

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

KARPAGAM ACADEMY OF HIGHER EDUCATION (Deemed to be University) (Established Under Section 3 of UGC Act 1956) COIMBATORE-21 DEPARTMENT OF CHEMISTRY

M.Sc Chemistry Syllabus

ELECTIVE-IIISemester-III18CHP305APOLYMER CHEMISTRY4H4C

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

Scope

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

Objectives

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

Methodology

Blackboard teaching, Powerpoint presentation and group discussion.

UNIT – I

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

UNIT – II

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

UNIT-III

Molecular Weight and Properties: Polydispersion – average molecular weight concept, number, weight and viscosityaverage molecular weights. Measurement of molecular weights. Viscosity, lightscattering, osmotic and ultracentrifugation methods. Polymer structure and physical properties – crystalline melting point T_m . The glass transition temperature. Determination of T_g . Relationship between T_m and T_g .

UNIT – IV

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

$\mathbf{UNIT} - \mathbf{V}$

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

SUGGESTED READINGS:

Text Books:

- 1. Billmeyer, F.W. (2003). *Text Book of Polymer Science* (III Edition). New York: John Wiley.
- 2. Gowariker, V. R., Viswanathan, N. V., &Sreedhar, J. (2015). *Polymer Science* (II Edition). New Delhi: New Age International Private Ltd.
- 3. Alcock, H. R., Lampe, F. W., & Mark, J. E. (2003). *Contemporary Polymer Chemistry* (III Edition). NJ: Prentice Hall.Englewood Cliffs.

Reference Books:

- 1. Flory, P. J. (1953). *Principles of Polymer Chemistry*. New York: Cornell University Press.
- 2. Odian, G. (2004). *Principles of Polymerization* (IV Edition). New York: John Wiley & Sons.



(Deemed to be University) (Established Under Section 3 of UGC Act 1956) Coimbatore - 641 021. (For the candidates admitted from 2018 onwards) **DEPARTMENT OF CHEMISTRY**

SUBJECT NAME: POLYMER CHEMISTRY

SEMESTER: III

SUBJECT CODE: 18CHP305A

CLASS: II M. Sc CHEMISTRY

LECTURE PLAN

<u>UNIT-</u>1

Polymer Basic Concepts

Total no. of hours: 10

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

Text book:

- **T1:** Gowariker, V. R., N. V. Viswanathan and J. Sreedhar, 1986. Polymer Science, *New Age International* Private Ltd., New Delhi.
- **T2**: Billmeyer, F.W., 2003. Text Book of Polymer Science. III Edition, John Wiley, New York.

Reference book

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

<u>UNIT-2</u>

Co-ordination Polymerization

Total no. of hours: 10

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

Text book:

- **T1:** Gowariker, V. R., N. V. Viswanathan and J. Sreedhar, 1986. Polymer Science, *New Age International* Private Ltd., New Delhi.
- **T2**: Billmeyer, F.W., 2003. Text Book of Polymer Science. III Edition, John Wiley, New York.

Reference book

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

<u>UNIT -3</u>

Molecular Weight and Properties

Total no. of hours: 10

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

Text book:

- **T1:** Gowariker, V. R., N. V. Viswanathan and J. Sreedhar, 1986. Polymer Science, *New Age International* Private Ltd., New Delhi.
- T2: Billmeyer, F.W., 2003. Text Book of Polymer Science. III Edition, John Wiley, New York

Reference book

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

Polyme	r Processing	Total no. of hours: 09				
S.NO LECTURE DURATION		TOPIC TO BE COVERED	SUPPORT MATERIALS			
1	1	Plastics, elastomers and fibres.	T1: 14, 221, 225, 29, 229, 449 T2: 351, 371,486,471-475			
2	1	Compounding	T1: 450-451			
3	1	Process techniques: Calendering,	T1: 452-453; T2:464-466			
4	1	Die casting	T1: 453-454; T2:464-466			
5	1	rotational casting, film casting	T1: 454-456; T2: 465-466			
6	1	injection moulding, blow moulding, Extrusion moulding	T1: 457-462; T2: 458-461, 461-464			
7	1	Thermoforming	T1: 462-464; T2: 467-469			
8	1	Foaming	T1: 462-464; T2: 467-469			
9	1	Reinforcing, Fiber spinning	T1: 465-469, T1: 470-474; T2: 491-496			
10	1	Discussion of important questions				

<u>UNIT -4</u>

Text book:

- **T1:** Gowariker, V. R., N. V. Viswanathan and J. Sreedhar, 1986(2014 re-print). "Polymer Science", *New Age International* Private Ltd., New Delhi.
- **T2**: Billmeyer, F.W., 2008(Re-print). "Text Book of Polymer Science". III Edition, John Wiley, New York.

Reference book:

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

Prepared by Dr. S. Manickasundaram, Department of Chemistry, KAHE

<u>UNIT -5</u>

Properties of Commercial Polymers Total no. of hours: 09							
S.NO	LECTURE DURATION	TOPIC TO BE COVERED	SUPPORT MATERIALS				
1	1	Polyethylene, Polyvinyl chloride	T1: 215-217, 236-238, 227-229				
2	1	Polyamides	T1: 215-217, 236-238, 227-229				
3	1	Polyesters and Silicon polymers	T1: 221-223,255-256; T2: 442-445,448-450				
4	1	Phenolic resins, Epoxy resins	T1: 251-254; T2: 436- 440,445-446				
5	1	Functional polymers, Fire retarding Polymers	W1				
6	1	Electrically conducting polymers	W1				
7	1	Bio-medical polymers- contact lens, dental polymers	W ₂ , Journals				
8	1	Artificial heart, kidney, skin and blood cells.	W ₂ , W ₃				
9	1	Recapitulation and discussion of Previous year question					

Text book:

- **T1:** Gowariker, V. R., N. V. Viswanathan and J. Sreedhar, 1986. Polymer Science, *New Age International* Private Ltd., New Delhi.
- **T2**: Billmeyer, F.W., 2003. Text Book of Polymer Science. III Edition, John Wiley, New York

Reference book

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

Web Address:

- W1: https://en.wikipedia.org/wiki/Fire-safe_polymers or Functional or Electrically conducting polymers.
- **W₂:** https://en.wikipedia.org/wiki/ Artificial-heart or https://biomedical polymers/applications.
- W3: https://en.wikipedia.org/wiki/ Artificial-kidney

Journals: Applications of polymers in the biomedical field, Current-Trends in Biomedical eng & biosensors, vol.4, issue.4 (2017), Ibrahim et al (mini review)



CLASS: II M.Sc CHEMISTRY COURSE NAME: POLYMER CHEMISTRY

	Questions	Opt-1	Opt-2	Opt-3	Opt-4	Answers
1	Which is more flexible than HDPE due to lower crystallinity?	Polyethylene	Low Density Polyethylene	Polyamide	Low density polyamide	Low Density Polyethylene
2	80-90% of all plasticizers used with?	DOP	DIOP	PVC	Colourants	PVC
3	It must not exude from the plastic material?	Primary plasticizers	Secondary plasticizers	Antioxidents	Colourants	Primary plasticizers
4	Limited compatibility with the polymers are?	Primary plasticizers	Secondary plasticizers	Antioxidents	Colourants	Secondary plasticizers
5	Inhibiting the oxidation of polymers is usually filled by a substance which itself is readily oxidized.	Antioxidants	Flame retardants	Colourants	Mgo	Antioxidants
6	In polymer industry 2- hydroxybenzophones are used as	Light stabilizers	Antioxidants	Polymer initiators	Fillers	Light stabilizers
7	Any of a group of substances that are used in plastics or other materials to impart viscosity, flexibility, softness or other properties to the finished product	Plasticizers	Antioxidants	Polymer initiators	Fillers	Plasticizers



CLASS: II M.Sc CHEMISTRY COURSE NAME:POLYMER CHEMISTRY

		1				
8	It often added to semicrystalline polymer to lower the value of Tg below room temperature.	Light stabilizers	Colouarants	Plasticizers	Flame retardents	Plasticizers
9	The basic requirement that must be met by a plasticizer are	Compatibility	Prevent oxidation	Retard flame	Impart a colour	Compatibility
10	Porosity increased as plasticizers content?	Increased	Decreased	Suddenly decreased	Never change	Increased
11	The substances which weaken the intermolecular forces between the polymer chains and decrease Tg.	Plasticizers	Antioxidants	Polymer initiators	Fillers	Plasticizers
12	Which content did not have a significant effect on the rate of erosion?	Light stabilizers	Colouarants	Plasticizers	Flame retardents	Plasticizers
13	Which type of compound is not used as a flame retardant in polymers	Aluminum Hydroxide	Halogen compounds	Phosphorous compounds	Ferrocene	Ferrocene
14	Chemical compounds capable of interfering with the physical and chemical processes of UV light- induced degradation.	Plasticizers	Antioxidants	Polymer initiators	Light stabilizer	Light stabilizer
15	which one of the following polymers is the product of a condensation polymerisation reaction?	Polypropylene	Polytetrafluoroethene	Polyacetic acid	PVC	Polyacetic acid



CLASS: II M.Sc CHEMISTRY COURSE NAME: POLYMER CHEMISTRY

16	The phenol-formaldehyde resins are formed by polymerisation of phenol and formaldehyde by	Addition polymerisation	Cationic polymerisation	Condensation polymerisation	Anionic polymerisation	Condensation polymerisation
17	The addition of polyethylene glycol in dielectric property significantly improves?	Electrolytic conductivity	Dielectric conductivity	Electric conductivity	Ionic conductivity	Ionic conductivity
18	Melamine is	White crystaline solid	Gas	Colourless liquid	Yellow liquid	White crystaline solid
19	Plastics are ?	Hydrocarbons	Aldehyde	Ester	Amide	Hydrocarbons
20	Which one is an inorganic pigment?	Barium sulfate	Perylenes	Pyrroles	Arylamides	Barium sulfate
21	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
22	Which one is more active flame retardant?	Aluminum hydroxide	Antimony oxychloride	Phosphorous	Halogen compounds	Antimony oxychloride
23	The most useful material imparting flame retardance to plastics is?	Antimony trioxide	Aluminum hydroxide	Halogen compounds	Antimony oxychloride	Antimony trioxide
24	Which one of the following flame retardant forms a gas shield layer?	Calcium	Phosphorous	Ammonium	Aluminium oxide	Phosphorous



CLASS: II M.Sc CHEMISTRY COURSE NAME: POLYMER CHEMISTRY

	Which one of the following					
25	flame retardant breaks down endothermic reaction?	Phosphorous	Ammonium	Aluminium oxide	Aluminum Hydroxide	Aluminum Hydroxide
26	Melting Point of Low Density Polyethylene (LDPE) is?	~115°C	~116°C	~135°C	~148 °C	~135°C
27	Which one is a synthetic polymer?	Cellulose	Cotton	Polyamide	Fibers	Polyamide
28	Polymethyl methacrylate is a colourless and transparent ?	Plastic	Rubber	Cotton	Nylon	Plastic
29	Polymethyl methacrylate can be prepared by using acetone cyanohydrin and	Nitric acid	Acetic acid	Sulphuric acid	Hydrochloric acid	Sulphuric acid
30	Silicones was commercially introduced in ?	1943	1930	1936	1947	1943
31	Polyvinyl chloride was commercially introduced in ?	1943	1930	1936	1947	1936
32	Polyvinyl acetate monomer is prepared by the reaction of acetic anhydride with ?	Benzaldehyde	Acetaldehyde	Acetic acid	Sodium acetate	Acetaldehyde
33	Polyvinyl acetate is used for the manufacture of ?	Polyvinyl chloride	Polyvinyl alcohol	Poly methyl methacrylate	Polyvinyl acetate	Polyvinyl alcohol



CLASS: II M.Sc CHEMISTRY COURSE NAME:POLYMER CHEMISTRY

34	Styrene(butadiene rubber) was commercially introduced during the year	1943	1930	1936	1947	1930
35	Polyvinyl acetate is insoluble in which solvent?	Alcohols	Aromatic solvents	Esters	Water	Water
36	Polythene was first synthesiedin ?	1877	1853	1890	1898	1898
37	Polythene was first produced in ?	German	England	India	USA	England c
38	Polyethylene was first synthesized by ?	Pechmann	Fawcett	Karl ziegler	Walter	Pechmann
39	Which one of the compound is used in the manufacture of terylene ?	Vinyl chloride	Ethylene glycol	Vinyl alcohol	Ethylene	Ethylene glycol
40	Which one of the following is an example of condensation polymer?	Terylene	PVC	Vinyl alcohol	Ethylene	Terylene
41	The synthetic polymer which resembles natural rubber is ?	Cotton	Nylon	Chloroprene	Neoprene	Neoprene
42	Which one is prepared by the melt polycondensation between dicarboxylic acids and diamides.	Polyamides	Polyester	Acrylic fibre	Polyethylene	Polyamides



CLASS: II M.Sc CHEMISTRY COURSE NAME: POLYMER CHEMISTRY

43	Aliphatic polyamides are generally known as ?	Cotton	Nylon	Polyamide	Polyester	Nylon
44	Which one of the following is obtained from dibasic acids and diamides.	Cotton	Nylon	Polyamide	Polyester	Nylon
45	The ring opening polymerization of lactometated is represented only by ?	Single number	Double number	Triple number	No number	Single number
46	It has good tensile strength and abrasion resistance	Polyamides	Polyester	Acrylic fibre	Polyethylene	Polyamides
47	It is used as a plastic as well as a fibre	Polyamides	Polyester	Acrylic fibre	Polyethylene	Polyamides
48	Which one is used in tires and ropes?	Cotton	Nylon	Polyamide	Polyester	Nylon
49	Which is used in clothes, belts and accessories?	Cotton	Nylon	Polyamide	Polyester	Nylon
50	It is prepared by polycondesation reaction between a dicarboxylic acid and a diol.	Polyamides	Polyester	Acrylic fibre	Polyethylene	Polyester
51	Which polymers contains ester groups in the main chain of the polymer itself.	Polyamides	Polyester	Acrylic fibre	Polyethylene	Polyester



CLASS: II M.Sc CHEMISTRY COURSE NAME:POLYMER CHEMISTRY

52	The molecular weight of cellulose varies between	20000 to 500000	10000 to 20000	10000 to 12000	1000 to 2000	20000 to 500000
53	Condensation polymerization is not used to produce	Polyester	Nylon 6	Nylon 66	Polypropylene	Polypropylene
54	Polyethylene terephthalte (PETP) has a high melting point because of the presence of ?	Aliphatic chain	Aromatic ring	Nitrogen bond	CN bond	Aromatic ring
55	Which one of the following is resistant to heat and moisture.	Polyamides	Polyester	Acrylic fibre	Polyethylene	Polyester
56	PETP melts at ?	275°C	266°C	267°C	265°C	265°C
57	Which one of the following is used in the manufacturing of magnetic recording tapes, aluminishedsheets for certain special applications?	Polyethylene terephthalte	Polyester	Acrylic fibre	Polyethylene	Polyethylene terephthalte
58	The polymer made from acrylenitrile ?	Polyacrylic fibres	Polyethylene	Polyester	Polyethylene terephthalte	Polyacrylic fibres
59	Polymer which contains between 35-65% of acrylonitrile are known as?	Orlon	Modaerylics	Acrilan	Verel	Modaerylics
60	Polymers which contain 85% or more acrylenitrile is?	Orlon	Modaerylics	Vinyl acetate	Verel	Orlon



COURSE CODE: 18CHU305A

CLASS: II M.Sc CHEMISTRY COURSE NAME:POLYMER CHEMISTRY **UNIT: I (Coordination Chemistry)**

	Questions	Opt-1	Opt-2	Opt-3	Opt-4	Answers
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



CLASS: II M.Sc CHEMISTRY COURSE NAME:POLYMER CHEMISTRY COURSE CODE: 18CHU305A

UNIT: I (Coordination Chemistry)

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	lonic 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	Non bonding 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



CLASS: II M.Sc CHEMISTRY COURSE NAME:POLYMER CHEMISTRY COURSE CODE: 18CHU305A

UNIT: I (Coordination Chemistry)

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 ^о С	50–70°C	80-90 ^o C	40-50 °C	50–70°C
25	Teflon is a polymer of the monomer or Teflon is obtained by the polymerisation of ?	Monofloroethene	Difloroethene	Trifloroethene	Tetrafloroethene	Tetrafloroethene



CLASS: II M.Sc CHEMISTRY COURSE NAME:POLYMER CHEMISTRY COURSE CODE: 18CHU305A

UNIT: I (Coordination Chemistry)

26	Which of the following is an example of condensation polymer?	PVC	Polyamide	Terylene	Polyester	Terylene
27	two trimers react together to form	Trimer	Hexamer	Monomer	Heptamer	Hexamer
28	Ionic vinyl polymerizations are very similar to	Free radical vinyl polymerizations	Step polymerizations	Self catalysted vinyl polymerization	Free radical polymerizations	Free radical vinyl polymerizations
29	A tetramer reacts with a trimer to form	Trimer	Dimer	Pentamer	Heptamer	Heptamer
30	A pentamer reacts with a trimer to form	Trimer	Dimer	Pentamer	Octamer	Octamer
31	Monomer concentration decreases steadily throughout reaction in?	Step polymerization	lonic polymerization	Radical polymerization	Self catalysted polymerization	lonic polymerization
32	Polymer molecular weight rises steadily throughout reaction in ?	Step polymerization	lonic polymerization	Radical polymerization	Self catalysted polymerization	Step polymerization
33	In which step of cationic polymerization follows the first order kinetics	Initiation	propagation	termination	transfermation	termination
34	A simple termination or chain transfer depending to	chain growth	degree of polymerization	kinetics	polymer deformation	degree of polymerization



CLASS: II M.Sc CHEMISTRY COURSE NAME:POLYMER CHEMISTRY COURSE CODE: 18CHU305A

UNIT: I (Coordination Chemistry)

35	The temperature would decreases	molecular weight	chain formation	initiator	monomer	molecular weight
	lie	of polymer				of polymer
36	In the radical polymerization, the propagation rate depends on	monomer	concentration of monomer radical	concentration of catalyst	reaction rate	concentration of monomer radical
37	In Cationic vinyl polymerization electron flow is ?	Same direction	Same and opposite direction	Opposite direction	Same or opposite direction	Opposite direction
38	Ionic polymerization necessarily carry along a?	Counter ion	Cation	Anion	Cation or anion	Counter ion
39	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
40	A dimer react with another dimer to form a	Trimer	Dimer	Pentamer	Tetramer	Tetramer
41	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
42	Which is impossible under any and all reaction conditions if it does not pass the test of thermodynamic feasibility?	Cationic vinyl polymerization	lonic polymerization	Polymerization	Wastage reactions	Polymerization
43	which of the following is a example of bifunctional monomer	methyl isonate	acetylene	malic acid	glycine	glycine



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CLASS: II M.Sc CHEMISTRY COURSE NAME:POLYMER CHEMISTRY **UNIT: I (Coordination Chemistry)**

44	Which of the following is the functionality of Gallic acid	monofunctional	bifunctional	tetra functional	tri functional	tetra functional
45	Monomers show high selectivity towards?	Cationic initiators	Cationic and anionic initiators	Ionic initiators	Anionic initiators	Ionic initiators
46	Most monomers will undergo polymerization with a radical initiator, although at?	Varying rates	Reliable rates	Stable rates	Positive rates	Varying rates
47	Polymerization is possible only if the free-energy difference -G between monomer and polymer is?	Positive	Negative	Both negative andpositive	Neither negative nor positive	Negative
48	The property of fabric which influences drape the most is?	Tensile	Compressional	Shear	Surface	Shear
49	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
50	To remove the residual metals, a process referred as ?	Ashing	Reashing	Ashing and reashing	Deashing	Deashing
51	3,4-Difluorophenylamine is a weaker base than ?	Phenylamine	Phenylacetate	Phenol	Henepthyl alcohol	Phenylamine
52	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



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CLASS: II M.Sc CHEMISTRY COURSE NAME: POLYMER CHEMISTRY **UNIT: I (Coordination Chemistry)**

53	Suspension free radical polymerization of styrene would be preferred over bulk polymerization to overcome the problem of ?	Branching	Cross-linking	Stereo-isomerism	Polymeric impurities	Branching
54	Polymers are ?	Large molecule	Small molecule	Small chain molecule	Large chain molecule	Large chain molecule
55	Polymers are high molecular weight in the range of ?	10 ⁴ to 10 ⁷	10 ³ to 10 ⁷	10 ² to 10 ⁷	10⁵ to 10 ⁷	10 ³ to 10 ⁷
56	Tetramer + monomer is ?	Trimer	Dimer	Pentamer	Tetramer	Pentamer
57	Which one is not a polymer?	Carbohydrates	Proteins	Carboxylic acid	Nucleic acid	Carboxylic acid
58	Due to the presence of carbon atom in polymers all large biological molecules are made of ?	lonic bond	Covalent bond	Triple bond	Metalic bond	Covalent bond
59	Amino acids are building blocks of ?	Carbohydrates	Proteins	Carboxylic acid	Lipids	Proteins
60	polyethylene is ?	Colourless liquid	Colourless gas	Gas	Liquid	Colourless gas



CLASS: II M.Sc CHEMISTRY COURSE NAME: POLYMER CHEMISTRY COURSE CODE:18CHP305A UNIT: II (CO-ORDINATION POLYMERIZATION) BATCH: 2018-2020

<u>UNIT – II</u> <u>Co-ordination Polymerization</u>

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

Coordination polymerization

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

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

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

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

Kinetics

A case of heterogeneous polymerization.

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

AR is the metal alkyl,

M is the monomer,

 M_X is the polymer.

Adsorption of metal alkyl from solution to form the active site

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

Adsorption of M from solution $H + M \stackrel{K_2}{\longrightarrow} M - H$ Initiation $M - H - AR \stackrel{K_i}{\longrightarrow} H - A - M - R$ Propagation $M - H - A - M_X - R \stackrel{K_P}{\longrightarrow} H - M_{X+1} - R$ Termination (transfer) $M - H - A - M_X - R \stackrel{K_{tr}}{\longrightarrow} H - A - M - R + M_X$ Termination (monomer forms an inactive site) $M - H - A - M_X - R \stackrel{K_1}{\longrightarrow} - H - A - M - + M_X R$

It is assumed that the process occurs in Langmuir isotherm condition and it is defined that : Θ_A and Θ_M are the fractions of the available surface covered by AR and M respectively,

[C*] is the concentration of growing chains,

Then the overall rate can be determined.

$$\theta_{A} = \frac{K_{1} [AR]}{1 + K_{1} [AR] + K_{2} [M]} \theta_{M} = \frac{K_{2} [M]}{1 + K_{1} [AR] + K_{2} [M]}$$

The overall rate :

 $R_{O} = - \frac{d [M]}{dt} = (k_{p} + k_{tr}) \theta_{M} [C^{*}]$

Assume that [C*] reaches steady state so that the initiation rate is similar to the termination rate. $k_i \theta_A \theta_M = k_t [C^*] \theta_M$

The overall rate :

$$R_{o} = - \frac{d[M]}{dt} = \frac{(k_{p} + k_{tr})k_{i}}{k_{t}} \frac{K_{1}K_{2}[AR][M]}{(1 + K_{1}[AR] + K_{2}[M])^{2}}$$

<u>Ziegler–Natta catalysis and polymerization</u> Historical Development of Ziegler–Natta Initiators

Various mechanisms have been proposed to explain the stereoselectivity of Ziegler- Natta initiators [Boor, 1979; Carrick, 1973; Corradini et al., 1989; Cossee, 1967; Ketley,

1967a,b; Tait and Watkins, 1989; Zambelli and Tosi, 1974]. Most mechanisms contain considerable details that distinguish them from each other but usually cannot be verified. In this

section the mechanistic features of Ziegler–Natta polymerizations are considered with emphasis on those features that hold for most initiator systems.

The major interest will be on the titanium-aluminum systems for isoselective polymerization, more specifically, TiCl₃ with Al(C₂H 5)₂Cl and TiCl₄ with Al(C₂H 5)₃ probably the most widely studied systems, and certainly the most important systems for industrial polymerizations. Before proceeding with the mechanistic consideration it is useful to review the evolution of the Ti-Al initiator system for industrial applications. The original initiator used by Ziegler for ethylene polymerization was obtained in situ as a precipitate on mixing the components TiCl₄ and Al(C_2H 5)₃ in a hydrocarbon solvent. The mixture was used directly for initiating polymerization. Natta, recognizing that the major product of the reaction was b-TiCl₃ (brown in color), explored various methods of preforming it outside the polymerization system, for example, by reduction of TiCl4 with hydrogen, aluminum, and various alkylaluminum compounds. The stereoselectivity of these early initiator systems was low with isotactic indices of only 20-40% for polypropene. The isotactic index, a measure of the isotactic content of a polymer, is the percentage of the sample insoluble in a hydrocarbon solvent such as boiling n-heptane. This is not as informative a technique as high-resolution NMR since insoluble molecules may contain some syndiotactic and atactic sequences and soluble molecules may contain some isotactic sequences. It does, however, give a simple measure of isotacticity that is usually within about 10% of the value obtained from NMR, especially for highly isotactic samples.

There was a dramatic increase in stereoselectivity when the α -, δ -, or γ -crystalline form of TiCl₃ (all violet in color) was used directly. The early generations of industrial processes used TiCl₃ together with Al(C₂H 5)₃ and/or Al(C₂H 5)₂Cl. Over a two decade period starting in the late 1950s, the isotactic indices for polypropene increased to the low 90 percentile range. The initiator activity was enhanced by various ball milling and heat treatments of the initiator components before and after mixing. Ball milling involves mechanical grinding and not only increases surface area but also facilitiates reactions between the initiator components.

However, the activities were too low to allow the polymer products to be used without purification (by treatment with base or acid) to remove the residual metals, a process referred to as deashing. Also, optimization of the physical properties of the product often required removal of the atactic fraction. The initiator systems were inefficient with less than 1% of the Ti being active in polymerization. The later generations of initiators, starting in the late 1970s, increased initiator efficiency and activity without sacrificing stereoselectivity [Bohm, 2001; Busico and Cipullo, 2001; Cecchin et al., 2001; Chadwick, 2001; Chadwick et al., 2001; Chien et al., 1982; Hu and Chien, 1988]. The effective surface area of the active component of the initiator system was increased by close to 2 orders of magnitude by using MgCl₂ as a solid support in which TiCl₄ is finely dispersed. Stereoselectivity was kept high and actually increased by the addition of electron-donor additives.

A typical recipe for a present-day superactive or high-mileage initiator system involve ball milling of MgCl₂ (or the alkoxide) and TiCl4 followed by the addition of Al(C₂H 5)₃ with an electron donor (such as dialkyl phthalate and alkoxysilane) usually added in each step of preparation. Activity is 50–200 kg polymer per gram of initiator system. Typically, the initiator system is no more than 2–4% Ti, which makes the activity about 1500–6000 kg polymer per gram of Ti. The high activity not only minimizes initiator and production costs but also avoids the costly task of initiator removal from the polymer product (except possibly for food- and medical-grade products). Isotactic indices for polypropene have been increased to 98% or higher with (mmmm) pentad fractions up to 98% and higher. This not only improves the product's physical properties but also avoids the need to remove the a tactic fraction.

Chemical Nature of Propagating Species

Some early polymerizations reported as Ziegler–Natta polymerizations were conventional free-radical, cationic, or anionic polymerizations proceeding with low stereoselectivity. Some Ziegler–Natta initiators contain components that are capable of initiating conventional ionic polymerizations of certain monomers, such as anionic polymerization of methacrylates by alkyllithium and cationic polymerization of vinyl ethers by TiCl₄. Most Ziegler–Natta components participate in a complex set of reactions involving alkylation and reduction of the transition-metal component by the group I–III component as shown below for TiCl₄+ AlR₃: TiCl₄ + AlR₃ —, TiCl₃ R + AlR₂ Cl

 $TiCl_4 + AlR2Cl \longrightarrow TiCl_3R + AlRCl_2$ $TiCl_3R + AlR_3 \longrightarrow TiCl_2 R_2 + AlRCl_2$

 $TiCl_3 R \longrightarrow TiCl_3 + R \bullet$

 $TiCl_3 + AlR_3 \longrightarrow TiCl_2 R + AlR_2 Cl$ R• \longrightarrow combination + disproportionation

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

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

Mechanism of Isoselective Propagation

A variety of structures have been proposed for the active species in Ziegler–Natta initiator systems [Allegra, 1971; Arlman and Cossee, 1964; Corradini et al., 1989; Natta, 1960a,b; Patat and Sinn, 1958; Rodriguez and van Looy, 1966; Tait and Watkins, 1989]. Structure XX is generally considered as the active species formed from titanium chloride and alkylaluminum components..



The Clin the structure represents an unoccupied (vacant) site of the octahedral titanium complex. XX represents an active titanium site at the surface of a TiCl₃ crystal after modification by reaction with the alkylaluminum component. The titanium atom shares four chloride ligands with its neighboring titanium atoms and has an alkyl ligand (incorporated via exchange of alkyl from the alkylaluminum for chloride) and a vacant orbital.

There are molecular mechanics calculations that indicate dimeric Ti₂Cl₆ may be theactive species instead of monomeric TiCl₃ [Monaco et al., 2000]. Other proposals for theactive species include bimetallic species that contain both titanium and aluminum [Liuet al., 2002]. To simplify matters, our discussions will center on the monomeric and monometallic titanium species, especially since the mechanistic details of stereoselectivity andactivity are essentially the same for both monomeric and dimeric titanium species as wellas titanium–aluminum species. The high-mileage supported initiators previously mentioned involve a species similar to XX as part of a mixed titanium–magnesium–chloride lattice, usually involving Mg-Cl-Ti bonds. Ti and Mg are interchangeable within the metal lattice.

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



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

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

Isotactic polymerization depends intimately on the crystal structure of the initiator surface. For a coordination lattice, as opposed to a molecular crystal lattice, the crystal contains a number of ligand vacancies in order to achieve overall electrical neutrality of the crystal. a-TiCl₃ crystals are made up of elementary crystal sheets of alternating titanium and chlorine layers aligned along the principal crystal axis [Natta et al., 1961a,b,c,d]. Figure 8-12 is a representation of a portion of the crystal [Corradini et al., 1989]. The titanium and chlorine atoms are represented by solid black and open spheres, respectively. The titaniums are at the octahedral interstices of the chlorine lattice while chlorines are hexagonally close-packed. Every third titanium in the lattice is missing, that is, there is a vacancy in between pairs of titanium atoms. Vacancies are represented by & in Fig. 8-12.

Polymerization occurs at active sites found on the edges (surfaces) of elementary sheets of the crystal and not in the basal planes. This is supported by microscopic observations of polymer growth at the crystal edges [Cossee, 1967; Kollar et al., 1968a,b; Rodriguez and van Looy, 1966]. A titanium atom at the surface is bonded to only five chlorines instead of six because of the imposed requirement of electroneutrality. Of the five chlorines, four are more strongly bonded since they are bridged to other titanium atoms. The fifth, nonbridged chlorine may be replaced by an alkyl group when the titanium component interacts with the group I–III component. The octahedral vacancy remains as a vacancy.Neighboring metal atoms (bridged by two chlorines) have opposite chirality [Allegra, 1971]. The two enantiomeric titaniums can be represented as XXI and XXII where one of the chlorine ligands has been



replaced by R via alkylation by the group I–III metal component.Propagation occurs by coordination of monomer at the vacancy, migratory insertion into the Ti__R bond, and migration of the newly formed bond to regenerate the vacancy in the original configuration. Considering either XXI or XXII, coordination of monomer can occur through either of the two monomer enantiofaces (si or re), which results in two diastereomeric transition states. The two diasteromeric states give rise to the two possible placements of monomer units in the polymerchain—meso and racemo [Corradini et al., 1984,1985; Zambelli et al., 1978, 1980]. The driving force for isoselective propagation results from steric and electrostatic interactionsbetween the substituent of the incoming monomer and the ligands of the transition metal vacancy primarily through one of the two enantiofaces. Actives sites XXI and XXII eachyield isotactic polymer molecules through nearly exclusive coordination with the re and simonomer enantioface, respectively, or vice versa. That is, we may not know which enantiofacewill coordinate with XXI while the opposite enantioface will coordinatewith XXII.

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

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

1. ¹³C NMR of isotactic polypropene shows the main error is pairs of racemic dyads instead of isolated racemic dyads (Table 8-3) [Heatley et al., 1969; Resconi et al., 2000; Wolfsgruber et al., 1975]. A stereoerror in the addition of a monomer molecule is immediately corrected when stereocontrol is by the chiral active site. If stereocontrol was due to the propagating chain end, an error would continue to propagate in an isotactic manner to yield a polymer, referred to as an isotactic stereoblock, containing long isotactic all-R and all-S stereoblocks on each side of the error.

2. ¹³C NMR of ethylene-propene copolymers of low ethylene content produced by initiators that yield isotactic polypropene shows that the isotactic propene units on each side of an ethylene unit have the same configuration (i.e., all-R or all-S) [Zambelli et al., 1971, 1978, 1979]. For stereocontrol by the propagating chain end, the amount of polymer in which the polypropene blocks on either side of an ethylene unit have the same configuration would equal that in which the blocks have the opposite configuration.

3. Statistical analysis of the stereochemical sequence distributions (Table 8-3 and Sec. 8-16) also supports the enantiomorphic site control model.

Isotactic Polymerization Mechanism



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



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

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



Natta- Bimetallic Polymerization mechanism



Copolymerization

Copolymerization of ethylene and α -olefins have been demonstrated soon after the discovery that Ziegler-Natta catalysts homopolymerize α -olefins. Copolymers have gained much interest in polymer field due to their elastomeric characteristics. Therefore, many research works were carried out to prepare better catalyst systems and to obtain more interesting elastomeric copolymers. The properties of the copolymers formed can be controlled by operating conditions, chemical composition and physical state of catalyst and comonomers structure. The most

important copolymer is prepared from ethylene and propylene. The production of ethylenepropylene copolymers were traditionally carried out with homogenous Ziegler-Natta catalyst based on vanadium compounds. The application of the Ziegler-Natta heterogenous catalytic system based on titanium compounds for the production of copolymers has recently become more important, due to high activity of the catalyst systems and low production costs. The best coordinated anionic type catalyst suitable for the production of ethylene-propylene copolymers are obtained by reaction of alklyaluminium compounds with transition metals such as vanadium, chromium, niobium and titanium. Recently, Soga and coworkers53 successfully copolymerized ethylene and propylene using a soluble chromium catalytic system composed of $Cr(C_{17}H_{35}COO)_3$ and AlEt₂Cl. The catalytic system produced random copolymer with a narrow molecular weight distribution.

Kinetics of Copolymerization

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

$M_1^* + M_1 \xrightarrow{K_{11}} M_1^* 1$	
$M_1^* + M_2 \xrightarrow{k_{12}} M_2^*$	2
$M_2^* + M_1 \xrightarrow{k21} M_1^*$	3
$M_2^* + M_2 \xrightarrow{K22} M_2^*$	4

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

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

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

5

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

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

 $d[M_1]/d[M_2] = (k_{11}[M_1^*][M_1] + k_{21}[M_2^*][M_1]) / (k_{12}[M_1^*][M_2] + k_{22}[M_2^*][M_2]) - 7$

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

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

8

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

 $\begin{aligned} d[M_1] / d[M_2] &= ((k_{11}k_{21}[M_2^*][M_1]^2 / k_{12}[M_2]) + k_{21}[M_2^*][M_1]) / k_{22}[M_2^*][M_2] + k_{21}[M2^*][M_1] & 9 \\ \text{Dividing the top and bottom of the right side of Eq. 6-10 by } k_{21}[M2^*][M_1] & \text{and combining the} \\ \text{result with the parameters } r_1 & \text{and } r_2, & \text{which are defined by} \\ r_1 &= k_{11} / k_{12} & \text{and} & r_2 = k_{22} / k_{21} & 10 \\ \text{one finally obtains} & \\ d[M_1] / d[M_2] &= [M_1] (r_1[M_1] + [M_2]) / [M_2] ([M_1] + r_2 [M_2]) & 11 \end{aligned}$

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

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

 $\begin{aligned} f_1 &= 1 - f_2 = [M_1] / ([M_1] + [M_2]) & 12 \\ \text{and} \\ F_1 &= 1 - F_2 &= d[M_1] / (d[M_1] + d[M_2]) & 13 \\ \text{Combining Eqs. 12 and 13 with above Eq. yields} \\ F_1 &= (r_1 f_1^2 + f_1 f_2) / (r_1 f_1^2 + 2 f_1 f_2 + r_2 f_2^2) \\ \text{or} \end{aligned}$

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

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

14

Types of copolymers



Different types of copolymers

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

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

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

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

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

• Stereoblock copolymers

$$\sim \stackrel{(-CH_2-C_{-})_m}{\underset{H}{\swarrow}} \stackrel{\sim}{\underset{X}{\longrightarrow}} \stackrel{(-CH_2-C_{-})_n}{\underset{X}{\longleftarrow}} \stackrel{\sim}{\underset{H}{\longrightarrow}} \stackrel{(-CH_2-C_{-})_n}{\underset{X}{\longrightarrow}} \stackrel{\sim}{\underset{H}{\longrightarrow}} \stackrel{(-CH_2-C_{-})_n}{\underset{X}{\longrightarrow}} \stackrel{\sim}{\underset{H}{\longrightarrow}} \stackrel{(-CH_2-C_{-})_n}{\underset{X}{\longrightarrow}} \stackrel{(-CH_2-C_{-})_n}{\underset{H}{\longrightarrow}} \stackrel{(-CH_2-C_{-})_n}{\underset{X}{\longrightarrow}} \stackrel{(-CH_2-C_{-})_n}{\underset{H}{\longrightarrow}} \stackrel{(-CH_2-C_{-})_n}{\underset{X}{\longrightarrow}} \stackrel{(-CH_2-C_{-})_n}{\underset{H}{\longrightarrow}} \stackrel{(-CH_2-C_{-})_n}{\underset{X}{\longrightarrow}} \stackrel{(-CH_2-C_{-})_n}{\underset{H}{\longrightarrow}} \stackrel{(-CH_2-C_{-})_n}{\underset{X}{\longrightarrow}} \stackrel{(-CH_2-C_{-})_n}{\underset{H}{\longrightarrow}} \stackrel{(-CH_2-C_{-})}{\underset{H}{\longrightarrow}} \stackrel{(-CH_2-C_{-})}{\underset{H}{\longrightarrow}} \stackrel{(-CH_2-C_{-})}{\underset{H}{\longrightarrow}} \stackrel{(-CH_2-C_{-})}{\underset{H}{\longrightarrow}} \stackrel{(-CH_2-C_{-})}{\underset{H}{\longrightarrow}} \stackrel{(-CH_2-C_{-})}{\underset{H}{\longrightarrow}} \stackrel{(-CH_2-C_{-})}{\underset{H}{\longrightarrow}} \stackrel{(-CH_2-C_{$$

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

Statistical copolymers

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

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

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

Graft copolymers

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

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

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

Block copolymers

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

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

Copolymer Composition

Terminal Model; Monomer <u>Reactivity Ratios</u>

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

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

Q-e Scheme

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

 $K_{12} = P_1 Q_2 \exp(-e_1 e_2)$

15

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

$r_1 = Q_1/Q_2 \exp[-e_1(e_1 - e_2)]$	16
$r_2 = Q_2/Q_1 \exp[-e_2(e_2 - e_1)]$	17

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

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

Consider now the use of the Q–e shceme to predict monomer reactivity ratios. Values of Q and e have been assigned to monomers on the basis of their r values and the arbitrarily chosen reference values of Q = 1 and e = -80 for styrene [Greenley, 1989b, 1999]. Table 6-7 shows the

average Q and e values for some common monomers. The practical success of the Q–e scheme in predicting the r_1 and r_2 values for comonomer pairs not previously copolymerized has been limited in its quantitative aspects. The reason for this is that the Q and e values for a monomer are not unique values for both experimental and theoretical reasons. The precision of the calculated Q and e values is often poor as a result of inaccuracies in the experimentally determined r values. Further, the Q and e values for a monomer vary considerably depending on the monomer with which it is copolymerized as a result of inherent deficiencies of the Q–e scheme. It does not explicitly take into account steric factors that may affect monomer reactivity ratios for certain radical–monomer combinations. The assumption of the same e value for a monomer and its corresponding radical is also inadequate. Attempts to refine the Q–e scheme by using separate e values for monomer and radical have not been successful.

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

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

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

THEEL: Q and C Values for Monomersa, a Data from Greenie J [19090, 1999].							
Monomer	Q	e					
Ethyl vinyl ether	0.018	-1.80					

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

Prepared by Dr. S. Manickasundaram, Assistant Professor, Dept. of Chemistry, KAHE

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

Text book:

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

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

Reference book

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

POSSIBLE QUESTIONS

Multiple choice questions (Each Carry 1 Marks)

1. The polyethene polymer formed by the addition polymerisation process using the Ziegler-Natta catalyst is a? a. High density and high melting point b. Low density and high melting point c. High density and low melting point d. Low density and low melting point 2. The catalyst used for the Ziegler–Natta polymerizations? b. BCl₃ with Al(C_2H_5)₂Cl c. TiCl₃ with Fe(C_2H_5)₂Cl a. TiCl₃ with Al(C₂H₅)₂Cl d. TiF₃ with Al(C₂H₅)₂F 3. Melting Point of Low Density Polyethylene (LDPE) is? c. ~117°C a. ~115° C b. ~116 °C d.~118°C 4. Which polymer is not an copolymer? a. CCDDDCCDDDCCD **b. AAAAAAAAA** c. BBBBBBBBAAAAAAA d. CCCDDCCCDDCCC 5. The metal in the co-catalyst is come from c. IV and V b. III to IV a.I to III d. IV-VIII 6.R-Ti-Cl₄ is an a.bi-metallic catalyst **b. mono metallic catalyst** c. tri metallic catalyst d. alkyl catalyst 7. Monometallic mechanism proposed by b. Cossee c. Robert d. Wilson a. Natta 8. The Ti metal have a ---- number of co-ordination a. 5 c. 7 b. 4 d. 6 9. Ti halide is acting as a a. adsorbate b. co-catalyst c. secondary catalyst d. Surface catalyst 10.In the zieglar-natta catalyst the aluminium halide ------ on Ti halide b. physisorbed d. absorped a. chemisorbed c. bonded 11. The insertition of monomer in the alternative spatial arrangement form the **b.** syndiotactic polymer c. copolymer a. isotactic polymer d. radical polymer 12. Which of the following is not depend on the formation of vaccant sites a. coming monomeric unit b. chlorine atom of catalyst c. substituent of monomer unit d. Transition metal atom 13. Which is the step to form the activesite catalyst in co-ordination polymerization b. propagation c. termination d. transfermation a. initiation 14. In the monometallic mechanism monmer attacks the b. Al-R bond c. Ti-R bond d. Al-Cl bond a. Ti-Cl bond 15. Who fractionated the vinyl chloride-vinyl acetate co-polymer a. Cossee b. Natta c. Staudinger d. Zieglar 16. Two or more monomers are combined to form a. Co-ordination polymer **b. Co-polymer** c. Crystalline polymer d. Homo polymer 17. The polymer production in the co-polymerisation depends on the a. anyone monomer unit **b. reactivity ratio** c. reaction path d. two monomers 18. The reactivity ratio is represented as a. r1 b. r2 c. r1/r2 d. m1/m219. [m1] and [m2] represents the a. mole fraction b. molar concentration d. number of moles c. molecular mass

20. The plot between r1(assumed values) Vs r2 (calculated values) is drawn in the method of **a. Mayo-Lewis method** b. Fineman-Rose method c. Lewis method d. molecular method

Questions(Each carry 6 Marks)

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

Compulsory Questions (Each carry 10 Marks)

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



CLASS: II M.Sc CHEMISTRY

HEMISTRY COURSE NAME:POLYMER CHEMISTRY UNIT: II(CO-ORDINATION POLYMERIZATION) I

BATCH-2018-2020

DUCATION COURSE CODE: 18CHP305A

	Questions	Opt-1	Opt-2	Opt-3	Opt-4	Answers		
1	The alternating copolymer contains ?	2 monomer units	3 monomer units	4 monomer units	1 monomer units	2 monomer units		
2	The copolymer is not an?	Alloy	Trimer	Monomer	Initiator	Alloy		
3	The polyethene polymer formed by the addition polymerisation process using the Ziegler- Natta catalyst is a?	High density and high melting point	Low density and high melting point	High density and low melting point	Low density and low melting point	High density and high melting point		
4	The catalyst used for the Ziegler–Natta polymerizations?	TiCl3 with Al(C2H 5)2Cl	BCl3 with Al(C2H 5)2Cl	TiCl3 with Fe(C2H 5)2Cl	TiF3 with Al(C2H 5)2F	TiCl3 with Al(C2H 5)2Cl		
5	Melting Point of Low Density Polyethylene (LDPE) is?	~115o C	~116 oC	~117oC	~118 oC	~115o C		
6	Which polymer is not an copolymer?	CCDDDCCDDDCC D	ААААААААААА	BBBBBBBAAAAAAA	CCCDDCCCDDCCC	ΑΑΑΑΑΑΑΑΑΑ		
7	Which, speeds up the oxidation process in polymerization?	Heat	Catalyst	Initiator	Reactants	Heat		



CLASS: II M.Sc CHEMISTRY

COURSE CODE: 18CHP305A

COURSE NAME:POLYMER CHEMISTRY

UNIT: II(CO-ORDINATION POLYMERIZATION)

8	Highly unsaturated polymers are much more sensitive to ?	Reduction	Addition	Oxidation	Redox	oxidation
9	Stability of a polymer depends on?	Physical structure	Chemical properties	Physical properties	Chemical structure	Chemical structure
10	Most polymers are?	Thermally stable	Physically stable	Chemically stable	Unstable	Thermally stable
11	Carbon Black and other colorants may also protect plastics from the effects of?	Temperature	Melting point	Pressure	Light	Light
12	Ultraviolet absorber is?	2-hydroxyphenyl benzotriazoles	Hydroxybenzop henones	Hindered amines	Benzophenones	Hydroxybenzophen ones
13	Any of a group of substances that are used in plastics to impart viscosity, flexibility, softness to the finished product is defined as?	Light stabilizers	Colouarants	Plasticizers	Flame retardents	Plasticizers
14	Which of the following is used to form a stereo regular polymer	co-polymer	Acid catalyst	Zieglar-natta catalyst	alkyl catalyst	Zieglar-natta catalyst
15	higher alpha olefins form the	isotactic polymer	syndiotactic polymer	stereo polymer	copolymer	isotactic polymer
16	Polymerization reaction done by the presence of organo-metallic compounds is	co-ordinaion polymerisation	co- polymerization	addition polymerisation	chain polymerization	co-ordinaion polymerisation



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COURSE NAME:POLYMER CHEMISTRY

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17	In the zieglar-natta catalyst, the alkyl metals from group	l to III	III to IV	IV and V	IV-VIII	l to III
18	The metal in the co-catalyst is come from	l to III	III to IV	IV and V	IV-VIII	IV-VIII
19	R-Ti-Cl4 is an	bi-metallic catalyst	mono metallic catalyst	tri metallic catalyst	alkyl catalyst	mono metallic catalyst
20	Monometallic mechanism proposed by	natta	cossee	Robert	Wilson	cossee
21	The Ti metal have a number of co-ordination	5	4	7	6	5
22	Ti halide is acting as a	adsorbate	co-catalyst	secondary catalyst	Surfae catalyst	Surfae catalyst
23	In the zieglar-natta catalyst the aluminium halide on Ti halide	chemisorbed	physisorbed	bonded	absorption	chemisorbed
24	In the Zieglar-natta catalyst, the Ti halide have a	vacant d-orbital	vacant p-orbital	filled d-orbitals	filled p-orbitals	vacant d-orbital
25	Which of the following is the active site of the zieglar- natta catalyst	metal in I-III group	metal in I group	metal in IV-VIII group	only in II group metal	metal in IV-VIII group



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COURSE NAME: POLYMER CHEMISTRY

UNIT: II(CO-ORDINATION POLYMERIZATION)

26	In the bi metallic mechanism forms the	bi-complex	intermediate compound	intermediate ion	Catalyst	bi-complex
27	Which of the following metal is not present in the zieglar- natta catalyst	Ti	Мо	v	Li	Li
28	The metal present in the zieglar-natta catalyst is	non-metal	semi metal	taransition metal	radio-active metal	taransition metal
29	Which of the following is used for the stereo-regular polymer	zieglar-natta catalyst	Acid catalyst	basic catalyst	intermediate	zieglar-natta catalyst
30	The insertition of monomer in the same spatial arrangement form the	isotactic polymer	syndiotactic polymer	copolymer	radical polymer	isotactic polymer
31	The insertition of monomer in the alternative spatial arrangement form the	isotactic polymer	syndiotactic polymer	copolymer	radical polymer	syndiotactic polymer
32	which of the following is not depent on the formation of vaccant sites	coming monomeric unit	chlorine atom of catalyst	substituent of monomer unit	Transition metal atom	Transition metal atom
33	In the syndiotactic polymer, the substituent monomer units are insert in the	alternative sites	same position	opposit position	regular postion	alternative sites
34	In the isotactic polymer, the monomer insertition in the	Same direction	opposite direction	alternative direction	either same or alternative	Same direction



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COURSE NAME:POLYMER CHEMISTRY

UNIT: II(CO-ORDINATION POLYMERIZATION) BAT

35	Which is the step to form the activesite catalyst	initiation	propagation	termination	transfermation	propagation
36	In the monometallic mechanism monmer attacks the	Ti-Cl bond	Al-R bond	Ti-R bond	Al-Cl bond	Ti-R bond
37	Who fractionated the vinyl chloride-vinyl acetate co- polymer	Cossee	natta	Staudinger	Zieglar	Staudinger
38	Two or more monomers are combined to form	co-ordination polymer	co-polymer	crystalline polymer	homo polymer	co-polymer
39	The polymer production in the co-polymerisation depends on the	anyone monomer unit	reactivity ratio	reaction path	two monomers	reactivity ratio
40	The reactivity ration is represented as	r1	r2	r1/r2	m1/m2	r1/r2
41	The r1>1 means the preference of the add	M1 monomer	M2 monomer	either M1 or M2	neither M1 nor M2	M1 monomer
42	The r2 > 1 prefer the addition of	M1 monomer	M2 monomer	either M1 or M2	neither M1 nor M2	M2 monomer
43	The two monomers in the co-polymerisation have same prefernce of addition to produce	ideal co-polymer	alternative co- polymer	block polymer	non-ideal polymer	ideal co-polymer



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		1				
44	In the ideal co-polymer, the reactivity ratio is equal to	1	0	not equal to 0	not equal to unity	1
45	In the alternating co- polymer, the reactivity ratio is equal to	0	1	not equal to 0	above 1	0
46	In which of the following condition form the block co- polymer	r1/r2 = 1	r1/r2 = 0	r1,r2<1	r1,r2>1	r1,r2>1
47	The over all rate of co- polymerization depends on the	inition step only	propagation step only	termination step only	both inition and termination	both inition and termination
48	Most of the graft polymers are formed by	chain polymerization	co-ordination polymerization	radical polymerization	lonic polymerization	radical polymerization
49	[m1] and [m2] represents the	mole fraction	molar concentration	molecular mass	number of moles	mole fraction
50	the plot between r1(assumed values) Vs r2 (calculated values) is drawn in the method of	Mayo-Lewis method	Finemann-Rose method	Lewis method	molecular method	Mayo-Lewis method
51	equation belongs to the	Mayo-Lewis method	Finemann-Rose method	Lewis method	molecular method	Finemann-Rose method
52	the slope of graph in the fineman-ross method give the value of	М	Ρ	r1	r2	r1



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53	In the fineman-Ross method, the ordinate intercept give the	r1 value	negative r1 value	negative r2 value	positive r1 value	negative r2 value
54	Which of the following condition make the M1 radical prefers to add M2 monomer and the M2 radical prefer to add M1 monomer	r1/r2 = 0	r1,r2<1	r1,r2>1	r1=r2=0	r1=r2=0
55	Which of the following condition make the both M1 and M2 radical have same preference for M1 and M2 monomers	r1=r2 = 1	r1,r2<1	r1,r2>1	r1=r2=0	r1=r2 = 1
56	The composition of two monomers are constant means it forms	azeotropic co- polymerisation	an azeotropic co- polymerisation	alternating co- polymerization	block co-polymer	azeotropic co- polymerisation
57	Which of the following conditions form the M1 richer co-polymer	r1,r2<1	r1,r2>1	r1=r2=0	r1>1 , r2<1	r1>1 , r2<1
58	The condition r1<1 and r2>1 condition preferse the	M1 radical prefer to M1 monomer	M2 radical prefer to the M2 monomer	M1 radical prefer to M2 monomer and M2 radical prefer the M1 monomer	M1 radical prefer to M1 and monomer and M2 radical prefer the M1 and M2 monomer	M1 radical prefer to M2 monomer and M2 radical prefer the M1 monomer
59	The r1 is less than r2, the azeotropic composition should be	increases	decreases	constant	first increases then decreases	decreases



CLASS: II M.Sc CHEMISTRY

COURSE NAME: POLYMER CHEMISTRY UNIT. II/CO ODDINATION DOI VMEDIZATION

RATCH-2018-2020

COURSE CODE: 18CHP305A

A	UNIT: II(CO-OR	DINATION POLYMERI	IZATION)	BATCH-2018-2

60	The r1 < 1 and r2 > 1 condition to form the polymer richer in	M1 monomer	M2 monomer	M1 radical	M2 radical	M2 monomer



CLASS: II M.Sc CHEMISTRYCOURSE NAME: POLYMER CHEMISTRYCOURSE CODE:18CHP305AUNIT: III (MOLECULAR WEIGHT PROPERTIES)BATCH: 2018-2020

<u>UNIT–III</u>

SYLLABUS

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 \mathcal{D} (pronounced D-stroke) which can refer to either molecular mass or degree of polymerization. It can be calculated using the equation $\mathcal{D}_{\rm M} = M_{\rm W}/M_{\rm n}$, where $M_{\rm W}$ is the weight-average molar mass and $M_{\rm n}$ is the number-average molar mass. It can also be calculated according to degree of polymerization, where $\mathcal{D}_{\rm X} = X_{\rm W}/X_{\rm n}$, where $X_{\rm W}$ is the weight-average degree of polymerization and $X_{\rm n}$ is the number-average degree of polymerization. In certain limiting cases where $\mathcal{D}_{\rm M} = \mathcal{D}_{\rm X}$, it is simply referred to as \mathcal{D} . 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 (\boldsymbol{D}), is a measure of the distribution of molecular mass in a given polymer sample. \boldsymbol{D} (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. D has a value equal to or greater than 1, but as the polymer chains approach uniform chain length, D 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	Typ e	Molecular Weight Range, g/mol	Mean Value Measured
1.	Membrane osmometry	А	$10^4 - 10^6$	M _n
2.	Ebullioscopy (boiling point elevation)	А	<104	M _n

3.	Cryoscopy (freezing point depression)	A	<104	M _n
4.	Isothermal distillation	A	<104	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	$10^2 - 10^8$	Mw
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	А	$10^{3}-10^{8}$	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,

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

so that

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

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 ,

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

Applying the formula previously analyzed for monodisperse M now yields

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

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 propertybased 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),

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

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,

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

where n_0 is the solvent refractive index, λ_0 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,

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

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

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

In light scattering, each molecule contributes to the overall measurement according to the square of its molecular weight. In osmometry, all molecules contribute equally, independently of molecular

weight.Turning to the analogous polydisperse molecular weight case, and using the same notation as before, contributions to R by each molecular weight fraction simply add,

$$R = K \sum c_i M_i$$

The M formula for the monodisperse sample now yields

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

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

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

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

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

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

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

Molecular Weight Distributions -

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



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

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



These bear no resemblance to the raw trace, and the significant polydispersity of the sample is amply evident. Indeed, the x(M) curve shows that the most common polymer species has a molecular weight of 7,200 g/mol even though M_n and M_W both exceed 100,000 g/mol. Approximately 10% of the molecules by weight have molecular weights in excess of 800,000

g/mol, while 10% by weight have molecular weights less than 50,000 g/mol. The value of M_n falls slightly above the maximum of w(M), whereas the value of M_w lies well above this maximum, a fact commonly mentioned in introductory polymer texts. The difference between x(M) and w(M) simply manifests that it takes many small chains to balance the mass of a few larger chains. By number, the short chains dominate, while by weight, the converse is true. Surveying a whole year of Macromolecules, one is likely to never see a x(M) curve and just a handful of w(M) curves.

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

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

$$y dx = y' dlog(x)$$

Solving,

$$\mathbf{y'} = \mathbf{y}\mathbf{x}$$

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 sensitivity with an increased chain length. The first measurements with this method were performed by Staudinger and Eder and gave determination limits of about 15,000 g·mol-1. Weber and Husemann treated cellulose with an alkaline copper sulfate solution to oxidize aldehydes to aldonic acids. Afterwards, they determined the so-called "*Monosezahl*" (number of glucose units per carboxyl group). With this method, they were able to determine molecular weights up to 200,000 g·mol⁻¹. However, due to processing, cellulose usually already contains oxidized end groups and additional carbonyl groups. Hence, a direct relationship between carboxyl groups (aldonic acid) and molecular weight determined with a high rate of accuracy.

Osmotic Pressure

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

based on colligative properties. Out of the four colligative methods, only membrane osmometry (MO) is of interest for cellulosic samples.

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

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

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

where Π is the osmotic pressure, *c* is the solute concentration, *R* is the ideal gas constant, *T* the temperature, *Mn* is the number average, and *A*2 and *A*3 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 *A*2. Note, that *A*2 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 η 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-Houwink equation (see Chapter 2.4).

Using VPO instruments with increased sensitivity, Kamide*et al.* detected an upper limit of $1 \times 105 \text{ g} \cdot \text{mol}^{-1}$. 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 $55,000 \pm 7000 \text{ g} \cdot \text{mol}^{-1}$. 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 ηsp 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:

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

Specific Viscosity: $\eta_{sp} = \frac{\eta - \eta_0}{\eta_0} = \eta_r - 1$
Reduced Viscosity: $\eta_{red} = \frac{\eta_{sp}}{c}$
Intrinsic Viscosity: $[\eta] = \lim_{c \to 0} \frac{\eta_{red}}{c}$
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 $[\eta]$ will give the molecular weight for an unknown molecule, which is normally done by plotting log $[\eta]$ 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:

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

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 Mvvalues, typically by using an Ubbelohde capillary viscometer. In industrial applications, the measurement of $[\eta]$ provides a quick and easy route to the molecular weight. For viscosity measurements, a minimum requirement is the knowledge of the dependence of $[\eta]$ 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 methods for 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 Mvtherefore is an approximation of Mw. In fact, Mvcan 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 Mvbe used as an approximation of Mw. MHS parameters found in the literature can be excessively variable, with Kvvalues ranging from 0.42 to 1.87 and v values ranging from 0.771 to 0.905.

In spite of these factors, viscometry remains a primary method for obtaining cellulose molecular weight averages because it does not require calibration. It is also a feasible method for

monitoring cellulose degradation during process steps, which results in relative data. This is mainly because it does not require advanced equipment, the method is relatively simple, and it is specifically recommended by industrial standards. It is essential to remember that the parameters for the Mark-Houwink equations arespecified for cellulose and that it is problematic to use such parameters for samples with, for example, high lignin or hemicellulose content.

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

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

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

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

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 [74]. As a standalone technique, it delivers the weight average Mw, the corresponding zaverage square radii $\langle r_2g \rangle_z$, and the second virial coefficient A2 of cellulose. Since it is an absolute method, it does not require calibration. One limitation of the LS method is that for a given concentration c (g·mL⁻¹), the scattered light signal is proportional to $c \times Mw$, such that molecules below a few thousand g·mol⁻¹need relatively high concentrations in order to produce a detectable signal. Raising the concentration of, for example, a broad distributed sample, leads to problems, especially in the SEC portion of the process in which cellulose is analyzed. Dust will also scatter light and contribute to the intensity; therefore, dust has to be removed using ultra-fine filters or centrifugation prior to measurements. The source of radiation is, in most cases, visible light from a laser; therefore, using colored solvents (e.g., Cu- and Fe-containing complexes) is challenging and cellulose is often derivatized and dissolved in an organic solvent or colorless solvent instead. Thus far, DMAc/LiCl is the solvent of choice for an LS experiment coupled to an SEC. Measuring cellulosic samples with fluorescence activity (e.g., pulp with high lignin content) also poses some challenges. Due to the laser excitation, even small amounts of fluorophores will disrupt a measurement. There are two types of LS experiments: the batch mode and the chromatographic (online) measurement. In the batch mode (off-line), MALLS detector can be used as a standalone instrument to characterize an unfractionated polymer sample; the online use of an LS detector is described in

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

The ratio:

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

depends on:

• The concentration of solution *c*;

• The specific refractive increment obtained at chemical equilibrium dn/dc or, more accurately, $(dn/dc)\mu$;

• The molecular weight of dissolved particles (*M*);

• Scattering angle θ .

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

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

Where K^* is the optical constant, $R(\theta, c)$ is the excess Rayleigh ratio of the solution as a function of scattering angle θ and concentration c, Mw is the molar mass weight average, $P(\theta)$ is the angular dependence of the scattered light, A2 is the second virial coefficient, and c is the concentration of the solute.

The optical constant is described by the following equation:

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

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

The measured data can be extrapolated to zero concentration and zero-degree scattering angle, which can be achieved for the batch mode by using the so-called Zimm-plot to derive three valuable quantities: the weight average Mw, the second virial coefficient of osmotic pressure A2

(both with extrapolation to zero angle), and the radius of gyration (z-average) by extrapolating the concentration to zero. The specific refractive increment at chemical equilibrium must be measured separately by using a differential refractometer.

Polymer morphology

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

Crystallinity

When applied to polymers, the term *crystalline* has a somewhat ambiguous usage. In some cases, the term *crystalline* finds identical usage to that used in conventional crystallography. For example, the structure of a crystalline protein or polynucleotide, such as a sample prepared for 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 threedimensional 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 Tg and Tm

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.



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

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

Determination of T_g

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

Differential Scanning Calorimetry (DSC)

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

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



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

Thermo Mechanical Analysis (TMA)

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

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

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

Dynamic Mechanical Analysis (DMA)

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



"Rubber plateau"

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

Text book:

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

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

Reference book

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

POSSIBLE QUESTIONS Multiple choice questions (Each carry 1 Marks)

- 1. The freezing point depression depends on the
- a. Number of dissolved solutes b. Average weight of solute c. Size and nature of solute d. solvent nature
- 2. The difference temperature between the freezing point of solute and solvent in the range of a. 10°C b. 0.01°C c. 0.001°C d. 0.1°C
- 3. By this method, accurately determine the molecular weights upto
- a. 10,000 b. 20,000 c. 30,000 d. 50,000
- 4. The method based on observation of boiling point of a solution and solvent is known as
- a. cryoscopic **b. Ebuliometry** c. membarane Osmometry
- d. Equlibrium Osmometry

 $\sum_{5,i=1}^{N_i} N_i$ the equation belongs to

a. **Number-average concept** b. Weight average concept c. Viscosity concept

- d. Osmostric concept
- 6. The weight average molecular degree of polymerisation indicates as
- a. $D_p b. (D_p)_w$ c. $(D_p)_n$ d. D
- 7. A simple chemical compounds which have same molecular weight to form
- **a.** monodispersion b. bi dispersion c. poly dispersion d. polymer solution 2. The same ball \overline{M} represents the
- 8. The symbol \overline{M}_v represents the
- a. Number-average molecular weight b. Weight average molecular weight

c. Viscosity average molecular weight d. Vapour pressure molecular weight 9. A polymer contains different molecular weight compounds to form b. bi dispersion c. poly dispersion a. monodispersion d. polymer solution 10. The symbol \overline{M}_{w} represents the a. Number-average molecular weight b. Weight average molecular weight c. Viscosity average molecular weight d. Vapour pressure molecular weight 11. The symbol $\overline{M}v$ represents the a. Number-average molecular weight b. Weight average molecular weight c. Viscosity average molecular weight d. Vapour pressure molecular weight 12. The phenomenon of depressing the freezing point of a liquid by the addition of solute is known as a. Cryoscopy c. Osmometry d. Vapour phase Osmometry b. Ebuliometry 13. The freezing point depression depends on the b. Average weight of solute c. Size and nature of solute a. Number of dissolved solutes d. solvent nature 14. The difference temperature between the freezing point of solute and solvent in the range of b. 0.01°C d. 0.1°C a. 10°C c. 0.001°C 15. By this method, accurately determine the molecular weights upto a. 10.000 b. 20,000 c. 30,000 d. 50,000 16. The method based on observation of boiling point of a solution and solvent is known as c. membarane Osmometry **b.** Ebuliometry a. cryoscopic d. Equlibrium Osmometry 17. $[\eta]$, dl/g is equal to the a. specific viscosity b. reduced viscosity c. inherent viscosity **d. intrinsic viscosity** 18. The intrinsic viscosity is also known as a. specific viscosity b. reduced viscosity c. inherent viscosity d. Staudinger viscosity 19. The rpm maintained for minute in the sedimentation equilibrium method is a. 30.000 b. 50.000 c. 15.000 d. 65,000 20. The error occurred in the viscometer due to the measurement of a. level of solute b. density d. flow time c. nature

Questions (Each Carry 6 Marks)

- 1. How to calculate the molecular weight of the polymer based on the number average method. Explain anyone of its experimental method?
- 2. Give an account of viscosity methods?
- 3. How to calculate the molecular weight of the polymer based on viscocity?
- 4. Give an account of light scattering method?
- 5. How to calculate the molecular weight of the polymer based on the weight average method. Explain anyone of its experimental method?
- 6. Give an account of vapour phase osmometry methods?
- 7. How to determine the molecular weight by osmometry?
- 8. Give an account of viscosity methods?
- 9. How to calculate the molecular weight of the polymer by Cryoscopic and Ebuliometric method?

- 10. What are the difference between T_g and T_m ?
- 11. What is Glass Transition Temperature? How to determine it experimently?

CompulsoryQuestions (Each Carry 10 Marks)

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



CLASS: II M.Sc CHEMISTRY COURSE NAME: POLYMER CHEMISTRY COURSE CODE: 18CHP305A UNIT: III(MOLECULAR WEIGHT AND PROPERTIES) BATCH-2018-2020

	Questions	Opt-1	Opt-2	Opt-3	Opt-4	Answers	
1	$\sum_{i=1}^{\infty} N_i$ the equation belongs to	Number- average concept	Weight average concept	Viscosity concept	Osmostric concept	Number-average concept	
2	The weight average molecular degree of polymerisation indicates as	Dp	(Dp)w	(Dp)n	D	(Dp)w	
3	A simple chemical compounds which have same molecular weight to form	monodispersio n	bi dispersion	poly dispersion	polymer solution	monodispersion	
4	A polymer contains different molecular weight compounds to form	monodispersio n	bi dispersion	poly dispersion	polymer solution	poly dispersion	
5	The symbol Mn represents the	Number- average molecular weight	Weight average molecular weight	Viscosity average molecular weight	Vapour pressure molecular weight	Number-average molecular weight	
6	The symbol Mw represents the	Number- average molecular weight	Weight average molecular weight	Viscosity average molecular weight	Vapour pressure molecular weight	Weight average molecular weight	
7	The symbol Mv represents the	Number- average molecular weight	Weight average molecular weight	Viscosity average molecular weight	Vapour pressure molecular weight	Viscosity average molecular weight	


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8	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
9	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
10	The freezing point depression depents on the	Number of dissolved solutes	Average weight of solute	solvent concentration	solvent nature	Number of dissolved solutes
11	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
12	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
13	The freezing point of the solvent indicates the	F	TF	Tf	Ts	Tf
14	ΔTf is the difference of	freezing point between solute and solvent	freezing point of solutes	freezing point between solvent molecules	the temperature between solute and solvent	freezing point between solute and solvent
15	In the cryoscopic method, the error occurred to measure the	weight of monomer	temperature	freezing point	melting point	temperature
16	The difference temperature between the freezing point of solute and solvent in the range of	10ºC	0.01ºC	0.001ºC	0.1ºC	0.001ºC



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			1			1
17	By this method, accurately determine the molecular weights upto	10,000	20,000	30,000	50,000	30,000
18	The method based on observation of boiling point of a solution and solvent is known as	cryoscopic	Ebuliometry	membaraneOs mometry	EqulibriumOsmom etry	Ebuliometry
19	The Ebuliometry is a method based on the observation of	freezing point	boiling point	meltinf point	crystalline point	boiling point
20	The difference in the heat of vapourisation is indicates as	ΔΗν	ΔSv	ΔΤν	ΔGv	ΔΗν
21	The Tb is the symbol for	freezing point of solvent	boiling point of solvent	meltinf point of solvent	crystalline point of solvent	boiling point of solvent
22	The osmosis based method is known as	membrane osmometry	Ebuliometry	Cryoscopic	Viscometry	membrane osmometry
23	The membrane osmometry method based on	freezing point	osmotic pressure	boiling point	crystaline point	osmotic pressure
24	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
25	The osmotic pressure is represented as	σ	θ	μ	π	π



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26	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
27	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
28	The Ebuliometry method is applicable for	volatile solute	non-volatile solute	ionised solute	low molecular weight solute	non-volatile solute
29	The solution and solvent levels are measured by using	cathetometer	anometer	thermometer	osmometry	cathetometer
30	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
31	1 atmosphere is equal to the	1033 g wt/cm2	1110 g wt/cm2	1200 g wt/cm2	1040 g wt/cm2	1033 g wt/cm2
32	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
33	The vapour pressure of a solution is than pure solvent	more	less	same	constant	less
34	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



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The ratio between the functionality divided by functional group equivalent is Ŵν 35 Ŵп Ŵw Ŵѕ Ŵп known as The viscosity of the polymer solution is 36 solute solvent monomer catalyst solvent high compared to The relative viscosity is equal to the $^{n}/^{n}0 = t/t0 = ^{n}r$ In nr /C 37 n/n0 = t/t0 = nrnsp nred 38 The specific viscosity is equal t the nr - 1 In nr /C nr - 1 nred ηr 39 The reduced viscosity is equal to the $\ln \eta r / C$ $\eta sp / C = \eta red$ $\eta sp / C = \eta red$ ηr - 1 ηr specific reduced inherent $\ln \eta r / C$ is the 40 intrinsic viscosity inherent viscosity viscosity viscosity viscosity specific reduced inherent $[\eta]$, dl/g is equal to the 41 intrinsic viscosity intrinsic viscosity viscosity viscosity viscosity reduced inherent Staudinger specific 42 The intrinsic viscosity is also known as Staudinger viscosity viscosity viscosity viscosity viscosity specific reduced inherent The limiting viscosity number known as 43 intrinsic viscosity intrinsic viscosity viscosity viscosity viscosity



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44	The USLV is the	osmometer	viscometer	cathetometer	speedometer	viscometer
45	The viscosity highly depends on the	temperature	density	size	nature	temperature
46	The range of constant temperature maintained at viscometer is	0.01ºC	± 0.001ºC	± 0.1ºC	± 0.01ºC	± 0.01ºC
47	The error occurred in the viscometer dur to the measurement of	level of solute	density	nature	flow time	flow time
48	All the solutions are free from impurities, it reduces the	Number of dissolved solutes	yield	error	density	error
49	Which one of the following is most complex method	viscometry	osmometry	ultracentrifugat ion	light scattering	ultracentrifugation
50	In the ultracentrifugation, which force is used for polymer separation	kinetic force	magnetic force	centrifugal force	vanderwalls force	centrifugal force
51	The sedimentation velocity depends on the	nature of polymer	size of polymer	molecular weight	number of solute	molecular weight
52	The sedimentation velocity method has revolution per minute	30,000	60,000	65,000	50,000	65,000



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53	The symbol ω represents the	angular viscosity	pressure	angular moment	angular velocity	angular velocity
54	The sedimentation constant is denoted as	ω0	S0	AO	CO	SO
55	The molecular weight distribution form a heterogenous system in the	sedimentation velocity method	sedimentatio n viscosity method	sedimentation equilibrium method	Osmometric method	sedimentation equilibrium method
56	The sedimentation equilibrium method is one of the	easy method	time consumuing	low cost	accurate	time consumuing
57	The rpm maintained for minute in the sedimentation equilibrium method is	30,000	50,000	15,000	65,000	15,000
58	The symbol iOis the equation	intensity of scattered light	intensity of incident light	intensity of solvent	intensity of both solute and solvent	intensity of scattered light
59	The symbol ț is equal to the	viscosity	velosity	turbidity	density	turbidity
60	the equation belongs to	Number- average concept	Weight average concept	Viscosity concept	Osmostric concept	Number-average concept



CLASS: II M.Sc CHEMISTRY COURSE NAME: POLYMER CHEMISTRY

COURSE CODE:18CHP305A UNIT: IV (POLYMER PROCESSING)

BATCH: 2018-2020

<u>Unit-IV</u>

SYLLABUS

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

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

Uses	sandwich bags, cling wrap, car	freezer bags, water pipes, wire and cable	
	covers, squeeze bottles, liners for	insulation, extrusion coating	
	tanks and ponds, moisture barriers		
	in construction		

<u>Elastomer</u>

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

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

<u>Fibres</u>

<u>Fiber</u>



A bundle of optical fibers

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

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

Compounding

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

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

Roles

During research and development

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

Patients with unique or unusual medication needs

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

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

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

Polymer processing Techniques

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

1. <u>Calendering</u>



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

2. <u>Casting Process</u>

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

1. Die casting

- 2. Rotational casting
- 3. Film casting

2.1 Die casting

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

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

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

Equipment

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

Hot-chamber die casting



Schematic of a hot-chamber machine

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



A schematic of a cold-chamber die casting machine.

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

Advantages and disadvantages

Advantages of die casting:

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

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

2.2 Rotational Casting

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



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

2.3 Film Casting

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

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



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

- Processing at low temperatures, which is valuable for thermally activated films or applications incorporating temperature-sensitive active ingredients.
- Ability to produce high-temperature resistant films from non-thermoplastic but soluble raw materials.
- Simplified incorporation of additives and fillers.
- Quicker changeovers for platforms with many part numbers that are differentiated based on formula.

- Single pass manufacturing of multi-layer films (g. the ability to cast a free film, then coat an adhesive and laminate release liner on one side, and coat a top coat on the other side).
- Wider range of material choices with casting from either aqueous or solvent-based solutions. Advantages of the resulting film include:
- Greater film thickness uniformity, as tight as +/-2%.
- Wider range of film thickness, from 150 microns down to less than 12 microns.
- Films that are gel and pinhole free.
- Excellent flatness and dimensional stability.
- Isotropic orientation (mechanical and optical) as film is not stretched during manufacture.
- Absence of typical extrusion process lubricants.

3. <u>Moulding</u>

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

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

3.1 Injection molding



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

3.2 Extrusion



Plastics extrusion is a high volume manufacturing process in which raw plastic material is melted and formed into a continuous profile. The process of extrusion is usually used to make products such as film, continuous sheeting, tubes, profile shapes, rods, coat wire, filaments, cords, and cables. As with injection molding, dry plastic material is placed into a hopper and fed into a long heating chamber. At the end of the chamber, however, the material is forced out of a small opening or a die in the shape of the desired finished product. As the plastic exits the die, it is placed on a conveyor belt where it is allowed to cool. Blowers are sometimes used to aid in this process, or the product may be immersed in water to help it cool. **3.3 Blow Molding**



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

3.4 Compression molding



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

3.5 Rotational molding

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

4. <u>Thermoforming</u>



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

4.1 Vacuum forming



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

5. <u>Polymeric Foams</u>

The most of the polymeric foams are formed by a process involving nucleation and growth of gas bubbles in a polymer matrix, except in the syntactic foam where micro-beads of encapsulated gas are compounded into a polymer system or latex. According to the nucleation mechanism, the fundamental principle for the formation of polymeric foam involves three different important stages such as, bubble formation, bubble growth and bubble stability. The foam is expanded by increasing the bubble size before stabilizing the system. As the bubbles grow, the foam structure changes through number of stages.5 These are the following characteristics observed during the formation of foam. fInitially, small dispersed spherical bubbles are produced in a liquid polymer matrix, with a small reduction in density. The further growth of cells leads to lower foam density, which involves distortion of cells to form polyhedral structures, sometimes idealized as pentagonal dodecahedrons. fEffects of viscosity and surface tension subsequently cause materials to flow towards the uniform cell formation. fExtensive rupture before the foam is stabilized may lead to foam collapse. Cooling of closed cell foam before stabilization may lead to shrinkage, because of the reduced pressure in cells. The foaming of polymeric materials can be carried out by mechanical, chemical, or physical methods.4 Some of the most commonly used methods are; ³/₄Thermal decomposition of a chemical blowing agent, generating either nitrogen or carbon dioxide or both, by application of heat or as a result of the exothermic reaction during polymerization. Chemical blowing agents are either inorganic materials such as carbonates, bicarbonates, borohydrides, etc., or organic materials such as, hydrazides, azides, and nitroso compounds, etc. Copyright IIT Kharagpur Chapter 1 4 ³/₄Mechanical whipping (frothing) of gases into a fluid polymer system (melt, solution, or suspension), then it hardens either by catalytic action or heat or both, thus entrapping the gas bubbles in the polymeric matrix. ³/₄Volatilization of low-boiling liquids (fluorocarbons or methylene chloride) within the polymer mass as a result of the exothermic reaction or by application of heat. ³/₄Chemical blowing action via in-situ reaction during polymerization. (In this in-situ reaction water reacts with isocyanate to form carbon dioxide which is responsible for polyurethane foam formation). ³/₄Expansion of dissolved gas in a polymer mass upon reduction of pressure in the system. ³/₄Incorporation of tiny beads or microspheres into a polymer mass.



Application of Polymeric Foams

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

6. <u>Reinforcement</u>

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



Process definition

A polymer is generally manufactured by step-growth polymerization or addition polymerization. When combined with various agents to enhance or in any way alter the material properties of polymers the result is referred to as a plastic. Composite plastics refer to those types of plastics that result from bonding two or more homogeneous materials with different material properties to derive a final product with certain desired material and mechanical properties. Fibre-reinforced plastics are a category of composite plastics that specifically use fibre materials to mechanically enhance the strength and elasticity of plastics.

The original plastic material without fibre reinforcement is known as the matrix or binding agent. The matrix is a tough but relatively weak plastic that is reinforced by stronger stiffer reinforcing filaments or fibres. The extent that strength and elasticity are enhanced in a fibre-reinforced plastic depends on the mechanical properties of both the fibre and matrix, their volume relative to one another, and the fibre length and orientation within the matrix.^[1] Reinforcement of the matrix occurs by definition when the FRP material exhibits increased strength or elasticity relative to the strength and elasticity of the matrix alone.

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

- 1. Two-dimensional fibreglass-reinforced polymer is characterized by a laminated structure in which the fibers are only aligned along the plane in x-direction, and y-direction of the material. This means that no fibers are aligned in the through-thickness or the zdirection, this lack of alignment in the through thickness can create a disadvantage in cost and processing. Costs and labor increase because conventional processing techniques used to fabricate composites, such as wet hand lay-up, autoclave and resin transfer molding, require a high amount of skilled labor to cut, stack and consolidate into a preformed component.
- 2. Three-dimensional fiberglass-reinforced polymer composites are materials with threedimensional fiber structures that incorporate fibers in the x-direction, y-direction and zdirection. The development of three-dimensional orientations arose from industry's need to reduce fabrication costs, to increase through-thickness mechanical properties, and to improve impact damage tolerance; all were problems associated with two-dimensional fibre-reinforced polymers.

Material requirements

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

Glass fibre

"Fibreglass reinforced plastics" or FRPs (commonly referred to simply as fibreglass) use textile grade glass fibres. These textile fibres are different from other forms of glass fibres used to deliberately trap air, for insulating applications (see glass wool). Textile glass fibres begin as varying combinations of SiO₂, Al₂O₃, B₂O₃, CaO, or MgO in powder form. These mixtures are then heated through direct melting to temperatures around 1300 degrees Celsius, after which dies are used to extrude filaments of glass fibre in diameter ranging from 9 to 17 μ m. These filaments are then wound into larger threads and spun onto bobbins for transportation and further processing. Glass fibre is by far the most popular means to reinforce plastic and thus enjoys a wealth of production processes, some of which are applicable to aramid and carbon fibres as well owing to their shared fibrous qualities.

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

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

Carbon fibre

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

Aramid fibre

Aramid fibres are most commonly known as Kevlar, Nomex and Technora. Aramids are generally prepared by the reaction between an amine group and a carboxylic acid halide group (aramid);^[1] commonly this occurs when an aromatic polyamide is spun from a liquid

concentration of sulphuric acid into a crystallized fibre. Fibres are then spun into larger threads in order to weave into large ropes or woven fabrics (Aramid). Aramid fibres are manufactured with varying grades to based on varying qualities for strength and rigidity, so that the material can be somewhat tailored to specific design needs concerns, such as cutting the tough material during manufacture.

Advantages and limitations

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

7. <u>Fiber Spinning</u>

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

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



Melt Spinning

General Information

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

Equipment Design

In melt spinning, as shown below, the molten or melted polymer is pushed vertically downwards through the spinneret. When the filaments emerge from the spinneret they are cooled by a gas,

usually air, which flows either perpendicularly across, cocurrently, or countercurrently to the filaments.



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

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



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

Usage Examples

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



Advantages and Disadvantages

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

Solution Spinning

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

Dry Spinning

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



Equipment Design

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

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



Advantages and Disadvantages

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

Wet Spinning

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



Equipment Design

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

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



Advantages and Disadvantages

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

Usage Examples

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



Text book:

- **T1:** Gowariker, V. R., N. V. Viswanathan and J. Sreedhar, 1986. Polymer Science, *New Age International* Private Ltd., New Delhi.
- T2: Billmeyer, F.W., 2003. Text Book of Polymer Science. III Edition, John Wiley, New York.

Reference book

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

POSSIBLE QUESTIONS

<u>Multiple Choice Questions</u> (Each Carry 1 Mark)

- 1. Which one of the following is obtained from acetaldehyde and hydrogen cyanide.
- a. Acrylonitrile monomer b. Polyamide c. Polyester d. Polyethylene terephthalte
- 2. Wet spinning technique is commercially used to produce filament yarn of
- a. Polypropylene b. Polyester c. Nylon 66 **d. Acrylic**

Too high resistivity leads to the development of static?
a. Mechanical charges
b. Positive charges
c. Negative charges
d. Electrical charges

- 4. Which properties of fibers are quite complex and have been subject of much experimental work?
 - a. Physical **b. Mechanical** c. Chemical d. Thermal

- 5. In which spinning, the polymer solution is forced through a spinneret? a. Melt spinning **b.** Dry spinning c. Wet spinning d. Spinning 6. Birefringence of filament yarn is related to its b. Filament denier c. Orientation Density d. Crystallinity 7. In melt spinning the temperature used for melting is about ? 29K **b. 30K** c. 31K d. 32K 8. Which one of the following is the most important fibers produced commercially? b. Wood **c.** Cotton d. Silk Nvlons 9. In which spinning, the polymer is melted by heating and then passed through a spinneret via Melt spinning b. Dry spinning c. Wet spinning d. Spinning 10. Which one of the following is used for self-lubricating gears and bearings? b. Wood **c.** Cotton Nvlons d. Silk 11. Crease resist finishing of cotton fabric does not lead to Reduction in tensile strength b. Increase in dimensional stability c. Increase in moisture regain d. Increase in bending length 12. Which property causes the fabric to cling unpleasantly and to be difficult to clean? a. Mechanical **b. Electrical** c. Chemical d. Thermal 13. In general, which is a difficult dye? a. Polyamide b. Polyester c. Hydrophobic fiber d. Acrylic fibre 14. In which spinning, Polymer solutions are converted into fibers by diluting a highly concentrated polymer solution in a coagulating bath? a. Melt spinning b. Dry spinning c. Wet spinning d. Spinning 15. Which is soluble only in specific solvents? **b.** Polymers d. Hydrophobic fibres a. Fibres c. Nylon 16. The PBNA is the standard b. anti-toxin c. anti-malarial d. anti-poisionus a. anti-oxidant 17. Which one of the following is used as the staining anti-oxidant a. DPPD **b. PBNA** c. TCS d. TMS 18. TCS is the example of the a. Standard anti-oxidant b. non standard anti-oxidant c. staining anti-oxidant d. non-staining anti oxidant 19. The rayon also known as a. nylon b. orelon c. viscose d. resin 20. The rayon polymers belongs to the
 - **a. silicon polymers** b. epoxy polymers c. organic polymer d. rubber

6 Marks (Each Carry 6 Marks)

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

10. How to prepare the fiber by spinning method?

CompulsoryQuestions (Each Carry 10 Marks)

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



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UNIT: IV (QSAR)

S.No	Question	Option 1	Option 2	Option 3	Option 4	Answer
	UNIT-IV					
1	In the QSAR studies, among the following one of them is a liphophilic parameter	Partition coefficient	Molar refractivity	Taft's steric constant	Molecular weight	Partition coefficient
2	In the QSAR studies, among the following one of them is a liphophilic parameter	Chromatographi c parameter	Molar refractivity	Taft's steric constant	Molecular weight	Chromatographic parameter
3	In the QSAR studies, among the following one of them is a liphophilic parameter	Pi-substitution constant	Molar refractivity	Taft's steric constant	Molecular weight	Pi-substitution constant
4	One among the following is a polarizability parameter in QSAR	Pi-substitution constant	Molar refractivity	Taft's steric constant	Molecular weight	Molar refractivity
5	One among the following is a polarizability parameter in QSAR	Pi-substitution constant	Molar volume	Taft's steric constant	Molecular weight	Molar volume
6	One among the following is a polarizability parameter in QSAR	Pi-substitution constant	Parachor	Taft's steric constant	Molecular weight	Parachor
7	An electronic parameter in QSAR studies	Hammet constant	Parachor	Taft's steric constant	Molecular weight	Hammet constant
8	An electronic parameter in QSAR studies	Field and resonance parameters	Parachor	Taft's steric constant	Molecular weight	Field and resonance parameters
9	An electronic parameter in QSAR studies	Spectroscopic data	Parachor	Taft's steric constant	Molecular weight	Spectroscopic data
10	An electronic parameter in QSAR studies	Charge transfer constat	Parachor	Taft's steric constant	Molecular weight	Charge transfer constant
11	An electronic parameter in QSAR studies	Dipole moment	Parachor	Taft's steric constant	Molecular weight	Dipole moment



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UNIT: IV (QSAR)

12	An electronic parameter in QSAR studies	Quantum chemical parameters	Parachor	Taft's steric constant	Molecular weight	Quantum chemical parameters
13	An example for a steric parameter	Quantum chemical parameters	Parachor	Taft's steric constant	Molecular weight	Taft's steric constant
14	An example for a steric parameter	Quantum chemical parameters	Parachor	Vander waals radii	Molecular weight	Vander waals radii
15	Partition coefficient is a	Liphophilic parameter	Polarazability parameter	Electronic parameter	Steric parameter	Liphophilic parameter
16	Chromatographic parameters is a	Liphophilic parameter	Polarazability parameter	Electronic parameter	Steric parameter	Liphophilic parameter
17	Pi-substitution constant is a	Liphophilic parameter	Polarazability parameter	Electronic parameter	Steric parameter	Liphophilic parameter
18	Molar refractivity is a	Liphophilic parameter	Polarazability parameter	Electronic parameter	Steric parameter	Polarazability parameter
19	Molar volume is a	Liphophilic parameter	Polarazability parameter	Electronic parameter	Steric parameter	Polarazability parameter
20	Parachor is a	Liphophilic parameter	Polarazability parameter	Electronic parameter	Steric parameter	Polarazability parameter
21	Hammett constant is a	Liphophilic parameter	Polarazability parameter	Electronic parameter	Steric parameter	Electronic parameter
22	Field and resonance measurements is a	Liphophilic parameter	Polarazability parameter	Electronic parameter	Steric parameter	Electronic parameter
23	Properties derived fron spectral data is a	Liphophilic parameter	Polarazability parameter	Electronic parameter	Steric parameter	Electronic parameter
24	Charge transfer constant is a	Liphophilic parameter	Polarazability parameter	Electronic parameter	Steric parameter	Electronic parameter
25	Dipole moment is a	Liphophilic parameter	Polarazability parameter	Electronic parameter	Steric parameter	Electronic parameter
26	Quantum chemical measurements are	Liphophilic parameter	Polarazability parameter	Electronic parameter	Steric parameter	Electronic parameter



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27	Taff's steric constant is a	Liphophilic	Polarazability	Electronic	Steric	Stearic parameter
		parameter	parameter	parameter	parameter	1
28	Vanderwaals radii is a	Liphophilic	Polarazability	Electronic	Steric	Stearic parameter
		parameter	parameter	parameter	parameter	1
29	Partitioning of a compound between an aqueous and non-aqueous phase is a	Liphophilic parameter	Polarazability parameter	Electronic parameter	Steric parameter	Liphophilic parameter
30	In determining the partition coefficient n-octanol/water system has more advantages because	Octanol have a long alkyl chain and a polar hydroxyl group	Octanol has a short alkyl chain	Octanol has a non polar hydroxyl group	Octanol has polar alkyl chain	Octanol have a long alkyl chain and a polar hydroxyl group
31	In determining the partition coefficient n-octanol/water system has more advantages because	Octanol has a low vapour pressure	Octanol has a short alkyl chain	Octanol has a non polar hydroxyl group	Octanol has polar alkyl chain	Octanol has a low vapour pressure
32	In determining the partition coefficient n-octanol/water system has more advantages because	Octanol is UV transparent	Octanol has a short alkyl chain	Octanol has a non polar hydroxyl group	Octanol has polar alkyl chain	Octanol is UV transparent
33	One of the disadvantages in determining the chromatographic parameter RM is	Compounds need not to be pure	Only traces of materials needed	Several compounds can be estimated simultaneously	Lack of precision and reproducibiity	Lack of precision and reproducibility
34	One of the disadvantages in determining the chromatographic parameter RM is	Compounds need not to be pure	Only traces of materials needed	Several compounds can be estimated simultaneously	Use of different solvent system renders deviation	Use of different solvent system renders deviation
35	The drugs which are more readily transported through membranes are	Non-polar drug	Polar drug	Drugs in their ionized form	Polar drug in its ionized form	Non-polar drug
36	The drugs which are more readily transported through membranes are	Polar non- ionised drug	Polar drug	Drugs in their ionized form	Polar drug in its ionized form	Polar non-ionised drug



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37	Ribbon presentation is used for	Nucleic acid and protein	Smaller molecules	ligands	Charged molecules	Nucleic acid and protein
38	The image type used to display the molecular graphics	Ball and stick	Coral draw	paint	Bright and dull	Ball and stick
39	The image type used to display the molecular graphics	Mesh	Coral draw	paint	Bright and dull	Mesh
40	The image type used to display the molecular graphics	Colour scheme	Coral draw	paint	Bright and dull	Colour scheme
41	Ribbon representations are usually used to depict	medium size molecule	small molecules	large molecules	tiny molecule	large molecules
42	refers to the process of predicting new chemical entities that would eventually inhibit a target (protein) related to some disease.	Steric parameter	Coral draw	Molar refractivity	Virtual Screening (VS)	Virtual Screening (VS)
43	can visualize the three dimensional shapes of both the ligands and their target sites.	doctors	Physicist	Medicinal Chemist	Organic chemist	Medicinal Chemist
44	Partition coefficient is a	Liphophilic parameter	Polarazability parameter	Electronic parameter	Steric parameter	Liphophilic parameter
45	Ribbon representations are usually					
15	used to depict large molecules such as	benzene	aliphatic amine	proteins	formaldehyde	proteins
46	used to depict large molecules such as Docking is used for calculating	benzene mass spectra	aliphatic amine three dimensional shapes	proteins proton and electron	formaldehyde functional groups	proteins three dimensional shapes
46	Noboli representations are usually used to depict large molecules such as Docking is used for calculating Very soluble means that Parts of solvent needed for 1 part solute	benzene mass spectra < 1	aliphatic amine three dimensional shapes >1	proteins proton and electron 1	formaldehyde functional groups ~1	proteins three dimensional shapes < 1



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	time					
49	The three dimensional shapes of both ligand and target site may be determined by	spectroscopy	computational methods	Electochemistry	NMR	computational methods
50	is the more useful source of the large structures of interest to the medicinal chemist.	Quantum chemistry	Molecular mechanics	Electochemistry	NMR	Molecular mechanics
51	The solubility of any substance is a function of	way of mixing	temperature	time	volume	temperature
52	The solubility of a drug in a given solvent is largely a function of the of the solvent	time	solubility	polarity	solvent	polarity
53	Very slightly soluble means that Parts of solvent needed for 1 part solute	1000-10,000	100-10,00	1000-10,0000	>10000000	1000-10,000
54	Liquids which form a homogenous system when mixed in any proportion are said to be	miscible in certain proportions	partially miscible	miscible	immiscible	miscible
55	The dielectric constant (δ) of a compound is an index of its	temperature	polarity	weight	boiling point	polarity
56	The solvents of increasing polarity will show a similar increase in	dielectric constant.	volume	weight	boiling point	dielectric constant.
57	Most substances are, absorbing heat in the process of dissolution.	polarity	Molecular weight	endothermic	exothermic	endothermic
58	A shift toward the molecular species	Molecular masst	non-polar solvents	polar solvents	Molecular weight	non-polar solvents



CLASS: I M.Sc CHEMISTRY COURSE CODE: 19CHP305A

UNIT: IV (QSAR)

COURSE NAME: MEDICINAL CHEMISTRY BATCH-2019-2021

improves solute solubility in liquids will not partially 59 Immiscible partially soulble miscible Immiscible produce a homogenous solution in miscible any proportions Insoluble means that Parts of solvent > 10,000 > 10,0 > 10,00000 60 > 10,00 > 10,000 needed for 1 part solute



CLASS: II M.Sc CHEMISTRY COURSE NAME: POLYMER CHEMISTRY COURSE CODE:18CHP305A UNIT:V (PROPERTIES OF COMMERCIAL POLYMERS) BATCH: 2018-2020

<u>UNIT – V</u> SYLLABUS

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

Commercial Polymers

Syntheticpolymers are human-made polymers. From the utility point of view they can be classified into four main categories:thermoplastics,thermosets,elastomersandsynthetic fibers. They are found commonly in a variety of consumer products such as money, super glue, etc.

A wide variety of synthetic polymers are available with variations in main chain as well as side chains. The back bones of common synthetic polymers such as polythene, polystyrene and poly acrylates are made up of carbon-carbon bonds, whereas hetero chain polymers such as polyamides, polyesters, polyurethanes, polysulfides and polycarbonates have other elements (e.g. oxygen, sulfur, nitrogen) inserted along the backbone. Alsosiliconforms similar materials without the need of carbon atoms, such assiliconesthrough siloxane linkages; these compounds are thus said to beinorganic polymers.Coordination polymersmay contain a range of metals in the backbone, with non-covalent bonding present.

Some familiar household synthetic polymers include:Nylonsin textiles and fabrics,Tefloninnonstick pans,Bakelitefor electrical switches,polyvinyl chloride(PVC) in pipes, etc. The common PET bottles are made of a synthetic polymer,polyethylene terephthalate. The plastic kits and covers are mostly made of synthetic polymers likepolytheneand tires are manufactured fromBuna rubbers.^[1]However, due to the environmental issues created by these synthetic polymers which are mostlynon-biodegradableand often synthesized from petroleum, alternatives likebioplasticsare also being considered. They are however expensive when compared to the synthetic polymers. **1.Polyethylene**

Polyethylene or **polythene** (abbreviated **PE**;IUPACname **polyethene** or **poly(ethylene**)) is the most commonplastic. The annual global production is around 80 milliontonnes. Its primary use is inpackaging(plastic bags,plastic films,geomembranes, containers includingbottles, etc.). Many kinds of polyethylene are known, with most having thechemical formula(C_2H_4)_n. PE is usually a mixture of similarpolymersofethylenewith various values of *n*.

<u>Properties</u>

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

Mechanical properties

Polyethylene is of low strength,hardnessand rigidity, but has a highductilityandimpact strengthas well as low friction. It shows strongcreepunder persistent force, which can be reduced by addition of short fibers. It feels waxy when touched.

Thermal properties

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

Chemical properties

Polyethylene consists of nonpolar, saturated, high molecular weight hydrocarbons. Therefore, its chemical behavior is similar toparaffin. The individual macromolecules are notcovalentlylinked. Because of their symmetric molecular structure, they tend to crystallize; overall polyethylene ispartially crystalline. Highercrystallinityincreasesdensityand mechanical and chemical stability.

MostLDPE, MDPE, and HDPE grades have excellent chemical resistance, meaning they are not attacked by strong acids or strong bases, and are resistant to gentle oxidants and reducing agents. Crystalline samples do not dissolve at room temperature. Polyethylene (other than cross-linked polyethylene) usually can be dissolved at elevated temperatures inaromatic hydrocarbonssuch astolueneorxylene, or in chlorinated solvents such astrichloroethaneortrichlorobenzene. Polyethylene absorbs almost nowater. The gas and water vapor permeability (only polar gases) is lower than for most plastics;oxygen, carbon dioxideandflavoringson the other hand can pass it easily.

PE can become brittle when exposed to sunlight, carbon blackis usually used as a UV stabilizer. Polyethylene burns slowly with a blue flame having a yellow tip and gives off an odour of paraffin (similar tocandleflame). The material continues burning on removal of the flame source and produces a drip.

Polyethylene cannot be imprinted or stuck together without pretreatment.

Electrical properties

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

Optical properties

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

High-density polyethylene (HDPE)



HDPE is defined by a density of greater or equal to 0.941 g/cm³. HDPE has a low degree of

HDPE pipe installation in storm drain project inMexico

branching. The mostly linear molecules pack together well, so intermolecular forces are stronger than in highly branched polymers. HDPE can be produced bychromium/silica catalysts,ZieglerNatta catalystsormetallocenecatalysts; by choosing catalysts and reaction conditions, the small amount of branching that does occur can be controlled. These catalysts prefer the formation offree radicalsat the ends of the growing polyethylene molecules. They cause new ethylene monomers to add to the ends of the molecules, rather than along the middle, causing the growth of a linear chain.

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

Low-density polyethylene (LDPE)

LDPE is defined by a density range of 0.910–0.940 g/cm³. LDPE has a high degree of short- and long-chain branching, which means that the chains do not pack into the trystal structureas well. It has, therefore, less strong intermolecular forces as the instantaneous-dipole induced-dipole attractionis less. This results in a lowertensile strengthand increased ductility. LDPE is created by free-radical polymerization. The high degree of branching with long chains gives molten LDPE unique and desirable flow properties. LDPE is used for both rigid containers and plastic film applications such as plastic bags and film wrap. In 2013, the global LDPE market had a volume of almost US\$33 billion.

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

Production

Production of LDPE byaddition polymerizationrequires:

- temperature range of 100-300°C
- very high pressure 1500-3000 atmospheres
- oxygen or an organic peroxide such as dibutyl peroxide, benzoyl peroxide or diethyl peroxide as initiator.

An initiator is a substance which is added in small quantities and is decomposed by light or heat to produce a free radical (\mathbb{R}). A free radical is formed when a covalent bond is broken and a bonding electron is left on each part of the broken molecule. Since the O-O covalent bond is weak, free radicals are easily formed from oxygen or peroxides.

• benzene or chlorobenzene used as the solvent since both polymer (polythene) and monomer (ethene) dissolve in these compounds at the temperature and pressure used. Water or other liquids may be added to dissipate the heat of reaction as the polymerization reaction is highlyexothermic.



Process continues to form polythene (polyethylene) [-CH₂-CH₂-]_n

Production of HDPE

- 1. Production of HDPE byaddition polymerization with a supported metal oxide catalyst requires:
 - temperature ~300°C
 - 1 atmosphere pressure (101.3kPa)
 - aluminium-based metal oxide catalyst (metallocene catalyst)

The catalyst can be used in a variety of operating modes including fixed-bed, movingbed, fluid-bed or slurry processes

- Theethene (ethylene)monomer is fed with a paraffin or cycloparaffin diluent (dilutingagent). After polymerization the polymer (polythene) is recovered by cooling or by solvent evaporation.
- 2. Production of HDPE by coordination polymerization requires:
 - \circ temperature 50-75°C \circ slight pressure
 - \circ Coordination catalyst is prepared as a colloidal suspension by reacting an aluminium alkyl and titanium chloride (TiCl₄) in a solvent such as heptane (C₇H₁₆).
 - The polymer (polythene) forms as a powder or granules which are insoluble in the reaction mixture. When the polymerization is completed, the catalyst is destroyed by adding water or alcohol to the reaction mixture. The polymer (polythene) is then filtered or centrifuged off, washed and dried.

2.Polyvinyl chloride


Polyvinyl chloride(/ pplivaməl'klə:raɪd/),also known as poly vinyl or**vinyl**,commonly abbreviated **PVC**, is the world's third-most widely produced syntheticplasticpolymer, afterpolyethyleneandpolypropylene.

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

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

Discovery

PVC was accidentally synthesized in 1872 by German chemistEugen Baumann. The polymer appeared as a white solid inside a flask ofvinyl chloridethat had been left exposed to sunlight. In the early 20th century the Russian chemistIvan OstromislenskyandFritz Klatteof the German chemical company Griesheim-Elektron both attempted to use PVC in commercial products, but difficulties in processing the rigid, sometimes brittle polymer thwarted their efforts. Waldo Semonand theB.F. Goodrich Companydeveloped a method in 1926 toplasticizePVC by blending it with various additives. The result was a more flexible and more easily processed material that soon achieved widespread commercial use.

Production

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



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

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

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

Properties

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

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

Mechanical

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

Thermal and fire

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

of oxygen, expressed as a percentage, that will support combustion of a polymer and noting that air has 20% content of oxygen.

Electrical

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

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

Chemical

PVC is chemically resistant to acids, salts, bases, fats, and alcohols; therefore, it is used in sewerage piping. It is also resistant to some solvents, mainly uPVC. Plasticized PVC, also known as PVC-P, is in some cases less resistant to solvents. For example, PVC is resistant to fuel and some paint

thinners. Some solvents may only swell it or deform it but not dissolve it, but some of them, like tetrahydrofuran or acetone, may damage it.

Applications



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

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

In February 2007 the California Building Standards Code was updated to approve the use ofchlorinated polyvinyl chloride(CPVC) pipe for use in residentialwater supplypiping systems. CPVC has been a nationally accepted material in the U.S. since 1982; California, however, has permitted only limited use since 2001. The Department of Housing and Community Development prepared and certified anenvironmental impact statementresulting in a

recommendation that the commission adopt and approve the use of CPVC. The commission's vote was unanimous, and CPVC has been placed in the 2007 California Plumbing Code.

Electric cables

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

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

Construction

"A modernTudorbethan" house with uPVC gutters anddownspouts,fascia, decorative imitation "half-timbering", windows, and doors

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

uPVC is extensively used in the building industry as a low-maintenance material, particularly inIreland, the United Kingdom, in the United States and Canada. In the U.S. and Canada it is known as vinyl orvinyl siding. The material comes in a range of colors and finishes, including a photo-effect wood finish, and is used as a substitute for painted wood, mostly for window frames andsillswhen installinginsulated glazingin new buildings, or to replace older single-glazed windows. Other uses includefascia, andsidingorweatherboarding. This material has almost entirely replaced the use ofcast ironforplumbinganddrainage, being used for waste pipes, drainpipes, gutters and downspouts. uPVC is known as having strong resistance against chemicals, sunlight, and oxidation from water.



Double glazed units

Signs

Polyvinyl chloride is formed in flat sheets in a variety of thicknesses and colors. As flat sheets, PVC is often expanded to create voids in the interior of the material, providing additional thickness without additional weight and minimal extra cost (seeClosed-cell PVC foamboard). Sheets are cut using saws and rotary cutting equipment. Plasticized PVC is also used to produce thin, colored, or clear, adhesive-backed films referred to simply as vinyl. These films are typically cut on acomputer-controlledplotter(seeVinyl cutter) or printed in awide-format printer. These sheets and films are used to produce a wide variety of commercial signageproducts, includingcar body stripesandstickers. Clothing and furniture

Prepared by Dr. S. Manickasundaram, Assistant Professor, Dept. of Chemistry, KAHE 8/27



Black PVC trousers

PVC has become widely used in clothing, to either create a leather-like material or at times

simply for the effect of PVC.PVC clothing is common inGoth,Punk,clothing fetishandalternative fashions. PVC is less expensive thanrubber, leather, andlatexwhich it is used to simulate.

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

Healthcare

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

Flooring

Flexible PVCflooringis inexpensive and used in a variety of buildings covering the home, hospitals, offices, schools, etc. Complex and3Ddesigns are possible, which are then protected by a clear wear layer. A middle vinyl foam layer also gives a comfortable and safe feel. The smooth, tough surface of the upper wear layer prevents the buildup of dirt, which prevents microbes from breeding in areas that need to be kept sterile, such as hospitals and clinics.

Wire rope

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



The handles of the Victorinox

ss Army knivesare made of PV

PVC has been used for a host of consumer products. One of its earliest mass-market consumer applications wasvinyl recordproduction. More recent examples include wallcovering,

greenhouses, home playgrounds, foam and other toys, custom truck toppers (tarpaulins), ceiling tiles and other kinds of interior cladding.

PVC piping is cheaper than metals used in musical instrument making; it is therefore a common alternative when making instruments, often for leisure or for rarer instruments such as the contrabass flute.**3.Polyamide**

A **polyamide** is amacromolecule with repeating units linked by amidebonds.

Polyamides occur both naturally and artificially. Examples of naturally occurring polyamides areproteins, such aswoolandsilk. Artificially made polyamides can be made throughstepgrowth polymerizationorsolid-phase synthesisyielding materials such asnylons, aramids, and sodium poly(aspartate). Synthetic polyamides are commonly used in textiles, automotive applications, carpets and sportswear due to their high durability and strength. The transportation manufacturing industry is the major consumer, accounting for 35% of polyamide (PA) consumption.

Classification

Polymers of amino acids are known aspolypeptidesorproteins.

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

Polyamide family	Main chain	Examples of polyamides	Examples of
			commercial products
Aliphatic	Aliphatic	NylonPA 6andPA 66	ZytelfromDuPont,
polyamides			Technyl fromSolvay,Rilsan
			and Rilsamid
			fromArkema,Radipol
			fromRadici Group
Polyphthalamides	Semi-	PA 6T	TrogamidT
	aromatic	=hexamethylenediamine+terephth	fromEvonikIndustries,
		alic acid	Amodel fromSolvay
Aramids= ar omatic	Aromatic	Paraphenylenediamine+	KevlarandNomexfrom
poly amide s		terephthalic acid	DuPont, Teijinconex, Twaron
			and Technora
			fromTeijin,Kermel from
			Kermel.

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

Polymerization

Production of polymers requires the repeated joining of two groups to form an amide linkage. In this case this specifically involvesamidebonds, and the two groups involved are anaminegroup, and a terminalcarbonylcomponent of afunctional group. These react to produce a carbon-nitrogen

bond, creating a singularamidelinkage. This process involves the elimination of other atoms previously part of the functional groups. The carbonyl-component may be part of either acarboxylic acidgroup or the more reactiveacyl halidederivative. The amine group and the carboxylic acid group can be on the same monomer, or the polymer can be constituted of two different bifunctional monomers, one with two amine groups, the other with two carboxylic acid or acid chloride groups.

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

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



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

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

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



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

Polyamides can also be synthesized from dinitriles using acid catalysis via an application of the

Ritter reaction. This method is applicable for preparation ofnylon 1,6fromadiponitrile,formaldehydeand water.Additionally, polyamides can be synthesized fromglycolsand dinitriles using this method as well.



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

Example: Nylon 66 Nylon 66



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

Synthesis and manufacturing



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

Nylon 66 is synthesized bypolycondensation of hexamethylenediamine and adipic acid. Equivalentamounts of hexamethylenediamine and adipic acid are combined with water in a reactor. This is crystallized to make nylon salt, an ammonium/carboxylatemixture. The nylon salt goes into a reaction vessel where polymerization process takes place either in batches or continuously. n HOOC-(CH₂)₄-COOH + n H₂N-(CH₂)₆-NH₂ \rightarrow [-OC-(CH₂)₄-CO-NH-(CH₂)₆-NH-]_n + (2n-1) H₂O

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

Applications

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

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

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

TheRemington Nylon 66was a .22 rifle manufactured byRemington Armsfrom 1959 to 1989. It had astockmade from nylon 66.

3. Polyester



Close-up of a polyester shirt

Stretching polyester fabric

Polyester is a category ofpolymersthat contain theesterfunctional groupin their main chain. As a specificmaterial, it most commonly refers to a type calledpolyethylene terephthalate(PET). Polyesters include naturally occurring chemicals, such as in thecutinofplant cuticles, as well as synthetics throughstep-growth polymerizationsuch aspolybutyrate. Natural polyesters and a few synthetic ones arebiodegradable, but most synthetic polyesters are not. The material is used extensively in clothing.

Depending on the chemical structure, polyester can be athermoplasticorthermoset. There are alsopolyester resinscured by hardeners; however, the most common polyesters are thermoplastics.

Fabricswoven or knitted from polyester thread or yarn are used extensively in apparel and home furnishings, from shirts and pants to jackets and hats, bed sheets, blankets, upholstered furniture and computer mouse mats. Industrial polyester fibers, yarns and ropes are used in car tire reinforcements, fabrics for conveyor belts, safety belts, coated fabrics and plastic reinforcements with high-energy absorption. Polyester fiber is used as cushioning and insulating material in pillows, comforters and upholstery padding. Polyester fabrics are highly stain-resistant—in fact,

the only class of dyes which *can* be used to alter the color of polyester fabric are what are known as disperse dyes.

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

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

Polyesters are also used to make bottles, films,tarpaulin, canoes,liquid crystaldisplays,holograms,filters,dielectricfilm forcapacitors,film insulationforwireandinsulating tapes. Polyesters are widely used as a finish on high-quality wood products such asguitars,pianosand vehicle/yacht interiors.Thixotropicproperties of spray-applicable polyesters make them ideal for use on open-grain timbers, as they can quickly fill wood grain, with a high-build film thickness per coat. Cured polyesters can be sanded and polished to a highgloss, durable finish.

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

Synthesis

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

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

Azeotrope esterification

In this classical method, analcoholand acarboxylic acidreact to form a carboxylic ester. To assemble a polymer, the water formed by the reaction must be continually removed by azeotropedistillation.

Alcoholic transesterification



Transesterification: An alcohol-terminated oligomer and an ester-terminated oligomer condense to form an ester linkage, with loss of an alcohol. R and R' are the two oligomer

chains, R" is a sacrificial unit such as amethyl group(methanolis the byproduct of the esterification reaction).

Acylation (HCl method)

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

Silyl method

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

Acetate method (esterification) Silyl acetate methodRing-opening polymerization

Aliphaticpolyesters can be assembled fromlactonesunder very mild conditions, catalyzedanionically, cationically ormetallorganically. A number of catalytic methods for the copolymerization of epoxides with cyclic anhydrides have also recently been shown to provide a wide array of functionalized polyesters, both saturated and unsaturated.

Cross-linking

Unsaturated polyesters are thermosetting resins. They are generally copolymers prepared by polymerizing one or morediolwith saturated and unsaturated dicarboxylic acids (maleic acid,fumaric acid...) or theiranhydrides. The double bond of unsaturated polyesters reacts with avinylmonomer, usuallystyrene, resulting in a 3-D cross-linked structure. This structure acts as a thermoset. The exothermiccross-linkingreaction is initiated through acatalyst, usually anorganic peroxidesuch asmethyl ethyl ketone peroxideorbenzoyl peroxide.

Example: Poly(ethylene terephthalate)

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



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

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

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

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

Making polyesters as an example of condensation polymerisation

In condensation polymerisation, when the monomers join together a small molecule gets lost. That's different from addition polymerisation which produces polymers like poly(ethene) - in that case, nothing is lost when the monomers join together. A polyester is made by a reaction involving an acid with two -COOH groups, and an alcohol with two -OH groups. In the common polyester drawn above:

Prepared by Dr. S. Manickasundaram, Assistant Professor, Dept. of Chemistry, KAHE 15/27

The acid is benzene-1,4-dicarboxylic acid (old name: terephthalic acid). The alcohol is ethane-1,2-diol (old name: ethylene glycol).



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



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



Hydrolysis of polyesters

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

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

If you spill dilute alkali on a fabric made from polyester, the ester linkages are broken. Ethane1,2-diol is formed together with the salt of the carboxylic acid.

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

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



5.<u>Phenol formaldehyde resin</u>



Phenol formaldehyde resins (PF) or **phenolic resins** are synthetic polymers obtained by the reaction of phenolor substituted phenol withformaldehyde. Used as the basis forBakelite, PFs were the first commercial synthetic resins (plastics). They have been widely used for the production of molded products including billiard balls, laboratory countertops, and as coatings and adhesives. They were at one time the primary material used for the production of circuit boardsbut have been largely replaced with poxy resinsand fiber glasscloth, as with fireresistant FR-4 circuit board materials.

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

Formation and structure

Phenol-formaldehyde resins, as a group, are formed by astep-growth polymerizationreaction that can be eitheracid- orbase-catalysed. Since formaldehyde exists predominantly in solution as a dynamic equilibrium of methylene glycololigomers, the concentration of the *reactive* form of formaldehyde depends on temperature and pH.

Phenol reacts with formaldehyde at theorthoandparasites (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 amethylene bridge, and the second forms anetherbridge:

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

 $2 \text{ HOC}_6\text{H}_4\text{CH}_2\text{OH} \rightarrow (\text{HOC}_6\text{H}_4\text{CH}_2)_2\text{O} + \text{H}_2\text{O}$

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



Novolac

Novolacs are phenol-formaldehyde resins with a formaldeh yde to phenol molar ratio of less than

one. The polymerization is brought to completion using acid-catalysis such as oxalic acid, hydrochloric acid or sulfonate acids. The phenol units are mainly linked by methylene and/or ether groups. Novolacs are commonly used asphotoresists. See alsophotolithography. The molecular weights are in the low thousands, corresponding to about 10–20 phenol units.

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

Applications

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

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

Phenolic resin is used as abinderinloudspeakerdriversuspension components which are made ofcloth.

Billiard ballsare made from solid Phenolic resin.

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

6.<u>Epoxy</u>

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



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



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

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

Epoxy resin



Structure of a cured epoxy glue. The triamine hardener is shown in red, the resin in black. The resin's epoxide groups have reacted with the hardener and are not present anymore. The material

Epoxy resins are low molecular weight pre-polymers or higher molecular weight polymers which is highlycrosslinked and contains many OH groups, which confer adhesive properties.

normally contain at least two epoxide groups. The epoxide group is also sometimes referred to as a glycidyl or oxirane group.

A wide range of epoxy resins are produced industrially. The raw materials for epoxy resin production are today largelypetroleumderived, although some plant derived sources are now becoming commercially available (e.g. plant derived glycerol used to makeepichlorohydrin). Epoxy resins are polymeric or semi-polymeric materials, and as such rarely exist as pure substances, since variable chain length results from the polymerisation reaction used to produce them. High purity grades can be produced for certain applications, e.g. using a distillation purification process. One downside of high purity liquid grades is their tendency to form crystalline solids due to their highly regular structure, which require melting to enable processing.

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

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

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

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

Examples: Bisphenol A epoxy resin

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



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

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

Bisphenol F epoxy resin

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

Applications

The applications for epoxy-based materials extensive and include are coatings, adhesives and composite materialssuch those usingcarbon as fiberandfiberglassreinforcements (althoughpolyester, vinyl ester, and otherthermosettingresinsare also used for glass-reinforced plastic). The chemistry of epoxies and the range of commercially available variations allows cure polymers to be produced with a very broad range of properties. In general, epoxies are known for their excellent adhesion, chemical and heat resistance, goodto-excellent mechanical properties and very goodelectrical insulating properties. Many properties of epoxies can be modified (for examplesilver-filled epoxies with goodelectrical conductivityare available, although epoxies are typically electrically insulating). Variations offering high thermal insulation, or thermal conductivity combined with high electrical resistance for electronics applications, are available.^[6]

Paints and coatings

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

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

Adhesives



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

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

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

Electrical systems and electronics





An epoxy encapsulated hybridcircui t on a printedcirc uit board. The interior of a pocket calculator. The dark lump of epoxy in the center covers the processor chip

Epoxy resin formulations are important in the electronics industry, and are employed in motors, generators, transformers, switchgear, bushings, and insulators. Epoxy resins are excellent electrical insulators and protect electrical components from short circuiting, dust and moisture. In

the electronics industry epoxy resins are the primary resin used in overmoldingintegrated circuits, transistors and hybrid circuits, and making printed circuit boards. The largest volume type of circuit board—an "FR-4board"—is a sandwich of layers of glass cloth bonded into a composite by an epoxy resin. Epoxy resins are used to bond copper foil to circuit board substrates, and are a component of the solder mask on many circuit boards.

Petroleum & petrochemical

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

Consumer and marine applications

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

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

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

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

Aerospace applications

In the aerospace industry, epoxy is used as a structural matrix material which is then reinforced by fiber. Typical fiber reinforcements includeglass,carbon,Kevlar, andboron. Epoxies are also used as a structuralglue. Materials likewood, and others that are 'low-tech' are glued with epoxy resin.

Biology

Water-soluble epoxies such asDurcupanare commonly used forembeddingelectron microscopesamples in plastic so they may be sectioned (sliced thin) with amicrotomeand then imaged. **Art**

Epoxy resin, mixed withpigment, may be used as a paintingmedium, by pouring layers on top of each other to form a complete picture.

Industry

These commodity epoxymanufacturersmentioned above typically do not sell epoxy resins in a form usable to smaller end users, so there is another group of companies that purchase epoxy raw

materials from the major producers and then compounds (blends, modifies, or otherwise customizes) epoxy systems from theserawmaterials. These companies are known as "formulators". The majority of the epoxy systems sold are produced by these formulators and they comprise over 60% of the dollar value of the epoxy market. There are hundreds of ways that these formulators can modify epoxies—by addingmineralfillers (talc,silica,alumina, etc.), by adding flexibilizers,viscosityreducers,colorants, thickeners, accelerators,adhesionpromoters, etc. These modifications are made to reduce costs, to improve performance, and to improve processing convenience. As a result, a typical formulator sells dozens or even thousands of formulations—each tailored to the requirements of a particular application or market.

7.Silicone





Silicones, also known as **polysiloxanes**, arepolymersthat include any inert, synthetic compound made up of repeating units ofsiloxane, which is a chain of alternatingsiliconatoms andoxygenatoms, frequently combined withcarbonand/orhydrogen. They are typically heatresistant andrubber-like, and are used in sealants, adhesives, lubricants, medicine, cooking utensils, and thermal and electrical insulation. Some common forms includesilicone oil,silicone grease,silicone rubber,silicone resin, and siliconecaulk.Silicones are of three types: 1. straight chain silicones; 2. cyclic silicones; 3. crosslinked silicones.

Synthesis

Most common are materials based onpolydimethylsiloxane, which is derived by hydrolysis ofdimethyldichlorosilane. This dichloride reacts with water as follows:

 $n \operatorname{Si}(\operatorname{CH}_3)_2\operatorname{Cl}_2 + n \operatorname{H}_2\operatorname{O} \rightarrow [\operatorname{Si}(\operatorname{CH}_3)_2\operatorname{O}]_n + 2n\operatorname{HCl}$

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 silylacetatesare used instead of silyl chlorides. The hydrolysis of the acetates produce the less dangerousacetic 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 siliconecaulkandadhesives.

Branchesor cross-links in the polymer chain can be introduced by using organosilicone precursors with fewer alkyl groups, such as methyltrichlorosilane andmethyltrimethoxysilane. Ideally, each molecule of such a compound becomes a branch point. This process can be used to

Prepared by Dr. S. Manickasundaram, Assistant Professor, Dept. of Chemistry, KAHE 24/27

produce hard silicone resins. Similarly, precursors with three methyl groups can be used to limit molecular weight, since each such molecule has only one reactive site and so forms the end of a siloxane chain.

Combustion

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

Properties

Silicones exhibit many useful characteristics, including:^[1]

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

Uses

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

Automotive

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

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

Sheet silicone is used to manufacturegasketsused inautomotive engines, transmissions, and other applications.

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

Coatings

Silicone films can be applied to such silica-based substrates as glass to form acovalentlybondedhydrophobiccoating.

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

Cookware







Soup ladle and pasta ladle made of silicone.

A silicone food steamer to be placed inside a pot of boiling water. Ice cube trays made of silicone.

♣ As a low-taint, non-toxic material, silicone can be used where contact with food is required. Silicone is becoming an important product in thecookwareindustry, particularlybakewareandkitchen utensils.

- Silicone is used as an insulator in heat-resistant potholders and similar items; however, it is more conductive of heat than similar less dense fiber-based products. Silicone oven mitts are able to withstand temperatures up to 260 °C (500 °F), allowing reaching into boiling water.
- 4 Moldsfor chocolate, ice, cookies, muffins and various other foods.
- 4 Non-stick bakeware and reusable mats used on baking sheets.
- Other products such assteamers, egg boilers orpoachers, cookware lids,pot holders,trivets, and kitchen mats.

Defoaming

Silicones are used as active compound indefoamersdue to their low water solubility and good spreading properties. **Dry cleaning**

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

Electronics

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

Silicones are used where durability and high performance are demanded of components under hard conditions, such as in space (satellite technology). They are selected overpolyurethaneorepoxyencapsulation when a wideoperating temperaturerange is required (-65 to 315 °C). Silicones also have the advantage of little exothermic heat rise during cure, low toxicity, good electrical properties and high purity.

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

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

Firestops

Silicone foamhas been used in North American buildings in an attempt tofirestopopenings within fire-resistance-rated wall and floor assemblies to prevent the spread of flames and smoke from one room to another. When properly installed, silicone-foam firestops can be fabricated for building code compliance. Advantages include flexibility and highdielectricstrength. Disadvantages include combustibility (hard to extinguish) and significant smoke development. Silicone-foam firestops have been the subject of controversy and press attention due to smoke development from pyrolysis of combustible components within the foam,hydrogengas escape, shrinkage, and cracking. These problems have led to reportable events among licensees (operators ofnuclear power plants) of theNuclear Regulatory Commission (NRC). Silicone firestops are also used in aircraft.



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COURSE CODE: 19CHP105B

COURSE NAME: MEDICINAL CHEMISTRY UNIT: V (Molecular Recognition in Drug-Receptor Binding)

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S.No	Question	Option 1	Option 2	Option 3	Option 4	Answer
	UNIT-V					
1	Antineoplastic agents are the drugs used in the treatment of	cancer	Bacterial infection	Viral infection	Central nervous system	cancer
2	Antineoplastic agents are the drugs used in the treatment of	Malignancy	Bacterial infection	Viral infection	Central nervous system	Malignancy
3	Antineoplastic agents are the drugs used in the treatment of	tumor	Bacterial infection	Viral infection	Central nervous system	Tumor
4	Antineoplastic agents are the drugs used in the treatment of	carcinoma	Bacterial infection	Viral infection	Central nervous system	carcinoma
5	Antineoplastic agents are the drugs used in the treatment of	Sarcoma	Bacterial infection	Viral infection	Central nervous system	Sarcoma
6	Antineoplastic agents are the drugs used in the treatment of	Leukemia	Bacterial infection	Viral infection	Central nervous system	Leukemia
7	A new and diseased form of tissue growth is called	neoplasm	Plasma membrane	Golgi bodies	mitichondria	neoplasm
8	An alkylating agent used to treat neoplasms	Nitrogen mustards	Pyrimidine analogues	Mitomycin	Vinca alkaloids	Nitrogen mustards
9	An alkylating agent used to treat neoplasms	Alkyl sulfonates	Pyrimidine analogues	Mitomycin	Vinca alkaloids	Alkyl sulfonates
10	An alkylating agent used to treat neoplasms	Nitroso ureas	Pyrimidine analogues	Mitomycin	Vinca alkaloids	Nitroso ureas
11	An alkylating agent used to treat neoplasms	Ethylimine	Pyrimidine analogues	Mitomycin	Vinca alkaloids	Ethylimine



cancer

KARPAGAM ACADEMY OF HIGHER EDUCATION

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12	An alkylating agent used to treat neoplasms	Methyl hydrazines	Pyrimidine analogues	Mitomycin	Vinca alkaloids	Methyl hydrazines
13	An antimetaboite used to treat neoplasms	Methyl hydrazines	Pyrimidine analogues	Mitomycin	Vinca alkaloids	Pyrimidine analogues
14	An antimetaboite used to treat neoplasms	Methyl hydrazines	Purine analogues	Mitomycin	Vinca alkaloids	Purine analogues
15	An antimetaboite used to treat neoplasms	Methyl hydrazines	Folic acid analogues	Mitomycin	Vinca alkaloids	Folic acid analogues
16	An antibiotics used to treat neoplasms	Methyl hydrazines	Purine analogues	Anthracyclines	Vinca alkaloids	Anthracyclines
17	An antibiotics used to treat neoplasms	Methyl hydrazines	Purine analogues	Bleomycin	Vinca alkaloids	Bleomycin
18	An antibiotics used to treat neoplasms	Methyl hydrazines	Purine analogues	Mitomycin	Vinca alkaloids	Mitomycin
19	A plant product used to treat neoplasm	Methyl hydrazines	Purine analogues	Mitomycin	Vinca alkaloids	Vinca alkaloids
20	A plant product used to treat neoplasm	Methyl hydrazines	Purine analogues	Mitomycin	Vincristine	Vincristine
21	A plant product used to treat neoplasm	Methyl hydrazines	Purine analogues	Mitomycin	Vincristine	Vinblastine
22	A plant product used to treat neoplasm	Methyl hydrazines	Purine analogues	Mitomycin	Taxol	Taxol
23	A plant product used to treat neoplasm	Methyl hydrazines	Purine analogues	Mitomycin	Etoposide	Etoposide
24	A radiotherapeutic agent used to treat cancer	Chromic phosphate P 32	Purine analogues	Mitomycin	Etoposide	Chromic phosphate P 32
25	An inorganic complex used to treat	Chromic phosphate P 32	Purine analogues	Mitomycin	cisplatin	cisplatin



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Antiviral drug which belongs to 26 Acyclovir Acyclovir Iodoxuridine Methisazone Rimantadine purine nucleoside Antiviral drug which belongs to Iodoxuridine Acyclovir Methisazone 27 Rimantadine Iodoxuridine pyrimidine nucleoside Antiviral drug which belongs to 28 Acyclovir Iodoxuridine Methisazone Rimantadine Methisazone Thiosemicarbazone class Antiviral drug which belongs to 29 Iodoxuridine Acyclovir Methisazone Rimantadine Rimantadine Adamantane amine class pyrimidine purine Adamantane Which class of antiviral drug 30 Thiosemicarbazone purine nucleoside nucleoside nucleoside amine Acyclovir belongs to pyrimidine pyrimidine Adamantane purine Which class of antiviral drug Thiosemicarbazone 31 nucleoside nucleoside amine nucleoside Iodoxuridine belongs to Thiosemicarbazon pyrimidine purine Adamantane Which class of antiviral drug 32 Thiosemicarbazone nucleoside nucleoside amine e Methisazone belongs to purine pyrimidine Adamantane Adamantane Which class of antiviral drug 33 Thiosemicarbazone nucleoside nucleoside amine amine Rimantadine belongs to Effect on Act on the brain Effect thought Act on the brain 34 system and mental function Mood elevating pattern and system and spinal Convulsant respiratory stimulants spinal cord and behavious perception cord Act on the brain Effect on Effect thought Effect on mental 35 mental function Mood elevating pattern and system and function and Psychomotor stimulants and behavious spinal cord behavious perception Act on the brain Effect on Effect thought Mood elevating pattern and Mood elevating 36 system and mental function Antidepressant drugs and behavious perception spinal cord Effect thought Act on the brain Effect on Effect thought mental function 37 system and Mood elevating pattern and pattern and Psycho mimetic drugs and behavious spinal cord perception perception Convulsant Convulsant Psychomotor Antidepressant Psycho Act on the brain system and spinal 38 respiratory respiratory stimulants drugs mimetic drugs cord stimulants stimulants



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39	Effect on mental function and behavious	Convulsant respiratory stimulants	Psychomotor stimulants	Antidepressant drugs	Psycho mimetic drugs	Psychomotor stimulants
40	Mood elevating	Convulsant respiratory stimulants	Psychomotor stimulants	Antidepressant drugs	Psycho mimetic drugs	Antidepressant drugs
41	Effect thought pattern and perception	Convulsant respiratory stimulants	Psychomotor stimulants	Antidepressant drugs	Psycho mimetic drugs	Psycho mimetic drugs
42	Act on the brain system and spinal cord	Analeptics	Psychomotor stimulants	Antidepressant drugs	Psycho mimetic drugs	Analeptics
43	An enzyme inhibitor is a molecule which binds to enzymes and	avearage their activity	decreases their activity	no effect on their activity	increases their activity	decreases their activity
44	is a molecule which binds to enzymes and decreases their activity.	enzyme inhibitor	enzyme booster	microorganisms	virus	enzyme inhibitor
45	is a molecule which binds to enzymes and increases their activity.	enzyme inhibitor	enzyme activators	microorganisms	bacteria	enzyme activators
46	An enzyme inhibitor is a molecule which binds toand decreases their activity.	bacteria	benzene	enzymes	metal	enzymes
47	Enzyme inhibitors also occur naturally and are involved in the regulation of	enzyme activators	metabolism	enzyme booster	activity	metabolism
48	There are kinds of reversible enzyme inhibitors	four	two	three	five	four
49	cellular enzyme inhibitors arethat specifically bind to	enzyme activators	proteins	enzymes	metabolism	proteins



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	and inhibit an enzyme target					
50	Reversible inhibitors generally do not undergowhen bound to the enzyme and can be easily removed by dilution or dialysis.			chemical reactions		chemical reactions
51	Mixed inhibition generally results from an allosteric effect where the inhibitor binds to a different site on an enzyme				$\mathbf{\mathbf{\mathbf{\mathbf{\mathbf{\mathbf{\mathbf{\mathbf{\mathbf{\mathbf{\mathbf{\mathbf{\mathbf{\mathbf{\mathbf{\mathbf{\mathbf{\mathbf{$	allosteric effect
52	Irreversible inhibitors modify key residues needed for enzymatic activity.	amino acid	DNA	protein	peptide	amino acid
53	usually react with the enzyme and change it chemically	enzyme activators	Irreversible inhibitors	reversible inhibitors	amino acid	Irreversible inhibitors
54	Reversible inhibitors bind to enzymes with	non-covalent interactions	covalent interactions	protein	metabolism	non-covalent interactions
55	,the substrate and inhibitor cannot bind to the enzyme at the same time	irreversible inhibition	reversible inhibition	competitive inhibition	chemical reactions	competitive inhibition
56	Give the example for irreversible protease inhibitor ?	DNA	Diisopropylfluo rophosphate (D FP)	protein	peptide	Diisopropylfluorop hosphate (DFP)
57	Diisopropylfluorophosphate (DFP) is a potent neurotoxin, with a lethal dose of	less than 1000 mg	more than 1000 mg	less than 100 mg	more than 100mg	less than 100 mg
58	The reactants that bind to the enzyme are known as the of the enzyme	product	catalyst	reactants	substrates	substrates



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fumarate ions

another

molecule

 59
 This enzyme catalyses the conversion of succinate ions to_____
 succinic acid
 fumarate ions
 Fumaric acid

	10					
60	The heavy metal ions arefor several enzymes.	non-competitive inhibitors	reversible inhibitors	irreversible inhibitors	chemical reactions	non-competitive inhibitors