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Paper: DSE-4 (Polymer Chemistry)

Topic: Introduction: Classification of polymers – Natural and synthetic; Thermoplastic and Thermosetting. Functionality – Degree of polymerization. Types and mechanism of polymerization: Addition (Free Radical, cationic and anionic); condensation and copolymerization. Properties of polymers: Tg, Tacticity, Molecular weight – weight average, number average and polydispersity index. Techniques of polymerization: Bulk, emulsion, solution and suspension. Preparation, properties and uses of Nylon 6,6, and Epoxy resin.

Comments: Read as much as you can. The highlighted and the quoted portions are must read.

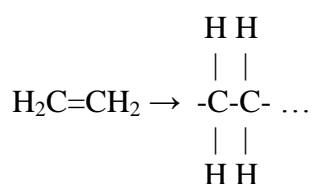
Reference:

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UNIT I POLYMER CHEMISTRY

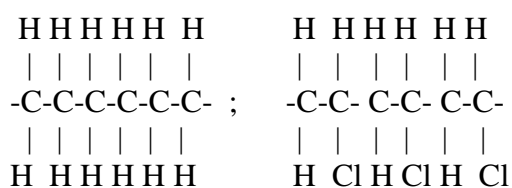
Introduction: Classification of polymers – Natural and synthetic; Thermoplastic and Thermosetting. Functionality – Degree of polymerization. Types and mechanism of polymerization: Addition (Free Radical, cationic and anionic); condensation and copolymerization. Properties of polymers: Tg, Tacticity, Molecular weight – weight average, number average and polydispersity index. Techniques of polymerization: Bulk, emulsion, solution and suspension. Preparation, properties and uses of Nylon 6,6, and Epoxy resin.

Polymers are high molecular weight materials / macromolecules, composed of large number of low molecular weight species. *The term polymer can be defined as a macromolecule with high molecular mass arising due to the joining of a large number of simpler / smaller molecules (called monomers).* The polymers are characterized by variable molecular weight (depending on the source or mode of synthesis or extraction), low specific gravity, better resistance to erosion, corrosion, insects or fungi etc. The advantageous aspect of polymeric materials over other materials is that they can be tailor-made i.e. polymers can be synthesized as per our property requirement or soft to rigid / tough, transparent to opaque, light to heavy, crystalline to amorphous materials can be synthesized. To cite an example, there are different types of polyethylene $\{(CH_2-CH_2)_n\}$ such as low density, medium density and high density polyethylene (abbreviated as LDPE, MDPE and HDPE). Polymers find applications as major class of materials such as plastics, fibres, rubbers, rexin (artificial leather) and explosives. *Polymerization is the union of two or more simpler molecules (effected under the influence of heat, pressure, catalyst etc.), resulting in the formation of new macromolecule with the characteristic C-C linkages. The resultant macromolecule is called polymer and the original / parent simpler molecule is called monomer.* The condition for a substance to be polymerized is the functionality. *The functionality of a monomer is defined as the number of reactive / bonding sites available in the molecule such as carbon-carbon multiple bond, condensible functional groups such as hydroxyl, carboxyl, amine, halo group etc.* E.g. carbon – carbon double bond is termed as bi-functional, because when the double bond is broken, two single bonds become available for combination i.e. ethylene can be polymerized but not ethane.

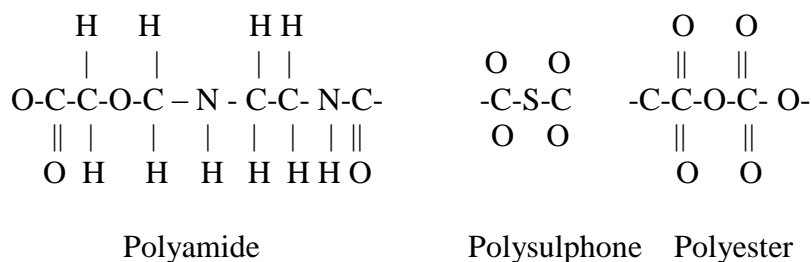


Polymers are classified based on their origin as natural and synthetic polymers. Natural polymers are the ones which are isolated from the natural sources. Cotton, silk, wool,

rubber etc. belong to this type. There are also polymers modified from these natural polymers viz., cellophane, cellulose rayon, leather etc. Synthetic polymers are the polymers obtained from the low molecular weight compounds such as ethylene, phenol, formaldehyde etc. polyethylene, polyvinyl chloride (PVC), nylon, bakelite etc. are some of the synthetic polymers. Polymers are further classified as homochain and heterochain polymers based on whether the polymeric chain is made of only carbon atoms or also of heteroatoms such as oxygen, nitrogen, sulphur, silicon etc. e.g. polyethylene, Teflon, polystyrene, PVC (polyvinyl chloride) are homochain polymers since their polymeric chain is made of only carbon atoms.

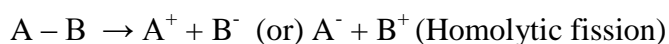
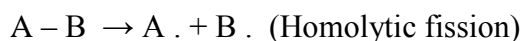


Polyesters, polyamides, polysulfones, silicones are examples of heterochain polymers since their polymeric chain is also made of hetero-atoms such as oxygen, nitrogen, sulphur, silicon etc.



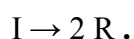
Polymers are characterized by their variable molecular weight depending upon the source of extraction and synthetic route adopted. Synthetic polymers may be either straight chain polymers or branched chain polymers. The chain length of a polymer and the degree of polymerization are the parameters to be carefully understood in the case of a branched chain polymer. The degree of polymerization (DP) may be defined as the total number of repeating units / monomers present in the given polymer macromolecules whereas the chain length of a polymer is the number of monomer units present in the main polymeric chain. Let us consider the following copolymer structure, where 'M' represents the monomer or the repeating unit.

of the covalent bond results in the formation of free radicals A. and B. i.e. the atoms A and B are separated with their unpaired electrons. In heterolytic fission, the covalent electron pair is transferred towards the more electronegative atom resulting in the formation of ions.

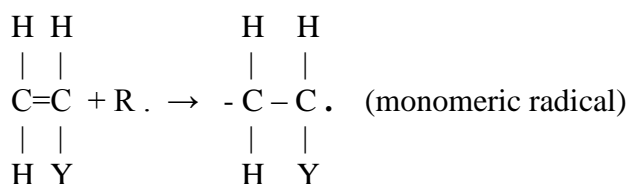
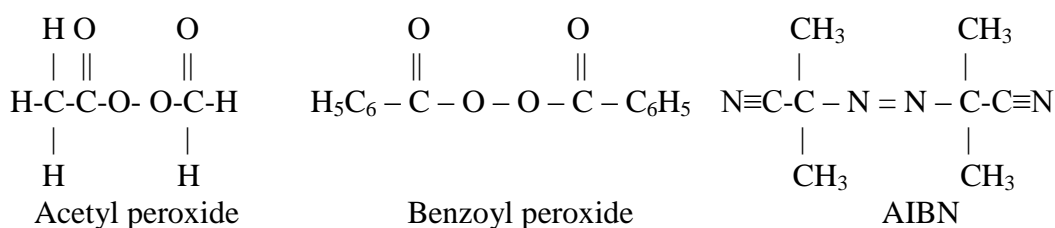


Addition or Chain polymerization is of types namely free radical polymerization, cationic polymerization and anionic polymerization based on whether the initiation of polymerization is caused by free radicals or cations or anions. Free radical polymerization is an important type, whose mechanism is discussed below:

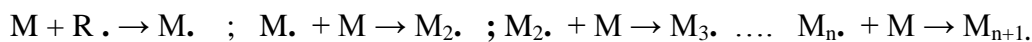
Chain initiation: The initiator molecule decomposes to give free radicals (highly reactive species).



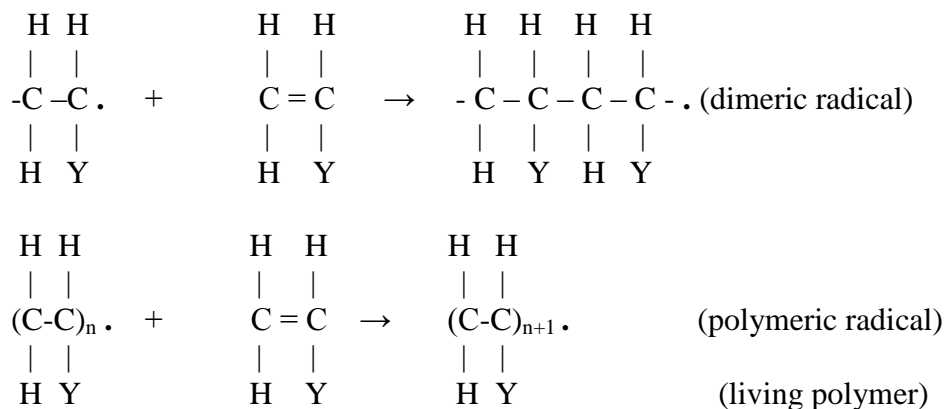
Here, the initiator species has to be distinguished from the catalyst in that the initiator starts the reaction between various species whereas the catalyst just speeds up the reaction that is already taking place but slowly. Organic peroxides such as alkyl peroxides or acyl peroxides are used as initiators for polymerization e.g. acetyl peroxide - $(\text{CH}_3\text{CO})_2\text{O}_2$, benzoyl peroxide - $(\text{C}_6\text{H}_5)_2\text{O}_2$ etc. Another important initiator used in free radical polymerization is AIBN – Azo bis (Iso Butyro Nitrile).



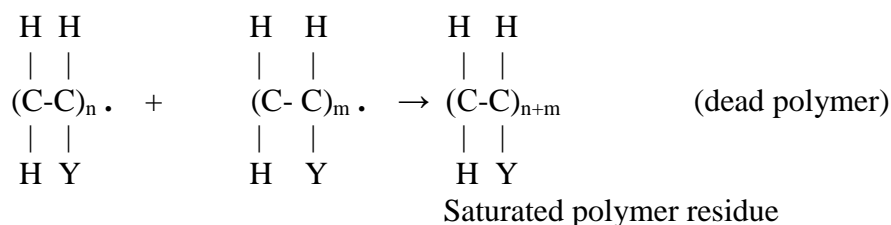
Chain propagation: The monomer molecule is attacked by the initiator radical to form a new reactive species monomeric radical; the monomeric radical, in turn, attacks another monomer molecule to form dimeric radical etc. this step proceeds continuously as long as polymeric radicals (reactive species) are available.



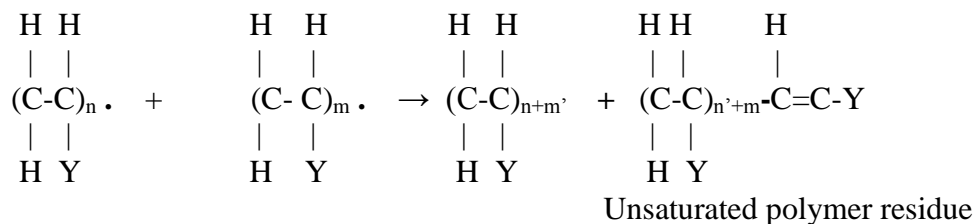
Here M_n represents the polymer with degree of polymerization 'n'. Thus, the degree of polymerization is the number of monomer units present in the polymer molecule. The polymeric radicals are also termed as living polymers as they can be further polymerized. Thus living polymers of various degrees of polymerization are formed in the chain propagation step.



Chain termination involves the recombination of polymer radicals to form dead polymers, which cannot be further polymerized. Chain termination may take place either by disproportionation or by coupling process, both of which are explained below with the example of a vinyl monomer $\text{H}_2\text{C}=\text{CHY}$ (Y is any group such as OH, X, COOH etc.).



(Recombination of polymeric radicals by coupling)



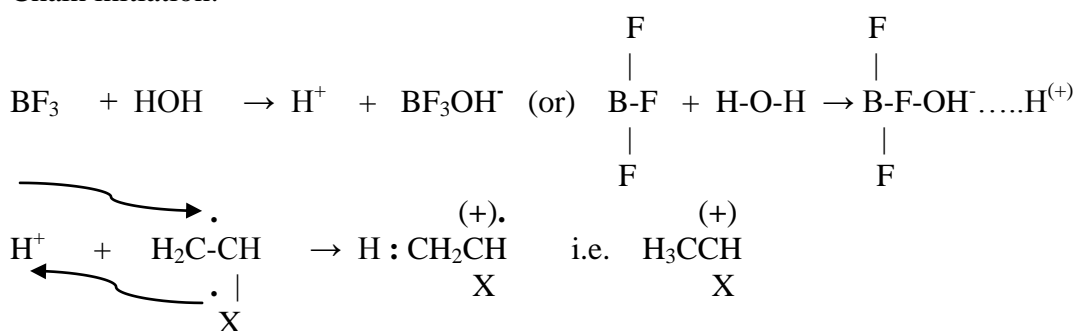
(Recombination of polymeric radicals by disproportionation)

The chain length is the number of monomers present in the main chain (carbon skeleton) of the polymer. (The term main chain signifies the chain with maximum carbon atoms, discarding the other chain branches). Another important salient feature of addition / chain polymerization is that the high molecular weight is formed at once / immediately.

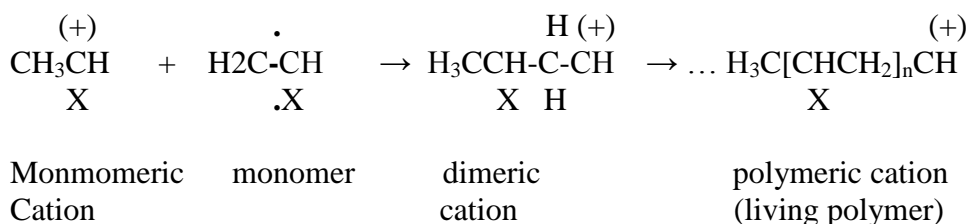
Ionic polymerization is a type of chain reaction or addition polymerization involving cations or the anion intermediates as the chain initiators. The main steps are of course, chain initiation, chain propagation and chain termination. The type of polymerization reaction initiated by the proton and the chain propagated by the carbonium ion is called **cationic polymerization**.

The chain initiation of cationic polymerization involves the attack of the π electron pair of the monomer. A proton (H^+) pulls the π electron pair towards it and the positive charge of the proton is transferred to the farther end of the monomer molecule, forming the carboium ion or carbo-cation (C^+), which acts as the cationic initiator. Here, a σ bond is formed between the proton, monomer unit and hence the polymeric chain further grows as a dimeric, trimeric, ..., polymeric cation, which constitutes the chain propagation process. The chain termination may be effected by the collision between the growing polymeric cation and a counter-ion i.e. an anion of other growing chain or a deliberately added anion. Lewis acids such as boron trifluoride (BF_3), aluminium chloride ($AlCl_3$), tin(IV)chloride ($SnCl_4$), titanium(IV)chloride ($TiCl_4$) etc. are used as the initiators / catalysts. Water is used as the co-catalyst. The catalyst and co-catalyst initially combine together forming the proton. The proton, in turn attacks the monomer, forming its cation which further acts as the chain carrier. The sequence of steps in this type of polymerization is represented below:

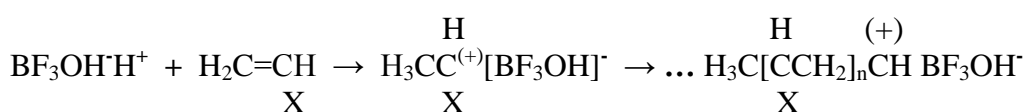
Chain initiation:



Chain propagation: (attack of second monomer by the carbonium ion of the first monomer, etc.)



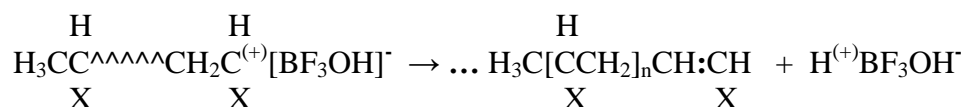
Here the electron pair transfer, as a whole is a unique process rather than one electron transfer. Lewis acid catalysts, in the presence of small amount of water as co-catalyst, form hydrates, which exist as ion pairs, as shown above. The net initiation and the propagation processes can be represented as



It is to be noted that the π electron pairs of the monomer units are pulled towards a direction opposite to that of the chain growth. The C^+ ion keeps on migrating in the direction of chain growth and the counter-ion also moves along with the carbonium ion.

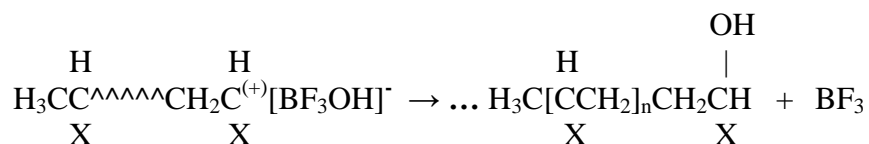
Chain termination: The possible reactions of this step are governed by the two facts mentioned below:

- (i) The proton donation to the counter-ion (reversal of the initiation step), resulting in the formation of a double bond at the end of the growing polymer molecule and hence the arrest of the chain growth.



This process of proton donation and the reformation of BF_3 hydrate is called ion-pair precipitation.

- (ii) Formation of covalent bond between the carbonium ion and the counter-ion and the termination being effected by coupling.

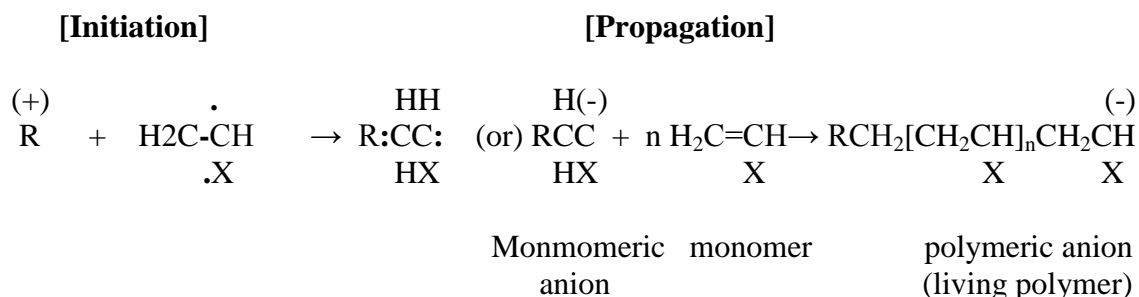


The termination by any of these two processes regenerates the initiator species (catalyst).

The monomers isobutylene, styrene, methyl styrene and vinyl ethers etc. undergo cationic polymerization.

Anionic polymerization: The type of polymerization reaction initiated and the chain propagated by the carbanion is called **cationic polymerization**.

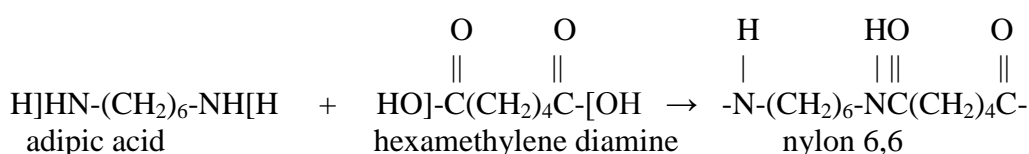
Here the attack on the π electron pair of the monomer by the anion takes place at the farthest end of the monomer substrate. At the same time, it forms a σ bond with the monomer molecule. The electron pair is pushed to the farthest end of the molecule, resulting in the formation of the carbanion – the chain carrier.



The carbanion formed in the initiation step attacks the π electron pair of the next monomer molecule and so on, pushing the π electron of the polymeric species to the farthest end and forming a σ bond with the new monomer unit. It is to be noted here that the electron pair movement is in the same direction as that of the chain growth, unlike the cationic mechanism.

The chain termination step of the anionic polymerization is not a spontaneous process. Hence the chain termination has to be made by the deliberate addition of strongly ionic impurities. In the absence of such materials, the anionic polymerization process continuously, once initiated and propagated. Thus the living polymers (species in the chain propagation process) grow as long as the fresh monomers are added. Hence this technique is called *living polymerization technique and is very useful in applications such as the preparation of block copolymers.*

Condensation polymerization may be defined as the reaction occurring between simple polar-group containing monomers. It proceeds by condensation mechanism i.e. takes place with the removal of minor molecules such as water, ammonia, hydrogen chloride etc e.g. condensation polymerization between adipic acid and hexamethylene diamine.

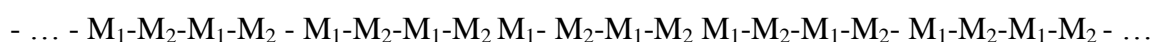


Co-polymerization is a type of addition polymerization involving two different monomers. Generally addition polymerization takes place with a similar monomer but addition polymerization can also take place between two different monomers (M_1 and M_2) with the resultant polymeric chain being composed alternatively of the two monomers.

The major differences between addition polymerization and condensation polymerization are tabulated below:

	Addition polymerization	Condensation polymerization
1	Growth reaction adds repeating units one at a time to the polymeric chain.	Any two molecular species can react.
2	Number of monomer units increases steadily throughout the reaction.	Monomer disappears early in the reaction.
3	High polymer is formed at once.	Polymer molecular weight (degree of polymerization) rises steadily throughout the reaction.
4	Longer reaction times have very little effect on molecular weight but gives higher yields.	Longer reaction times are essential to obtain higher molecular weights i.e. reaction time influences molecular weight of the polymer.
5	The reaction mixture contains only monomers, high polymers and very small amount (10^{-8}) of growing chains.	All types of molecular species are present at any stage.
6	E.g. polymerization of ethylene, styrene, vinyl chloride, propylene etc.	Polymerization to get nylon, PET, polycarbonate, polyurethane etc.

The polymeric chain of a copolymer of two monomers (M_1 and M_2) will be as follows:

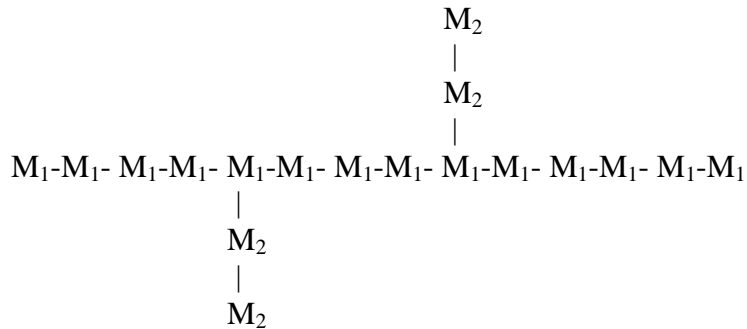


(the above structure is that of a linear co-polymer)

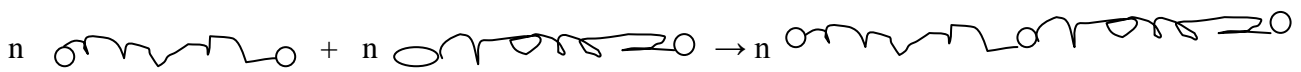
E.g. SBR – styrene butadiene rubber – a copolymer is composed of alternative units of styrene and butadiene. SBR structure will be discussed in detail under the topic rubbers.

Based on the mechanism of polymerization, polymers are classified as addition polymers, condensation polymers and copolymers (addition polymers). Based on branching of the polymeric chain, polymers are classified as linear polymers, branched chain polymers and cross-linked polymers. Cross-linked polymers are the polymers, which have the adjacent polymeric chains, connected together by means of covalent linkages such as ether linkage, methylene linkage etc. e.g. Bakelite is a cross-linked polymer. Copolymers may be either

linear with alternately placed two different monomers or branched chain polymers where one monomer is attached as a side chain / branch. (*Structure below*)

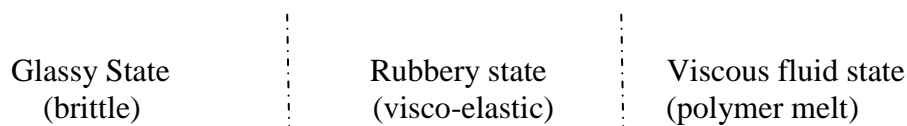


The schematic of a block copolymer is given below:



Properties of polymers:

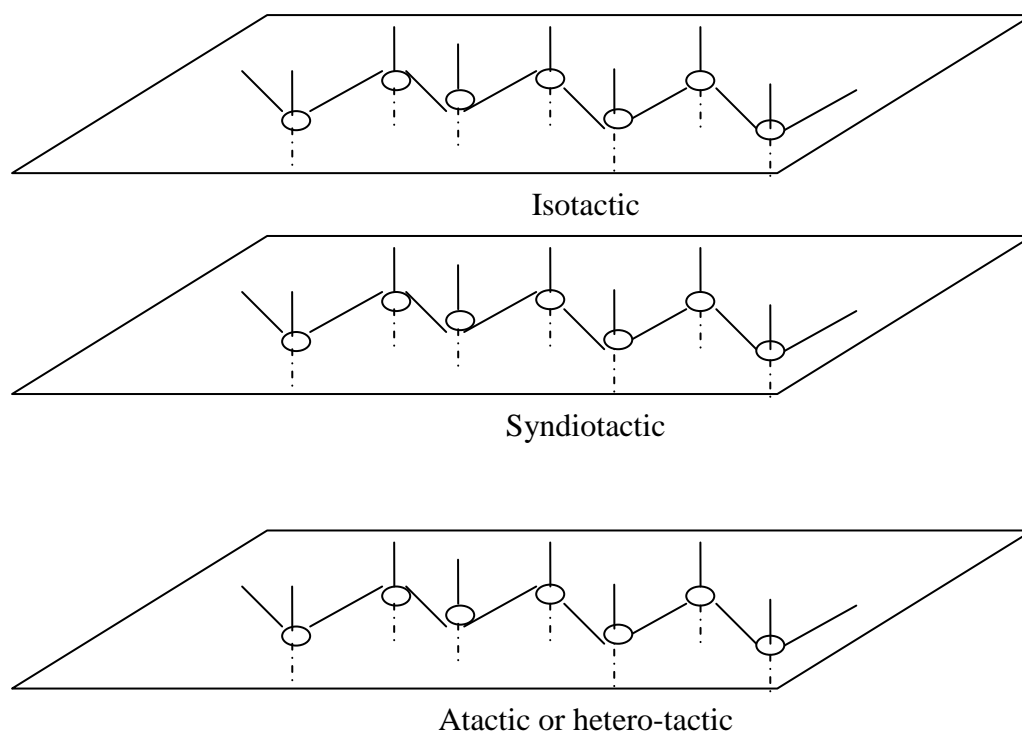
Glass Transition Temperature (T_g) : It is obvious that the polymers can be synthesized for wide range of properties such as those from flexibility to rigidity, crystalline to amorphous nature etc. A polymeric sample on heating may transform itself from a state of softness to a state of hardness or brittleness. Thus the temperature below which a polymer is hard and above this temperature, it becomes so soft that it transforms from glassy (brittle) state to a rubbery (elastic) or a visco-elastic state is termed as glass transition temperature (T_g). On further heating the polymer sample beyond the T_g value, it starts melting, acquiring the flow properties. The temperature at which the polymer becomes a fluid is called flow temperature (T_f). The phase transition of the polymer in these temperature ranges can be represented as



Depending on whether the polymer is more crystalline or more amorphous, the T_g, T_f or melting temperatures are either sharp or a temperature range respectively. These temperature values of a polymer are indicative of other mechanical properties of the polymer and hence become more significant. Thus if rubber (originally known for its elastic behavior), if cooled below its T_g value of -70°C, it becomes brittle and resembles glass in its brittleness.

Tacticity: Polymers may be synthesized as stereo regular compounds. Stereo regularity is a phenomenon of regular or orderly, spatial arrangement of groups or radicals of the monomer

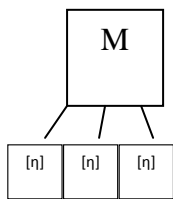
on either side of the main polymeric chain. Co-ordination polymerization is a type of chain polymerization where Ziegler_Natta catalysts (organo-metallic compounds containing transition metals such as Ti, Mo, Cr, V, Ni, Rh etc.) are used for achieving the stereo regularity in the polymer structure. Based on tacticity / stereo regularity, the polymers are classified as atactic, isotactic and syndiotactic polymer. Atactic polymer is one in which the stereo regularity is lacking or the groups / radicals are randomly / disorderly arranged on either side of the polymeric chain. Isotactic polymer is one in which the stereo regularity exists such that the groups / radicals are orderly arranged on same (one or other) side of the polymeric chain. Syndiotactic polymer is one in which the stereo regularity exists such that the groups / radicals are orderly arranged on either side of the polymeric chain. This can be illustrated with the vinyl ($H_2C=CHY$) monomer (Y is a substituent radical such as alkyl / R, halogen / X etc). Thus propylene ($H_2C=CHCH_3$) is a vinyl monomer where the alkyl group is the simplest methyl group ($R = CH_3$). Propylene can be polymerized with Ziegler_Natta catalysts to get stereo regular polymers such as isotactic polypropylene or syndiotactic polypropylene or atactic polypropylene if polymerized with other initiators / catalysts. The relative arrangement of the methyl groups attached to the alternate carbon atoms of the monomers in the polymeric chain decides the type of polypropylene. These three types are shown in fig. below:



(R has to be incorporated in these figures – important before print-out / mailing)

Isotactic and syndiotactic polymers are collectively termed as homo-tactic polymers whereas the atactic polymers are termed as hetero-tactic polymers. Poly buta-dienes and their derivatives, used as repeating units / monomers in synthetic rubber (co-polymers) can be synthesized as stereo regular polymers in this way.

It is obvious that the molecular weight of a polymer is not a fixed parameter but variable dependent on the synthetic method. Hence there are three important versions—of representation of polymer molecular weight as number average molecular weight (\overline{M}_n), weight average molecular weight (M_w), and viscosity average molecular weight (M_v). First two types of parameters are discussed in detail below:



Let us consider a polymer system containing ‘ n_1 ’ numbers of the monomer species with molecular weight ‘ M_1 ’, ‘ n_2 ’ numbers of the monomer species with molecular weight ‘ M_2 ’, ‘ n_3 ’ numbers of the monomer species with molecular weight ‘ M_3 ’, and so on. The total number of monomers in this system is ‘ $(\sum n_i)$ ’, with ‘ i ’ ranging from ‘1’ to ‘ n ’. the total weight (W) of the polymer sample is $W = (\sum n_i M_i)$.

The number fraction of fraction 1 (i.e. fraction of monomers with molecular weight ‘ M_1 ’) is given by $[n_1 / (\sum n_i)]$

Thus the molecular weight contribution by the fraction 1 is given by $(n_1 M_1) / (\sum n_i)$

Similarly, the molecular weight contribution by the fraction 2 is given by $(n_2 M_2) / (\sum n_i)$

Hence, The number average molecular weight (\overline{M}_n) is defined as

$\overline{M}_n = (\sum n_i M_i) / (\sum n_i)$, where ‘ n_i ’ is the number of monomers each with molecular weight ‘ M_i ’ and ‘ i ’ varies from ‘1’ to ‘ n ’ i.e. ‘ n_1 ’ is the number of monomers each with molecular weight ‘ M_1 ’, ‘ n_2 ’ is the number of monomers each with molecular weight ‘ M_2 ’, so on.

The weight fraction of fraction 1 (i.e. weight fraction of monomers with molecular weight ‘ M_1 ’) is given by $[n_1 M_1 / (W)] = [n_1 M_1 / (W)] = [n_1 M_1 / (\sum n_i M_i)]$.

Thus the molecular weight contribution by the fraction 1 is given by $[n_1 M_1 \cdot M_1 / (\sum n_i M_i)]$
i.e. $= [n_1 M_1^2 / (\sum n_i M_i)]$.

Similarly, the molecular weight contribution by the fraction 2 is given by

$$[n_2 M_2 \cdot M_2 / (\sum n_i M_i)] \text{ i.e. } = [n_1 M_1^2 / (\sum n_i M_i)].$$

Hence, The weight average molecular weight ($\overline{M_w}$) is defined as

$\overline{M_w} = (\sum n_i M_i^2) / (\sum n_i M_i)$, where 'n_i' is the number of monomers each with molecular weight 'M_i' and 'i' varies from '1' to 'n' i.e. 'n₁' is the number of monomers each with molecular weight 'M₁', 'n₂' is the number of monomers each with molecular weight 'M₂', so on.

For synthetic polymers, $\overline{M_w}$ is greater than $\overline{M_n}$, i.e. $\overline{M_w} > \overline{M_n}$. For a given polymer, these two molecular weight values may be same or different i.e. more than unity. Accordingly, the polymer is said to be mono-disperse or poly-disperse. Mono-disperse polymers are considered as homogenous and the poly-disperse ones as heterogenous polymers. But in practice, homogenous polymers are not realizable. Thus the Poly Dispersity Index (PDI) of a polymer is defined as the ratio of the weight average molecular weight to the number average molecular weight i.e.

$$PDI = \overline{M_w} / \overline{M_n}$$

Typical PDI values for the synthetic polymers are given below for reference:

Free radical polymers: obtained by solution / suspension / emulsion methods: 1.5 – 2

: obtained by bulk polymerization method: 2 – 5

: obtained by auto-acceleration methods: 8 – 10

Polymers by cationic / anionic mechanism: Using homogenous catalysts: < 1.5 (less than)

Using heterogenous catalysts: > 10 (higher than)

Polymers obtained by poly-condensation / poly-addition / ring opening mechanisms: 2 – 3

Branched chain polymers: > 20 (greater than 20)

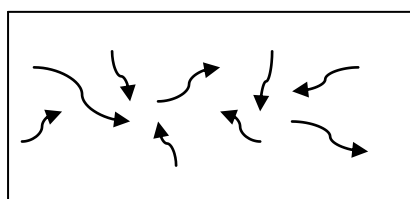
The polymerization techniques used in practice are of types such as bulk polymerization, solution polymerization, emulsion polymerization, suspension polymerization etc.

Bulk polymerization: In this method, the monomer is taken in the liquid state and the initiator is dissolved in the monomer. The chain transfer reagent, if required, is also dissolved in the monomer. The function of chain transfer reagent is to control the molecular weight of the final polymer and result in a homogenous phase. The resultant mass is heated or exposed to radiations of particular wavelength for the initiation of the polymerization. As the polymerization reaction proceeds, the viscosity of the medium increases and hence the mixing becomes progressively difficult, which is the disadvantage. Another disadvantage of this process is the restricted diffusibility of the growing polymer chain, because of the higher viscosity of the medium. Moreover, the accumulation of active radical sites causes the

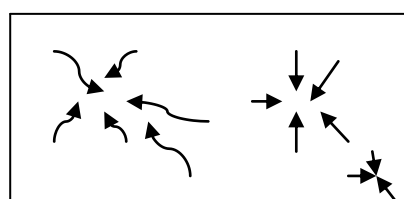
enormous increase in the polymerization rate, leading to the auto-acceleration mechanism and ultimately to explosion, if not controlled properly. The advantages of bulk polymerization technique are (i) simplicity, (ii) higher purity of the polymer obtained, (iii) no requirement of additives other than the initiator and the chain transfer reagent and (ii) direct utility of the polymer with no isolation requirement (due to higher purity). Bulk polymerization is used in the free radical polymerization of methyl methacrylate ($\text{H}_2\text{C}=\text{C}(\text{CH}_3)\text{COOCH}_3$) or styrene ($\text{H}_2\text{C}=\text{CHC}_6\text{H}_5$) to get transparent powders of PMMA or polystyrene (thermocole) and also the cast sheets of poly vinyl chloride (PVC) .

Emulsion polymerization: Here, the monomer is dispersed in aqueous phase as emulsion. The emulsion is stabilized by the addition of surfactants (surface active agents), protective colloids and some buffers. Anionic surfactants such as sodium or potassium aryl sulphonates or cationic surfactants such as alkyl amino hydro chlorides or alkyl ammonium halides or non-ionic surfactants such as alkyl glycosides or saccharic esters of higher fatty acids are used. They function by lowering the surface tension at the water-monomer interface and hence facilitate the emulsion of monomer in water. Due to their low solubility, surfactants are molecularly dispersed even at low concentrations. At a particular concentration, the excess un-dissolved ones form as molecular aggregates, called micelles and an equilibrium is established between the dissolved surfactant molecules and the aggregated micelles. *The highest concentration of surfactants wherein all the molecules are in the dispersed state and the concentration beyond which the micelle formation is possible is termed as critical micelle concentration (CMC).*

The emulsifier molecules are made of two parts – a long, non-polar hydrocarbon (H/C) moiety, to which is attached a polar entity such as $-\text{COONa}$, $-\text{SO}_3\text{Na}$, $-\text{NH}_2\cdot\text{HCl}$, $-\text{NBr}$ etc. in micelle formation, the emulsifier molecules aggregate in such a way that the polar ends align outward and the H/C ends come close to each other at the interface.



Randomly aligned but complete
Distribution at low concentration



Micelles

[——— - non-polar H/C chain (tail) ; → polar end (head)

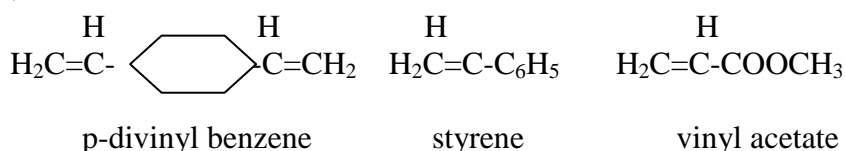
Due to the proximity of the H/C entities of all emulsifier molecules, the interiors of the micelles act as the H/C phases, where the monomers can be made soluble. On further addition of the monomer followed by agitation, emulsification takes place. The resultant emulsion is a complex system. These micelles possess favourable condition for polymerization to occur. The initiator molecules are available at the surface layers whereas the interior of the monomer is filled with the solubilized monomer. Hence the polymerization starts at the surface and proceeds inwards. On consumption of the monomer in the micelle, more amount of monomer diffuses from the aqueous phase, into the micelle. The polymer chain growth continues until another radical species enters and arrests the chain growth. With more and more amount of polymer formed, the polymer chains aggregate into fine particles and get surrounded and stabilized by the emulsifier layer. At the end of polymerization, the fine particles of the polymer are stabilized by the emulsifier layer and dispersed uniformly in the aqueous phase. The resultant milky white dispersion is termed as latex, which can be used as such for applications like adhesives, emulsion paints or the polymer can be isolated from the latex by the de-stabilization of the emulsified polymer mass using electrolytes or by spray drying or by freezing. Depending upon the relative solubility of the monomer and initiator in water and the ratios of amounts of monomer / water and emulsifier water, the polymerization occurs either at the dissolved phase or at the interface or at the surface or inside the monomer droplets.

Emulsion polymerization is the most widely used industrial technique for the polymerization of monomers such as vinyl chloride ($\text{H}_2\text{C}=\text{CH}.\text{Cl}$), buta-diene ($\text{H}_2\text{C}=\text{CH}.\text{CH}=\text{CH}_2$), chloroprene ($\text{H}_2\text{C}=\text{CCl}.\text{CH}=\text{CH}_2$), vinyl alcohol ($\text{H}_2\text{C}=\text{CH}.\text{OH}$), acrylates ($\text{H}_2\text{C}=\text{CH}.\text{COO}-$) and methacrylates ($\text{H}_2\text{C}=\text{C}(\text{CH}_3).\text{COO}-$) etc. It is to be noted that the heat transfer is very difficult with this technique and hence the viscosity build up of the polymer mass is quite low compared to the bulk and solution polymerization techniques.

Solution polymerization: In this technique, the monomer and the free radical initiator are dissolved in a suitable solvent, along with the ionic co-ordination catalyst and the chain transfer reagent, if any. The selection of some inert solvent enables viscosity control and prevents heat transfer. The advantage of this method lies in its use when the polymer is used in solution form or when the polymer is insoluble in monomer or any other solvent or precipitates out as slurry and is amenable for easy isolation. The industrial production of poly

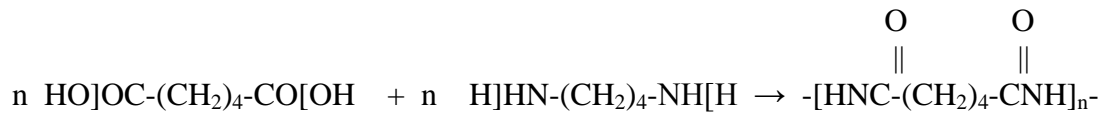
acrylo nitrile (PAN) by free radical mechanism, that of poly isobutylene by cationic initiation and manufacture of block co-polymers are effected by solution polymerization technique.

Suspension polymerization: Water-insoluble monomers are polymerized by this technique. The monomer is suspended in water in the form of fine droplets, which are then stabilized against coalescence, using stabilizers, surfactants, protective colloids and by stirring. But the initiators are monomer-soluble. Each monomer droplet is isolated and is independent of other droplets and hence acts as an independent bulk polymerization nucleus (where the polymer chain growth starts and proceeds). The continuous aqueous phase separating the monomer droplets, acts as the efficient heat transfer medium and hence the exothermicity is controlled. The size of the monomer droplets depends upon the monomer/water ratio, type and concentration of stabilizers and the mode and speed of agitation. This technique is more economical compared to solution polymerization technique, since water is used as the heat transfer medium. As the entire bulk of the monomer is divided into numerous tiny droplets, the control of the kinetic chain length (chain length of living polymer; that in chain propagation stage) of the formed polymer is quite good and results in a fairly narrow molecular weight distribution of the product. Thus the polymerization proceeds to 100% conversion levels and the product is obtained as '*spherical beads or pearls*'. The technique is so termed as *bead or pearl polymerization*. The isolation of the product is easy as it involves only the filtration of pearls or beads and the removal of surfactants and other additives by mere washing with water. The water-washed and dried polymer sample is as such used for molding purposes or can be dissolved in a suitable medium for use as adhesives / coatings. Expanded polystyrene beads (for making polystyrene foams), styrene-divinyl benzene copolymers (for the preparation of ion exchange resins) and poly vinyl acetates (for further conversion to poly vinyl alcohol) are produced by suspension polymerization technique



Preparation, properties and uses of nylon 6,6:

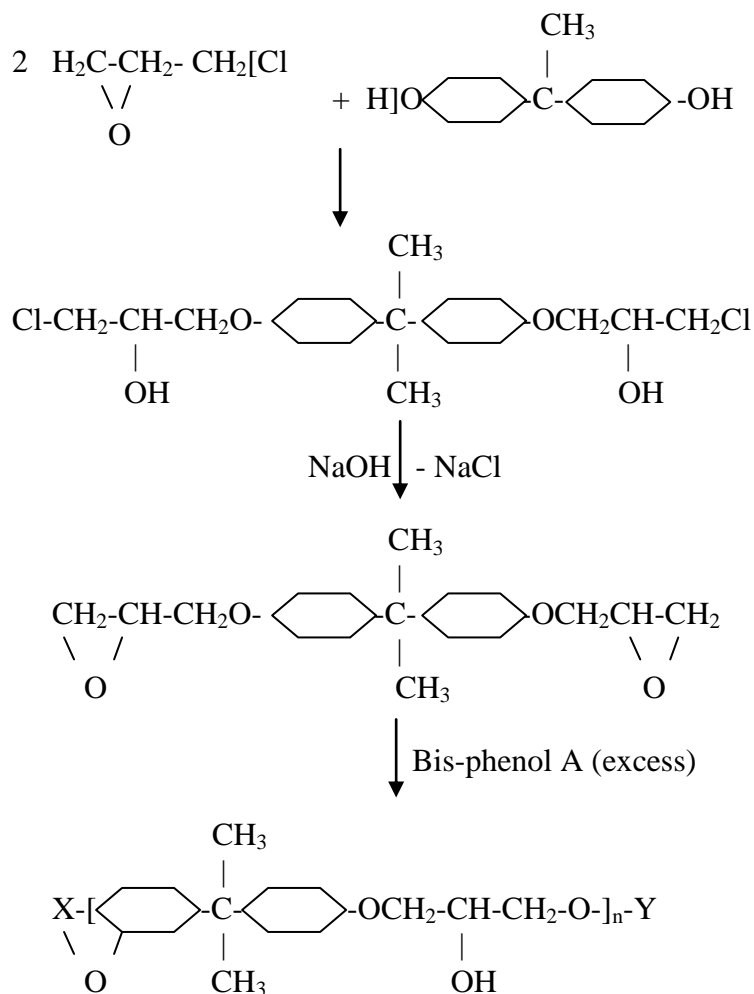
Nylon 6,6 is a polyamide prepared by the condensation polymerization between / polycondensation of the monomers hexamethylene diamine and adipic acid. Here two water molecules are removed from each set of monomers.

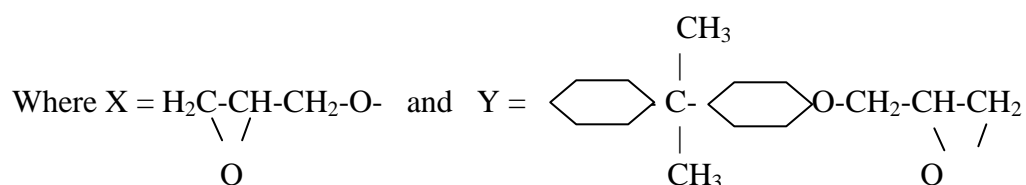


Nylon 6,6 is a tough, fairly crystalline material with the melting point of 270°C. It has good tensile strength and abrasion resistance up to 150°C. It is resistant to the action of solvents but soluble in formic acid, cresols and phenols. Its high tensile strength and rigidity / stiffness are due to the high degree of polymerization.

Nylon 6,6 is largely used to produce tyre chord and to make filaments and ropes. Due to its toughness, it is used as a good substitute for metals in gears and bearings. Its fibre forming tendency is used to yarn textile fibres and dress materials.

Epoxy resins: these are basically poly-ethers. The common types of epoxy resins are prepared from the condensation polymerization between epichlorohydrin and bis-phenol A. The reaction is carried out with excess of epichlorohydrin.





Instead of bis-phenol A, other compounds with OH groups such as glycols, glycerols and resorcinols can also be used. The epoxy resins obtained through these reactions will be either highly viscous liquids or solids with high melting points. The epoxy resins can be further cured with substances such as amines, poly sulfides and poly amides. The thiol (-SH) covalent linkages are established between the polymer chains, during curing, to get the resultant strong, highly cross-linked polymers.

Epoxy resins find enormous applications due to their remarkable chemical resistance and good adhesion properties. They are used as excellent structural adhesives. On proper curing, they yield tough materials as used in industrial floorings, as foaming materials, as potting materials in electrical insulation etc. A principal constituent of most of the fibre reinforced plastic (FRP) materials is the epoxy resins. Also, the EPI coating in lorries carrying corrosive chemicals contains the epoxy resin formulations.



Questions

1. What is meant by T_g ?
2. What is meant by tacticity of a polymer?
3. What is meant by co-polymer? How is it classified?
4. State the techniques of polymerization.
5. Outline the comparison of techniques of polymerization.
6. What is meant by functionality of a monomer?
7. Write the repeating units of nylon and epoxy resins.
8. List the types of chain polymerization.
9. Define number average molecular weight.
10. Define weight average molecular weight.
11. What is meant by poly dispersity index? State its significance.
12. Discuss the classification of polymers with examples.
13. Discuss the mechanism of free radical / cationic / anionic polymerization.
14. List the differences between addition polymerization and condensation polymerization.
15. List the differences between thermo plastics and thermosetting plastics.
16. Explain the preparation, properties and uses of nylon 6, 6 and epoxy resins.
17. Discuss the method, advantages and limitations of solution / suspension/ emulsion / bulk polymerization techniques.
