$$

and v_s and v_r are the volumes of a solvent molecule and of a polymer repeat unit, respectively. Obviously, the solvent needs not necessarily to be made of a single unit. The solvent may, in fact, consist of several repeat units or of another polymer.

The Gibbs free energy of mixing, ΔG_{mix}, often includes an enthalpy part, that is, mixing can be an endothermic or an exothermic process

$$\Delta G_{mix} = \Delta H_{mix} - T\,\Delta S_{mix}$$

where ΔH_{mix} is the heat of mixing. Flory and Huggins introduced a new parameter, the so called Flory-Huggins interaction parameter to describe the the polymer-solvent interaction:[5]

$$\chi_{ps} = \Delta H_{mix} / (kT\, N_s\, \varphi_p)$$

which combined with the entropy term leads to the free energy of mixing:

$$\Delta G_{mix} / kT = N_p \ln \varphi_p + N_s \ln \varphi_s + \chi_{ps}\, N_s\, \varphi_p$$

Assuming equal lattice volumes for both repeat units, the free energy per lattice site can be written

$$\Delta g_{mix} / kT \approx \varphi_p / r \cdot \ln \varphi_p + \varphi_s \ln \varphi_s + \chi_{ps}\, \varphi_s\, \varphi_p$$

A more general expression for the free energy of mixing is

$$\Delta g'_{mix} / kT = \varphi_p / (r \cdot v_r) \cdot \ln \varphi_p + \varphi_s / v_s \cdot \ln \varphi_s + \chi_{ps}\, \varphi_s\, \varphi_p / \sqrt{(v_r v_s)}$$

where $\Delta g'_{mix}$ is the free energy of mixing per unit volume. These equations are the starting point for many other important equations. For example, the *partial molar free energy of mixing* (*chemical potential*) can be obtained by differentiation of the expression above with respect to N_s. This gives

$$\Delta\mu_s/RT = \ln [1- \varphi_p] + (1 - 1/\mathrm{r})\, \varphi_p + \chi_{ps}\, \varphi_p^2$$

where μ_s is the chemical potential of the solvent per mole. Substitution of this expression into the osmotic pressure relation $\Pi = - \Delta\mu_s / V_s$ gives

$$\Pi \approx RT\, V_s^{-1} \cdot \{\ln [1- \varphi_p] + \varphi_p + \chi_{ps}\varphi_p^2\}$$

where V_s is the molar volume of the solvent.

III.A THERMODYNAMICS OF POLYMER SOLUTIONS

The behavior of polymers towards a given solvent is characteristic and different from that of other solvents. This is quite expected as the differences in molecular weight of a polymer and that of a low molecular weight substance (solvent) is quite large. The size and conformations of dissolved polymer molecules require special theoretical treatment to explain their solution properties. Conversely, it is possible to obtain information about the *size* and *shape* of polymer molecules from studies of their solution properties.

III.A.1 Ideal Solutions

The *ideal solution* is defined as one which obey the *Raoult's* law. This law states that the partial vapor pressure of each component in the mixture is proportional to its mole-fraction, i.e.,

$$p_1 = p_1^0 \frac{n_1}{\sum n_1} = p_1^0 N_1 \qquad \text{(III.1)}$$

where p_1^0 is the vapor pressure of the solvent, p_1 is the vapor pressure of the same solvent in the solution and N_1 is the mole-fraction.

For a binary solution, the Eq.(III.1) can be written as

$$p_1 = p_1^0 \frac{n_1}{n_1 + n_2} = p_1^0 N_1 \quad \text{and} \quad p_2 = p_2^0 \frac{n_2}{n_1 + n_2} = p_2^0 N_2$$

From the condition of equilibrium between two phases, the free energy of dilution of a solution is given by, the *Claussius-Clayperon* equation

$$\Delta G_1 = K_BT \ln \left(\frac{p_1}{p_1^0} \right) \qquad \text{(III.2)}$$

where ΔG_1 is the free-energy of dilution resulting from the transfer of one mole of liquid one from a pure liquid state with vapor pressure p_1^0 to a large amount of solution with vapor pressure p_1.

From Eq.(III.1) and (III.2) it is clear that

$$\Delta G_1 = K_BT \ln N_1 \qquad \text{(III.3)}$$

So, the total free-energy of mixing for a binary mixture is,

$$\Delta G = n_1 \Delta G_1 + n_2 \Delta G_2$$

$$\Rightarrow \Delta G = K_BT (n_1 \ln N_1 + n_2 \ln N_2) \qquad \text{(III.4)}$$

$$\Rightarrow \Delta G = K_BT (n_1 \ln N_1 + n_2 \ln N_2) \qquad \text{(III.4)}$$

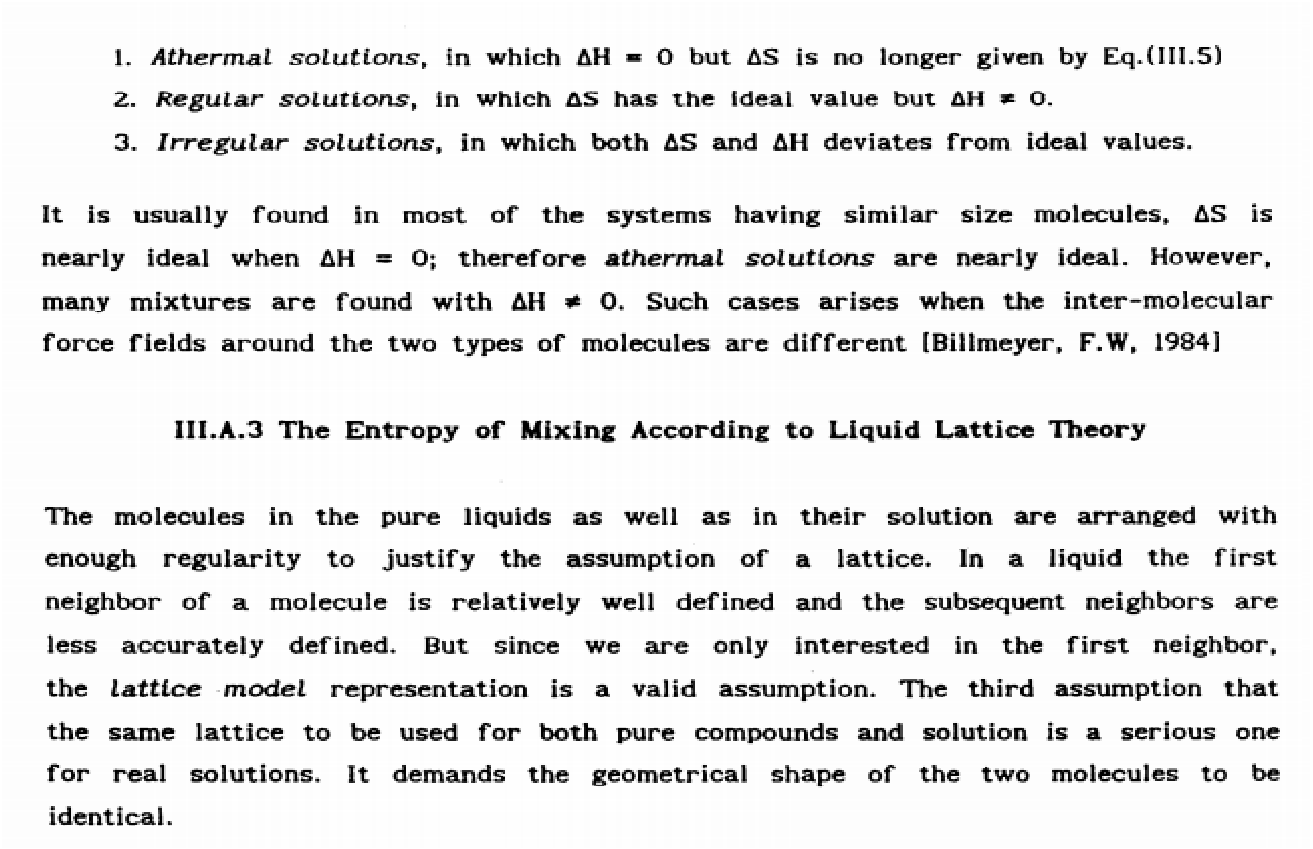
The condition for *ideal mixing* demands that the heat of mixing $\Delta H = 0$, i.e., the components mix without change in enthalpy. Since $\Delta G = \Delta H - T\Delta S$, the *ideal entropy of mixing* is given by

$$\Delta S_{mix} = -K_B(n_1 \ln N_1 + n_2 \ln N_2) \qquad \text{(III.5)}$$

The expression for *ideal entropy of mixing* as given in Eq.(III.5) is true for a binary solution, consisting of two types of molecules virtually identical in size, spatial configuration and external field so that if one type of molecule in the solution is replaced by the other types, it does not affect the immediate neighbor in the solution.

III.A.2 Non-Ideal Solutions

But in practice, few mixtures are *ideal*. They can deviate from the ideality in one of these three ways.

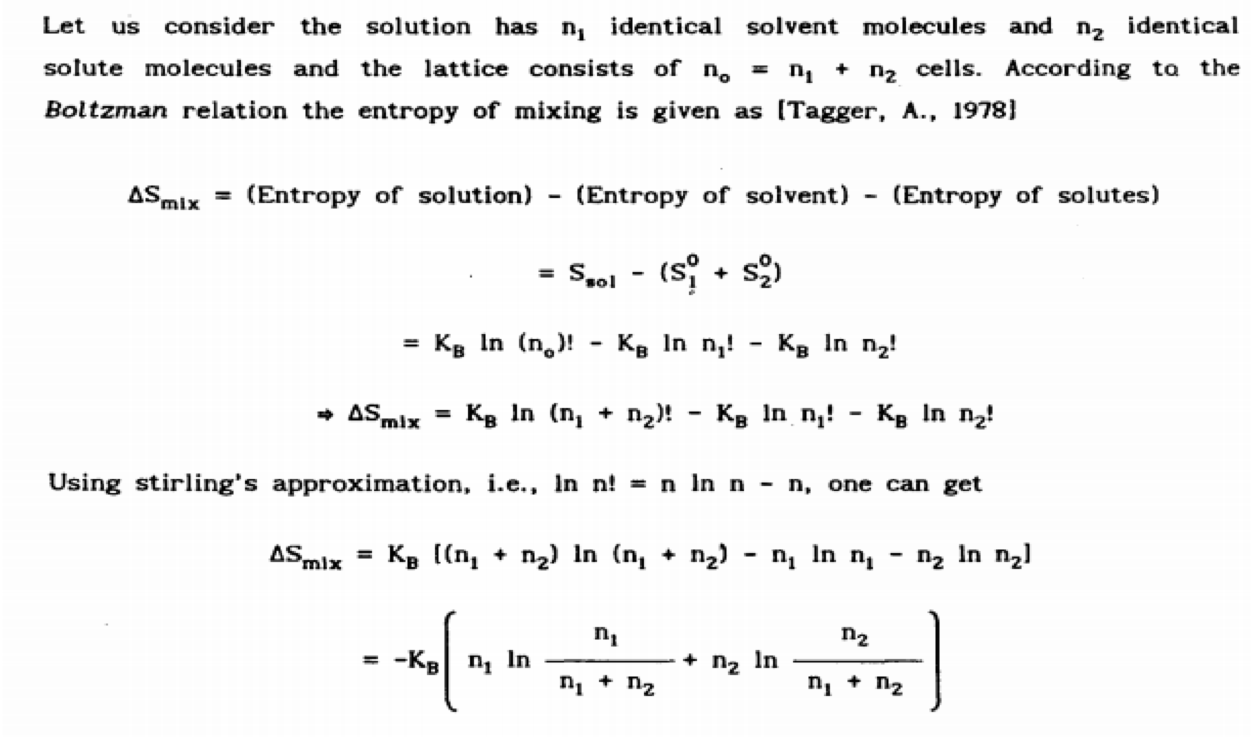


1. *Athermal solutions*, in which ΔH = 0 but ΔS is no longer given by Eq.(III.5)
2. *Regular solutions*, in which ΔS has the ideal value but ΔH ≠ 0.
3. *Irregular solutions*, in which both ΔS and ΔH deviates from ideal values.

It is usually found in most of the systems having similar size molecules, ΔS is nearly ideal when ΔH = 0; therefore *athermal solutions* are nearly ideal. However, many mixtures are found with ΔH ≠ 0. Such cases arises when the inter-molecular force fields around the two types of molecules are different [Billmeyer, F.W, 1984]

III.A.3 The Entropy of Mixing According to Liquid Lattice Theory

The molecules in the pure liquids as well as in their solution are arranged with enough regularity to justify the assumption of a lattice. In a liquid the first neighbor of a molecule is relatively well defined and the subsequent neighbors are less accurately defined. But since we are only interested in the first neighbor, the *lattice model* representation is a valid assumption. The third assumption that the same lattice to be used for both pure compounds and solution is a serious one for real solutions. It demands the geometrical shape of the two molecules to be identical.



Let us consider the solution has n_1 identical solvent molecules and n_2 identical solute molecules and the lattice consists of $n_o = n_1 + n_2$ cells. According to the *Boltzman* relation the entropy of mixing is given as [Tagger, A., 1978]

$$\Delta S_{mix} = \text{(Entropy of solution)} - \text{(Entropy of solvent)} - \text{(Entropy of solutes)}$$

$$= S_{sol} - (S_1^o + S_2^o)$$

$$= K_B \ln (n_o)! - K_B \ln n_1! - K_B \ln n_2!$$

$$\Rightarrow \Delta S_{mix} = K_B \ln (n_1 + n_2)! - K_B \ln n_1! - K_B \ln n_2!$$

Using stirling's approximation, i.e., $\ln n! = n \ln n - n$, one can get

$$\Delta S_{mix} = K_B [(n_1 + n_2) \ln (n_1 + n_2) - n_1 \ln n_1 - n_2 \ln n_2]$$

$$= -K_B \left(n_1 \ln \frac{n_1}{n_1 + n_2} + n_2 \ln \frac{n_2}{n_1 + n_2} \right)$$

$$\Rightarrow \Delta S_{mix} = -K_B(n_1 \ln N_1 + n_2 \ln N_2) \qquad \text{(III.6)}$$

which is same as Eq.(III.5). In spite of such drastic approximations, the ideal entropy of mixing also looks valid for solutions in which the components differ considerably in molecular shape as much as two fold in size.

III.A.4 The Entropy of Mixing of Polymer Solutions

The above treatment rests on the assumption of interchangeability of molecules of solute and solvent which is not the case where the solute is a polymer, since the polymer molecule is at least a 1000 times larger in size than the solvent molecule. In this case one can think of a polymer having 'x' chain segments, each having the size of a solvent molecule. 'x' is roughly defined as molar volume of solute divided by the molar volume of solvent. This is equivalent to a solution having an equal proportion of monomers to replace a polymer except in the case of a polymer 'x' continuous cell in the lattice are to be filled up by a polymer. This is shown in Fig.(III.1). In this case a solvent molecule can interchange its position with a polymer segment.

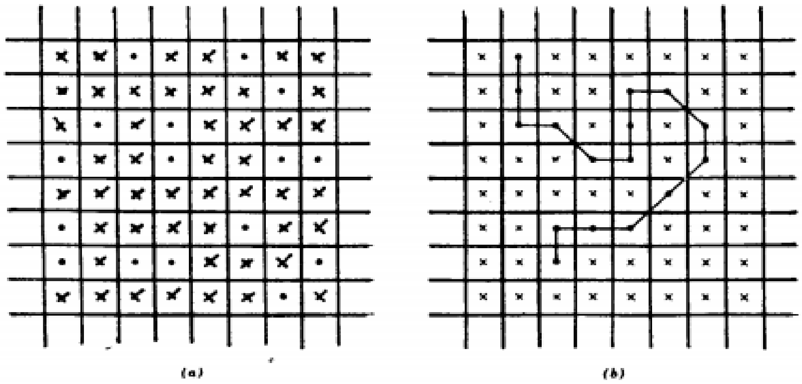


Fig.III.1 Two-dimensional representation of (a) nonpolymer liquids and (b) a polymer molecule in the liquid lattice.

Let us calculate the *configurational entropy* of the polymer solution arising from variety of ways of arranging the polymer and solvent molecules. The solution has n_1 solvent molecules and n_2 solute molecules, each having 'x' chain segments. So the total number of sites in the lattice is $(n_1 + xn_2) = n_o$. Let us consider the filling of these lattice sites. Let the solute molecule be introduced first. At any point of time n_1 solute molecules is already introduced. n_1 can vary from 0 to n_2. Let f_1 be the fraction of lattice sites occupied, i.e.,

$$f_1 = \frac{x.n_1}{(n_1 + xn_2)} \qquad \text{(III.7)}$$

Then the next step is to find out the number of ways to put $(n_1+1)^{st}$ solute molecule in the lattice. The 1st segment can be put in any one of the free sites of the lattice, i.e., in $(1 - f_1).(n_1 + xn_2)$ ways. The second segment can only be put in any one of the nearest neighbor of the 1^{st} segment. Let 'z' be the nearest neighbor coordination number. It can vary from 6 (for cubic lattice) to 12 (for hexagonal lattice), so the 2^{nd} segment of the polymer can be filled by $(1 - f_1).z$ ways. The number of ways the third segment can be filled is $(z - 1).(1 - f_1)$. But it also depends on the flexibility of the polymer. For a less flexible molecule it is less than $(z - 1).(1 - f_1)$ and is '1' for completely rigid polymer. The number of ways of placing 4^{th} segments and onwards is equal to the number of ways 3^{rd} can be placed, i.e., $(z - 1).(1 - f_1)$.

So, the number of ways of introducing $(n_1+1)^{st}$ polymer molecule (ν_{1+1}) [Tanford, C, 1961] is

$$\nu_{1+1} = \frac{1}{2}(1 - f_1)^x.(n_1 + xn_2).z.(z - 1)^{x-2} \qquad \text{(III.8)}$$

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$$\nu_{1+1} = \frac{1}{2}(1 - f_1)^x.(n_1 + xn_2).z.(z - 1)^{x-2} \qquad (III.8)$$

The reason for 1/2 is that the two sides of the polymer is indistinguishable. The total number of ways of putting n_2 polymer in the lattice is the product of ν_{1+1} with n_1 ranging from '0' to n_2-1. Then n_1 solvent molecules has to be introduced. Since all the solvent molecules are indistinguishable, there is only one distinguishable way of arranging them. So the total number of distinguishable ways of arranging the total mixture is

$$\Omega = \frac{1}{n_2!}\prod_{1=0}^{n_2-1} \nu_{1+1} \qquad (III.9)$$

It is divided by $n_2!$, since n_2 polymers are indistinguishable. Taking the logarithm of Eq.(III.9) and putting the value of ν_{1+1}, one gets,

$$\ln \Omega = -\ln n_2! + n_2 \ln \frac{1}{2}(n_1 + xn_2).z.(z-1)^{x-2} + x.\sum_{i=0}^{n_2-1} \ln(1-f_i) \qquad (III.10)$$

Since a real solution contains a large number of molecules the summation in Eq.(III.10) can be replaced by an integration

$$\rightarrow \sum_{i=0}^{n_2-1}(1-f_i) = \int_{n=0}^{n_2}\left[1 - \frac{x.n}{n_1 + xn_2}\right].dn$$

$$= -\frac{n_1}{x}\ln\frac{n_1}{n_1 + xn_2} - n_2 \qquad (III.11)$$

Applying stirling's formula ln n! = n ln n-n and putting Eq.(III.11) in Eq.(III.10) we get,

$$\ln \Omega = n_2 \ln \frac{z(z-1)^{x-2}}{2n_2} n_2(x-1) + (n_1 + n_2)\ln(n_1 + xn_2) - n_1 \ln n_1 \qquad (III.12)$$

The entropy of mixing is given by

The entropy of mixing is given by

$$\Delta S_{mix} = S_{sol} - (S_1^0 + S_2^0)$$

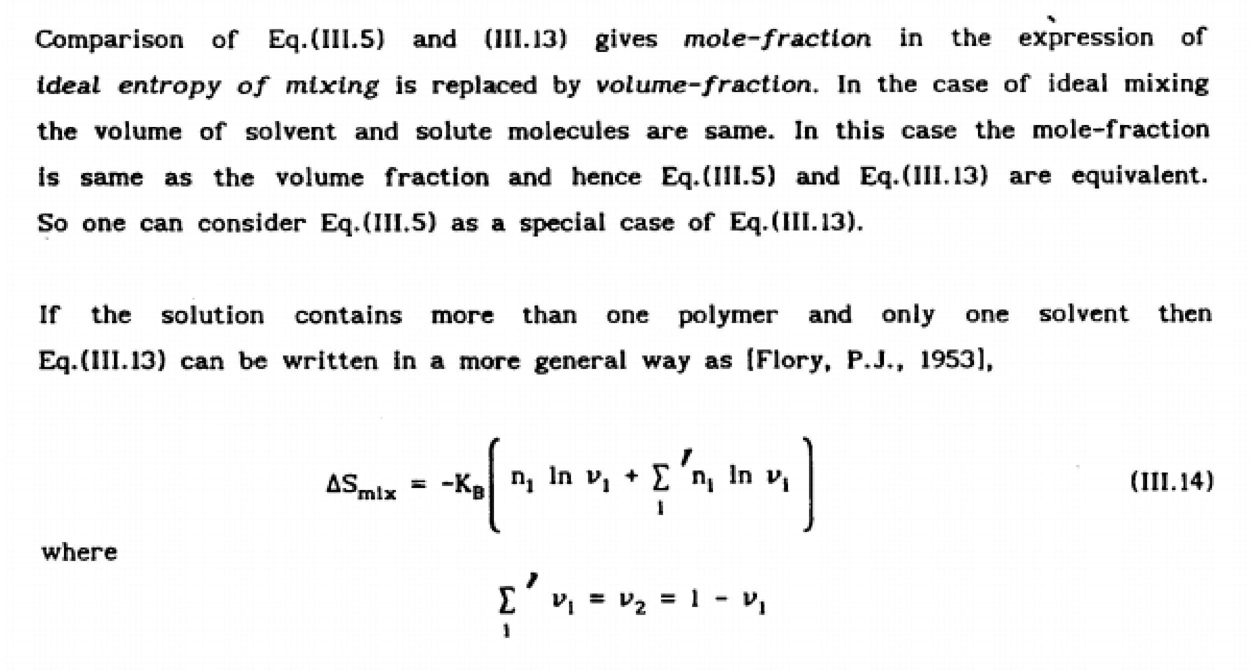
$$\rightarrow \Delta S_{mix} = K_B \ln \Omega - K_B \ln \Omega_1^0 - K_B \ln \Omega_2^0$$

for: S_1^0 ; $n_2 = 0$ and for: S_2^0 ; $n_1 = 0$.

$$\Delta S_{mix} = -K_B(n_1 \ln \nu_1 + n_2 \ln \nu_2) \qquad (III.13)$$

where $\nu_1 = n_1/(n_1+xn_2)$ and $\nu_2 = xn_2/(n_1+xn_2)$ are the volume fraction of the solvent and solute respectively.

This is called as *configurational entropy*. This is called so, because only the external arrangements of molecules and their segments are considered without bothering about the contribution to the entropy term because of the interaction between the segments of the polymers.



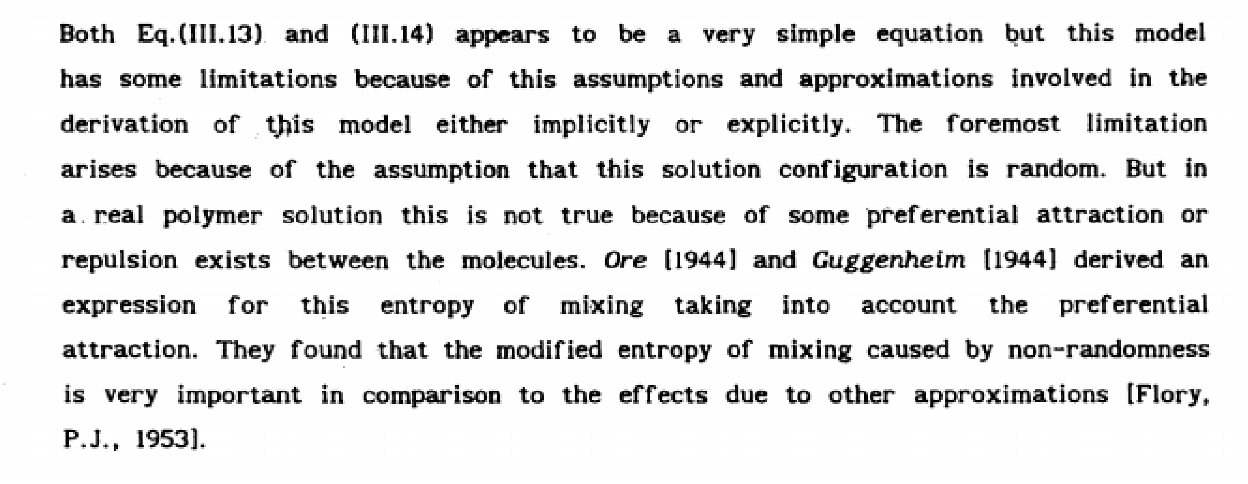
Comparison of Eq.(III.5) and (III.13) gives *mole-fraction* in the expression of *ideal entropy of mixing* is replaced by *volume-fraction*. In the case of ideal mixing the volume of solvent and solute molecules are same. In this case the mole-fraction is same as the volume fraction and hence Eq.(III.5) and Eq.(III.13) are equivalent. So one can consider Eq.(III.5) as a special case of Eq.(III.13).

If the solution contains more than one polymer and only one solvent then Eq.(III.13) can be written in a more general way as [Flory, P.J., 1953],

$$\Delta S_{mix} = -K_B\left(n_1 \ln \nu_1 + \sum_i{}' n_i \ln \nu_i \right) \qquad \text{(III.14)}$$

where

$$\sum_i{}' \nu_i = \nu_2 = 1 - \nu_1$$



Both Eq.(III.13) and (III.14) appears to be a very simple equation but this model has some limitations because of this assumptions and approximations involved in the derivation of this model either implicitly or explicitly. The foremost limitation arises because of the assumption that this solution configuration is random. But in a real polymer solution this is not true because of some preferential attraction or repulsion exists between the molecules. *Ore* [1944] and *Guggenheim* [1944] derived an expression for this entropy of mixing taking into account the preferential attraction. They found that the modified entropy of mixing caused by non-randomness is very important in comparison to the effects due to other approximations [Flory, P.J., 1953].

TEXT BOOK

T1: F.W. Billmeyer.(1972). *Text Book of Polymer Science*. 1984, ^{3d} Edition, John Wiley and sons, Delhi.

REFERENCE BOOK

R1: *V.R.Gowariker, N.V.Viswanathan and Jayadev sreedhar, polymer science, (2014),* New Age international publishers, New Delhi.

POSSIBLE QUESTIONS

UNIT-II

PART-A (20 MARKS)

(Q.NO 1 To 20 Online Examination)

PART-B (2 MARKS)

1. Define Glass transition temperature.
2. How will you calculate Enthalpy of a polymer solution?
3. How will you calculate entropy of a polymer solution?
4. What is mean by Lower critical solution temperature of a polymer solution?
5. What is mean by Upper critical solution temperature of a polymer solution?
6. What are the factors affecting glass transition temperature?

7. PART-C (6 MARKS)

(Either or Type questions)

8. What are the difference between T_g and T_m?
9. What is Glass Transition Temperature? How to determine it experimentally?
10. What is glass transition temperature and how will you determine the T_g by experimentally?
11. Explain the Flory-Huggins theory of polymer solutions.
12. Discuss in detail about entropy, enthalpy, and free energy change of mixing of polymers solutions thermodynamically.
13. What are factors affecting glass transition temperature? Explain in detail.
14. Derive WLF equation.

KARPAGAM ACADEMY OF HIGHER EDUCATION

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Coimbatore – 641 021.

UNIT-IV- MULTIPLE CHOICE QUESTIONS

DEPARTMENT OF CHEMISTRY
B.Sc CHEMISTRY

STAFF NAME : Dr. M.MAKESWARI
SUBJECT NAME : POLYMER CHEMISRY
SUB. CODE : 16CHU502A
SEMESTER : V
CLASS : III- B. Sc-CHEMISTRY

S.No	Questions	Option 1	Option 2	Option 3	Option 4	Answer
1	The glass transition temperature of a polymer is represented by the symbol of	Ts	Tg	Gt	tg	Tg
2	The symbol Tg represents the ------- of a polymer	Glass transition temperature	Transition temperature	Temperature constant	Viscosity constant	Glass transition temperature
3	An ordinary rubber ball if cooled below -70°C, it becomes	Soft	Liquefied	Vaporized	Hard	Hard
4	The hard and brittle state of a polymer is known as	Rubbery state	Glassy state	Viscoelastic state	Viscofluid state	Glassy state

5	The soft flexible state of a polymer is known as	Glassy state	Viscoelastic state	Viscofluid state	Rubbery state	Rubbery state
6	On heating the polymer becomes a highly viscous liquid and starts flowing, this state is termed as	Glassy state	Viscoelastic state	Viscofluid state	Rubbery state	Viscofluid state
7	In the glassy state, the polymer becomes	Soft and flexible	Hard and brittle	Soft and brittle	Hard and flexible	Hard and brittle
8	In the rubbery state of a polymer, it becomes	Soft and flexible	Hard and brittle	Soft and brittle	Hard and flexible	Soft and flexible
9	In Viscofluid state of a polymer, it becomes	High viscous liquid	Soft and flexible	Hard and brittle	Hard and flexible	High viscous liquid
10	The Brownian movement is possible only in	Amorphous solid	Crystalline solid	Liquid substance	Emulsions	Crystalline solid
11	A polymer can exists only as	Emulsion	Solid or liquid	Liquid	gas	Solid or liquid
12	What is the glass transition temperature of Nylon 6 is	50ºC	-102ºC	-73ºC	81ºC	-73ºC
13	The glass transition temperature of PVC is	-18ºC	18ºC	-81ºC	81ºC	81ºC
14	What is the glass transition temperature of Nylon 6, 6 is	-54ºC	58 ºC	50ºC	-73ºC	58ºC
15	The glass transition temperature of polystyrene is	69 ºC	-8ºC	8ºC	-69ºC	-8ºC
16	If in the process of dissolution, there is increase in enthalpy, Δf values become	More positive	Zero	Remains constant	More negative	More negative
17	For a good solvent, the Flory-Huggins parameter value is	Constant	High	Very low	Zero	Very low
18	For a poor solvent, the Flory-Huggins parameter value is	Constant	High	Very low	Zero	High
19	Among the following, The viscosity of a	Nature of	Temperature	Nature of	Pressure	Pressure

	polymer solution does not depends on	polymer		Solvent		
20	Viscosity-molecular weight constants for natural Rubber-Benzene system is	0.74	0.77	0.66	0.67	0.74
21	The viscosity of a polymer solution depends on which of the following factor	Pressure	Origin of the polymer	Kind of polymer	Nature of Solvent	Nature of Solvent
22	The glass transition is a property of only for which portion of a polymer	Amorphous	Powdered	Crystalline	Liquefied	Amorphous
23	During the glass transition, the crystalline portion of a polymer remains	Amorphous	Powdered	Crystalline	Liquefied	Crystalline
24	When a polymer is heated beyond Tg it passes from glassy state to	Liquefied state	rubbery state	Emulsion state	Crystalline state	rubbery state
25	The temperature at which the polymer starts flowing is known as its.	Flow temperature	Melting temperature	Boiling temperature	Transition temperature	Flow temperature
26	The Flow temperature of a polymer is known as temperature at which the polymer starts	Liquefied	Solidified	Flowing	Melting	Flowing
27	The temperature below Tg which the polymer is in which state	Liquefied state	rubbery state	Emulsion state	Crystalline state	rubbery state
28	The glass transition temperature is directly proportional to	Intermolecular force	Plasticization	Flexibility	Molecular weight	Molecular weight
29	The glass transition temperature is inversely proportional to	Intermolecular force	Plasticization	Cross links	Molecular weight	Plasticization
30	The presence of cross-links between chains restricts rotational motion and Tg will	Rises	Lowered	No change	Remains zero	Rises
31	Free volume of a polymer is represented by the symbol of	V_f	F_v	v_F	f_V	V_f
32	The decrease in Tg of a polymer is explained by	Free volume theory	WLF - equation	Flory–Huggins Theory	Thermodynamic factors	Free volume theory
33	The Free volume theory of polymer	Transition	Decrease in	Increase in Tg	Molecular weight	Decrease in Tg

	explains	temperature	Tg		change	
34	By the addition of plasticizer to a polymer , the Tg will be	Increases	Decreases	Constant	Zero	Decreases
35	By increasing the polymer molar mass the Tg will be	Increases	Decreases	Constant	Zero	Increases
36	The free volume is high in which state of polymer	Glassy state	Liquid State	Powdered state	Crystalline state	Liquid State
37	When a critical value of free volume V_f is reached so that the polymer chains can be considered as	Block in fixed positions	Blend in fixed positions	frozen in fixed positions	Trozen in fixed positions	frozen in fixed positions
38	Above the glass transition temperature, the value of V_f is	High	Constant	Low	Negative	Constant
39	Below the glass transition temperature, the value of V_f is	Constant	Zero	Increases	Decreases	Increases
40	The free volume fraction value in the glassy state is	Constant	Zero	Increases	Decreases	Constant
41	The solubility parameter of a polymer solution is represented by the symbol of	δ	υ	α	T	δ
42	The symbol δ indicates that which of the polymer property	Entropy	Enthalpy	Solubility	Viscosity	Solubility
43	The approach of polymer solubility is pioneered by	Hoy	Hildebrand	Billmeyer	Burrell	Burrell
44	Burrell explore the approach of the polymer solubility in the year of	1956	1954	1955	1957	1955
45	The Extensive values of the solubility parameter have been published by	Burrell and Hildebrand	Burrell and Billmeyer	Burrell and Hoy	Hoy and Billmeyer	Burrell and Hoy
46	The Extensive values of the solubility parameter have been published in the year of	1975	1957	1978	1967	1975

47	The molar attraction constant value E^a for OH aromatic group is	340 ((Jcm^{-3})$^{1/2}$/mole)	360 ((Jcm^{-3})$^{1/2}$/mole)	350 ((Jcm^{-3})$^{1/2}$/mole)	370 ((Jcm^{-3})$^{1/2}$/mole)	350 ((Jcm^{-3})$^{1/2}$/mole)
48	The molar attraction constant value E^a for –CHO group is	540 ((Jcm^{-3})$^{1/2}$/mole)	599 ((Jcm^{-3})$^{1/2}$/mole)	590 ((Jcm^{-3})$^{1/2}$/mole)	5990 ((Jcm^{-3})$^{1/2}$/mole)	599 ((Jcm^{-3})$^{1/2}$/mole)
49	The free energies for the polymer solutions were calculated from which measurements	Viscosity measurements	Calorimetric measurements	Vapor –pressure measurements	Conductivity measurements	Vapor –pressure measurements
50	The heat of polymer solution were measured in	Manometer	Calorimeter	Viscometer	Potentiometer	Calorimeter
51	Raoult's law says that the partial vapor pressure of each component in the mixture is proportional to its	Enthalpy	Temperature	Concentration of solvent molecules	Mole fraction	Mole fraction
52	The Boltzmann relation for the entropy of mixing is given by	$\Delta G = k \ln W$	$\Delta S = k \ln W$	$\Delta E = k \ln W$	$\Delta H = k \ln W$	$\Delta S = k \ln W$
53	$\Delta S = k \ln W$ is known as	Entropy of mixing	Enthalpy of mixing	Free energy change	Entropy change	Entropy of mixing
54	The calculation of W value is known as	Flory-Huggins theory	Flory theory	Huggins Theory	Burrell-Flory theory	Flory-Huggins theory
55	The Boltzmann constant value is calculated by the	Flory-Huggins theory	Flory theory	Huggins Theory	Burrell-Flory theory	Flory-Huggins theory
56	The Flory-Huggins theory can be used to calculate	Boltzmann constant	Enthalpy	Entropy	Moe fraction	Boltzmann constant
57	The solubility parameter value for the solvent Toluene is	18.5	18.4	18.3	18.7	18.3
58	The solubility parameter value for the solvent water is	28.5	47.9	48.5	14.8	47.9
59	The solubility parameter value for the polymer polyethylene is	16.6	16.7	16.8	16.2	16.2
60	The solubility parameter value for the polymer Poly(Vinyl Acetate) is	21.7	21.5	21.4	31.5	21.7

UNIT-V

SYLLABUS

Properties of Polymers (Physical, thermal, Flow & Mechanical Properties).

Brief introduction to preparation, structure, properties and application of the following polymers: polyolefins, polystyrene and styrene copolymers, poly(vinyl chloride) and related polymers, poly(vinyl acetate) and related polymers, acrylic polymers, fluoro polymers, polyamides and related polymers. Phenol formaldehyde resins (Bakelite, Novalac), polyurethanes, silicone polymers, polydienes, Polycarbonates, Conducting Polymers, [polyacetylene, polyaniline, poly(p-phenylene sulphide polypyrrole, polythiophene)].

LECTURE NOTES

Properties of Polymers

Physical Properties

- As chain length and cross-linking increases the tensile strength of the polymer increases.
- Polymers do not melt, they change state from crystalline to semi crystalline.

Chemical properties

- Compared to conventional molecules with different side molecules, the polymer is enabled with hydrogen bonding and ionic bonding resulting in better cross-linking strength.
- Dipole-dipole bonding side chains enable the polymer for high flexibility.
- Polymers with Van der Waals forces linking chains are known to be weak, but give the polymer a low melting point.

Optical Properties

Due to their ability to change their refractive index with temperature as in the case of PMMA and HEMA: MMA, they are used in lasers for applications in spectroscopy and analytical applications.

The following variables can be controlled when producing a polymer.

- The monomer polymerized or the monomers copolymerized.

- The reagent used to initiate the polymerization reaction.
- The identity and amount of the reagent used to crosslink the polymer chains.
- The temperature and pressure at which the polymerization occurs.
- The solvent in which the monomer is polymerized.
- The way the polymer is collected, which can produce either a more or less random alignment of the polymer chains or a fabric in which the chains are aligned in one direction.

Changing one or more of these parameters can affect the linearity of the polymer,

its average molecular weight, the tacticity of side chains on the polymer backbone, and the density of the product.

It is also possible to change the properties of a polymer by adding either stabilizers or plasticizers. *Stabilizers* are used to increase the ability of a plastic to resist oxidation, to make it less sensitive to either heat or light, or as flame retardants. *Plasticizers* increase the flexibility of a plastic by acting as a lubricant, decreasing the friction between molecules as one polymer chain moves past another. They also increase the amount of empty space — the so-called free volume — within the polymer by opening up space between the polymer chains to increase the ease with which the chain ends, the side chains, and the main chain can move.

The result of all of these manipulations can be a polymer as strong as Kevlar, which is used to make bullet-proof vests, or a material as easy to rip as a piece of paper. It can be as hard as a bowling ball or as soft as a piece of tissue paper. It can be as brittle as the disposable polystyrene glasses used at parties or as elastic as a Styrofoam coffee cup.

The following list describes some of the important properties of a polymer

Heat capacity/ Heat conductivity — The extent to which the plastic or polymer acts as an effective insulator against the flow of heat. (The polystyrene in disposable plastic glasses isn't a very good insulator. However, blowing air through styrene while it is being polymerized gives the Styrofoam used for disposable coffee cups, which is a much better insulator.)

Thermal expansion — The extent to which the polymer expands or contracts when heated or cooled. (Silicone is often used to seal glass windows to their frames because it has a very low coefficient of thermal expansion.) Thermal expansion is also concerned with the question of whether the polymer expands or contracts by the same amount in all directions. (Polymers are usually anisotropic. They contain strong covalent bonds along the polymer chain and much weaker dispersive forces between the polymer chains. As a result, polymers can expand by differing amounts in different directions.)

Crystallinity **—** The extent to which the polymer chains are arranged in a regular structure instead of a random fashion. (Some polymers, such as Silly Putty and Play Dough, are too amorphous and lack the rigidity needed to make a useful product. Polymers that are too crystalline often are also too brittle.)

Permeability **—** The tendency of a polymer to pass extraneous materials. (Polyethylene is used to wrap foods because it is 4000 times *less* permeable to oxygen then polystyrene.)

Elastic modulus **—** The force it takes to stretch the plastic in one direction.

Tensile strength **—** The strength of the plastic. (The force that must be applied in one direction to stretch the plastic until it breaks.)

Resilience **—** The ability of the plastic to resist abrasion and wear.

Refractive index **—** The extent to which the plastic affects light as it passes through the polymer. (Does it pass light the way PMMA does, or does it absorb light like PVC?)

Resistance to electric current **—** Is the material an insulator, like most polymers, or does it conduct an electric current? (There is a growing interest in conducting polymers, which can be charged and discharged, and photoconducting polymers that can pick up an electric charge when exposed to light.)

Preparation and applications of thermosetting plastics

Phenol-formaldehyde

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:

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

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

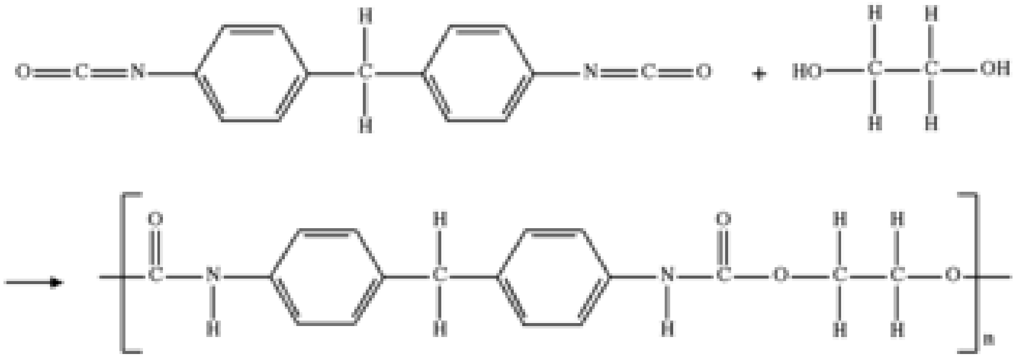
The diphenol $(HOC_6H_4)_2CH_2$ (sometimes called a "dimer") is called bisphenol F, which is an important monomer in the production of epoxy resins. Bisphenol-F can further link generating tri- and tetra-and higher phenol oligomers.

Uses

- Soft Bakelite are used as binding glue for laminated wooden planks, in varnishes and lacquers.
- Hard bakelite is used as a thermosetting polymer.
- It is used for the manufacture of combs, formica-table –tops, electrical switches and gramophone records.

Polyurethanes

Polyurethane (PUR and PU) is a polymer composed of organic units joined by carbamate (urethane) links. While most polyurethanes are thermosetting polymers that do not melt when heated, thermoplastic polyurethanes are also available.



Polyurethane polymers are traditionally and most commonly formed by reacting a di- or poly-isocyanate with a polyol. Both the isocyanates and polyols used to make polyurethanes contain, on average, two or more functional groups per molecule.

Some noteworthy recent efforts have been dedicated to minimizing the use of isocyanates to synthesize polyurethanes, because the isocyanates raise severe toxicity issues. Non-isocyanate based polyurethanes (NIPUs) have recently been developed as a new class of polyurethane polymers to mitigate health and environmental concerns.[1][2][3][4][5]

Polyurethane products often are simply called "urethanes", but should not be confused with ethyl carbamate, which is also called urethane. Polyurethanes neither contain nor are produced from ethyl carbamate.

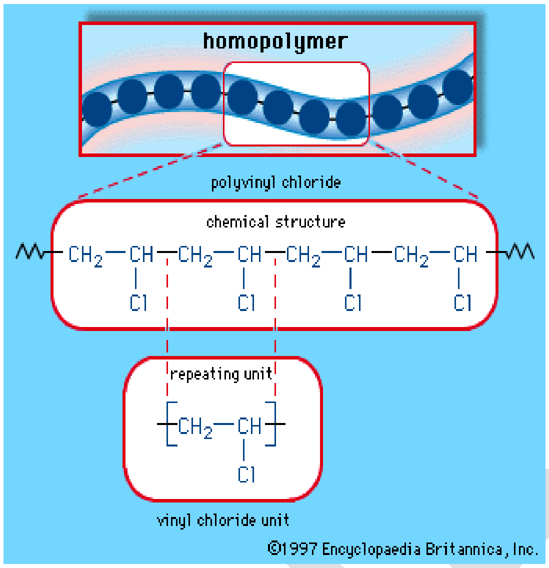
Uses

Polyurethanes are used in the manufacture of high-resilience foam seating, rigid foam insulation panels, microcellular foam seals and gaskets, durable elastomeric wheels and tires (such as roller coaster, escalator, shopping cart, elevator, and skateboard wheels), automotive suspension bushings, electrical potting compounds, high performance adhesives, surface coatings and surface sealants, synthetic fibers (e.g., Spandex), carpet underlay, hard-plastic parts (e.g., for electronic instruments), condoms,[6] and hoses.

Preparation and applications of Thermoplastic polymers

PVC

Polyvinyl chloride (PVC), a syntheticresin made from the polymerization of vinyl chloride. Second only to polyethylene among the plastics in production and consumption, PVC is used in an enormous range of domestic and industrial products, from raincoats and shower curtains to window frames and indoor plumbing. A lightweight, rigid plastic in its pure form, it is also manufactured in a flexible “plasticized” form.



USES

- It is a good electrical insulator and hence is used for coating wires and cables.
- It is also used in making gramophone records and pipes.
- It is used for making rain coats, hand bags, plastic dols, upholstery, shoe soles and vinyl flooring.

Polyethene

Low density poly(ethene) (LDPE)

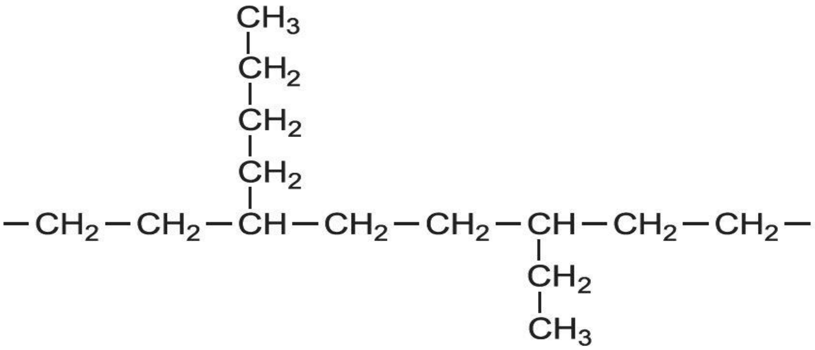
The process is operated under very high pressure (1000-3000 atm) at moderate temperatures (420-570 K) as may be predicted from the reaction equation:

$$nC_2H_4 \longrightarrow \left[CH_2 - CH_2 \right]_n \qquad \Delta H^{\ominus} = -92\ kJ\ mol^{-1}$$

This is a radical polymerizationprocess and an initiator, such as a small amount of oxygen, and/or an organic peroxide is used.

Ethene (purity in excess of 99.9%) is compressed and passed into a reactor together with the initiator. The molten poly(ethene) is removed, extruded and cut into granules. Unreacted ethene is recycled. The average polymer molecule contains 4000-40 000 carbon atoms, with many short branches.

For example,



There are about 20 branches per 1000 carbon atoms. The relative molecular mass, and the branching, influence the physical properties of LDPE. The branching affects the degree of crystallinity which in turn affects the density of the material. LDPE is generally amorphous and transparent with about 50% crystallinity. The branches prevent the molecules fitting closely together and so it has low density.

High density poly(ethene) (HDPE)

Two types of catalyst are used principally in the manufacture of HDPE:

a Ziegler-Natta organometallic catalyst (titanium compounds with an aluminium alkyl).

an inorganic compound, known as a Phillips-type catalyst. A well-known example is chromium(VI) oxide on silica, which is prepared by roasting a chromium(III) compound at *ca* 1000 K in oxygen and then storing prior to use, under nitrogen.

HDPE is produced by three types of process. All operate at relatively low pressures (10-80 atm) in the presence of a Ziegler-Natta or inorganic catalyst. Typical temperatures range between 350-420 K. In all three processes hydrogen is mixed with the ethene to control the chain length of the polymer.

i)Slurry process

The Ziegler-Natta catalyst, as granules, is mixed with a liquid hydrocarbon (for example, 2-methylpropane (isobutane) or hexane), which simply acts as a diluent. A mixture of hydrogen and ethene is passed under pressure into the slurry and ethene is polymerized to HDPE. The reaction takes place in a large loop reactor with the mixture constantly stirred (Figure 4). On opening a valve, the product is released and the solvent is evaporated to leave the polymer, still containing the catalyst. Water vapour, on flowing with nitrogen through the polymer, reactswith the catalytic sites, destroying their activity. The residue of the catalyst, titanium(IV) and aluminium oxides, remains mixed, in minute amounts, in the polymer.

Fabrics

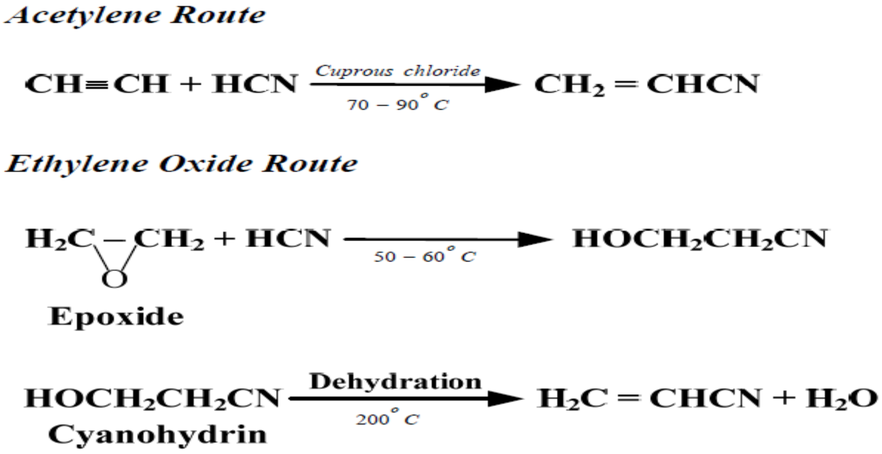
In general, the term fabric describes the way different parts of something work together to form a single entity. In this context, fabric is used as a metaphor to illustrate the idea that if someone were to document computer components and their relationships on paper, the lines would weave back and forth so densely that the diagram would resemble a woven piece of cloth.

The term fabric is commonly used to describe data or storage area networks (SANs). Increasingly, however, vendors are using the term to describe the servers, high-speed connections and switches that make up a cloud computing platform.

Acrylic fabrics

Acrylonitrile(CH_2=CH-CN)

Acrylic nitrile is one of the important monomer for manufacture of acrylic fibres, however,earlier routes of acrylonitrile manufacture by acetylene, ethylene oxide or acetaldehyde route hasbeing replaced by propylene route due to availability of cheaper propylene from steam crackerplant. This involves ammono-oxidation of propylene. Other uses of acrylonitrile are in themanufacture of nitrile rubber, ABS and SAN plastics, adiponitrile and acrylamide. In addition it is also used in the manufacture of acrylates, intermediates for flocculants, pharmaceuticals,antioxidants, dyes and surface active agents



Acrylonitrile (CH_2=CH-CN)

Acetaldehyde Route

$$CH_3CHO + HCN \longrightarrow CH_3CHOHCN$$

$$CH_3CHOHCN \xrightarrow{\text{Dehydration}} CH_2 = CHCN + H_2O$$

Propylene Route

$$CH_2 = CH - CH_3 + NH_3 + 3/2\ O_2 \xrightarrow[\text{400-500 }^{0}\text{C}]{\text{Ammoxidation}} CH_2 = CHCN$$

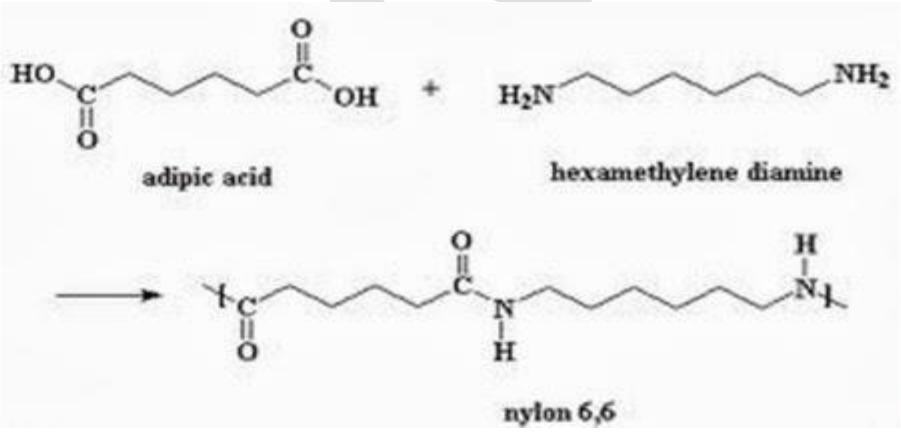
Uses

- Polyacrylontrile is a hard and high melting material
- It is used in the manufacture of orlon and Acrrilan fibres used for making clothes, carpets and blankets.
- It is blended with other polymers to improve their qualities.

Polyamide fabrics

Polyester

Nylon-66 (polyhexamethylene diamine adipamide) is a polyamide made from adipic acid and hexamethylenediamine by polycondensation. The resulting polymer is extruded into a wide range of fiber types. The fibers are drawn, or stretched, in a process that increases their length and reorients the material's molecules parallel to one another to produce a strong, elastic filament. The thermo-plasticity of nylon permits permanent crimping or texturing of the fibers and provides bulk and stretch properties.



Polyester

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 :

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

Rubbers

“Rubber” refers to elastomeric compounds that consist of various monomer units forming polymers that are heat cured (vulcanized). Polymers are long molecular chains that are connected together (cross-linked) to improve their toughness and resilience. The base monomer (or monomers, when blended) is used to classify the type of rubber. For example: Neoprene, SBR or Nitrile.

Natural Rubber

Natural rubber is an addition polymer that is obtained as a milky white fluid known as latex from a tropical rubber tree. Natural rubber is from the monomer isoprene (2-methyl-1,3-butadiene), which is a conjugated diene hydrocarbon as mentioned above. In natural rubber, most of the double fonds formed in the polymer chain have the Z configuration, resulting in natural rubber's elastomer qualities.

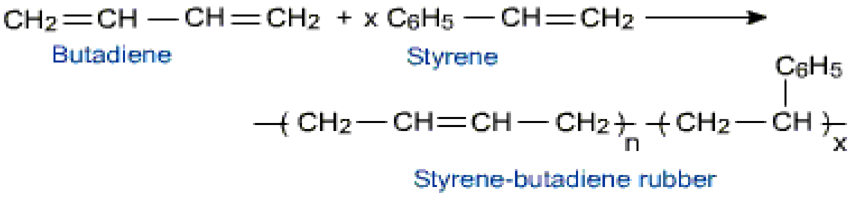
Synthetic Rubber

Important conjugated dienes used in synthetic rubbers include isoprene (2-methyl-1,3-butadiene), 1,3-butadiene, and chloroprene (2-chloro-1,3-butadiene). Polymerized 1,3-butadiene is mostly referred to simply as polybutadiene. Polymerized chloroprene was developed by DuPont and given the trade name Neoprene.

Natural Rubber-Buna –S Rubber

The synthesis of rubber in nature in somewhat similar the artificial synthesis of rubber except that it takes place within a plant. Instead of the 2-chloro-1,3-butadiene used in the synthesis of neoprene, natural rubber is synthesized from 2-methyl-1,3-butadiene. As an electrophile, the plant synthesizes the pyrophosphate 3-methyl-3-butenyl pyrophosphate is from phosphoric acid and 3-methyl-3-buten-1-ol. This pyrophosphate then catalyzes the reaction that leads to natural rubber.

The 3-methyl-3-butenyl pyrophosphate (OPP) is then used in the polymerization of natural rubber as it pulls electrons off 2-methyl-1,3-butadiene



$$CH_2{=}CH-CH{=}CH_2 + x\,C_6H_5-CH{=}CH_2 \longrightarrow -\!\!\left(CH_2-CH{=}CH-CH_2\right)_n\!\left(CH_2-\overset{\overset{\displaystyle C_6H_5}{|}}{CH}\right)_x$$

Neoprene

Neoprene or polychloroprene is a family of synthetic rubbers that are produced by polymerization of chloroprene. Neoprene is produced by free-radical polymerization of chloroprene. In commercial production, this polymer is prepared by free radical emulsion polymerization. Polymerization is initiated using potassium persulfate. Bifunctional nucleophiles, metal oxides (e.g. zinc oxide), and thioureas are used to crosslink individual polymer strands.

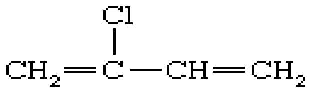
Uses

It can be used as a base for adhesives, noise isolation in power transformer installations, and as padding in external metal cases to protect the contents while allowing a snug fit. It resists burning better than exclusively hydrocarbon based rubbers, resulting in its appearance in weather stripping for fire doors and in combat related attire such as gloves and face masks. Because of its tolerance of extreme conditions, neoprene is used to line landfills. Neoprene's burn point is around 260°C (500°F). Neoprene foam is also used in many applications. Neoprene foam can be produced in either closed-cell or open-cell form. The closed-cell form is waterproof, less compressible and more expensive. The open-cell form can be breathable.

Chloroprene

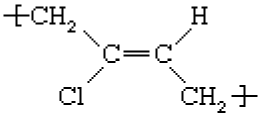
Polychloroprene is the polymer name for the synthetic rubber known as neoprene (a proprietary trade name of DuPont that has become generic). One of the first successful synthetic elastomers, neoprene was first prepared in 1931 by Arnold Collins, a chemist in Wallace Hume Carothers' research group at DuPont, while he was investigating by-products of divinylacetylene. It is a good general-purpose rubber, but it is limited to special-properties applications because of its high cost.

Polychloroprene is prepared by emulsionpolymerization of chloroprene, or 2-chlorobutadiene,



$CH_2{=}C(Cl){-}CH{=}CH_2$

which is obtained by the chlorination of butadiene or isoprene. Of the several structures adopted by the chloroprene repeating unit, the most common is *trans*-1,4 polychloroprene, which can be represented as follows:



Properties

This polymer tends to crystallize and harden slowly at temperatures below about 10° C (50° F). It also crystallizes on stretching, so that cured components are strong even without fillers. Because the double bond between the carbon atoms is shielded by the pendant atoms and CH_2 groups, the molecular interlinking necessary for producing a cured rubber is usually effected through the chlorine atom. The presence of chlorine in the molecular structure causes this elastomer to resist swelling by hydrocarbon oils, to have greater resistance to oxidation and ozone attack, and to possess a measure of flame resistance.

Applications

Principal applications are in products such as hoses, belts, springs, flexible mounts, and gaskets where resistance to oil, heat, flame, and abrasion are required.

Vulcanization

Vulcanization, chemical process by which the physical properties of natural or syntheticrubber are improved; finished rubber has higher tensile strength and resistance to swelling and abrasion, and is elastic over a greater range of temperatures. In its simplest form, vulcanization is brought about by heating rubber with sulfur.

In modern practice, temperatures of about 140°–180° C are employed, and in addition to sulfur and accelerators, carbon black or zinc oxide is usually added, not merely as an extender, but to improve further the qualities of the rubber. Anti-oxidants are also commonly included to retard deterioration caused by oxygen and ozone. Certain synthetic rubbers are not vulcanized by sulfur but give satisfactory products upon similar treatment with metal oxides or organic peroxides.

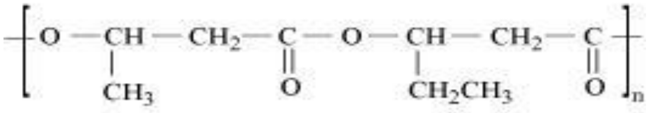
Biodegradable polymers

A polymer that can be decomposed by bacteria is called a biodegradable polymer.

The biodegradable polymer are the polymers which are degraded by the micro-organism within a suitable period so that biodegradable polymers & their degraded products do not cause any serious affects on the environment. They degrade by enzymatic hydrolysis & oxidation.The decomposition reactions involves hydrolysis(either enzymatically induced or by non –enzymatic mechanism) to non- toxic small molecules which can be metabolized by or excreted from the body.
The common examples of aliphatic biodegradable polymers are polyglycolic acid(PGA), Polyhydroxy butyrate (PHB), Polyhydroxy butyrates-co-beta hydroxyl valerate(PHBV), Polycaprolactone(pcl), Nylon-2-nylon-6.

These polymers are used mainly for medical goods such as surgical sutures, tissues in growth materials, for controlled drug release,plasma substitutes etc.They are also used in agriculture materials,such as films,seed coatings,fast food wrappers,personal hygiene products etc.

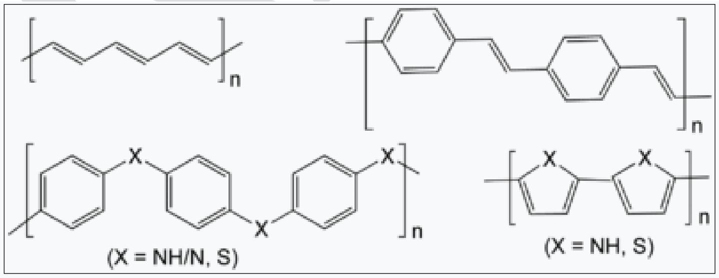
Poly-β-hydroxybutyrate-CO-β- hydroxyvalerate (PHBV) is a biodegradable aliphatic polyester.



$$\left[-O-\underset{CH_3}{CH}-CH_2-\overset{}{\underset{O}{\overset{\|}{C}}}-O-\underset{CH_2CH_3}{CH}-CH_2-\underset{O}{\overset{\|}{C}}- \right]_n$$

PHBV

Conductive polymer



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 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 double bonds	• **Poly(p-phenylene vinylene) (PPV)**		

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.

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.

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.

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. 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.

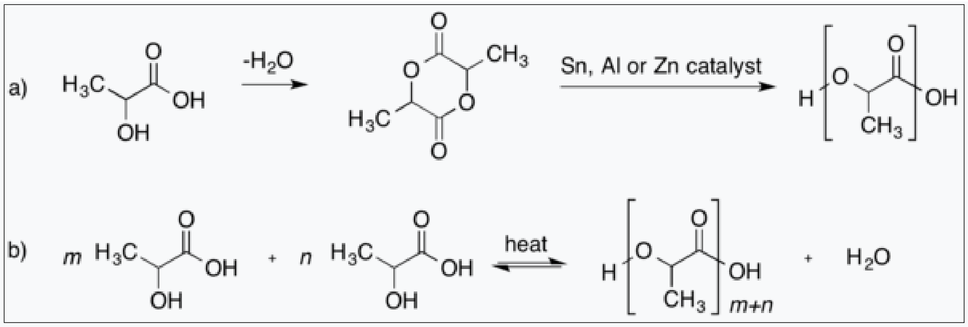
Other properties of biodegradable polymers that are common among those used for medicinal usages include

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.

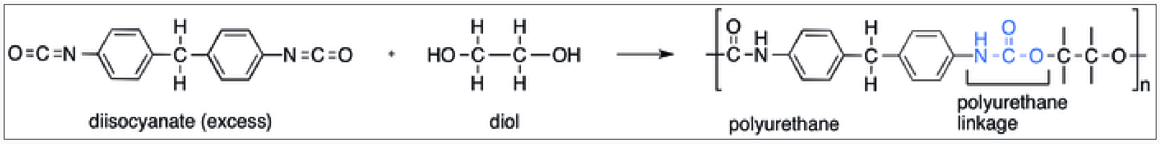
Synthesis

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. 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. 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). 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. 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. 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. 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. 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.

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.

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.

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.

TEXT BOOK

T1: F.W. Billmeyer.(1972). *Text Book of Polymer Science*. 1984, ^{3d} Edition, John Wiley and sons, Delhi.

REFERENCE BOOK

R1: *V.R.Gowariker, N.V.Viswanathan and Jayadev sreedhar, polymer science, (2014),* New Age international publishers, New Delhi.

WEB SITE

W1: WW.rsc.org/polymer/,https://en.wikipedia.org/wiki/IUPAC_polymer_nomenclature

W2: https://en.wikipedia.org/wiki/

UNIT-V-POSSIBLE QUESTIONS

PART-A (20 MARKS)

(Q.NO 1 To 20 Online Examination)

PART-B (2 MARKS)

1. What is SBR? How is it synthesized?

2) Write the preparation and uses of PVC.

3) Write the preparation and uses of phenol-formaldehyde.

4) Write the preparation and uses of fluoro polymers.

5) How will you prepare polyethene?

6) Define vulcanization.

7) Write the thermal behaviour of polymers.

PART-C (6 Marks)

(Either or type Questions)

1) How will you classify polymers on the basis of their thermal behaviour?

2) Give the preparation and uses of i) Polyethene ii) Polyester
iii) Phenol- formaldehyde iv) PolyStyrene

3) Give the preparation and uses of i) poly(p-phenylene sulphide) ii) polypyrrole iii) polythiophene

4) Write the synthesis and applications of (i)Polythene (ii)Buna-S rubber (iii) Polyurethanes

5) Write the synthesis, structure and applications of polyamide polymers

6) Write the preparation, properties, structure and uses of i)polyacetylene ii)polyaniline

KARPAGAM ACADEMY OF HIGHER EDUCATION

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

Coimbatore – 641 021.

UNIT-V- MULTIPLE CHOICE QUESTIONS

DEPARTMENT OF CHEMISTRY
B.Sc CHEMISTRY

STAFF NAME : **Dr. M.MAKESWARI**
SUBJECT NAME : **POLYMER CHEMISRY**
SUB. CODE : **16CHU502A**
SEMESTER : **V**
CLASS : **III- B. Sc-CHEMISTRY**

S.No	Questions	Option 1	Option 2	Option 3	Option 4	Answer
1	Which is soluble only in specific solvents?	Fibres	Polymers	Nylon	Hydrophobic fibres	Polymers
2	Cellulose acetate, polyacrylonitrile, and polyurethane are spun by this technique?	Melt spinning	Dry spinning	Wet spinning	Spinning	Dry spinning
3	Nylon ends in?	Building	Ropes	Chair	Watch	Ropes
4	Which one of the following is a polyamide?	Terylene	Nylon 6	Cotton	Watch	Nylon 6
5	Synthetic fibers are consisting of?	Linear	Nonlinear	Copolymers	Chain polymers	Linear polymers

		polymers	polymers			
6	The alkyd resins are condensation polymers obtained from dibasic acids and	Glycol	Phenol	Acetaldehyde	Benzaldehyde	Phenol
7	Nylon threads are made of	Polyester polymer	Polyamide polymer	Polyvinyl chloride	Acrylic polymer	Polyamide polymer
8	Acrylic resins are	Brown colour	Colourless	Gold colour	White colour	Colourless
9	Which one of the following can be polymerised to polythene	Ethylene	Ethyl amide	Ethyl ketone	Ethyl acetate	Ethylene
10	Hydrolysis of cellulose gives	D-glucose	L- glucose	D-fructose	L-fructose	D-glucose
11	Orlon is a polymer of	Polyamide	Polyester	Hydrophobic fibre	Acrylic fibre	Acrylic fibre
12	Condensation product of caprolactum is	Nylon 6	Cotton	Nylon 6,10	Nylon 66	Nylon 6
13	Nylon is a example of	condensation polymer	copolymer	coordination polymer	chain polymer	condensation polymer
14	The DPPD is the	Diphenyl phenylene diamine	Diphenyl phenylene diamide	Diphenyl phospho diamine	Diphenyl phospho diamine	Diphenyl phenylene diamine
15	PBNA is the	phenylα naphthyl amine	phenyl ρ naphthalene amide	phenyl β naphthyl amine	phenyl γ naphthyl amine	phenyl β naphthyl amine
16	The PBNA is the standard	anti-oxidant	anti-toxin	anti-malarial	anti-poisionus	anti-oxidant
17	Which one of the following is used as the staining anti-oxidant	DPPD	PBNA	TCS	TMS	PBNA
18	TCS is the example of the	Standard anti-oxidant	non standard anti-oxidant	staining anti-oxidant	non-staining anti oxidant	non-staining anti oxidant
19	The rayon also known as	nylon	orelon	viscose	resin	viscose
20	The rayon polymers belongs to the	silicon	epoxy	organic polymer	rubber	silicon polymers

		polymers	polymers			
21	Which one of the following should give the strength to the paper	urea-formaldehyde	phenol-formaldehyde	polysulphides	polychloroprene	urea-formaldehyde
22	Which one of the following is used as a core binders	urea-formaldehyde	phenol-formaldehyde	polysulphides	polychloroprene	phenol-formaldehyde
23	Which one of the following is used as fuel material	urea-formaldehyde	phenol-formaldehyde	polysulphides	polychloroprene	polysulphides
24	which one of the following is used to coating the wires and cables	urea-formaldehyde	phenol-formaldehyde	polysulphides	polychloroprene	polychloroprene
25	Which one of the following is used as the insulation material in electrical industry	urea-formaldehyde	phenol-formaldehyde	polybutadiene	polysulphides	polybutadiene
26	Which one of the following is consider as lifesaving substance	urea-formaldehyde	phenol-formaldehyde	polybutadiene	polyvinyl pyrrolidine	polyvinyl pyrrolidine
27	Which one of the following is used in the paints and surface coatings	polybutadiene	polysulphides	polyvinyl pyrrolidine	polyvinyl fluoride	polyvinyl fluoride
28	Which one of the following is used to form the thermoplastic material	polyvinylidene chloride	PVC	polybutadiene	polysulphides	polyvinylidene chloride
29	Which one of the following is the liquid resins	PPG	PVC	PEG	PABA	PPG
30	PEG also known as	alcowax	carbowax	hydrowax	rubber	carbowax
31	Which one of the following is used as the surface coating in the supersonic airgraft	polyamines	polyamides	polyimides	polyvinyls	polyimides
32	Which one of the following is used to making the toys	HDPE	LDPE	PPG	PEG	HDPE
33	Nylon is not a?	Homo polymer	Polyamide	Caprolactum	Condensation polymer	Homo polymer
34	Which is more flexible than HDPE due to lower crystallinity?	Polyethylene	Low Density Polyethylene	Polyamide	Low density polyamide	Low Density Polyethylene
35	80-90% of all plasticizers used with?	DOP	DIOP	PVC	Colourants	PVC

36	It must not exude from the plastic material?	Primary plasticizers	Secondary plasticizers	Antioxidents	Colourants	Primary plasticizers
37	Limited compatibility with the polymers are?	Primary plasticizers	Secondary plasticizers	Antioxidents	Colourants	Secondary plasticizers
38	Inhibiting the oxidation of polymers is usually filled by a substance which itself is readily oxidized.	Antioxidants	Flame retardants	Colourants	Mgo	Antioxidants
39	In polymer industry 2-hydroxybenzophones are used as	Light stabilizers	Antioxidants	Polymer initiators	Fillers	Light stabilizers
40	The addition of polyethylene glycol in dielectric property significantly improves?	Electrolytic conductivity	Dielectric conductivity	Electric conductivity	Ionic conductivity	Ionic conductivity
41	Melamine is	White crystaline solid	Gas	Colourless liquid	Yellow liquid	White crystaline solid
42	Plastics are?	Hydrocarbons	Aldehyde	Ester	Amide	Hydrocarbons
43	Which one is an inorganic pigment?	Barium sulfate	Perylenes	Pyrroles	Arylamides	Barium sulfate
44	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
45	Which one is more active flame retardant?	Aluminum hydroxide	Antimony oxychloride	Phosphorous	Halogen compounds	Antimony oxychloride
46	The most useful material imparting flame retardance to plastics is?	Antimony trioxide	Aluminum hydroxide	Halogen compounds	Antimony oxychloride	Antimony trioxide
47	Which one of the following flame retardant forms a gas shield layer?	Calcium	Phosphorous	Ammonium	Aluminium oxide	Phosphorous
48	Which one of the following flame retardant breaks down endothermic reaction?	Phosphorous	Ammonium	Aluminium oxide	Aluminum Hydroxide	Aluminum Hydroxide
49	Which one of the compound is used in	Vinyl chloride	Ethylene	Vinyl alcohol	Ethylene	Ethylene glycol

	the manufacture of terylene?		glycol			
50	Which one of the following is an example of condensation polymer?	Terylene	PVC	Vinyl alcohol	Ethylene	Terylene
51	The synthetic polymer which resembles natural rubber is?	Cotton	Nylon	Chloroprene	Neoprene	Neoprene
52	Which one is prepared by the melt polycondensation between dicarboxylic acids and diamides.	Polyamides	Polyester	Acrylic fibre	Polyethylene	Polyamides
53	Aliphatic polyamides are generally known as?	Cotton	Nylon	Polyamide	Polyester	Nylon
54	Which one of the following is obtained from dibasic acids and diamides.	Cotton	Nylon	Polyamide	Polyester	Nylon
55	The ring opening polymerization of lactometated is represented only by?	Single number	Double number	Triple number	No number	Single number
56	It has good tensile strength and abrasion resistance	Polyamides	Polyester	Acrylic fibre	Polyethylene	Polyamides
57	It is used as a plastic as well as a fibre	Polyamides	Polyester	Acrylic fibre	Polyethylene	Polyamides
58	Which one is used in tires and ropes?	Cotton	Nylon	Polyamide	Polyester	Nylon
59	Which is used in clothes, belts and accessories?	Cotton	Nylon	Polyamide	Polyester	Nylon
60	PVC 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

[6CHU502A] **Reg. No…………..**

KARPAGAM ACADEMY OF HIGHER EDUCATION

COIMBATORE-641 021

(For the candidates admitted from 2016 & Onwards)

B.Sc., DEGREE INTERNAL EXAMINATION, JULY 2018

CHEMISTRY

POLYMER CHEMISTRY

Time: 2 Hours **Maximum :50 marks**

<u>PART A</u> (20 x 1 =20)

Answer all Questions

1. Polyvinyl chloride was commercially introduced in?
(a)1943 (b)1930 **(c)1936** (d)1947

2. Which of the following is an example of condensation polymer?
(a)PVC (b) Polyamide **(c) Terylene** (d)Polyester

3. Which of the following is a example of bifunctional monomer
(a)methyl isonate (b) acetylene (c) malic acid **(d)glycine**

4. Which of the following is the functionality of Gallic acid
(a)monofunctional (b)bifunctional
(c) tetra functional (d) tri functional

5. Monomers show high selectivity towards?
(a)Cationic initiators (b)Cationic and anionic initiators
(c)Ionic initiators (d)Anionic initiators

6. Most monomers will undergo polymerization with a radical initiator, although at?
(a)Varying rates (b)Reliable rates (c)Stable rates (d)Positive rates

7. Polymers are?
(a)Large molecule (b)Small molecule
(c)Small chain molecule **(d)Large chain molecule**

8. The alternating copolymer contains?
(a)2 monomer units (b)3 monomer units
(c)4 monomer units (d)1 monomer units

9. Monomer concentration decreases steadily throughout reaction in?

(a)Step polymerization **(b)Ionic polymerization**

(c)Radical polymerization (d)Self catalysted polymerization

10. Styrene(butadiene rubber) was commercially introduced during the year

(a)1943 **(b)1930** (c)1936 (d)1947

11. Polyvinyl acetate is insoluble in which solvent?

(a)Alcohols (b) Aromatic solvents (c) Esters **(d)Water**

12. Polythene was first synthesized in?

(a)1877 (b)1853 (c) 1890 **(d) 1898**

13. Polythene was first produced in?

(a)German **(b)England** (c) India (d)USA

14. Polyethylene was first synthesized by?

(a)Pechmann (b) Fawcett (c)Karl ziegler (d)Walter

15. Which of the following polymer type is not classified on the basis of its application and properties?

(a) rubbers (b) plastics (c) fibres **(d) synthetic**

16. Which of the following is a thermosetting polymer?

(a) polystyrene (b) polyolefins (c) nylons **(d)phenolic resins**

17. What is the range of tensile strength, exhibited by fibres?

(a) 300-3,000 (b) 4,000-15,000 (**c) 20,000-150,000** (d) 5,000-10,000

18. Which of the following kind of polymers are known for their high crystallinity?

(a)isotactic (b)syndiotactic (c)atactic (d)iso-atactic

19. Which of the following byproduct is released when an amine reacts with acid chloride?

(a) HCl (b)H_2O (c)NH_3 (d) SO_2

20. Which of the following category does cellulose nitrate fall into?

(a) natural (b)synthetic (c) **semi-synthetic** **(d)** Fibre

PART B

Answer All the Questions (3x2=6)

21. Define Degree of polymerization.

22. What do you mean by the ‘Addition polymerization” Give two examples?

23. Write a note on molecular forces in polymers.

PART C

Answer All the Questions (3x8=24)

24. a) How will you classify polymers on the basis of their physical properties.

(OR)

b) Based on structure, how polymers are classified?

25. a) Explain the solution polymerization technique. Write their advantages and disadvantages also.

(OR)

b) How will you synthesis polymers using emulsion polymerization technique?

26. a) Give mechanism of step growth polymerization.

(OR)

b) Discuss the mechanism of one of the type of radical chain growth polymerization.

[6CHU502A] **Reg. No……………**

KARPAGAM ACADEMY OF HIGHER EDUCATION

COIMBATORE-641 021

(For the candidates admitted from 2016 & Onwards)

B.Sc., DEGREE INTERNAL EXAMINATION, JULY 2018

CHEMISTRY

ANSWER KEY -POLYMER CHEMISTRY

Time: 2 Hours **Maximum :50 marks**

PART A (20 x 1 =20)

Answer all Questions

1. (c)1936
2. (c) Terylene
3. (d)glycine
4. (c) tetra functional
5. (c)Ionic initiators
6. (a)Varying rates
7. (d)Large chain molecule
8. (a)2 monomer units
9. (b)Ionic polymerization
10. (b)1930
11. (d)Water
12. (d) 1898
13. (b)England
14. (a)Pechmann
15. (d) synthetic
16. (d)phenolic resins
17. (c) 20,000-150,000
18. (a)isotactic
19. (a) HCl
20. (c) semi-synthetic

PART B

Answer All the Questions (3x2=6)

21. Degree of polymerization.

The degree of polymerization, is the number of monomeric units in a macromolecule or polymer or oligomer molecule. ... an oligomer molecule, a block, or a chain.

It is represented by the symbol Dp.

22. Addition polymerization

In addition polymerization, monomers react to form a polymer without the formation of by-products. Addition polymerizations usually are carried out in the presence of catalysts.

Example : PVC, Poly ethylene.

23. Molecular forces in polymers.

The intermolecular forces for polymers are the same as for small molecules. Because polymer molecules are so large, though, the magnitude of their intermolecular forces can vastly exceed those between small molecules.

The presence of strong intermolecular forces is one of the main factors leading to the unique physical properties of polymers.

Types of forces

1. Dispersion Forces
2. Dipole-Dipole Forces
3. Hydrogen Bonds

PART C

Answer All the Questions (3x8=24)

24. a) classification of polymers on the basis of their physical properties.

Depending on its ultimate form and use a polymer can be classified as

Rubber(Elastomers):- Rubber is high molecular weightpolymer with longflexible chains and weak intermolecular forces. They exhibits tensile strength in the range of 300-3000 psi and elongation at break ranging between 300-1000% . Examples are natural and syntheticrubber.

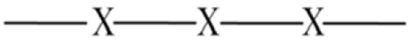
Plastics:- Plastics are relatively tough substances with high molecular weight that can be molded with (or without) the application of heat. These are usually much stronger than rubbers. They exhibit tensile strength ranging between 4000-15000 psi and elongation at break ranging usually from 20 to 200% or even higher. The examples of plastics are, polyethylene, polypropylene, PVC, polystyrene,etc.

Fibers:-Fibers are long- chain polymers characterized by highly crystalline regions resulting mainly from secondary forces. They have a much lower elasticity than plastics and elastomers. They also have high tensile strength ranging between 20,000- 150,000 psi., are light weight and possess moisture absorption properties.

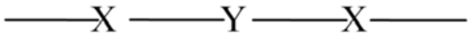
b) Classification of polymers on the basis of their structure

On the basis of structure, polymers are of three types.

Linear polymer:- If the monomer units are joined in a linear fashion, polymer is said to be linearpolymer.

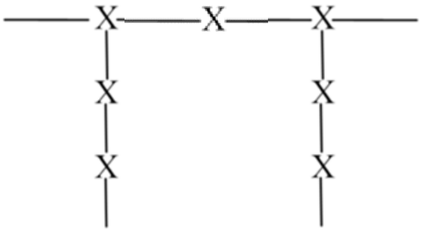


Linear Homopolymer

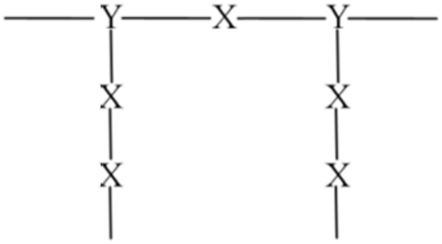


Linear Copolymer

Branched polymer:-monomer units are joined in branched manner, it isWhen called branchedpolymer.

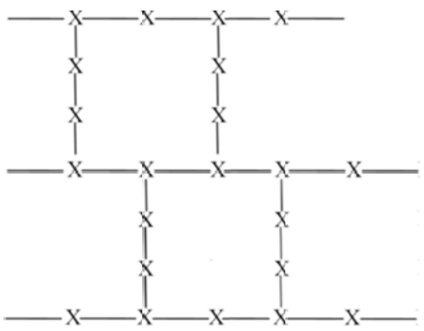


Branched Homopolymer

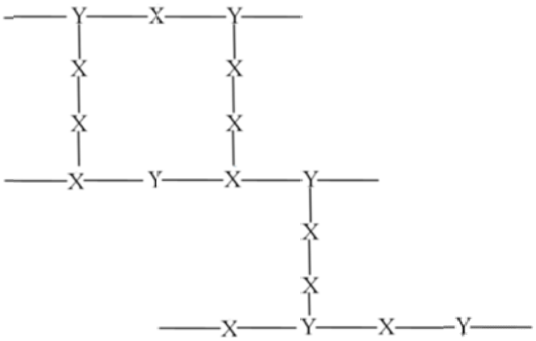


Branched Copolymer

Cross linked polymer:- A polymer is said to be a cross linked polymer, if the monomer units are joined together in a chain fashion.



Crosslinked Homopolymer



Cross linked Copolymer

25. a) Solution polymerization technique

The mixture is kept at polymerizaion temperature′Monomer along with initiator dissolved in solvent, formed polymer stays dissolved. ′ Some disadvantages of bulk polymerization are eliminated in solution polymerization. ′

Depending on concentration of monomer the viscosity of solution does not increase.′constantly agitated.

It is used for the production of Polyacrylonitrile, PVC, Polyacrylic acid, Polyacrylamide, Polyvinyl alcohol, PMMA, Polybutadiene, etc′ Polymer so formed can be used for surface coating. ′After the reaction is over, the polymer is used as such in the form of polymer solution or the polymer is isolated by evaporating the solvent.

Solution Polymerization Is Very Suitable For Polycondensation Reaction Which Requires Higher Temperature . It Is Used On Large Industrial Scale.

Advantages

- The solvent acts as a diluent & helps in facilitating continuous transfer of heat of polymerization. Therefore temperature control is easy.
- The solvent allows easy stirring as it decreases the viscosity of reaction mixture. • Solvent also facilitates the ease of removal of polymer from the reactor.
- Viscosity build up is negligible.

Disadvantages

- To get pure polymer, evaporation of solvent is required additional technology, so it is essential to separate & recover the solvent.
- The method is costly since it uses costly solvents.
- Polymers of high molecular weight polymers cannot be formed as the solvent molecules may act as chain terminators.
- The technique gives a smaller yield of polymer per reactor volume, as the solvent waste the reactor space. • The purity of product is also not as high as that of bulk polymerization. Removal of last traces of solvent is difficult.

b) How will you synthesis polymers using emulsion polymerization technique?

Emulsion polymerization is a type of radical polymerization that usually starts with an emulsion incorporating water, monomer, and surfactant. The most common type of emulsion polymerization is an oil-in-water emulsion, in which droplets of monomer (the oil) are emulsified (with surfactants) in a continuous phase of water. Water-soluble polymers, such as certain polyvinyl alcohols or hydroxyethyl celluloses, can also be used to act as emulsifiers/stabilizers. The name "emulsion polymerization" is a misnomer that arises from a historical misconception. Rather than occurring in emulsion droplets, polymerization takes place in the latex/colloid particles that form spontaneously in the first few minutes of the process. These latex particles are typically 100 nm in size, and are made of many individual polymer chains. The particles are stopped from coagulating with each other because each particle is surrounded by the surfactant, the charge on the surfactant repels other particles electrostatically. When water-soluble polymers are used as stabilizers instead of soap, the repulsion between particles arises because these water-soluble polymers form a 'hairy layer' around a particle that repels other particles, because pushing particles together would involve compressing these chains.

Emulsion polymerization is used to manufacture several commercially important polymers. Many of these polymers are used as solid materials and must be isolated from the aqueous dispersion after polymerization. In other cases the dispersion itself is the end product.

Advantages

- High molecular weight polymers can be made at fast polymerization rates. By contrast, in bulk and solution free-radical polymerization, there is a tradeoff between molecular weight and polymerization rate.
- The continuous water phase is an excellent conductor of heat, enabling fast polymerization rates without loss of temperature control.
- Since polymer molecules are contained within the particles, the viscosity of the reaction medium remains close to that of water and is not dependent on molecular weight.
- The final product can be used as is and does not generally need to be altered or processed.

Disadvantages

- Surfactants and other polymerization adjuvants remain in the polymer or are difficult to remove
- For dry (isolated) polymers, water removal is an energy-intensive process
- Emulsion polymerizations are usually designed to operate at high conversion of monomer to polymer. This can result in significant chain transfer to polymer.
- Can not be used for condensation, ionic, or Ziegler-Natta polymerization, although some exceptions are known.

26. a) Give mechanism of step growth polymerization.

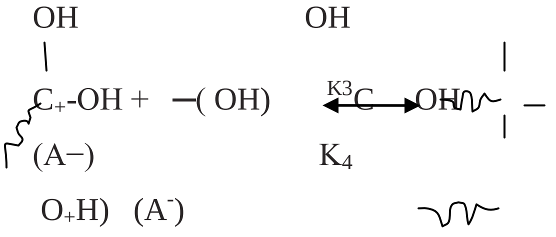
A monomer with functionality of 3 or more will introduce branching in a polymer and will ultimately form a cross-linked macrostructure or network even at low fractional conversion. The point at which a tree-like topology transits to a network is known as the gel point because it is signalled by an abrupt change in viscosity. One of the earliest so-called thermosetsis known as bakelite. It is not always water that is released in step-growth polymerization: in acyclic diene metathesis or ADMET dienes polymerize with loss of ethylene.

KINETICS OF STEP 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,

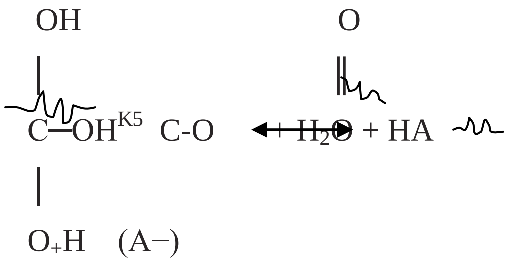
$$\sim(C{-}OH) + HA \underset{K_2}{\overset{K_1}{\rightleftharpoons}} (HO{-}C_+{-}OH(A^-)) \qquad 2.12$$

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



$$\overset{OH}{\underset{(A-)}{C_+}}{-}OH + \sim(OH) \underset{K_4}{\overset{K_3}{\rightleftharpoons}} \overset{OH}{\underset{O_+H)\ (A^-)}{C}}{-}OH\sim \qquad 2.13$$

II



$$\sim\overset{OH}{\underset{O_+H\ \ (A-)}{C}}{-}OH\sim \overset{K_5}{\rightleftharpoons} \overset{O}{\overset{\|}{C}}{-}O\sim + H_2O + HA \qquad 2.14$$

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. 2-14).

Under these conditions the kinetics of polymerization can be handled by considering the reactions in Eqs. 2-13 and 2-14 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. 2-13 and 2-14 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

$$R= -d[COOH]/dt \quad = k_3[C^+(OH)_2][OH] \qquad 2.15$$

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 2-15 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

$$K = k_1/k_2 = [C^+(OH)_2] / [COOH][HA] \qquad 2.16$$

for the protonation reaction (Eq. 2-12). Combination of Eqs. 2-15 and 2-16 yields

$$-d[COOH]/dt = k_3K[COOH][OH][HA] \qquad 2\text{-}17$$

Two quite different kinetic situations arise from Eq. 2-17 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. 2-17 can be written in the usual form [Flory, 1953]

$$-d[\mathrm{COOH}]/dt = k[\mathrm{COOH}]^2\,[\mathrm{OH}] \qquad \text{2-18}$$

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. 2-18 can be written as

$$-d[M]/dt = k[M]^3 \qquad \text{2-19a}$$

Or

$$-d[M]/[M]^3 = kdt \qquad \text{2-19b}$$

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

Integration ofEq. 2-19b yields

$$2kt = 1/[M]^2 - 1/[M_0]^2 \qquad \text{2-20}$$

where $[M_0]$ is the initial (at t = 0) concentration of hydroxyl or carboxyl groups. It is convenient at this point to write Eq. 2-20 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

$[M]=[M_0]-[M_0]p=[M_0](1-p)$ 2-21

Combination of Eqs. 2-20 and 2-21 yields

$1/(1-p)^2=2[M_0]^2kt+1$ 2-22

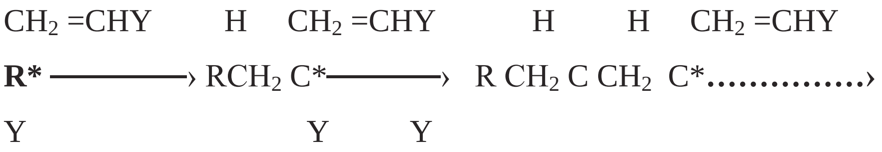
b) Mechanism of radical chain growth polymerization.

RADICAL CHAIN POLYMERIZATION

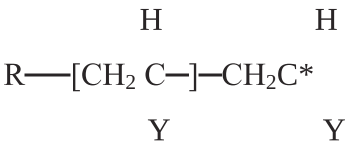
In the previous chapter, the synthesis of polymers by step polymerization was considered. Polymerization of unsaturated monomers by chain polymerization will be discussed in this and several of the subsequent chapters. Chain polymerization is initiated by a reactive species R* produced from some compound I termed an initiator:

$\mathbf{I\rightarrow\rightarrow R^*}$ 3-1

The reactive species, which may be a free radical, cation, or anion, adds to a monomer molecule by opening the p-bond to form a new radical, cation, or anion center, as the case may be. The process is repeated as many more monomer molecules are successively added to continuously propagate the reactive center:



$$\underset{Y}{\mathbf{R^*}} \xrightarrow{CH_2=CHY} RCH_2\underset{Y}{\overset{H}{C^*}} \xrightarrow{CH_2=CHY} RCH_2\overset{H}{C}CH_2\underset{Y}{\overset{H}{C^*}}\ldots\ldots\ldots\ldots\ldots\rightarrow$$



$$R-[CH_2\underset{Y}{\overset{H}{C}}-]-CH_2\underset{Y}{\overset{H}{C^*}}$$ 3.2

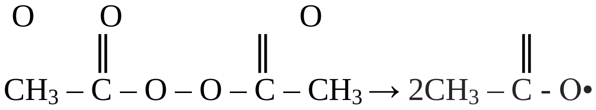
Polymer growth is terminated at some point by destruction of the reactive center by an appropriate reaction depending on the type of reactive center and the particular reaction conditions.

INITIATION

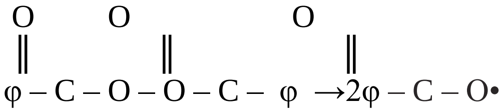
The derivation of Eq. 3-25 is general in that the reaction for the production of radicals (Eq. 3-13) is not specified and the initiation rate is simply shown asRi. Avariety of initiator systemscan be used to bring about the polymerization. (The term catalyst is often used synonomouslywith initiator, but it is incorrect in the classical sense, since the initiator is consumed.The use of the term catalyst may be condoned since very large numbers of monomer moleculesare converted to polymer for each initiator molecule that is consumed.) Radicals can beproduced by a variety of thermal, photochemical, and redox methods [Bamford, 1988;Denisova et al., 2003; Eastmond, 1976a,b,c; Moad et al., 2002]. In order to function as auseful source of radicals an initiator system should be readily available, stable under ambientor refrigerated conditions, and possess a practical rate of radical generation at temperatures
which are not excessive (approximately <150_C).

Types of Initiators

The thermal, homolytic dissociation of initiators is the most widely used mode of generatingradicals to initiate polymerization–for both commercial polymerizations and theoretical studies.Polymerizations initiated in this manner are often referred to as thermal initiated orthermal catalyzed polymerizations. The number of different types of compounds that can beused as thermal initiators is rather limited. One is usually limited to compounds with bonddissociation energies in the range 100–170 kJ mol^{-1}. Compounds with higher or lower dissociationenergies will dissociate too slowly or too rapidly. Only a few classes of compounds—including those with O─O, S─S, or N─O bonds–possess the desired range ofdissociation energies. However, it is the peroxides which find extensive use as radicalsources. The other classes of compounds are usually either not readily available or not stableenough. Several different types of peroxy compounds are widely used [Sheppard, 1988].These are acyl peroxides such as acetyl and benzoyl peroxides

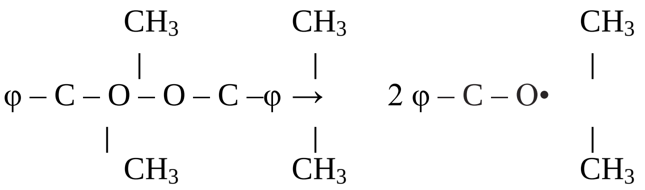


$$CH_3-\overset{O}{\overset{\|}{C}}-O-O-\overset{O}{\overset{\|}{C}}-CH_3 \rightarrow 2CH_3-\overset{O}{\overset{\|}{C}}-O\bullet \qquad 3.26a$$



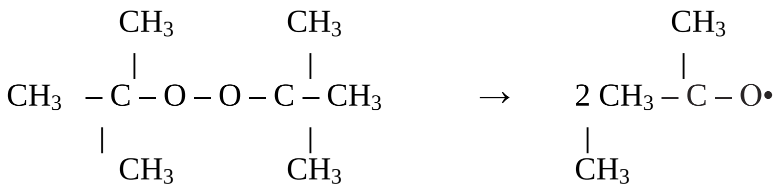
$$\varphi-\overset{O}{\overset{\|}{C}}-O-O-\overset{O}{\overset{\|}{C}}-\varphi \rightarrow 2\varphi-\overset{O}{\overset{\|}{C}}-O\bullet \qquad 3.26b$$

alkyl peroxides such as cumyl and t-butyl peroxides



$$\varphi - \underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{C}}} - \mathrm{O} - \mathrm{O} - \underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{C}}} - \varphi \rightarrow 2\ \varphi - \underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{C}}} - \mathrm{O}\bullet$$

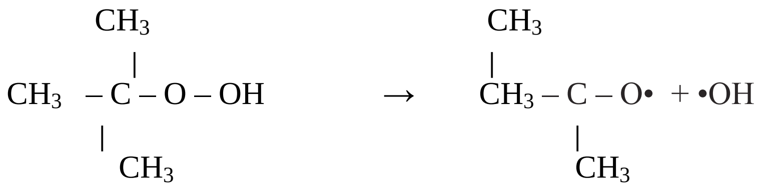
3.26c



$$\mathrm{CH_3} - \underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{C}}} - \mathrm{O} - \mathrm{O} - \underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{C}}} - \mathrm{CH_3} \rightarrow 2\ \mathrm{CH_3} - \underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{C}}} - \mathrm{O}\bullet$$

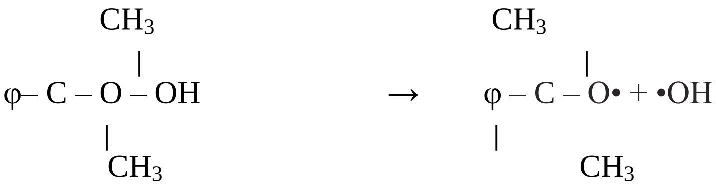
3.26d

hydroperoxides such as t-butyl and cumyl hydroperoxides



$$\mathrm{CH_3} - \underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{C}}} - \mathrm{O} - \mathrm{OH} \rightarrow \mathrm{CH_3} - \underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{C}}} - \mathrm{O}\bullet + \bullet\mathrm{OH}$$

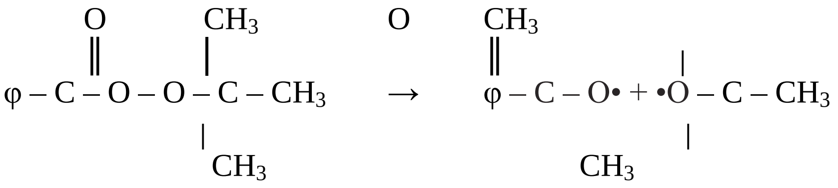
3.26e



$$\varphi - \underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{C}}} - \mathrm{O} - \mathrm{OH} \rightarrow \varphi - \underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{C}}} - \mathrm{O}\bullet + \bullet\mathrm{OH}$$

3.26f

and peresters such as t-butyl perbenzoate:



$$\varphi - \overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}} - \mathrm{O} - \mathrm{O} - \underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{C}}} - \mathrm{CH_3} \rightarrow \varphi - \overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}} - \mathrm{O}\bullet + \bullet\mathrm{O} - \underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{C}}} - \mathrm{CH_3}$$

3.26g

Other peroxides used to initiate polymerization are acyl alkylsulfonyl peroxides (Va), dialkylperoxydicarbonates (Vb), diperoxyketals (Vc), and ketone peroxides (Vd).

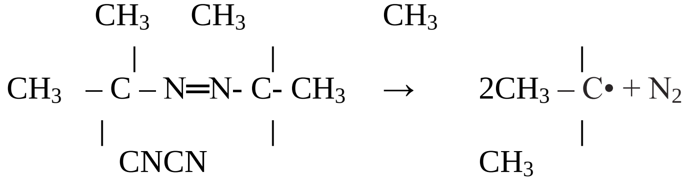
$\mathrm{R\text{-}\ SO_2\text{-}OO\text{-}CO\text{-}R'}$ **Va**

$\mathrm{RO\ –CO\text{-}\ OO\text{-}\ CO\text{-}\ OR}$ **Vb**

$\mathrm{(ROO)_2C(R')_2}$ **Vc**

$\mathrm{RR'C(OOH)_2}$ **Vd**

Aside from the various peroxy compounds, the main other class of compound used extensivelyas initiators are the azo compounds. 2,20-Azobisisobutyronitrile (AIBN) is themost important member of this class of initiators, although other azo compounds such as



$$CH_3-\underset{CN}{\overset{CH_3}{C}}-N{=}N-\underset{CN}{\overset{CH_3}{C}}-CH_3 \rightarrow 2CH_3-\underset{CH_3}{\overset{CH_3}{C}}\bullet + N_2 \qquad 3.26h$$

2,2′-azobis(2,4-dimethylpentanenitrile), 4,40-azobis(4-cyanovaleric acid), and 1,10-azobis(cylohexanecarbonitrile)are also used [Sheppard, 1985]. The facile dissociation of azo compoundsis not due to the presence of a weak bond as is the case for the peroxycompounds. The C─N bond dissociation energy is high (~290 kJ mol -^{1}), but the drivingforce for homolysis is the formation of the highly stable nitrogen molecule.

Among other initiators that have been studied are disulfides

$$RS-SR \longrightarrow 2RS\bullet \qquad 3\text{-}26i$$

and tetrazenes

$$R_2N-N=N-NR_2 \longrightarrow 2R_2N\bullet + N_2 \qquad 3\text{-}26j$$

[Oda et al., 1978; Sato et al., 1979a,b].

The various initiators are used at different temperatures depending on their rates ofdecomposition. Thus azobisisobutyronitrile (AIBN) is commonly used at 50–70^{O}C, acetylperoxide at 70–90^{O}C, benzoyl peroxide at 80–95^{O}C, and dicumyl or di-t-butyl peroxide at120–140^{O}C. The value of the decomposition rate constant kd varies in the range10^{-4}-10^{-9} s^{-1},depending on the initiator and temperature [Eastmond, 1976a,b,c]. Mostinitiators are used at temperatures where kd is usually 10^{-4}–10$^{-6s-1,}$ The great utilityof peroxide and azo compounds results from the availability in stable form of many differentcompounds with a range of use temperatures.The differences in the rates of decomposition of the various initiators are related to differencesin the structures of the initiators and of the radicals produced. The effects of structureon initiator reactivity have been discussed elsewhere [Bamford, 1988; Eastmond,1976a,b,c; Sheppard, 1985, 1988]. For example, *kd*is larger for acyl peroxides than for alkylperoxides since the RCOO•radical is more stable than the RO•radical and for R-N=N-R, kd increases in the order R =allyl, benzyl >tertiary >secondary >primary [Koenig, 1973].

The differences in the decomposition rates of various initiators can be convenientlyexpressed in terms of the initiator half-life t(1/2) defined as the time for the concentration ofI to decrease to one half its original value. The rate of initiatordisappearance by Eq. 3-13 is

$$-d[I]/dt=K_d[I] \qquad 3\text{-}27$$

which on integration yields

$$[\,I\,] = [\,I\,]_O\, e^{-Kd\,t} \qquad 3\text{-}28a$$

or

$\ln([I]_o/[I]) = K_d t$ 3-28b

where $[I]_0$ is the initiator concentration at the start of polymerization. T(1/2) is obtained as

$t1/2 = 0{:}693/\ k_d$ 3-29

by setting$[I] = [I]_0/2$.

Half-Lives of Initiators^{a,b}$_{;}$ atvarious temp,

[16CHU502A] **Reg. No……………**

KARPAGAM ACADEMY OF HIGHER EDUCATION

COIMBATORE-641 021

(For the candidates admitted from 2016 & Onwards)

B.Sc., DEGREE INTERNAL EXAMINATION, SEPTEMBER 2018

CHEMISTRY

INTERNAL TEST-II

POLYMER CHEMISTRY

Time: 2 Hours **Maximum : 50 marks**

Date : 10.09.18 (AN)

PART A **(20 x 1 =20)**

Answer all Questions

1) Which of the following kind of polymers are known for their high crystalline nature?
a) Isotactic b) Syndiotactic c) Atactic d) Iso-atactic

2) The polyesterification becomes a much more economically feasible reaction when it is catalyzed by an?
a) Base b) Acid c) Alkali d) Neutral

3) 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

4) In Cationic vinyl polymerization electron flow is?
a) Same direction b) Same and opposite direction
c) Opposite direction d) Same or opposite direction

5) The helical structure of DNA was determined by
a) Watson and Crick b) Walden c)Einstein d) Nobel

6) Who won the noble prize for the determination of helical structure in DNA?
a) Watson and Crick b) Walden c)Einstein d) Nobel

7) [η], dl/g is equal to the

a) Specific viscosity b) Reduced viscosity
c) Inherent viscosity d) Intrinsic viscosity

8) Light scattering method is used to determine the _______ of the polymer

a) Molecular weight b) Kinetic force c) Magnetic force d) Centrifugal force

9) In the membrane osmometry, the pressure applied to the solution should prevent

a) Nature of solvent b) Flow of solvent
c) Nature of solute d) Concentration of solvent

10) In the ebuliometry method, the boiling point of solution is

a) Higher than solvent b) Less than solvent
c) Same to the solvent d) Decrease than solvent

11) The viscosity highly depends on the

a) Temperature b) Density c) Size d) Nature

12) The range of constant temperature maintained at viscometer is

a) 0.01ºC b) ± 0.001ºC c) ± 0.1ºC d) ± 0.01ºC

13) A polymer contains different molecular weight compounds to form

A) Monodispersion b) bi dispersion c) poly dispersion d) polymer solution

14) The difference in temperature between the freezing point of solute and solvent is

a) 10ºC b) 0.01ºC c) 0.001ºC d) 0.1ºC

15) The limiting viscosity number is known as

a) Specific viscosity b) Reduced viscosity
c) Inherent viscosity d) Intrinsic viscosity

16) 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) Vapor phase Osmometry

17) Cryoscopy method is applied to determine the

a) Weight average molecular weight b) Number-average molecular weight
c) Viscosity average molecular weight d) Vapour pressure molecular weight

18) ΔT_f is the difference of

a) Freezing point between solute and solvent
b) Freezing point of solutes
c) Freezing point between solvent molecules
d) The temperature between solute and solvent

19) A simple chemical compounds which have same molecular weight to form

a) Monodispersion b) bi dispersion c) poly dispersion d) polymer solution

20) The freezing point depression depends on the

a) Number of dissolved solutes b) Average weight of solute

c) Solvent concentration d) Solvent nature

PART B (3x2=6)

Answer All the Questions

21. Define Degree of crystallinity.

22. Define weight average molecular weight.

23. What is polydispercity index?

PART C (3x8=24)

Answer All the Questions

24. a) Give a detailed note on the crystalline melting point of polymers.

(OR)

b) What are the factors affecting crystalline melting point of a polymer?

25. a) Write a note on structure property relationship of polymers.

(OR)

b) How to calculate the molecular weight of the polymer based on viscosity?

26. a) How to calculate the molecular weight of the polymer based on the number average Method, Explain anyone of its experimental method?

(OR)

b) Define molecular weight distribution. Explain the significance of molecular weight distribution.

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KARPAGAM ACADEMY OF HIGHER EDUCATION

COIMBATORE-641 021

(For the candidates admitted from 2016 & Onwards)

B.Sc., DEGREE INTERNAL EXAMINATION, AUGUST 2018

CHEMISTRY

INTERNAL TEST-II

POLYMER CHEMISTRY

Time: 2 Hours **Maximum :50 marks**

PART A **(20 x 1 =20)**

Answer all Questions

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a) Isotactic b) Syndiotactic c) Atactic d) Iso-atactic

2) The polyesterification becomes a much more economically feasible reaction when it is catalyzed by an?
a) Base **b) Acid** c) Alkali d) Neutral

3) 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

4) In Cationic vinyl polymerization electron flow is?
a) Same direction b) Same and opposite direction
c) Opposite direction d) Same or opposite direction

5) The helical structure of DNA was determined by
a) Watson and Crick b) Walden c)Einstein d) Nobel

6) Who won the noble prize for the determination of helical structure in DNA?

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a) Specific viscosity b) Reduced viscosity
c) Inherent viscosity **d) Intrinsic viscosity**

8) Light scattering method is used to determine the _______ of the polymer
a) Molecular weight b) Kinetic force c) Magnetic force d) Centrifugal force

9) In the membrane Osmometry, the pressure applied to the solution should prevent
a) Nature of solvent **b) Flow of solvent**
c) Nature of solute d) Concentration of solvent

10) The Ebuliometry method, the boiling point of solution is
a) Higher than solvent b) Less than solvent
c) Same to the solvent d) Decrease than solvent

11) The viscosity highly depends on the
a) Temperature b) Density c) Size d) Nature

12) The range of constant temperature maintained at viscometer is
a) 0.01ºC b) ± 0.001ºC c) ± 0.1ºC **d) ± 0.01ºC**

13) A polymer contains different molecular weight compounds to form
A) Monodispersion b) bi dispersion **c) poly dispersion** d) polymer solution

14) The difference in 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) The limiting viscosity number is known as
a) Specific viscosity b) Reduced viscosity
c) Inherent viscosity **d) Intrinsic viscosity**

16) 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) Vapor phase Osmometry

17) Cryoscopy method is applied to determine the
a) Weight average molecular weight **b) Number-average molecular weight**
c) Viscosity average molecular weight d) Vapour pressure molecular weight

18) ΔT_f is the difference of
a) Freezing point between solute and solvent
b) Freezing point of solutes
c) Freezing point between solvent molecules
d) The temperature between solute and solvent

19) A simple chemical compounds which have same molecular weight to form

a) Monodispersion b) bi dispersion c) poly dispersion d) polymer solution

20) The freezing point depression depends on the

a) Number of dissolved solutes b) Average weight of solute

c) Solvent concentration d) Solvent nature

PART B (3x2=6)

Answer All the Questions

21. Define Degree of crystallinity.

22. Define number average molecular weight.

23. What is polydispercity index?

PART C (3x8=24)

Answer All the Questions

24. a) Give a detailed note on the crystalline melting point of polymers.

(OR)

b) What are the factors affecting crystalline melting point of a polymer?

25. a) Write a note on structure property relationship of polymers.

(OR)

b) How to calculate the molecular weight of the polymer based on viscocity?

26. a) How to calculate the molecular weight of the polymer based on the number average Method, Explain anyone of its experimental method?

(OR)

b) Define molecular weight distribution. Explain the significance of molecular weight distribution.

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COIMBATORE-641 021

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B.Sc., DEGREE INTERNAL EXAMINATION, AUGUST 2018

CHEMISTRY

INTERNAL TEST-II

POLYMER CHEMISTRY

Time: 2 Hours **Maximum :50 marks**

PART A (20 x 1 =20)

Answer all Questions

1) a) Isotactic
2) b) Acid
3) a) Edges (surfaces) of elementary sheets of the crystal
4) c) Opposite direction
5) a) Watson and Crick
6) a) Watson and Crick
7) d) Intrinsic viscosity
8) a) Molecular weight
9) b) Flow of solvent
10) a) Higher than solvent
11) a) Temperature
12)d) ± 0.01ºC
13)c) poly dispersion
14) c) 0.001ºC
15)d) Intrinsic viscosity
16) a)Cryoscopy
17) b) Number-average molecular weight
18) a) Freezing point between solute and solvent
19) a) Monodispersion
20) a) Number of dissolved solutes

PART B (3x2=6)

Answer All the Questions

21. Degree of crystallinity.

The Degree of Crystallinity. The degree of crystallinity is defined as the fractional amount of polymer that is crystalline and it is either expressed in terms of the mass fraction, w_c or the volume fraction, j_c.

22. Define number average molecular weight.

Number average molecular weight: Mn. The number average molecular weight is the statistical average molecular weight of. all the polymer chains in the sample, and is defined by: Mn = SN.

23. Polydispercity index

The dispersity index, or formerly polydispersity index (PDI), or heterogeneity index, or simplydispersity (Đ), is a measure of the distribution of molecular mass in a given polymer sample. ... Thedispersity indicates the distribution of individual molecular masses in a batch of polymers.

PART C (3x8=24)

Answer All the Questions

24. a) crystalline melting point of polymers.

Definition

The temperature at which polymer changes from a viscous liquid to a micro-crystalline solid is the crystalline melting point of the polymer.

- Tm is not as sharp as melting point of other solids but is analogous to it.
- Accompanied by changes in density, refractive index, heat capacity,etc.
- Tg=0.5Tm Or Tg=(2/3)Tm (for most of the polymers)

Crystallinity depends on the molecular structure of polymers

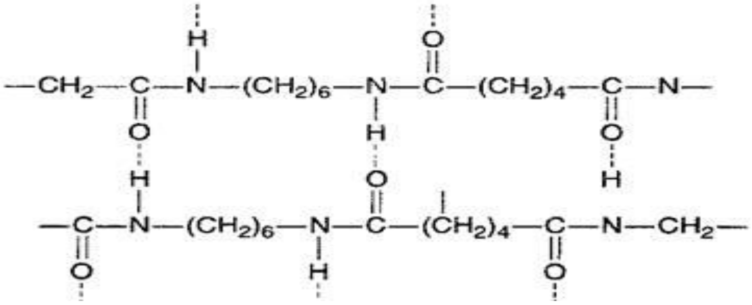
- No bulk polymer is completely crystalline
- In semi-crystalline polymers, regular crystalline units are linked by un-orientated, random conformation chains that constitute amorphous regions
- Presence of crystalline structures has a significant influence on physical, thermal and mechanical properties
- Highly crystalline: polyolefins
- Totally amorphous: atactic PS and PMMA

Crystallinity and its effects on hydrogen bonding

Specific interactions (hydrogen bonding between chains) enhance crystallinity

- Within nylons, hydrogen bonding between;

- Amide carbonyl group on one chain
- Hydrogen atom of an amide group of another chain



(OR)

b) What are the factors affecting crystalline melting point of a polymer?

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 x-ray 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.

In semicrystalline polymers there at least three different, more or less independently variable quantities which describe the polymer. One is the degree of crystallinity which can be calculated from the crystalline/amorphous areas of the X-ray diffractogram or form the integral melting heat determined by DCS.

The second is the long period or folding length (and its distribution) which can be determined from the shape of the DSC curve or from SAXS measurements. The third is spherulite size (and its distribution) which can be determined from polarization optical microscopy or light scattering. Of these the second is related to the observed minimum of the DSC curves which is sometimes called the melting point. In fact we have a distribution of metling points: the lonher the folding length, the higher the corresponding melting point (the closer to the ideal isngle crystal melting point). It is true that longer folding length usually involves higher crystallinity, but not necessarily. Thus it is better to speak of a relation between folidng length and melting point than between crystallinity and melting point.

25. a) Write a note on structure property relationship of polymers.

Homologous series

The simplest precedent is the sequence of properties for the saturated paraffin hydrocarbons (normal alkanes). Such a series of compounds is known as an **homologous series**. The lowest members are gases like methane and ethane, but as the length of the chain increases the hydrocarbons become first liquids and then waxy solids. Both the melting points and densities increase in a regular manner. When many hundreds of carbon atoms are linked together the properties reach a plateau, and it is only here that one can talk of true polymeric properties. During investigations of other types of repeat unit, considerable efforts were and still are made to determine how properties vary with increasing chain length for the lower members (oligomers) of the family, and how it may affect the final properties of the true polymers.

Polymer families

An example of slight changes in the repeat unit structure is exhibited by polyamides, polyesters and polyurethanes. They are all polymers linked together by a particular kind of functional group, which gives the name to each family. Their backbone chain may either be aliphatic or aromatic in nature, although here we'll only be examining trends for the aliphatic polymers. One way of looking at their structure is to regard them as comprising a polyethylene chain into which is inserted the functional group of interest.

They are crystalline polymers which show a distinct melting point (T_m) and we are interested in the effect on T_m of changing the chain length of the sectors between functional groups. Since such polymers are made from two separate monomers (cf. the repeat unit in nylon 6,6, only one of the sectors will be varied. The melting temperatures are shown in **Figure 11** as a function of increasing sector chain length. The constant melting point of HDPE is shown on the same figure for comparison.

The first point of interest is that the polyamides and polyurethanes always have melting points above that of HDPE, an effect due to **hydrogen-bonding** between adjacent chains. This is a secondary kind of bonding between hydrogen and oxygen or nitrogen, which occurs in water and ice as well as many natural polymers. Hydrogen bonds occur between the functional groups on neighbouring chains and effectively tie the chains together in a weak kind of crosslink. This means that the crystalline chains are held together in an energetically more stable conformation than in polyethylene itself, so a higher temperature is needed to melt or decompose the crystals. Hydrogen bonding is absent from polyesters, so the crystals actually show a lower melting temperature than PE because the functional groups make for a less well packed, and hence less stable, structure.

The effect of increasing the number of carbon atoms in the intervening PE chains in the amides and urethanes is similar, lowering T_m in a regular way and approaching the limiting value for HDPE. The decrease is not smooth, however, values oscillating about the line. This effect is caused by packing effects in the crystal structure, odd numbers of carbon atoms fitting together less easily than even numbered chains. With the polyesters, the packing effect still creates oscillations, but increasing chain length has a minimal overall effect on melting temperature.

(OR)

b) How to calculate the molecular weight of the polymer based on viscocity?

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 (η/η0) 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:

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

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

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

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

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

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

$$\boxed{[\eta] = K_v M^v}$$

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; *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.

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

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

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.

26. a) How to calculate the molecular weight of the polymer based on the number average
Method, Explain anyone of its experimental method?

When polymer chains form their lengths and thus their weights differ. It is important to be able to characterize the polymer structure. Determining the weight-average molecular weight or the number-average molecular weight is a part of any polymer characterization.

Number-average molecular weight

Properties such as strength are more sensitive to the numbers of molecules in each weight fraction than to the actual weight. Hence, a "number-average" molecular weight, M_n, has some significance:

$M_n = \{Sum\ [(W_i)(MW)_i]\}/\{Sum\ X_i\}$

The value X_i is the number of molecules in each size fraction.

Number-average molecular weight and molecular weight distributions are determined from osmotic pressure and intrinsic viscosity determinations.

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

$$\boxed{\frac{\Pi}{c} = RT\left(\frac{1}{M_n} + A_2c + A_3c^2 + \cdots\right)}$$

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.

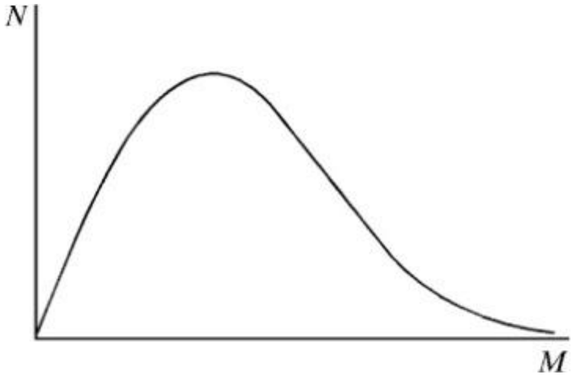
(OR)

b) Define molecular weight distribution. Explain the significance of molecular weight distribution.

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.

A typical synthetic polymer sample contains chains with a wide distribution of chain lengths. This distribution is seldom symmetric and contains some molecules of very high molecular weight. A representative distribution is illustrated in Figure 1. The exact breadth of the molecular-weight distribution depends upon the specific conditions of polymerization, as will be described in Chapter 2. For example, the polymerization of some olefins can result in molecular-weight distributions that are extremely broad. In other polymerizations, polymers with very narrow molecular-weight distributions can be obtained. As will be shown in subsequent chapters, many polymer properties, such as melt viscosity, are dependent on molecular weight and molecular-weight distribution. Therefore, it is useful to define molecular-weight averages associated with a given molecular-weight distribution as detailed in this section.



A representation of a continuous distribution of molecular weights shown as a plot of the number of moles of chains, *N*, having molecular weight *M*, against *M*.

[16CHU502A] **Reg. No…………..**

KARPAGAM ACADEMY OF HIGHER EDUCATION

COIMBATORE-641 021

(For the candidates admitted from 2016 & Onwards)

B.Sc., DEGREE INTERNAL EXAMINATION, OCTOBER 2018

III B.Sc., CHEMISTRY

INTERNAL TEST-III

POLYMER CHEMISTRY

Time: 2 Hours **Maximum: 50 marks**

Date : 08.10.18 (AN)

PART A (20 x 1 =20)

Answer all Questions

1) If an ordinary rubber ball is cooled below -70ºC, it becomes
a) Soft b) Liquefied c) Vaporized d) Hard

2) The temperature below Tg, the polymer is in
a) Liquefied state b) rubbery state c) Emulsion state d) Crystalline state

3) For a poor solvent, the Flory-Huggins parameter value is
a) Constant b) High c) Very low d) Zero

4) If in the process of dissolution, there is increase in enthalpy, Δf values become
a) More positive b) Zero c) Remains constant d) More negative

5) ΔS = k lnW is known as
a) Entropy of mixing b) Enthalpy of mixing
c) Free energy change d) Entropy change

6) The decrease in Tg of a polymer is explained by
a) Free volume theory b) WLF -equation
c) Flory–Huggins Theory d) Thermodynamic factors

7) The Extensive values of the solubility parameter have been published by

a) Burrell and Hildebrand b) Burrell and Billmeyer

c) Burrell and Hoy d) Hoy and Billmeyer

8) When a critical value of free volume V_f is reached so that the polymer chains can be considered as

a) Block in fixed positions b) Blend in fixed positions

c) frozen in fixed positions d) Trozen in fixed positions

9) Which one of the following is used to coating the wires and cables?

a) Urea-formaldehyde b) phenol-formaldehyde

c) Polysulphides d) Polychloroprene

10) Which one of the following should give the strength to the paper?

a) Urea-formaldehyde b) phenol-formaldehyde

c) Polysulphides d) Polychloroprene

11) 80-90% of all plasticizers used with?

a) DOP b) DIOP c) PVC d) Colourants

12) Which one of the following is used as fuel material?

a) Urea-formaldehyde b) phenol-formaldehyde

c) Polysulphides d) Polychloroprene

13) Which is used in clothes, belts and accessories?

a) Cotton b) Nylon c) Polyamide d) Polyester

14) Which one of the following is consider as lifesaving substance

a) Urea-formaldehyde b) phenol-formaldehyde

c) Polybutadiene d) polyvinyl pyrrolidine

15) Which is more flexible than HDPE due to lower crystallinity?

a) Polyethylene b) Low Density Polyethylene

c) Polyamide c) Low density polyamide

16) Which one of the following is used as the insulation material in electrical industry?

a) Urea-formaldehyde b) phenol-formaldehyde

c) Polybutadiene d) Polychloroprene

17) Limited compatibility with the polymers is?

a) Primary plasticizers b) Secondary plasticizers

c) Antioxidents d) Colourants

18) Which one of the following is an example of condensation polymer?

a) Terylene b) PVC c) Vinyl alcohol d) Ethylene

19) Aliphatic polyamides are generally known as?
a) Cotton b) Nylon c) Polyamide d) Polyester

20) Which one of the following flame retardant breaks down endothermic reaction?
a) Phosphorous b) Ammonium c) Aluminium oxide d) Aluminum Hydroxide

PART B (3x2=6)

Answer All the Questions

21) What is mean by Lower critical solution temperature of a polymer solution?
22) Write the thermal behaviour of polymers.
23) Write the preparation and uses of PVC.

PART C (3x8=24)

Answer All the Questions

24) a) i) What is Glass Transition Temperature? How to determine it experimentally?
ii) What are the factors affecting Glass transition Temperature? Explain any two of them.

(OR)

b) Explain the Flory-Huggins theory of polymer solutions

25) a) Discuss in detail about entropy, enthalpy and free energy change of mixing of polymer solutions thermodynamically.

(OR)

b) How will you explain the decrease of Tg using WLF equation?

26) a) Write the preparation, properties, structure and uses of i)polyacetylene
ii)Phenol– formaldehyde (iii) Nylon-6,6 (iv) Silicon polymers

(OR)

b) Write a note on mechanical property of polymers.

[16CHU502A] **Reg. No……………**

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3) For a poor solvent, the Flory-Huggins parameter value is
a) Constant **b) High** c) Very low d) Zero

4) If in the process of dissolution, there is increase in enthalpy, Δf values become
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c) Polyamide c) Low density polyamide

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PART B (3x2=6)

Answer All the Questions

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22) Write the thermal behaviour of polymers.
23) Write the preparation and uses of PVC.

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Answer All the Questions

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B.Sc., DEGREE INTERNAL EXAMINATION, OCTOBER 2018

III B.Sc., CHEMISTRY
INTERNAL TEST-III
ANSWER KEY-POLYMER CHEMISTRY

Time: 2 Hours **Maximum: 50 marks**
Date : 08.10.18 (AN)

PART A (20 x 1 =20)

Answer all Questions

1) d) Hard
2) b) rubbery state
3) b) High
4) d) More negative
5) a) Entropy of mixing
6) a) Free volume theory
7) c) Burrell and Hoy
8) c) frozen in fixed positions
9) d) Polychloroprene
10) a) Urea-formaldehyde
11)c) PVC
12) c) Polysulphides
13)b) Nylon
14)d) polyvinyl pyrrolidine
15)b) Low Density Polyethylene
16) c) Polybutadiene
17) b) Secondary plasticizers
18) a) Terylene
19) b) Nylon
20) d) Aluminum Hydroxide

PART B (3x2=6)

Answer All the Questions

21) What is mean by Lower critical solution temperature of a polymer solution?

The lower critical solution temperature (LCST) or lower consolute temperature is the critical temperature below which the components of a mixture are miscible for all compositions. The word *lower* indicates that the LCST is a lower bound to a temperature interval of partial miscibility, or miscibility for certain compositions only.

22) Write the thermal behaviour of polymers.

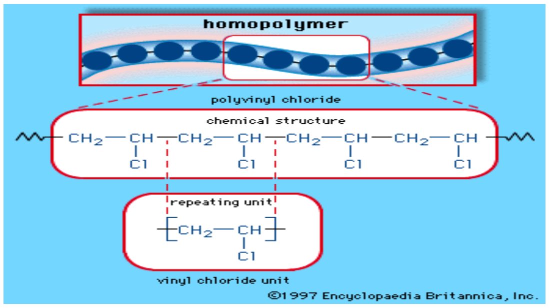
Thermal Behavior of Polymers •At low temperatures, all amorphous polymers are stiff and glassy, sometimescalled as the Vitreous State, especially for inorganic polymers.

•On Warming, polymers soften in a characteristic temperature range known as theglass-rubber transition region.

•The glass transition temperature (Tg), is the temperature at which the amorphous phase of the polymer is converted between rubbery and glassy states.

•Tg constitutes the most important mechanical property for all polymers. In fact,upon synthesis of a new polymer, the glass transition temperature is among thefirst properties measured.The following physical properties undergo a drastic change at the glass transition temperature of any polymer:

23) Write the preparation and uses of PVC.



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USES

- It is a good electrical insulator and hence is used for coating wires and cables.
- It is also used in making gramophone records and pipes.
- It is used for making rain coats, hand bags, plastic dols, upholstery, shoe soles and vinyl flooring.

PART C (3x8=24)

Answer All the Questions

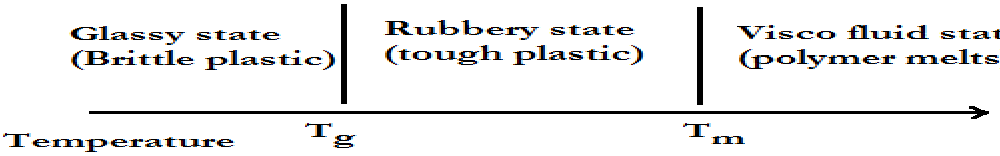
24) a) i) What is Glass Transition Temperature? How to determine it experimentally?

Glass transition temperature

When plastic or rubber is cooled up to certain temperature, it becomes so hard and brittle that it breaks into pieces on application of stress.

The temperature below which the polymer becomes hard, brittle and glassy and above which it is softener and flexible, is known as glass transition temperature (TG).

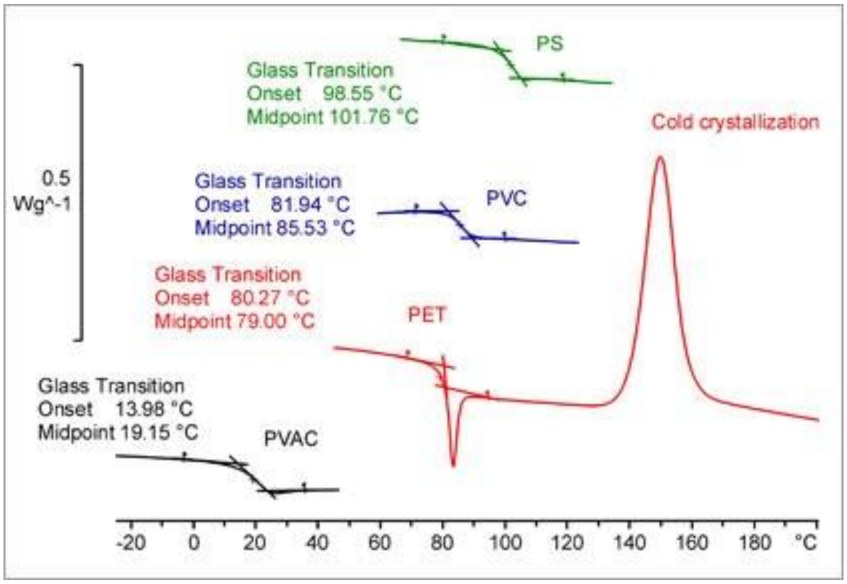
The glass transition is a property of only amorphous portion of a semi-crystalline solid. The crystalline portion remains crystalline during the glass transition.



When a polymer is heated beyond TgTg,TgTg, it passes from glassy state to rubbery state. Further heating much above, causes melting of the polymer and it starts flowing and it starts flowing. The temperature below which the polymer is in rubbery state and above which it is a liquid is called melting temperature of the polymer, while the temperature at which the polymer starts flowing is known as its flow temperature.

Determination of Glass Transition Temperature

A comprehensive coverage of TA techniques for the determination of glass transition temperature



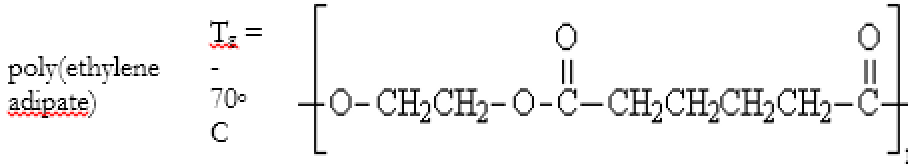
The determination of glass transition temperature (Tg) is critical for understanding a material's properties. It indicates the temperature at which a substance transforms from a glassy state to a rubbery state or vice versa. The formation of such amorphous glasses is a universal phenomenon observed in practically all materials.

For practical applications, it is important to realize that the properties of glasses differ significantly from those of other solids. For example, the solubility of glasses is higher than for crystals; this influences the biological activity of pharmaceutical substances.

ii) What are the factors affecting Glass transition Temperature? Explain any two of them.

Factors affecting glass transition temperature are-

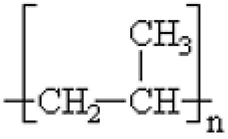
1) Chain Stiffness-Stiffening groups: in the polymer chain reduce the flexibility of the chain and raise the value of TgTg .



poly(ethylene terephthalate) Tg=69oCTg=69oC

2) Intermolecular Forces-

Stronger intermolecular forces lead to a higher Tg. PVC has stronger intermolecular forces than polypropylene because of the dipole-dipole forces from the C-Cl bond.



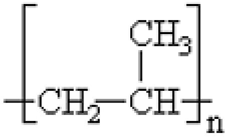
$$\left[CH_2-\underset{}{\overset{CH_3}{\overset{|}{C}H}} \right]_n$$

Atactic Polypropylene Tg=−20oCTg=−20oC

3) Pendant Groups-

The influence of pendant groups on the glass transition temperature is somewhat more complicated.

1. Bulky pendant groups, such as a benzene ring, can catch on neighboring chains like a "fish hook" and restrict rotational freedom34freedom34. This increases TgTg.



$$\left[CH_2-\overset{CH_3}{\overset{|}{C}H} \right]_n$$

Atactic Polypropylene Tg=−20oCTg=−20oC

4) Cross-Linking-

The presence of cross-links between chains restricts rotational motion and raises Tg.

5) Plasticizers-

Plasticizers are low molecular weight compounds added to plastics to increase their flexibility and workability. They weaken the intermolecular forces between the polymer chains and decrease Tg.

(OR)

b) Explain the Flory-Huggins theory of polymer solutions

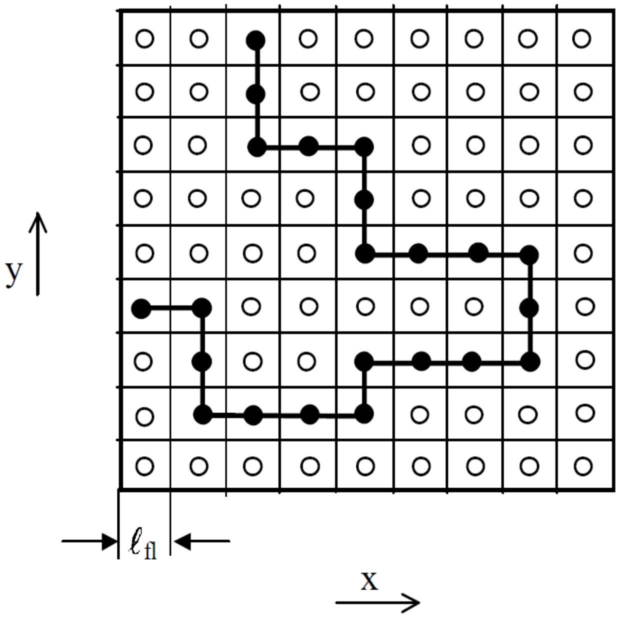
Florry- Huggins theory

The thermodynamics of (binary) regular polymer solutions[1] were first investigated by Paul Flory[2] and Maurice Huggins[3] independently in the early 1940s. They assumed a rigid lattice frame, that is, the molecules in the pure liquids and in their solution / mixture are considered to be distributed over N_0 lattice sites, as illustrated in the figure below. The total number of lattice sites, N_0, is assumed to be equal to the number of solvent molecules, N_s, and polymer repeat units, $N_p r$:

$$N_0 = N_s + N_p r$$

where N_p is the number of polymer molecules each consisting of r repeat units.

TWO-DIMENSIONAL LATTICE



The model has been described in great detail by Flory in his famous book "*Principles of Polymer Chemistry*" (1953).[4] Following the standard theory of mixing for small molecules of similar size and using Stirling's approximation $\ln M! = M \ln M - M$, Flory and Huggins obtained following expression for the entropy of mixing:

$$\Delta S_{mix} \approx -k\,(N_p \ln \varphi_p + N_s \ln \varphi_s\,)$$

Alternately, the entropy of mixing can be written as

$$\Delta s_{mix} = \Delta S_{mix} / N_0 \approx -k\,\{\varphi_p / (r \cdot v_r) \cdot \ln \varphi_p + \varphi_s / v_s \cdot \ln \varphi_s\}$$

where φ_s and φ_p are the volume fractions of the solvent and polymer,

$$\varphi_s = N_s v_s / (N_s v_s + N_p r v_r), \quad \varphi_p = N_p r v_r / (N_s v_s + N_p r v_r)$$

and v_s and v_r are the volumes of a solvent molecule and of a polymer repeat unit, respectively. Obviously, the solvent needs not necessarily to be made of a single unit. The solvent may, in fact, consist of several repeat units or of another polymer.

The Gibbs free energy of mixing, ΔG_{mix}, often includes an enthalpy part, that is, mixing can be an endothermic or an exothermic process

$$\Delta G_{mix} = \Delta H_{mix} - T\,\Delta S_{mix}$$

where ΔH_{mix} is the heat of mixing. Flory and Huggins introduced a new parameter, the so called Flory-Huggins interaction parameter to describe the the polymer-solvent interaction:[5]

$$\chi_{ps} = \Delta H_{mix} / (kT\, N_s\, \varphi_p)$$

which combined with the entropy term leads to the free energy of mixing:

$$\Delta G_{mix} / kT = N_p \ln \varphi_p + N_s \ln \varphi_s + \chi_{ps}\, N_s\, \varphi_p$$

Assuming equal lattice volumes for both repeat units, the free energy per lattice site can be written

$$\Delta g_{mix} / kT \approx \varphi_p / r \cdot \ln \varphi_p + \varphi_s \ln \varphi_s + \chi_{ps}\, \varphi_s\, \varphi_p$$

A more general expression for the free energy of mixing is

$$\Delta g'_{mix} / kT = \varphi_p / (r \cdot v_r) \cdot \ln \varphi_p + \varphi_s / v_s \cdot \ln \varphi_s + \chi_{ps}\, \varphi_s\, \varphi_p / \sqrt{(v_r v_s)}$$

where $\Delta g'_{mix}$ is the free energy of mixing per unit volume. These equations are the starting point for many other important equations. For example, the *partial molar free energy of mixing* (*chemical potential*) can be obtained by differentiation of the expression above with respect to N_s. This gives

$$\Delta \mu_s / RT = \ln [1 - \varphi_p] + (1 - 1/\mathrm{r})\, \varphi_p + \chi_{ps}\, \varphi_p^2$$

where μ_s is the chemical potential of the solvent per mole. Substitution of this expression into the osmotic pressure relation $\Pi = -\Delta \mu_s / V_s$ gives

$$\Pi \approx RT\, V_s^{-1} \cdot \{\ln [1 - \varphi_p] + \varphi_p + \chi_{ps} \varphi_p^2\}$$

where V_s is the molar volume of the solvent.

25) a) Discuss in detail about entropy, enthalpy and free energy change of mixing of polymer solutions thermodynamically.

III.A THERMODYNAMICS OF POLYMER SOLUTIONS

The behavior of polymers towards a given solvent is characteristic and different from that of other solvents. This is quite expected as the differences in molecular weight of a polymer and that of a low molecular weight substance (solvent) is quite large. The size and conformations of dissolved polymer molecules require special theoretical treatment to explain their solution properties. Conversely, it is possible to obtain information about the *size* and *shape* of polymer molecules from studies of their solution properties.

III.A.1 Ideal Solutions

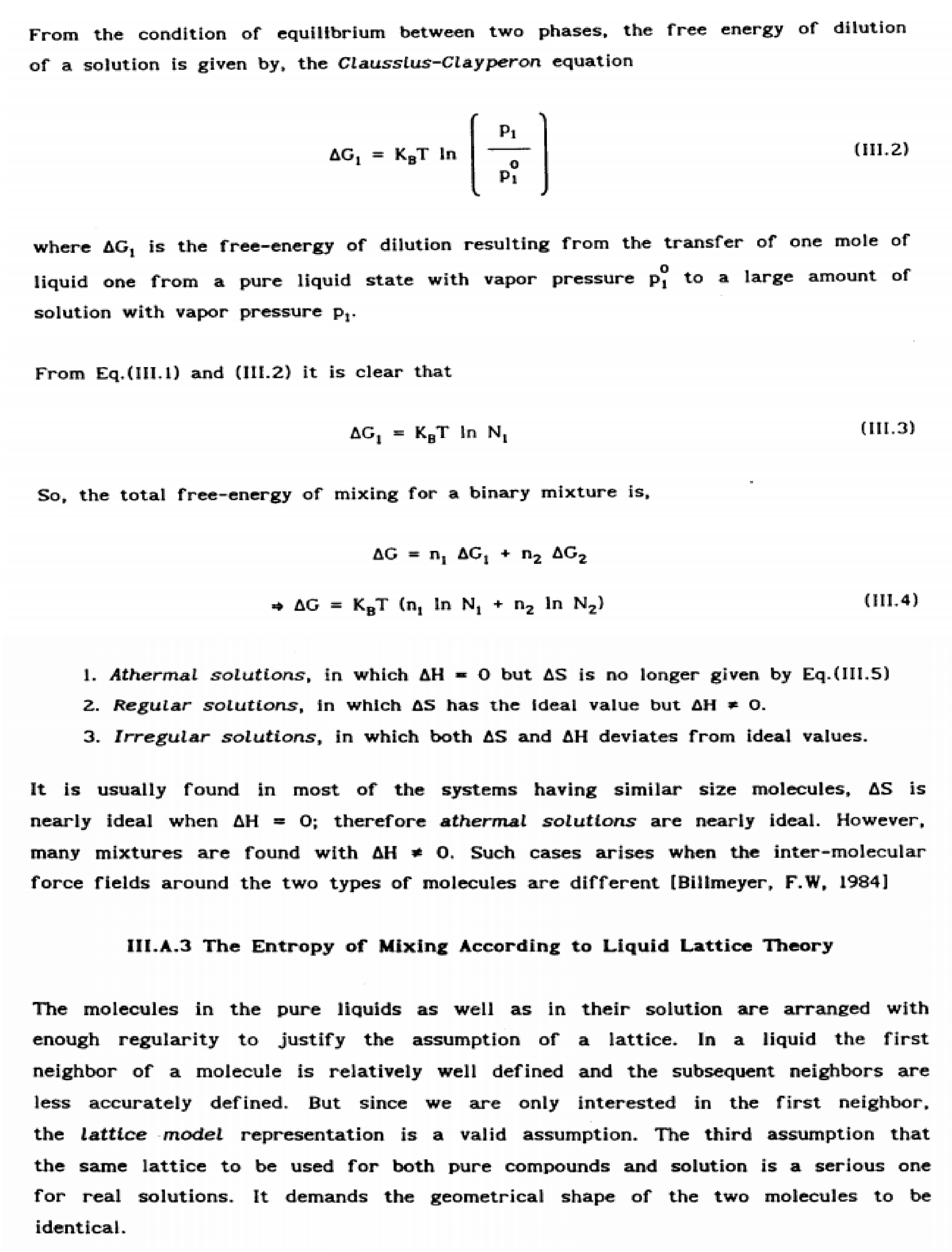
The *ideal solution* is defined as one which obey the *Raoult's* law. This law states that the partial vapor pressure of each component in the mixture is proportional to its mole-fraction, i.e.,

$$p_1 = p_1^0 \frac{n_1}{\sum n_1} = p_1^0 N_1 \qquad \text{(III.1)}$$

where p_1^0 is the vapor pressure of the solvent, p_1 is the vapor pressure of the same solvent in the solution and N_1 is the mole-fraction.

For a binary solution, the Eq.(III.1) can be written as

$$p_1 = p_1^0 \frac{n_1}{n_1 + n_2} = p_1^0 N_1 \quad \text{and} \quad p_2 = p_2^0 \frac{n_2}{n_1 + n_2} = p_2^0 N_2$$



From the condition of equilibrium between two phases, the free energy of dilution of a solution is given by, the *Claussius-Clayperon* equation

$$\Delta G_1 = K_B T \ln \left(\frac{p_1}{p_1^0} \right) \qquad \text{(III.2)}$$

where ΔG_1 is the free-energy of dilution resulting from the transfer of one mole of liquid one from a pure liquid state with vapor pressure p_1^0 to a large amount of solution with vapor pressure p_1.

From Eq.(III.1) and (III.2) it is clear that

$$\Delta G_1 = K_B T \ln N_1 \qquad \text{(III.3)}$$

So, the total free-energy of mixing for a binary mixture is,

$$\Delta G = n_1 \Delta G_1 + n_2 \Delta G_2$$

$$\Rightarrow \Delta G = K_B T (n_1 \ln N_1 + n_2 \ln N_2) \qquad \text{(III.4)}$$

1. *Athermal solutions*, in which $\Delta H = 0$ but ΔS is no longer given by Eq.(III.5)
2. *Regular solutions*, in which ΔS has the ideal value but $\Delta H \neq 0$.
3. *Irregular solutions*, in which both ΔS and ΔH deviates from ideal values.

It is usually found in most of the systems having similar size molecules, ΔS is nearly ideal when $\Delta H = 0$; therefore *athermal solutions* are nearly ideal. However, many mixtures are found with $\Delta H \neq 0$. Such cases arises when the inter-molecular force fields around the two types of molecules are different [Billmeyer, F.W, 1984]

III.A.3 The Entropy of Mixing According to Liquid Lattice Theory

The molecules in the pure liquids as well as in their solution are arranged with enough regularity to justify the assumption of a lattice. In a liquid the first neighbor of a molecule is relatively well defined and the subsequent neighbors are less accurately defined. But since we are only interested in the first neighbor, the *lattice model* representation is a valid assumption. The third assumption that the same lattice to be used for both pure compounds and solution is a serious one for real solutions. It demands the geometrical shape of the two molecules to be identical.

(OR)

b) How will you explain the decrease of Tg using WLF equation?

WLF THEORY

Polymers exhibit behavior during flow and deformation which depends on both temperature and time (frequency), that is, the viscoelastic response of a polymer will depend on the shear history. Only for Newtonian liquids, and in a first approximation for low molecular weight polymers, is the viscosity independent of the shear history. In this case, the temperature dependence of the viscosity may be decribed by an Arrhenius equation of the form

$$\eta = A\,\mathrm{e}^{E/RT}$$

where T is the absolute temperature, R the universal gas constant, A a material constant, and E the activation energy. Knowledge of the two material-dependent parameters E and A allows for the prediction of the viscosity for any temperature. The two parameters are usually determined from a plot of log η against $1/T$ which yields a straight line:

$$\log \eta = \log A + E \,/\, RT$$

For most polymer melts a straight line can only be drawn over a fairly small temperature range of about 50°C. In general, the lower the shear rate and the molecular weight the better the agreement.

Doolittle provided another equation that is much more accurate for entangled polymer systems. He postulated that the viscosity is an exponential function of the reciprocal of the fractional free volume f:

$$\eta = A\,\mathrm{e}^{B/f(T)}$$

or

$$\log \eta = \log A + B \,/\, f(T)$$

where A and B are constants and f is the free volume fraction,

$$f = v_f \,/\, v = (v - v_{hc}) \,/\, v$$

v_{hc} is the inaccessible volume and v the measured (molar) volume. Similar to the (molar) polymer volume, it can be assumed that the fractional free volume f increases linearly with temperature. Choosing the free volume at the glass transition temperature Tg as the reference state, the free volume as a function of temperature may be written as

$$f = f_g + \alpha_f (T - T_g)$$

where f_g is the fractional free volume at Tg and α_f is the thermal expansion coefficient. It has been suggested that the two parameters have the univerals values

$$f_g \approx 0.025$$

$$\alpha_f \approx 4.8 \times 10^{-4}\ \mathrm{K}^{-1}$$

Williams, Landel and Ferry (1955) have suggested that the viscosity η at a temperature T may be related to the viscosity η_g at the glass transition temperature:

$$\log a_T = \log \eta(T) - \log \eta_g = B \left\{ \frac{1}{f(T)} - \frac{1}{f_g} \right\}$$

or

$$\log_{10} a_T = \log_{10} \frac{\eta(T)}{\eta(T_g)} = \frac{B}{2.303 f_g} \left\{ \frac{-\alpha(T - T_g)}{f_g + \alpha(T - T_g)} \right\}$$

where a_T is the so called WLF shift factor. Using the universal values of f_g and α_f yields two new constants:

$$C_1 = \mathrm{B} \,/\, f_g \approx 17.44$$

$$C_2 = f_g \,/\, \alpha_f = 51.6\ \mathrm{K}$$

The two constants are not universal at all. Only polymers with isoviscose behavior will obey the WLF equation. For all other polymers, the two parameters might be very different.
Many polymers have melt viscosities of about 10^{13} poise at their glass transition temperature. Lets assume a polymer has a glass transition temperature of about 373 K then the viscosity at 423 K is:

$$\log_{10} a_T = \log_{10} \frac{\eta(T)}{\eta(T_g)} = -\frac{17.44\ (T - T_g)}{51.6 + T - T_g}$$

$$\log_{10} \eta(423\ \text{K}) = 13 - \frac{17.44\ (423 - 373)}{51.6 + 423 - 373} = 4.42$$

or $\eta = 2.61 \times 10^4$ Poise.

26) a) i)polyacetylene

Polyacetylene is the simplest linear synthetic polymer. Fundamental unit consists from one carbon and one hydrogen atoms, as has been called simply (CH),. Each carbon is u bonded by sp2 hybrid orbital to one hydrogen and two adjacent carbon atoms to form a planar chain molecule.

ii)Phenol– formaldehyde

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:

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

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

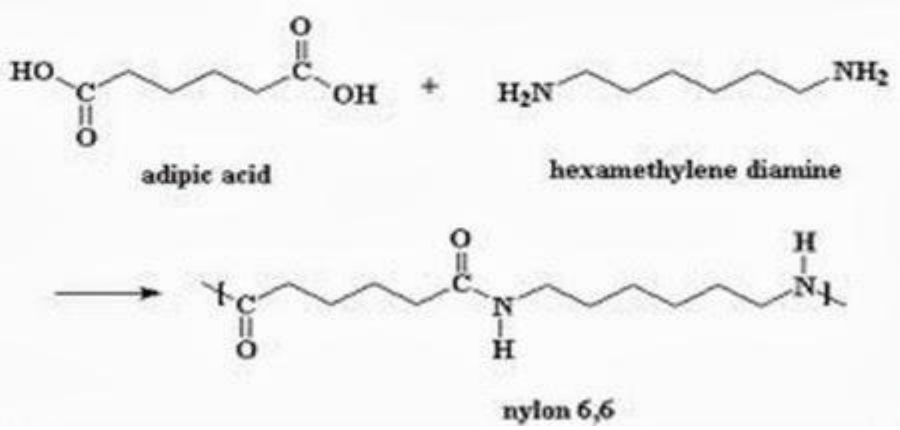
The diphenol $(HOC_6H_4)_2CH_2$ (sometimes called a "dimer") is called bisphenol F, which is an important monomer in the production of epoxy resins. Bisphenol-F can further link generating tri- and tetra-and higher phenol oligomers.

Uses

- Soft Bakelite are used as binding glue for laminated wooden planks, in varnishes and lacquers.
- Hard bakelite is used as a thermosetting polymer.
- It is used for the manufacture of combs, formica-table –tops, electrical switches and gramophone records.

(iii) Nylon-6,6

Nylon-66 (polyhexamethylene diamine adipamide) is a polyamide made from adipic acid and hexamethylenediamine by polycondensation. The resulting polymer is extruded into a wide range of fiber types. The fibers are drawn, or stretched, in a process that increases their length and reorients the material's molecules parallel to one another to produce a strong, elastic filament. The thermo-plasticity of nylon permits permanent crimping or texturing of the fibers and provides bulk and stretch properties.



Polyester

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 :

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

(iv) Silicon polymers

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

n Si(CH3)2Cl2 + n H2O → [Si(CH3)2O]n + 2n 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.

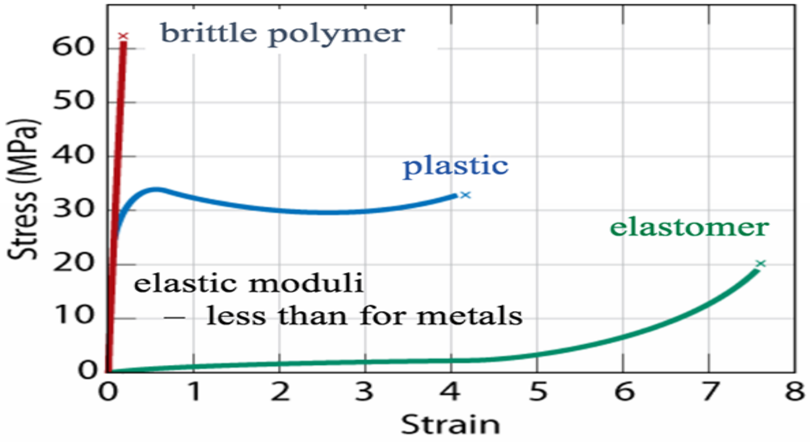
Uses

Silicones are used in many products. 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 and dentistry (e.g., tooth impression molds), textiles and 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.

(OR)

b) Write a note on mechanical property of polymers.

Polymers exhibit a wide range of stress-strain behaviors as shown in the figure below. The brittle polymer (red curve) elastically deforms and fractures before deforming plastically. The blue curve is a plastic polymer and is similar to curves for many metals. Its behavior begins in the linear elastic deformation region. As the curve transitions from the elastic to plastic deformation typically there is a peak stress. For polymer materials, this peak stress is identified as the yield stress. As the material is pulled further, fracture occurs. The stress value when fracture occurs is defined as the tensile strength for polymer materials. The tensile strength can be greater than, equal to, or less than the yield strength. The green curve is a class of polymers known as elastomers. These materials exhibit rubber-like elasticity and will return to their original shape and form unless they are extended to the point of fracture.



Mechanical properties of polymers: stress-strain behavior.