

Polymer

What is Polymer?

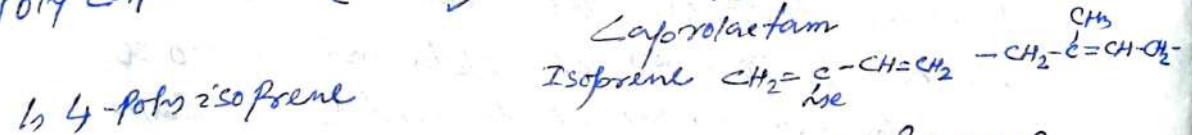
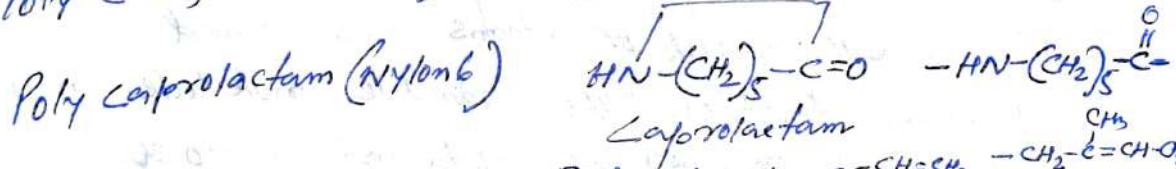
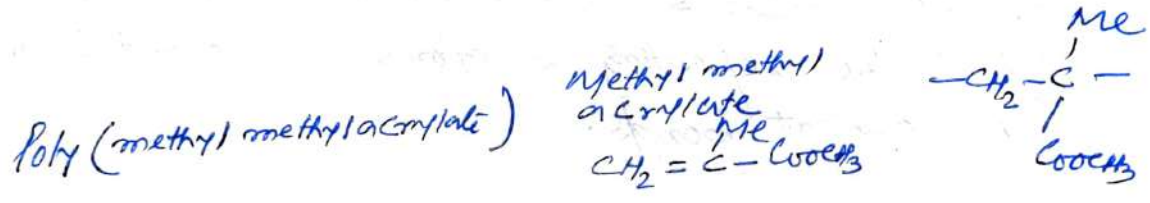
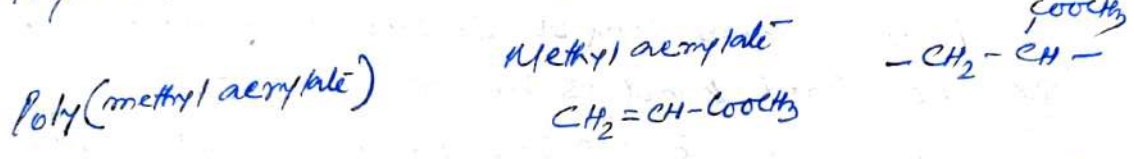
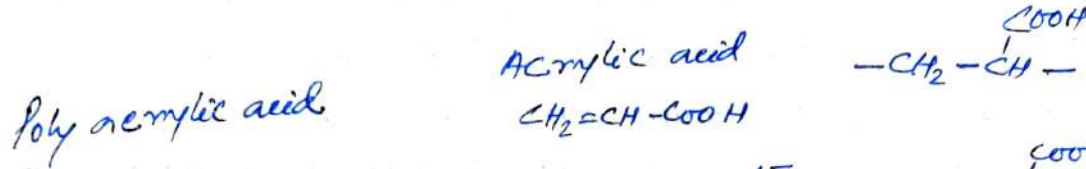
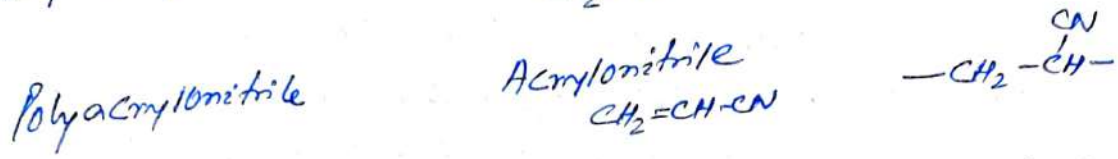
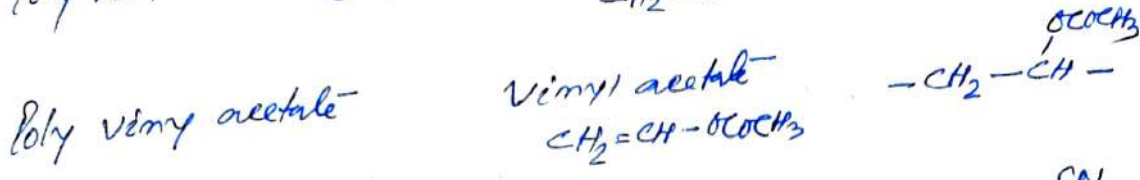
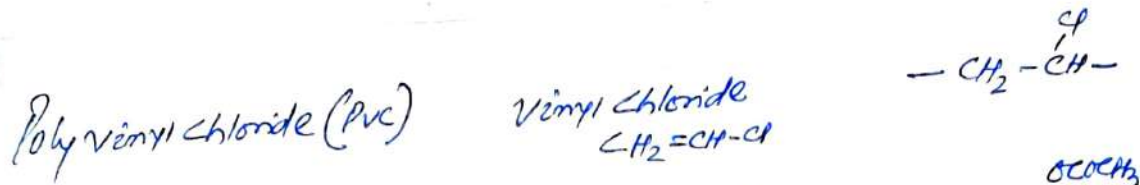
✓ The word Polymer literally means many (poly) units (mer). A simple chemical unit repeats itself a very large number of times in the structure of a polymer molecule; this unit may consist of a single atom, or more commonly, a small group of atoms linked chemically. An example of the first kind is the well known plastic Sulphur, $-S-S-S-S-S-S-$, in the molecules of which the repeating 'S' atoms are joined together by covalent bonds.

What is monomer?

In bulk of the polymers, the repeating unit or simply the repeat unit is constituted of small group of atoms combined in specific fashion. The simple molecule from which its polymer is obtained or to which a polymer may be degraded is called the monomer.

* The number of repeat units in a given polymer molecule is known as its chain length or degree of polymerization (DP). The molecular weight of the polymer is the product of the molecular weight of the repeat unit and DP.

| <u>Polymer</u> | <u>Monomer</u> | <u>Repeat unit</u> |
|----------------|-----------------------------------|-----------------------------|
| Polyethylene | Ethylene $CH_2=CH_2$ | $-CH_2-CH_2-$ |
| Polypropylene | Propylene $CH_2=\overset{Me}{CH}$ | $-CH_2-\overset{CH_3}{CH}-$ |
| Polystyrene | Styrene $CH_2=CH-Ph$ | $-CH_2-\overset{Ph}{CH}-$ |



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* What is copolymer, low polymer and high polymer?

When more than one kind of repeat units are present in a polymer, it is known as a copolymer. Polymers having molecular weight roughly in the range of 1000-20,000 are called low polymers and those having molecular weights higher than 20,000 as higher polymers.

* Why the Properties of Polymer differ from that of monomer?

~~Ans~~ length to diameter ratio of a polymer molecule is very high compared to that of a simple molecule. If a small molecule such as the ethylene molecule is represented by a dot (.), then the molecule of a polymer say polyethylene of 1000 DP will be represented by a line (-) formed by addition or sticking together of 1000 dots in a linear fashion. The characteristic difference in length to diameter ratio between a small molecule and a polymer or a high polymer molecule makes all the difference in their physical properties.

Due to their long lengths, molecules in a given sample of a polymer material remain in a state of entanglements, both intermolecular and intramolecular. High melting or softening temperature, high melt or solution viscosity exhibited by polymer materials arise as a consequence of big size of their molecules and the entanglements of the molecular chains.

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* Classification of Polymers:

| Basic of Classification | Polymer types |
|-------------------------------------|---|
| Origin | Natural, Semisynthetic, Synthetic |
| Thermal response | Thermoplastic, thermosetting |
| Mode of formation | Addition, Condensation |
| Line structure | Linear, branched, cross-linked |
| Application and Physical Properties | Rubbers, Plastics, fibres |
| Tacticity | Isotactic, Syndiotactic, atactic |
| Crystallinity | amorphous, semicrystalline, crystalline |

- * **Natural Polymers:** They are available in nature. Examples of such polymers are: natural rubber, natural silk, cellulose, starch.
- * **Semisynthetic Polymer:** They are chemically modified natural polymers such as hydrogenated, halogenated or hydrohalogenated natural rubber. -i.e. Cellulose nitrate-
- * **Synthetic Polymers:** They are man-made polymers prepared synthetically. Polyethylene, polystyrene,
- * **Thermoplastic Polymer:** They can be softened or plasticized repeatedly on application of thermal energy, without much change in properties if treated with certain precautions, e.g. Polyolefins, polystyrene, Dr. Santanu Chakravorty
- * **Thermosetting Polymers:** They can be obtained in soluble and fusible forms in early or intermediate stages of their synthesis, but they get set or cured and become insoluble and infusible when further heated or thermally treated; the curing or setting process involves chemical reactions leading to further growth and cross linking of the polymer chain molecules and producing giant molecules, e.g. phenolic resins, diene rubbers.
- * **Addition Polymers:** They are formed from olefinic, diolefinic, vinylic and related monomers. They all have $-C-C-$ linkages along the main chains of the polymer molecules and no other atom appears in the main chain. These polymers are formed by simple additions of monomer molecules to each

Other in quick succession by a chain mechanism. This is known as addition polymerisation or chain growth polymerisation. example: Polyethylene, Polystyrene etc. ✓

* **Condensation Polymer:** They are formed from intermolecular reaction between bifunctional or polyfunctional monomer molecules having reactive functional group such as $-OH$, $-COOH$, $-NH_2$, $-NCO$ etc. The related functional groups react with each other in a stepwise manner producing condensed structural linkages, usually with the elimination of a simple, small byproduct molecule in each step of reaction. Beside $-C-C-$ linkages, they contain such atoms as O , N , S , etc; at regular intervals in the main chain. The process of their formation is called Condensation Polymerization. Polyamides, Polyesters, Polyurethanes etc. are example of Condensation Polymer.

* **Linear Polymers:** They can schematically be represented by lines of finite lengths. They are formed from olefinic, vinyl or related polymerization under suitable ~~condensation~~ conditions or by condensation polymerization of bifunctional monomers. Linear polymers such as high density Polyethylene, Poly(vinyl chloride).

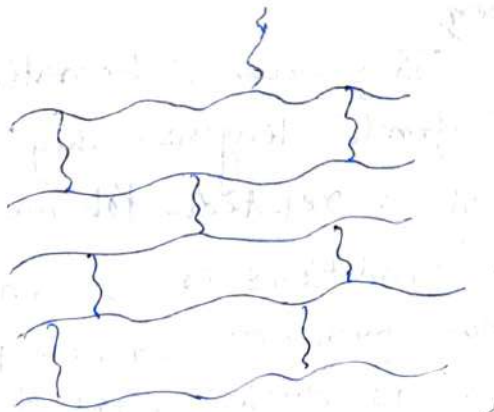
Schematic representation
of linear polymer:

* **Branched Polymers:** They can be schematically represented by lines of finite lengths with short or long branch structures of repeat units. The branches

appear as a consequence of uncontrolled side reactions during polymerization or by design of polymerization. Branched polymers are usually more readily soluble and fusible than linear polymers of comparable chain length or molecular weight.



Cross-linked or Network Polymer: They can be represented by a network structure, planar-network as in graphite or space-network as in diamond. Cross-linked polymers are insoluble and infusible as the molecules are giant molecules, often of unusually high or infinite molecular weight. Depending on the nature and frequency of cross-links, such polymers may show different orders of swelling in solvents. Examples are phenol-formaldehyde resins, epoxy resins.



* Rubbers:

These polymers are characterized by long-range ~~capacity~~ elasticity. On consideration of mechanical strength, they are rather weak, dimensionally unstable and undergo high elongations even on application of low stresses. They exhibit tensile strength in the range of 300-3000 psi and elongation at break ranging between 300-1000%. Examples are natural rubber and synthetic rubber.

* Plastics:

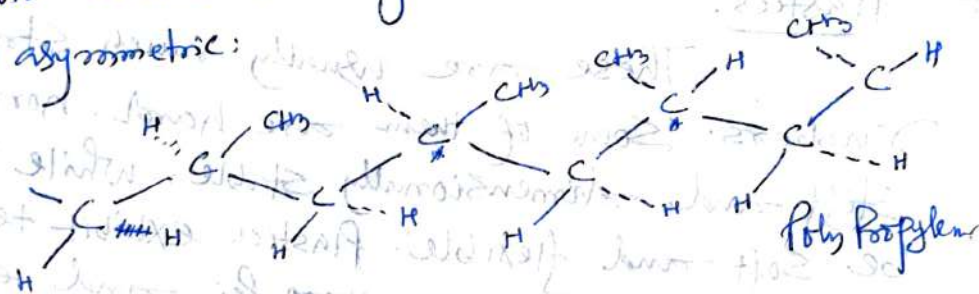
These are usually much stronger than rubbers. Some of them are hard, horny, rigid, stiff and dimensionally stable, while others may be soft and flexible. Plastics exhibit tensile strength ranging between 4000-15000 psi and elongation at break ranging from 20 to 200% even higher. The examples of plastics are: polyethylene, polypropylene.

* Fibers:

They are the strongest of the three different types of polymers mentioned here. Among the natural polymers of industrial importance, the foremost place is occupied by fibres, which may be either plant or animal origin. The suitability of fibres, natural or synthetic, for use as textile materials is unique and it is ~~range of 20000-15000 psi~~ associated not only with high mechanical strength but also with other useful properties such as warmth or thermal insulation, softness and flexibility. Cotton, cellulose, wool, silk, synthetic polyamides etc. are example of fibres.

Tacticity:

A vinyl polymer $-(CH_2-CHR)_n$ is characterized by an asymmetric carbon atom in each of the repeat units of the chain molecule, and a type of stereochemical difference that may arise in the segments of the chain is d, l-isomerism. In a polymer of this kind, such as polypropylene or polystyrene, every alternate carbon atom indicated by an asterisk along the chain backbone is asymmetric:



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Considering head to tail linkage of the repeat units, the first two asymmetric carbon atoms in each case have a different configuration in comparison with the last two, giving stereochemical sequences represented as -d-d-l-l.

Depending on the tacticity or spatial disposition of the substituents attached to ~~the~~ asymmetric carbon atoms in the chain, we can have three major and distinctive sequences;

- (i) isotactic sequence represented as -d-d-d-d-d- or -l-l-l-l-l-, giving similar or identical spatial disposition of the substituent in the repeat units.
- (ii) Syndiotactic sequence represented as -d-l-d-l-d-l- where the steric placements

density for a few commonly used polymers is listed below which clearly show variation in this parameter depends on molecular structure.

Among the different type of secondary valance forces known, one type arises from polarity of the molecules and it is manifested through interaction of dipoles. The magnitude of such interaction energy is dependent on the mutual alignment of the interacting dipoles. As molecular alignments are opposed by thermal agitation, the dipole forces are very much dependent on temperature.

| Polymer | Repeat unit | Cohesive energy density, $\frac{\text{cal/cm}^3}$ |
|-------------------|---|---|
| | | 56-64 |
| Polyethylene | $-\text{CH}_2-\text{CH}_2-$ | 55-88 |
| Polystyrene | $-\text{CH}_2-\text{CH}(\text{Ph})-$ | 56-64 |
| Polyisobutylene | $-\text{CH}_2-\text{C}(\text{Me}_2)-$ | 89-94 |
| Polyvinyl acetate | $-\text{CH}_2-\text{CH}(\text{OCOCH}_3)-$ | 60-67 |
| Polyisoprene | $-\text{CH}_2-\text{C}(\text{Me})=\text{CH}-\text{CH}_2-$ | 180-220 |
| nylon-66 | $-\text{HN}(\text{CH}_2)_6\text{NHCO}(\text{CH}_2)_4\text{CO}-$ | 180-230 |
| Polyacrylonitrile | $-\text{CH}_2-\text{CH}(\text{CN})-$ | |

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Another kind of intermolecular interaction is that induced by polar molecules or segments through the dipoles on surrounding molecules or segments that do not have permanent dipoles.

The secondary bond forces consequent to interactions between permanent dipoles

and induced dipoles are known as the induction forces. The cohesive energy corresponding to the induction force is small and it does not depend on temperature.

There are also dispersion forces which are not dependent on polarity or permanent dipoles but which are consequences of different instantaneous configurations of electrons and nuclei of all kind of molecules, resulting in time-varying dipole moments that average out to zero. The dispersion forces exist in all molecular systems, polar or non-polar and constitute a major part of the cohesive forces except in systems having strong dipoles. In non-polar materials the molar cohesion is due only to the dispersion forces which are also independent of temperature. The energy of all the above secondary forces usually ranges between 2-5 kcal/mol.

A fourth but an important and major kind of intermolecular attraction, particularly in polar molecules containing fluorine, nitrogen, oxygen and occasionally chlorine atoms is due to hydrogen bonding. The energy of hydrogen bonds usually ranges between 5-10 kcal/mol and its overall cumulative effect in polymer material systems is very pronounced and sometime overwhelming, so much so that suitable polymers having frequent and extensive hydrogen bonds along the chain such as cellulose, polyamides etc are inherently crystalline and resistant to heat and solvents. The exact nature of the hydrogen bond depends on the chemical nature and environment of the concerned polar groups and it is considered, in most systems, electrostatic or ionic in character.

The average attractive force between sections of polymer molecules in an oriented domain or crystal lattice is higher than that between sections that are not in a lattice. Crystallites are usually 10-15% more dense than the supercooled melt at the same temperature.

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* Melting point and first order transition:

Melting of a crystalline solid or boiling of a liquid is associated with change of phase. Many high polymers possess enough molecular symmetry and/or structural regularity that they crystallize sufficiently to produce a solid-liquid phase transition phenomenon or melting, i.e. they have a crystalline melting point T_m . The melting is quite sharp for a few polymer such as, the nylons, while in polystyrene, different rubbers, etc, the phase change take place over a range of temperature. Phase transition of this kind, particularly in low molecular weight materials, being associated with sharp discontinuities in some primary physical properties such as the density or volume and entropy, which are first derivatives of free energy; which are first derivatives of free energy, are commonly called first order transitions.

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* Glass transition or second order transition:

Glass transition or second order transition is not a phase transition and almost each polymeric or high polymeric material is characterized by a specific glass transition temperature (T_g), appearing well below its (crystalline melting point T_m).

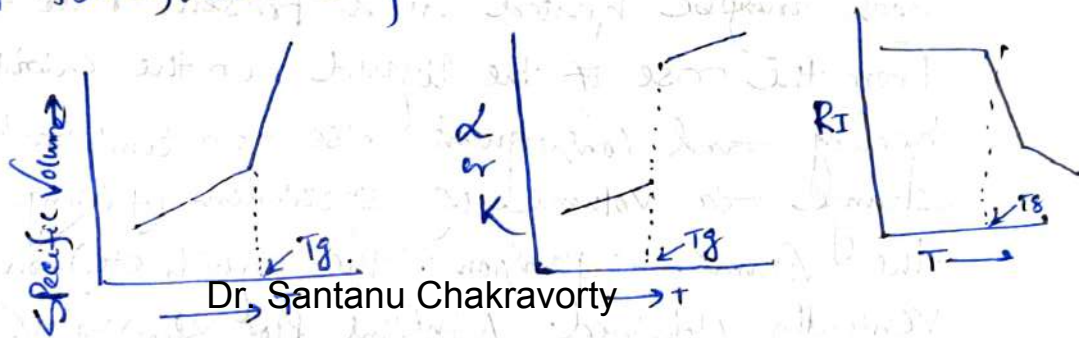
The glass transition is not a phase transition and so, it involves no latent heat.

Below this temperature normally rubber-like polymers become rigid, hard and dimensionally stable and they are considered to be in a glassy state while above this temperature, all normally rigid, hard and stiff polymers become soft, and readily susceptible to cold flow or creep and they turn into a rubbery state.

The difference between the glassy and rubbery states of the polymer lies not in their geometrical structure, but in the state and level of molecular motion. Below the glass transition temperature, T_g , the molecular segments or groups constituting the chain backbone can undergo only limited degrees of vibration and they do not possess the energy required to rotate about bonds and change their positions with respect to segments of neighbouring chains. At or slightly above T_g , rotation sets in and it is conceivable, that only the molecular segment rather than the entire high polymer molecule would rotate at this stage of transition.

* When plastic or rubber is cooled up to certain temperature, it becomes so hard and brittle that it breaks into pieces on application of stress. The temperature below which the polymer becomes hard, brittle and glassy and above which it is softer and flexible, is known as glass transition temperature (T_g).

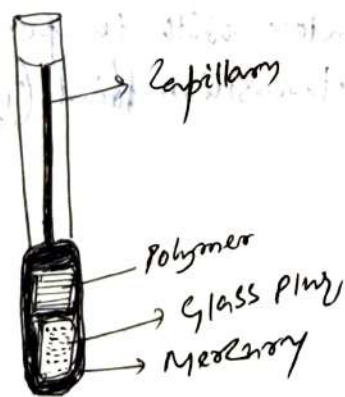
* At T_g , the variables S , V and n merely undergo change of slope when plotted against temperature without showing sharp changes or discontinuities as observed in case of first order transitions. The properties which undergo discontinuities at the glass transition temperature are: heat capacity C_p , coefficient of thermal expansion α , and isothermal compressibility K , which are second order transition temperature. T_g is commonly referred to as the second order transition temperature.



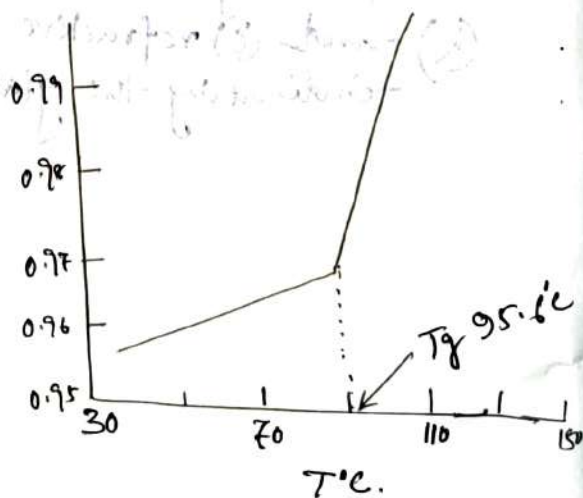
* Trend of change of (a) Specific Volume (b) Coefficient of thermal expansion or isothermal compressibility (K) and (c) refractive index with temperature indicating the glass transition point (T_g)

Measurement of Glass Transition Temperature: (Free Volume theory):

The glass transition temperature, T_g , is conveniently measured in the laboratory by taking help of dilatometry. The polymer appropriately confined in the bulb at the bottom is kept immersed in a suitable liquid, usually mercury so as to give a column of the liquid in the capillary up to a convenient height for measurement. The positioning of the glass plug, as shown, enables heating the test specimens avoiding overheating. The dilatometer placed in an outer bath may be heated at a preset rate and pattern. From the rise of the liquid in the capillary on heating and consequent rise in temperature, the change in volume of specimen (taking into account the volume expansion of the liquid, etc.) may be conveniently obtained. A typical plot showing variation of specific volume with change of temperature for polystyrene is shown below:



A dilatometric set up for measurement of change in volume of polymer with change in temperature.



Volume expansion of polystyrene with rise in temperature; the inflection point corresponds to T_g .

Williams-Landel-Ferry equation (WLF equation):

WLF equation is an empirical equation associated with time-temperature superposition.

The WLF equation has the form:

$$\log(a_T) = \frac{-C_1(T-T_r)}{C_2 + (T-T_r)}$$

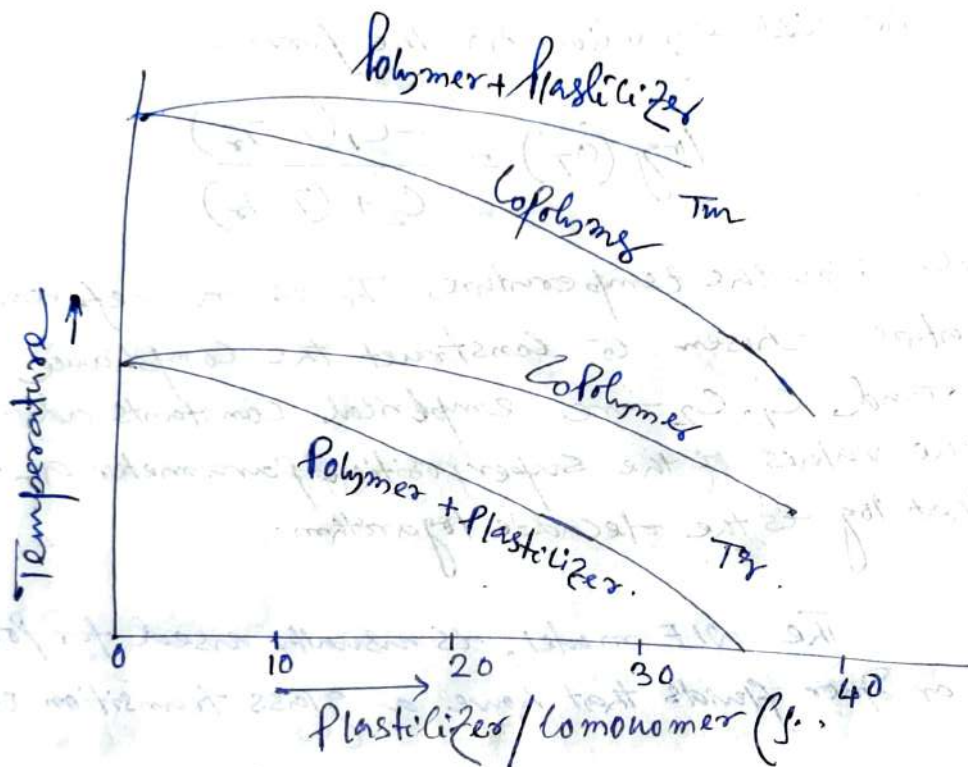
Where T is the temperature, T_r is a reference temperature chosen to construct the compliance master curve and C_1, C_2 are empirical constants adjusted to fit the values of the superposition parameter a_T . Note that \log is the decadic logarithm.

The WLF model, is usually used for polymer melts or other fluids that have a glass transition temperature.

* Factor affecting glass transition temperature: Dr. Santanu Chakravorty

Molecular weight, external tension or pressure, plasticizer incorporation, copolymerization and cross-linking are some of the more important factors that influence the glass transition temperature and the melting point of polymers. The comparative lowering of T_m and T_g for polymer modification by plasticizer incorporation and by copolymerization is shown in fig. 1. In general, a comonomer incorporation i.e. copolymerization is more effective than plasticization in lowering the melting point, while plasticization is normally more effective than copolymerization in lowering the glass transition point. Cross-linking tends to increase the glass transition temperature as the cross-links restrict the freedom of chain segments to rotate, necessitating a higher temperature for inception of rotation. Similarly, higher molecular weight of linear chains

restricts slope for segmental rotation and hence, rise in T_g , with a levelling off effect in the higher molecular weight range, however.



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fig: Schematic plots showing comparative lowering of T_m and T_g of polymers by separately incorporating: (i) a plastilizer and (ii) a comonomer by copolymerization.

Polymerization

Polymerization may be generally defined as intermolecular reaction between bifunctional or polyfunctional compounds avoiding formation of ring or cyclic structures and in a manner that makes the process functionally capable of proceeding to infinity. Functional groups or atoms through disappearance of which polymerizations of different kinds take place are: reactive hydrogen atom ($-H$), hydroxyl group ($-OH$), carboxyl group ($-COOH$), amino group ($-NH_2$), halogen ($-Cl, -Br$), isocyanate ($-NCO$), aldehyde group ($-CHO$), double bond ($C=C$), etc.

According to the functionality principle and concept, for polymerization to take place, each of the reacting molecules must be at least bifunctional, giving average functionality for the system as 2. For reacting compounds containing two different kind of functional groups, the average functionality is calculated on the basis of stoichiometric equivalence of the two kinds of functional groups. Thus, for reaction between a dicarboxylic acid and a trihydric alcohol, to strike stoichiometric equivalence of $-COOH$ and $-OH$ groups, the acid and the alcohol should be taken in molar ratio 3:2, which would express the average functionality for the system as $12/5$, i.e. 2.4. On this basis, any system consisting of a polyfunctional compound bearing a given kind of functional group and a related monofunctional compound bearing a different kind of functional group would always give an average functionality less than 2. So for any system, if one type of the reacting molecules is monofunctional, then the system would fail to produce polymer molecules. On consideration of functionality, a double bond is bifunctional, as on thermal or photo activation, the π bond may open up to yield a diradical intermediate.

Types of Polymerization:

Polymerization usually takes place by two basically different mechanisms. Depending on the mode of formation, one kind of polymerization is called condensation polymerization and other kind is known as addition polymerization.

* Relationship between Average Functionality, Extent of Reaction and Degree of Polymerization:

W.H. Carothers derived a general expression, relating average functionality (f), extent of reaction (p) and average degree of polymerization (\bar{X}_n), for polycondensation reactions carried out for a time period t . The expression is commonly known as Carothers' Equation.

Let N_0 be the total number of reacting molecules initially present giving average functionality for the system as f . The related functional groups are also considered to be present in stoichiometric equivalence. Let N be the number of molecules present at time ' t ' when the extent of reaction is p .

Then, number of molecules lost during the process over the time period t is $(N_0 - N)$; for each molecule lost, the number of functional groups lost is 2 (one of each kind) and hence the total number of functional groups lost is $2(N_0 - N)$ against the initial total number of $N_0 f$ functional groups.

$$\text{Hence the extent of reaction } p = \frac{2(N_0 - N)}{N_0 f}$$

$$\text{or } p = \frac{2}{f} \left(1 - \frac{N}{N_0}\right) \quad \text{--- (1)}$$

The average degree of polymerization \bar{X}_n , is defined as the average number of structural units per polymer molecule which can simply be expressed as:

$$\bar{X}_n = \frac{N_0}{N} \quad \text{--- (2)}$$

Combining eqs. (1) and (2), one obtains

$$P = \frac{2}{f} \left(1 - \frac{1}{\bar{X}_n}\right) \quad \text{--- (3)}$$

Eqⁿ (3), known as Carothers' Equation is very important for the ~~understanding~~ understanding and control of the growth of polymers through polycondensations. The critical extent of reaction P_c at the gel point (for $\bar{X}_n \rightarrow \infty$) is given by:

$$P_c = \frac{2}{f} \quad \text{--- (3a)}$$

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Bifunctional System

For a bifunctional system, $f=2$ eqⁿ (3) reduce to:

$$P = \left(1 - \frac{1}{\bar{X}_n}\right) \quad \text{--- (4)}$$

for $P=1$, $\bar{X}_n = \infty$, which means that for complete reaction, the average degree of polymerization will be infinity; but short of complete reaction, the degree of polymerization is always a finite quantity. Polymer obtained in a bifunctional system is, under all practical situations, linear and hence soluble and fusible. The upper theoretical limit in the degree of polymerization is infinity and this can be attained only in the hypothetical condition of completion of reaction between the functional groups ($P=1$). For bifunctional system eqⁿ (4) may be rearranged to express \bar{X}_n as

$$\bar{X}_n = \frac{1}{1-P}$$

If the mean molecular weight of the repeat unit in the polymer molecule is M_0 , then the average molecular weight \bar{M}_n of the polymer system is expressed as:

$$\bar{M}_n = \bar{X}_n \cdot M_0 = \frac{M_0}{(1-P)}$$

Polyfunctional System:

A typical polyfunctional system in condensation polymerization is exemplified by the reaction between phthalic anhydride or phthalic acid and glycerol, i.e. by allowing ~~an~~ a bifunctional acid to react with trihydric alcohol. As discussed before, this system is characterized by an average functionality of 2.4. For this system eqn (3) will assume the form:

$$P = \frac{2.4}{2.4} \left(\frac{\bar{X}_n}{M_0} \right)$$

We may now easily find out the critical extent of reaction, P_c at which gelation or cross-linking would commence, i.e. at which point \bar{X}_n would first assume a value of infinity; the calculated value of P_c , according to eqn (3) will be $\frac{2}{2.4} = 0.83$

Thus, it is clearly seen that at the point of a theoretical extent of reaction $P=0.83$, i.e. when the reaction is 83% complete, the polymer being formed in the polycondensation system gets cross-linked and, hence, turns into an insoluble infusible gelled mass. Technically, such a condensation polymerization cannot and should not be allowed to proceed beyond this point (83% completion), or otherwise reaction mass would turn into an unstable product. In fact, it is

advisable to arrest the reaction nearly 10-15% earlier in 'p' to avoid damage of the reaction kettle and to collect a good quality product which would be useful and which could be easily manipulated in subsequent steps.

Characteristics of Polymerization

The Concept of Average Molecular Weight:

A given polymer material is mostly mixture of molecules of identical structure but varying in chain length or molecular weight. The molecule produced in polymerization reactions have lengths that are distributed in accordance with a probability function which is governed by the mechanism of the reaction and by the conditions under which it has been carried out. The concept of average molecular weight is, therefore, important and relevant and the assignment of numerical value to the molecular weight of polymer requires the definition of a particular average. An average molecular weight \bar{M} may generally be expressed as

$$\bar{M} = f_1 M_1 + f_2 M_2 + f_3 M_3 + \dots = \sum f_i M_i \quad \text{--- (I)}$$

Where M_1, M_2, M_3 etc are the molecular weights of different sizes of molecules and the coefficients f_1, f_2, f_3 etc, are fractions such that their summation, i.e., $\sum f_i$ equals to unity. The average molecular weight \bar{M} may also be conveniently expressed as

$$\bar{M} = \frac{\sum N_i M_i^a}{\sum N_i M_i^{(a-1)}} \quad \text{--- (II)}$$

Where N_i is the number of molecules with molecular weight M_i and the index i may have any real value. Two most important average are: (i) number average molecular weight and (ii) weight average molecular weight. Setting $\alpha=1$, one obtains the expression for number average molecular weight, \bar{M}_n from eqn-①, i.e.

$$\bar{M}_n = \frac{\sum N_i M_i}{\sum N_i} \quad \text{--- ②}$$

Eqn-②, in effect, can be expressed as a summation series eqn-① where the fractional coefficients represent mole fractions of the respective molecular species present in the system. Knowing the total weight $W = \sum N_i M_i$ and total number of molecules $N = \sum N_i$, thus,

Dr. Santanu Chakravorty

$$\begin{aligned} \bar{M}_n &= \frac{W}{N} = \frac{\sum N_i M_i}{\sum N_i} = \frac{N_1}{N} M_1 + \frac{N_2}{N} M_2 + \dots \\ &= f_1 M_1 + f_2 M_2 + f_3 M_3 + \dots \end{aligned} \quad \text{--- ④}$$

On the other hand, setting $\alpha=2$ in eqn-② one obtains the expression for weight average molecular weight (\bar{M}_w), i.e.

$$\bar{M}_w = \frac{\sum N_i M_i^2}{\sum N_i M_i} \quad \text{--- ⑤}$$

Eqn ⑤ may also be rearranged and expressed as a summation series as given by Eqn-①, but in this case the fractional coefficients correspond to weight fractions of different molecular species present. Thus

$$\begin{aligned}\bar{M}_w &= \frac{\sum N_i M_i \cdot M_i}{\sum N_i M_i} = \frac{\sum w_i M_i}{\sum w_i} = \frac{\sum w_i M_i}{w} \\ &= \frac{w_1}{w} M_1 + \frac{w_2}{w} M_2 + \frac{w_3}{w} M_3 + \dots \\ &= f_1 M_1 + f_2 M_2 + f_3 M_3 + \dots\end{aligned}$$

Here w_1, w_2, w_3 etc., stand for weights of different species having molecular weights, M_1, M_2, M_3 etc. respectively and $\sum w_i = w$ is the total weight of all the molecules present.

The consequence of definitions given above is that $\bar{M}_w \gg \bar{M}_n$; the equality, however, correspond to limiting case of perfectly mono-disperse sample. The deviation from unity of the ratio \bar{M}_w/\bar{M}_n , known as the distribution ratio, is taken as a measure of polydispersity of polymer sample. Higher value of the ratio indicating greater polydispersity.

Number Average Molecular Weight
determination by Membrane Osmometry:

Consider a solution of polymer separated from the pure solvent by a semipermeable membrane; the chemical potential of the solvent in solution (μ_s) is less than that of the pure solvent (μ_0) and consequently, to keep the system in equilibrium, the chemical potential of the solvent on either side of the membrane must be balanced or made equal. This may be conveniently done by applying an excess pressure, called the osmotic pressure π to

the solution side to compensate for the deficiency in chemical potential. Thus the condition of equilibrium for the chemical potential of the solvent over the two sides of the osmometer membrane gives

$$\mu_0 - \mu_s = \Delta \mu_1 = -\bar{n} \bar{V}_1$$

$$RT \ln f_1 x_1 = -\bar{n} \bar{V}_1$$

Where R is the universal gas constant, T , the absolute temperature, \bar{V}_1 the partial molar volume and f_1 the activity coefficient of the solvent in solution. For a very dilute solution, $f_1 \rightarrow 1$ and \bar{V}_1 may be taken as equal to the molar volume, V_1^0 of the pure solvent. Replacing solvent mole fraction x_1 by $(1-x_2)$ where x_2 is the mole fraction of the solute in solution, and expanding logarithm factor, one obtains for a very dilute solution:

$$\bar{n} \bar{V}_1^0 = RT \left(x_2 + \frac{x_2^2}{2} + \frac{x_2^3}{3} + \dots \right) \quad \text{--- (1)}$$

Dr. Santanu Chakravorty

If c is the concentration in grams per unit volume of solution, then x_2 is given by

$$x_2 = \frac{c/M_2}{1/V_1^0 + c/M_2} \approx \frac{V_1^0 c}{M_2} \quad \text{--- (2)}$$

Combining eqn (1) and eqn (2) one obtains,

$$\bar{n} c = \frac{RT}{M_2} \left\{ 1 + \frac{1}{2} \left(\frac{V_1^0}{M_2} \right) c + \frac{1}{3} \left(\frac{V_1^0}{M_2} \right)^2 c^2 + \dots \right\}$$

Polymer solutions largely deviate from ideality and the activity coefficient f_1 is less than unity even at the lowest concentration at which accurate osmometric measurement can be made. The real coefficients of the concentration terms are somewhat higher in magnitude than those in the equation above. Even then, $\bar{n} c$ may be expressed as a power series

in C using empirical coefficients, viz.

$$\eta/c = RT(A_1 + A_2c + A_3c^2 + \dots)$$

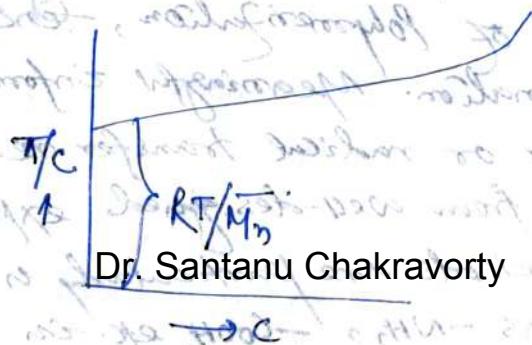
or alternatively
$$\eta/c = \frac{RT}{M_0} (1 + \Gamma_2 c + \Gamma_3 c^2 + \dots)$$

where $\Gamma_2 = A_2/A_1$ $\Gamma_3 = A_3/A_1$ and so on

and $A_1 = \frac{1}{M_0}$.

The coefficients A_2, A_3 etc. are known as the second, third etc. virial coefficients.

This η/c is measured as a function of c and plotted on a graph paper and extrapolation of the plot to $c \rightarrow 0$ gives an intercept on the η/c axis which is equal to RT/M_0 .



Tyland Plot Showing η/c vs c
for determination of M_0

End-Group Analysis:

Analysis of functional groups in polymers, particularly of those incorporated at chain ends is a very important mean of polymer characterization. Polymer characterization by this approach is meaningful specially when it is clear cut case with well-defined mechanism of polymer growth under a specified condition, and purification from low molecular weight monomers, additives and spurious contaminants has been meticulously accomplished. For high polymers desired purifications

are satisfactorily accomplished by repeated precipitations

In well-defined polymer systems, a knowledge of the number of specific end group in a given mass of polymer permits determination of number average molecular weight from the results of end-group analysis, which in effect, gives a count of the molecules in a given weight of the sample. Or else, if the number average molecular weight is determined by an independent technique, end-group gives an idea of the number of a specific end-group per polymer chain which further throws light on the detailed mechanism of polymerization, including initiation and termination. Meaningful information about chain transfer or radical transfer reactions may also be obtained from well-designed experiments.

Dr. Santanu Chakravorty
Titrimetric methods are particularly useful to estimate such groups as $-NH_2$, $-COOH$, etc. in relatively low molecular weight polyamide, polyester and related polymers.

Spectroscopic method (UV, IR spectroscopy) have been conveniently used for polymer end-group characterization on many occasions. Radioactive tracer technique has also been used for some system for studies of the mechanism of polymerization and for end-group characterization. Sensitive colorimetric methods of selective nature have also been extensively used for characterization of end groups.

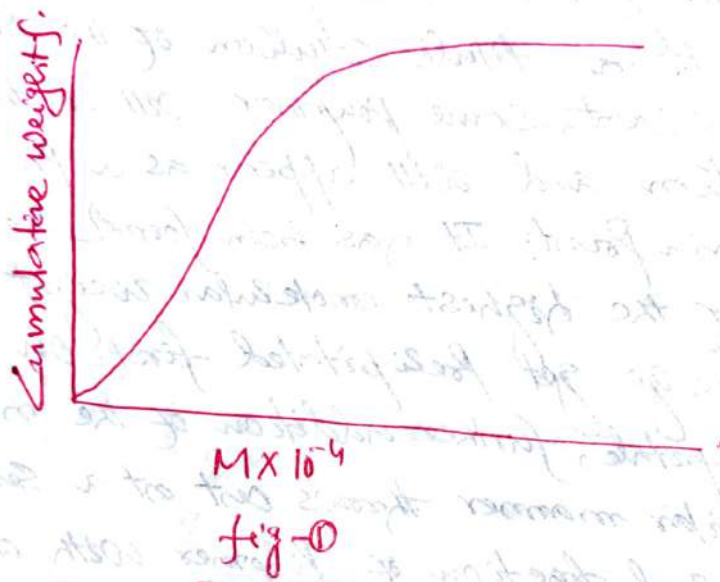
Polymer fraction and Molecular Weight Distributions:

In a very poor solvent, or more appropriately, in a non-solvent, the polymer will not dissolve. On gradual or dropwise addition of a non-solvent to a dilute solution of the polymer in a good solvent, some polymer will be thrown out of solution and will appear as a precipitate at a certain point. It has been found that polymer molecules of the highest molecular weight or molecular range get precipitated first. On separation of the precipitate, further addition of the non-solvent in a similar manner throws out at a subsequent point a second fraction of polymer with somewhat lower molecular weight or molecular weight range.

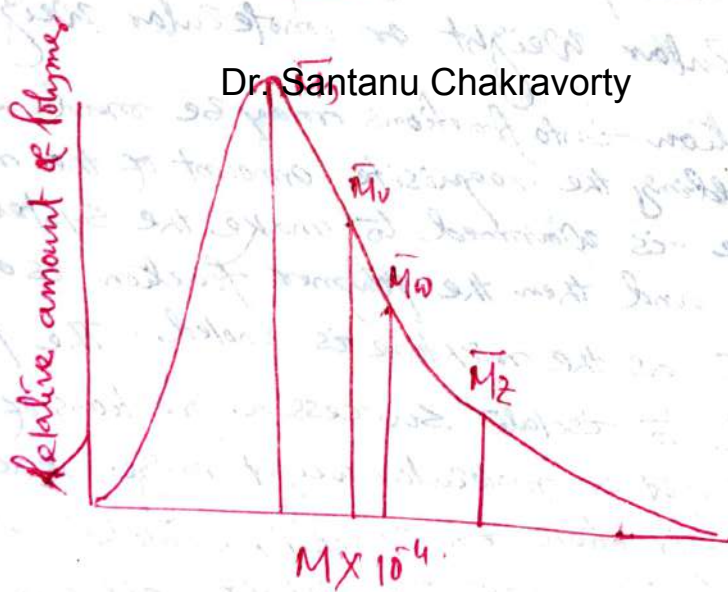
The separation into fractions may be made sharper if after adding the requisite amount of the non-solvent the mixture is warmed to make the system just homogeneous and then the polymer fraction is allowed to precipitate as the mixture is cooled. The process is repeated to isolate successive fractions of decreasing molecular weight or molecular weight range. Each of the successive fractions is carefully isolated, dried, weighed and its molecular weight determined by one of the techniques discussed in the preceding sections.

It is then possible to draw an integral molecular weight distribution curve as shown in fig-① showing cumulative weight percent plotted against molecular weight. Another useful curve based on differential molecular weight distribution shown in fig-② is - obtained by differentiating the integral distribution curve. The relative positions of \bar{M}_w , \bar{M}_n , \bar{M}_w and \bar{M}_z are shown on this curve.

Fractionation based on the above approach separates the various species in a given polymer sample mainly on the basis of their solubility characteristics rather than on the basis of their molecular weight.



Dr. Santanu Chakravorty



Polydispersity index:

Polydispersity index is the ratio of \bar{M}_w to \bar{M}_n . where \bar{M}_w and \bar{M}_n are weight average molecular weight and number average molecular weight respectively. PDI is basically the molecular weight distribution throughout the polymer.

$$PDI = \frac{\bar{M}_w}{\bar{M}_n}$$

Polyethylene

Polyethylene of different density ranges can be obtained by chain polymerization of ethylene, the simplest olefinic monomer.

Low density polyethylene (LDPE) is produced by free radical polymerization of ethylene under very high pressure (1500-3000 atm), using oxygen, peroxides or azo-compounds as initiators. The polymerization reaction, simply written as



High Density Polyethylene (HDPE) -

Use of coordination catalysts or supported metal oxide catalysts allows polymerization of ethylene at much lower pressure as well as at a relatively low temperature; the polymers thus produced are by and large linear having much fewer branches than found in the product obtained by the high pressure free radical process. The HDPE synthesis is ~~conveniently~~ conveniently done by ① the Ziegler process using an aluminum trialkyl - TiCl_4 complex as the catalyst dispersed in a hydrocarbon solvent such as n-heptane and employing a slightly elevated pressure and a temperature in the range of 70-100°C

② the Phillips process using ZrO_2 supported on finely divided silica- Alumina (75-90% silica) base as the catalyst.

Structure and Properties:

Due to the high chain transfer in the radical polymerization effected under high pressure, the resultant polymer, LDPE has nearly 20-25 branches (20th long and short branches) per 1000 linear carbon atoms in the chain molecules. The loss of molecular symmetry due to the high degree of branching results in lower density range and lower softening or melting temperature ($110-117^\circ C$) for LDPE. The low pressure polymers HDPE, are long and large linear, having only 2-5 short-branches or side chains per 1000 carbon atoms in the main chain, thus having a higher density range ($0.945-0.963 \text{ g/cm}^3$) and higher melting temperature ($125-130^\circ C$) compared to LDPE.

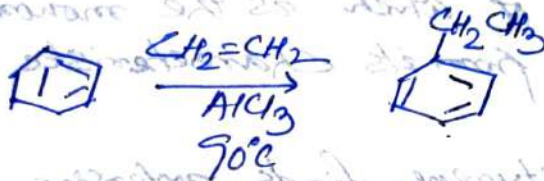
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Uses

Polyethylene being thermoplastic in nature, are conveniently processed by injection moulding, blow moulding, extrusion and thermoforming techniques. They find extensive uses and applications as moulded or formed objects, films, sheets, bottles, and containers, pipes and tubes and in wire insulation and cables.

Poly Styrene:

Poly Styrene is high tonnage, general purpose thermoplastic polymer. The monomer, Styrene, or vinyl benzene, $\text{CH}_2=\text{CH}-\text{Ph}$ is made from benzene and ethylene in two steps. The first step involves alkylation of benzene through reaction with ethylene in the presence of a Friedel-Crafts catalyst such as AlCl_3 .



In a subsequent step, ethylbenzene is dehydrogenated to styrene by heating its stream over iron oxide or magnesium oxide catalyst at about 600°C .

Polymerisation of styrene is mostly done following bulk polymerization technique. The bulk polymerization is done in two stages. In the first stage, the stabilizer-free monomer containing dissolved initiator is allowed to polymerize at about 80°C in one or more "prepolymerizer" batch reactors, each fitted with an efficient stirrer and an outer jacket for circulation of heat transfer fluid until a conversion of about 35% is reached. The viscous monomer-polymer mixture is then forced into the top of a tower reactor which is fitted with heating and cooling jackets and coils for external and internal control of temperature respectively. The temperature down the tower changes from 100°C at the top to nearly $180-200^\circ\text{C}$ at the bottom. The melt containing polystyrene and traces of the monomer passes through an extruder at the bottom from which it emerges as narrow strands or filaments which are then cooled, granulated and packed.

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Structure and Properties:

Commercial polystyrene is a radically initiated linear atactic polymer. It is amorphous and transparent. The polymer is hard, brittle and transparent at room temperature. It is soluble in aromatic hydrocarbon solvents, cyclohexane and chlorinated hydrocarbons. It decomposes at elevated temperature into a mixture of volatiles, a significant part of which is the monomer which can be identified from its characteristic smell.

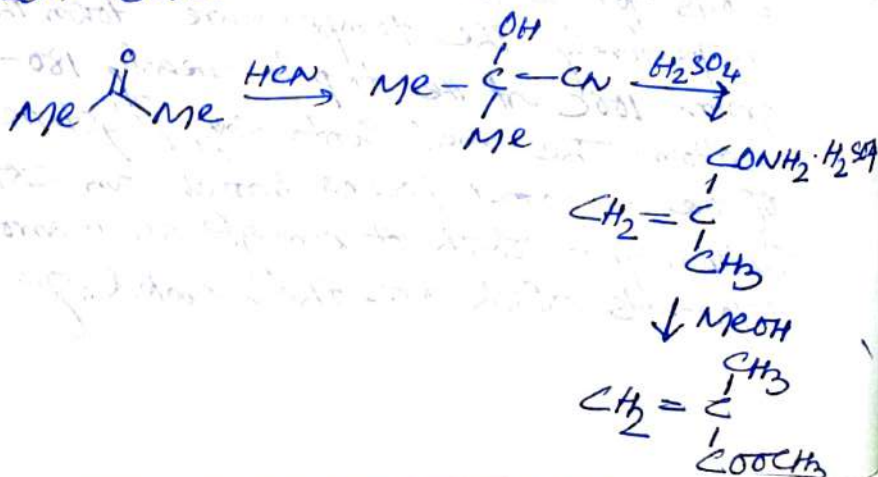
Use: Polystyrene finds extensive use in packaging and ~~set~~ shock absorbing applications, in thermal insulation and as acoustics improves in halls and auditoria.

Acrylic Plastics: Poly (Methyl Methacrylate):

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Plastics based on acrylate and methacrylate monomers are commonly known as acrylic plastic. Most important among the acrylic plastics is poly (methyl methacrylate) prepared by the polymerization of methyl methacrylate monomer. Methyl methacrylate is prepared from acetone through the cyanohydrin route.

The synthetic scheme is shown in the reaction below:



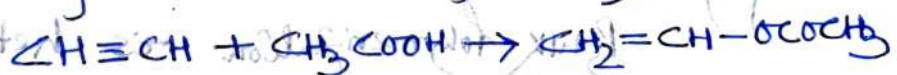
Moulding grade poly(methyl methacrylate) is made by bulk or suspension polymerization of the monomer, using peroxide or azobisisobutyronitrile initiators at about 100°C, preferably in the absence of air.

Use A combination of excellent optical clarity, total lack of colour, some toughness and outstanding outdoor weathering behaviour makes poly(methyl methacrylate) very useful as automotive tail lamp and signal light lenses, jewellery, lenses of optical equipment and contact lenses.

Poly(vinyl acetate):

Vinyl acetate monomer is most conveniently prepared by catalytic addition of acetic acid to acetylene, which may be accomplished by a liquid phase or vapour phase process.

The vapour-phase synthesis is more in commercial practice and is accomplished by passing a mixture of acetylene and acetic acid through a reaction tube packed with such catalyst as cadmium acetate or zinc acetate at a temperature of 200-250°C. The monomer formed is purified by distillation.



Properties and uses:

Poly(vinyl acetate) as formed commercially is atactic in nature and hence amorphous and it is transparent if free from contaminants such as emulsifiers. Because of soft and gummy nature of poly(vinyl acetate), the polymer has poor dimensional stability.

It rarely finds an application as moulded or formed objects and is seldom processed like common thermoplastics. The polymer is widely used in emulsion form and hence, emulsion polymerization of vinyl acetate is widely employed for commercial purpose.

Poly (vinyl chloride):

Historically, vinyl chloride is definitely an acetylene derivative and as late as 1965, more than 45% of ~~all~~ all vinyl chloride produced was still based on acetylene derived from coal via ~~the~~ calcium carbide or from petroleum sources. ~~However~~

The earliest route to vinyl chloride (VC) was from acetylene and HCl. In a typical synthesis

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Commercial polymerization is heterogeneous in view of ~~insolubility~~ ~~of~~ done by using free radical catalysts and employing bulk, suspension and emulsion techniques. Suspension and emulsion techniques are however, most commonly employed.

Bulk polymerization is heterogeneous in view of the polymer in the monomer. Peroxy dicarbonates are conveniently used as initiators in the bulk or suspension polymerization. Bulk polymerization may be done in rotating ~~stirrer~~ cylindrical reactors with tumbling steel balls inside to facilitate removal of heat of polymerization from the monomer-polymer heterogeneous system.

Structure and Properties of PVC:

Poly(vinyl chloride), PVC is a long and large linear polymer, colorless and thermoplastic in nature, and having a chlorine content of about 56.8%.

The polymer is thermally unstable and extensive heating transforms it into a dark coloured residue. PVC is insoluble in all hydrocarbon solvents. It is soluble in acetone and nitrobenzene.

Application:

Both rigid and flexible applications of PVC have been developed. Rigid applications include chemical plants and equipments, storage tanks, building items, pipes, sheets, specific moulded objects and containers. Other flexible applications include toys, packaging items, tubes, pipes, footwear etc.

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Polytetrafluoroethylene (PTFE):

Among the fluorocarbon polymers, the use of polytetrafluoroethylene is relatively widespread and it is popular in certain specific areas of application.

The monomer tetrafluoroethylene is obtained by pyrolysis of monochlorodifluoromethane in contact with platinum at about 700°C. Monochlorodifluoromethane is obtained by reacting chloroform with hydrofluoric



Commercial polymerization of tetrafluoroethylene is essentially aqueous polymerization accomplished by using free radical initiators (K₂S₂O₈ or hydrogen peroxide). An elevated pressure is maintained during polymerization. Polymer

is obtained either in a granular form or in the form of a fine aqueous dispersion.

Structure/Properties/Use:

PTFE is essentially a linear polymer having a density of about 2.2 gm/cm^3 . PTFE has a waxy feel and it is self-lubricant in nature, having coefficient of friction lower than any other solid.

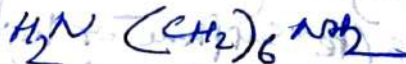
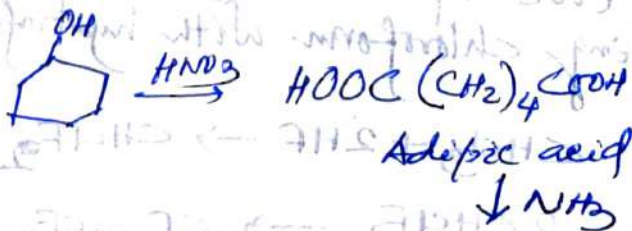
Major application of PTFE are as seals, films, gaskets, laboratory equipments or component thereof, packings in pumps and valves, stopcocks, machine components, kitchen-ware etc.

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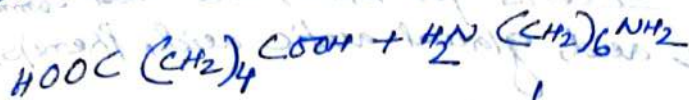
Nylon 66

Nylon 66 or Poly (hexamethylene adipamide) is synthesized by polycondensation of adipic acid and hexamethylene diamine. Adipic acid can be prepared by oxidation of cyclohexane.

Hexamethylene diamine is conveniently prepared from adipic acid via adiponitrile.



The first step of Nylon 66 is the formation of Nylon 66 Salt. The adipic acid and hexamethylene diamine are reacted in boiling methanol to the insoluble nylon 66 salt which precipitates out. The salt is then dissolved in water.



Nylon 66 Salt

mixed with about 0.5-0.1 mole percent of acetic acid to act as the viscosity stabilizer, i.e. to limit the molecular weight, and pumped into autoclave. The autoclave is closed and the temperature is raised to nearly 220°C. The steam generated purges the air and a pressure of nearly 250 psi is allowed to develop. After about 2h the temperature is raised to 280°C and steam is bled off to maintain the pressure at 250 psi. Pressure is then reduced over a period of 1-2h to the normal level. The molten polymer is then extruded out under nitrogen pressure through a valve at the bottom of the autoclave onto a water-cooled casting wheel forming ribbons which are then chipped into granules and stored.

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Preparation of Nylon 6:

Caprolactam is made from cyclohexanone oxime through reactions involving Beckmann-rearrangement. Nylon 6 may be made by a batch or continuous process. Caprolactam, water and traces of acetic acid are charged into a reactor and heated at 250°C under blanket of Nitrogen for 10-12h. Poly-caprolactam formed remains in equilibrium with unreacted monomer (about 10%) which may be removed from the product by washing with water.

Properties, uses and applications of the Nylon polyamides.

The nylons are polar, crystalline materials with excellent resistance to hydrocarbons. There are only a limited number of solvents for them, the most common ones being formic acid, glacial acetic acid, phenols, and cresols.

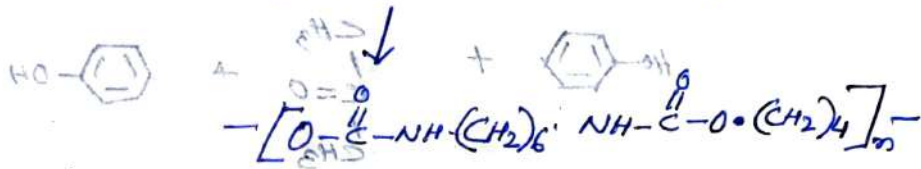
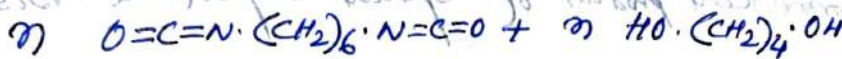
The nylons are polymers of low specific gravity. The specific gravity of nylon 66 and nylon 6 are very close. The properties of the nylons are considerably affected by the amount of crystallization. The glass transition temperature (T_g) of the nylons are below room temperature, thus making them somewhat flexible and reasonably tough despite high order of crystallinity.

Nylon 6 and Nylon 66 are melt-spun into fibres or filaments and the fibres and cords made from them are extensively used as reinforcing agents for plastics and rubbers. Other applications of the nylons include textiles, ropes, tows, nets, pipes, tubes, rods, bottles and containers, toys

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Polyurethanes:

Polymers formed through interactions of isocyanate groups of di- or polyisocyanates and hydroxyl groups of monomeric ~~and~~ or polymeric diols or polyols are commonly known as polyurethanes. The reaction between hexamethylene diisocyanate and 1,4-butanediol yields a fibre-forming polyurethane. The reaction is better considered as rearrangement polymerization characterized by step growth mechanism:



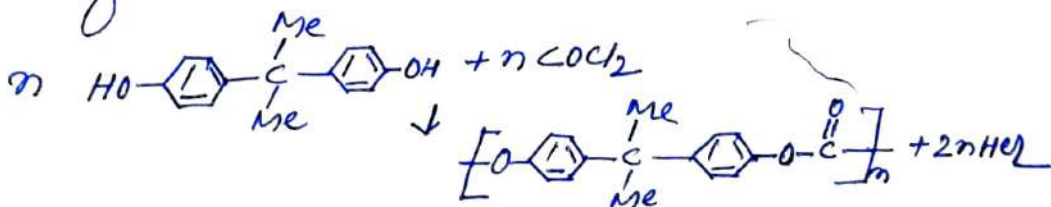
Different kinds and grades of polyurethanes have been developed for applications as fibres, resins, rubbers, adhesives and surface coatings. However, their applications as flexible or rigid foams are of special importance.

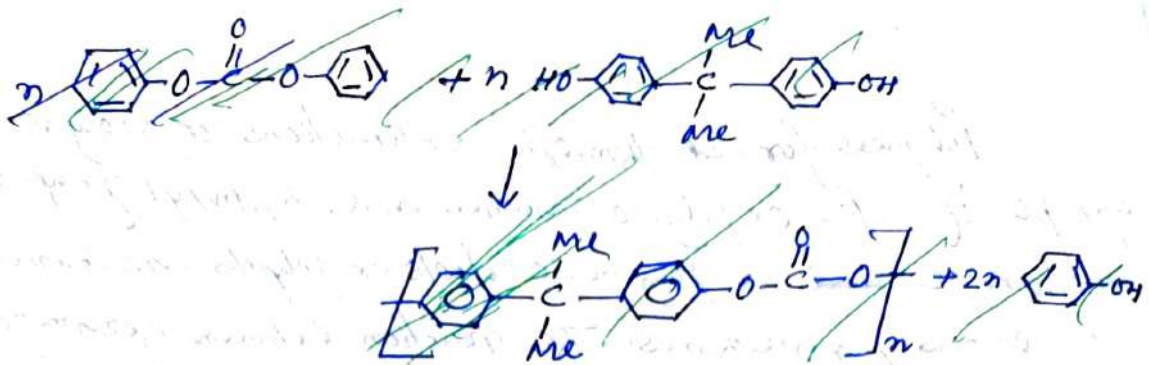
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The polyurethane rubbers have good tensile strength (or scopsi), higher than any other rubber, and excellent tear and abrasion resistance, and they exhibit excellent resistance to oxygen and ozone. They are, however, less resistant to acids and alkalis and steaming than the conventional rubbers.

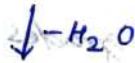
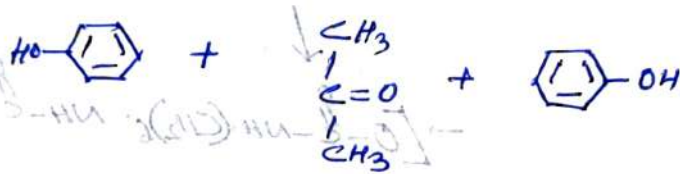
Polycarbonates:

Polycarbonates are characterized by repeat units having carbonate ($-\text{O}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-$) interunit linkages. Linear polycarbonates are formed either by reaction of dihydroxy compounds and phosgene or by means of ester interchange reactions involving dihydroxy compounds and organic carbonates.

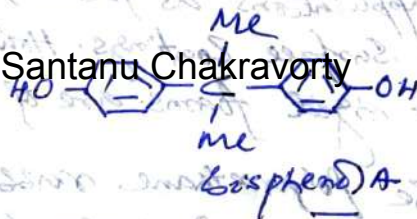




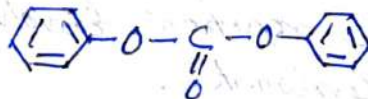
The Poly carbonate based on Bisphenol A and diphenyl carbonate is the only one that has been developed into a commercial product of special importance. Bisphenol A



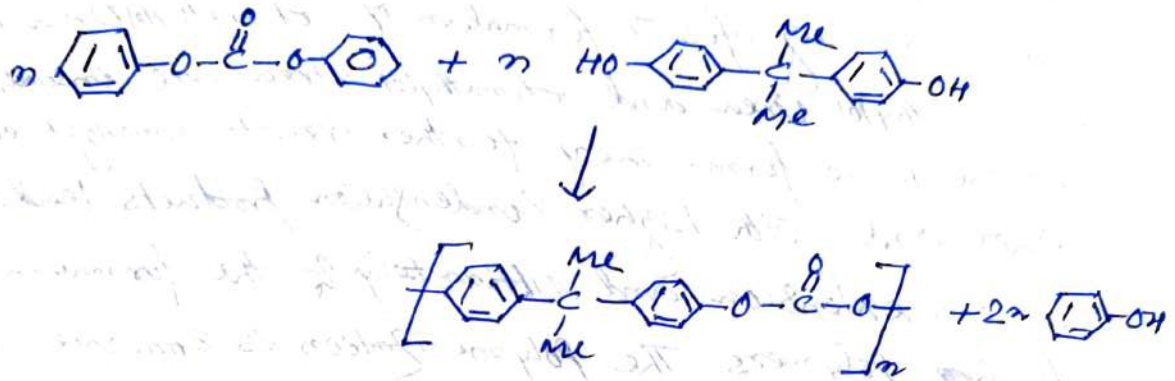
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is readily produced by the condensation of acetone and phenol under acidic condition at temperature below 70°C. An excess of phenol is used in order to achieve a high yield. Diphenyl carbonate is conveniently obtained by reacting phenol with phosgene in aqueous NaOH solution in presence of a tertiary amine catalyst. The diphenyl carbonate is purified by redistillation.



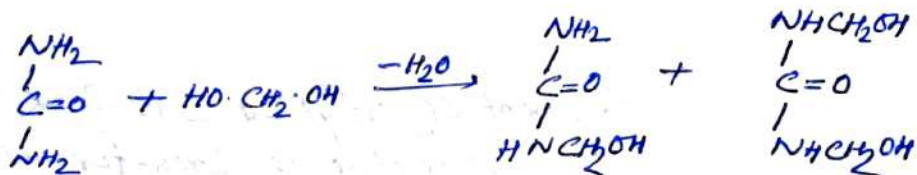
The ester interchange reaction leading to polycarbonate is shown below. The reaction is normally accomplished at nearly 200°C at reduced pressure, until about 90% of the phenol liberated has been removed. The temperature is then raised to about 290-300°C and pressure further reduced to below 1 mmHg to complete the reaction.



The polycarbonates ~~can be processed by~~ appear in crystal-clear grades, if prepared from high purity ingredients. The refractive index at 25°C is 1.58. Their low water absorption ~~and~~ ^{good insulation} properties, transparency and toughness coupled with heat and flame resistance make them suited for many areas of application including electrical insulation.

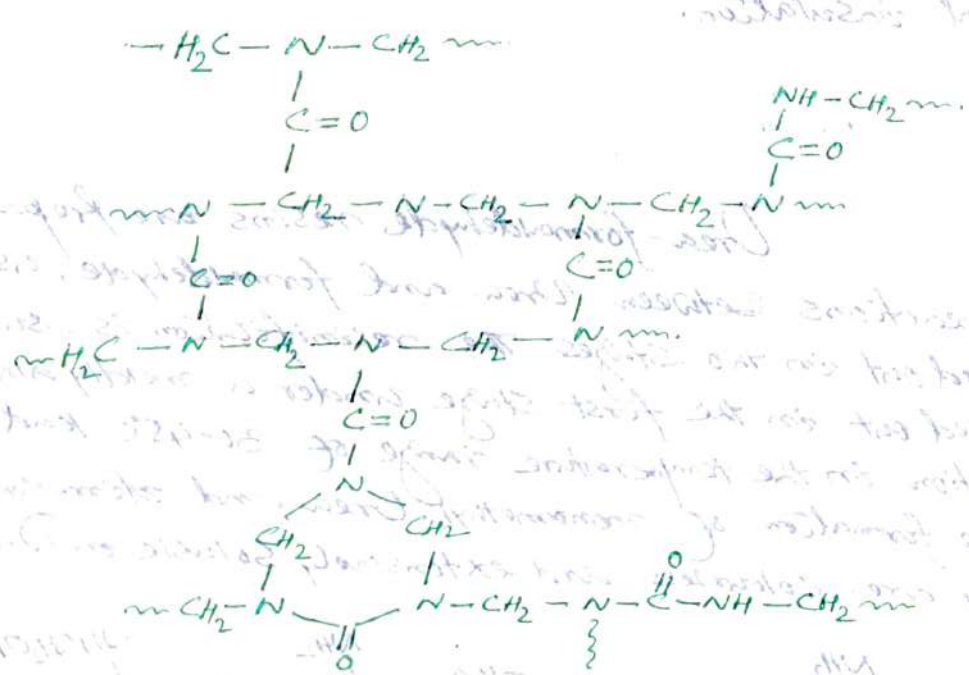
Urea-Formaldehyde Resins:

Urea-formaldehyde resins are prepared by reactions between urea and formaldehyde, usually carried out in two stages. The resinification is usually carried out in the first stage under a mildly alkaline condition in the temperature range of 30-45°C leading to the formation of monomethyl urea and dimethylol urea. They are colourless and extensively soluble in water.



The relative proportions of mono- and dimethylol Ureas would depend on the molar ratio of Urea to formaldehyde. Urea is potentially tetrafunctional and use of nearly 1.5 to 2 moles of formaldehyde for each mole of urea has been found to yield useful resins. There should be enough formaldehyde to permit measurable and significant formation of dimethylol Urea. Both monomethylol Urea and dimethylol Urea are insoluble in the pure form. They further react amongst each other and with higher condensation products leading to chain extension and ultimately to the formation of higher polymers. The polymerization is conveniently carried out in the second stage under acidic condition, the acid acting as a strong catalyst for the polymerization, leading to the formation of insoluble infusible cross-linked products. The chain extension and cross-linking are accompanied with loss of water and formaldehyde:

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Segment of typical cross-linked structure of Urea-formaldehyde resins

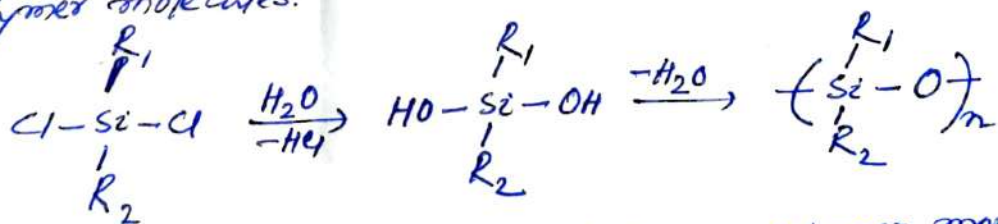
Properties and uses:

The cured urea resins are hard and rigid and resistant to stain and scratching. They are non-inflammable but they char around 200°C. They exhibit good impact properties and excellent electrical insulation properties under dry conditions. They do not impart taste and odour to food and drinks with which they may come in contact.

Urea-formaldehyde resins ~~also~~ find extensive use as wood adhesive and in the manufacture of plywood and laminates.

Silicons:

Polymers in which the backbone consists of repeat units having organic side group linked with silicon atoms are commonly known as silicons or polyorgano siloxanes. The polyorgano siloxanes are usually prepared by allowing chlorosilanes such as $\text{Cl}_2\text{SiR}_1\text{R}_2$ to react with water to form the corresponding hydroxy compounds which subsequently condense with each other leading to the production of polymer molecules.



Only dichloroalkyl silanes yield linear polymer, monochloro silanes fail to produce any polymer and trichloroalkyl silanes yield network polymers. The intermediates silanes $\text{R}_n\text{SiX}_{4-n}$ ($n=0-4$), where X is hydrolyzable group or atom such as chlorine or alkoxy, may be made by direct synthesis involving reactions between alkyl/aryl halides and elementary silicon e.g.

