Dr. Akhilesh Prasad *M.Sc. II Semester* *Physical III(Macromolecules)*

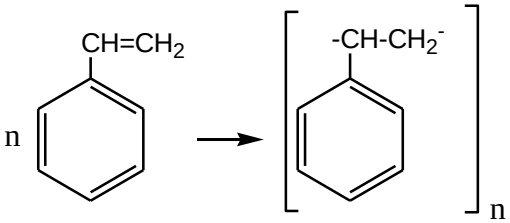
MACROMOLECUELS

Macromolecules or polymers are high molecular mass containing large number of structural units which is connected by covalent bonds. Polymer consists of large number of monomeric units which are repeated over and over again to form a giant molecule called a macromolecule. Fundamental research in polymer chemistry was done by German Chemist, Herman Staudinger who won the 1953 Chemistry Nobel Prize. Karl Ziegler, Giulio Natta and Paul J. Flory made significant contribution the subject. Flory was awarded the 1974 Chemistry Nobel Prize and later the French physicist was awarded the 1991 Physics Noble Prize for studying polymer liquid crystal and developing the scale concept in polymer dynamics.

Some examples are:

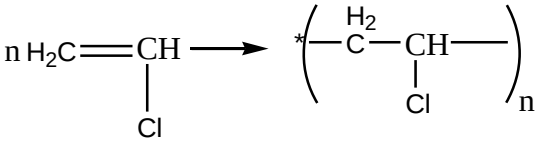
1. Polythene $nCH_2=CH_2 \rightarrow (-CH_2-CH_2-)_2$

2. Polystyrene



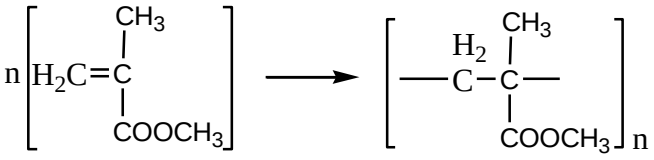
(Styrene) (Polystyrene)

3. Polyvinyl Chloride(PVC)



(Vinyl chloride) (Poly Vinyl chloride)

4. Poly(methyl methacrylate(PMMA)



Methyl methacrylate Poly methyl methacrylate

The degree of polymerization represents the number structural or monomeric units contained in a polymer. It is designated by the symbol, p. Molar mass M of the polymer is related to p by the equation, p = M/m where m is the molar mass of monomeric unit.

Classification of Polymers – Polymers may be of two types

(i) Naturally Occurring Polymers – Proteins, Starches, Cellulose

(ii) Synthetic Polymers – Plastics

Parameters for classification of Polymers

(i) Chemical Structure

(a) Homopolymer – It consist of identical monomers

(b) Copolymer - It is a mixture of more than one type of monomers

(ii) Polymeric Structure

(a) Linear structure – Consist of a long string of monomers, attached in a linear manner.

(b) Branched Structure – It consist of branches at irregular intervals along the polymer chain.

(c) Cross linked – It consists of short side chains that connect different polymers chains into a network.

(iii) Arrangement of Monomers

(a) Block Polymers – It consist of relatively long sequences of identical monomers.

(b) Graft Copolymers – Branched polymers whose backbone is formed form one type of monomer and branches are formed of other type.

(iv) Tacticity – On the basis of orientation of monomer units in a polymer molecule with respect to the main chain. It may noted that α carbon atoms of the polymers are asymmetric since each of them is attached to H, R and molecular chains of different lengths. This results in optical isomerisation of the monomer units which may thus have *d*- and *l*- configuration.

(a) Isotactic Polymer – The side groups of the monomers lie on the same side of the chain.

(b) Syndiotactic Polymer - The side groups of the polymers are arranged in an alternate manner.

(c) Atactic Polymer – The side groups are arranged in an irregular or random manner around the chain.

(v) Thermal Behavior – Behavior upon on heating

(a) Thermoplastic – Those polymers which are easily softened upon heating. Ex. Polythene, Polystyrene.

(b) Thermosets – Those polymers which change irreversibly into hard and rigid materials on heating and cannot be reshaped. Ex Bakelite, Melamine Formaldehyde

(vi) Molecular Forces

(a) Elastomers – Polymers that can be easily stretched by applying small stress. Ex. Natural Rubber.

(b) Fibers – Polymers which have strong intermolecular force like hydrogen bonds or dipole-dipole interaction between the polymer chains. Ex. Nylon 6,6, Dacron.

(vii) Method of Synthesis

(a) Addition Polymers

(b) Condensation Polymers

MOLAR MASSES OF POLYMERS

The molar mass of a polymer increases continuously during the polymerization however polymerization chains might be broken at different stages, the final product generally contain macromolecules of different masses. So, an average molar mass is taken. Two types of molar masses are calculate-

(a) Average molar mass ($\overline{Mn}$)

$$\overline{M}_n = \frac{n_1M_1 + n_2M_2 + \ldots}{n_1 + n_2 + \ldots\ldots}$$

(b) Mass-average molar mass ($\overline{Mm}$)

$$\overline{M}_m = \frac{n_1M^2_1 + n_2M^2_2 + \ldots}{n_1M_1 + n_2M_2 + \ldots\ldots}$$

DETERMINATION OF MOLAR MASSES OF MACROMOLECULES

(i) VISCOMETERY

This method was introduced by Staudinger, is the one most commonly used method. Accurate measurement of absolute viscosity being difficult, it is convenient to measure relative viscosity.

$$\eta_{rel} = \eta/\eta_0 \quad (1)$$

where η and η_0 are respectively, the viscosity of the solution and the viscosity of the solvent. The relative viscosity is related to some other quantities as follows:

$$\eta_{sp} = \eta_{rel} - 1 \quad (2)$$

$$\eta_{red} = \eta_{sp}/c \quad (3)$$

$$[\eta] = \lim_{c \to 0}\left(\frac{\eta sp}{c}\right) \quad (4)$$

where η_{sp} is **specific viscosity**, η_{red} is **reduced viscosity** and [η] is **intrinsic viscosity** (also called the **viscosity number or Staudinger index**) and c is the concentration.

Einstein in 1906 derived the flowing relation between the viscosity of a dilute suspension of hard spherical molecules and the volume fraction, ϕ of the solute molecule:

$$\eta = \eta_0(1+2.5\phi)$$

$$\text{or} \qquad \eta/\eta_0 = \eta_{sp} = 2.5\phi \qquad (5)$$

Hence from eq. 4 and 5,

$$[\eta] = \lim_{c\to 0}\left(\frac{\eta sp}{c}\right) = 2.5\phi/c \qquad (6)$$

In 1950, Staudinger gave new relation, which relates the intrinsic viscosity with molar mass of the polymer known as **Mark-Kuhn-Houwink-Sakurada equation.**

$$[\eta] = K(\bar{M}_{visc})^a$$

where M_{visc}^{-} is the viscosity-average molar mass of the polymer and K and a are constant.

(ii) OSMOMETRY

Osmotic pressure measurements are used for macromolecules because osmotic changes are larger than the change in boiling point elevation, freezing point depression and vapor pressure lowering.

If Π is the osmotic pressure of a solution in which the mole fraction of the solvent is x_1, the condition for equilibrium for the chemical potential of the solvent on both sides of the semi permeable membrane gives

$$RT\ln\Upsilon_1 x_1 + \Pi\bar{V}_1 = 0$$

where Υ_1 is the activity coefficient of the solvent and $\bar{V}_1$ is the partial molar volume of the solvent in the solution. For dilute solution, $x_1 \rightarrow 1$ and $\bar{V}_1 \rightarrow \bar{V}^0_1$, the molar volume of the pure solvent. If we replace x_1 by $(1-x_2)$, where x_2 is the mole fraction of the solvent, then expansion of the logarithm gives

$$\Pi\bar{V}^0_1 = RT(x_2 + x_2^2/2 + x_2^3/3 + \ldots.)$$

For a polymer solution of concentration c, x_2 is given by

$$x_2 = \frac{c/M}{\frac{1}{V^0} + c/M} = \frac{V_1^0 c}{M} \text{ for dilute solution.}$$

(iii) LIGHT SCATTERING

When a beam of light is passed through a colloidal solution, it suffers scattering. This phenomenon is called **tyndal effect.** Lord Rayleigh found that the ration of the intensity I_0, scattered at angel θ from the direction of transmitted beam, to the intensity I_0 of the incident unpolarized, monochromatic light is given by

$$\frac{I_\theta}{I_0} = \frac{8\pi a \alpha \lambda^2}{\lambda^4 r^2}(1 + cos^2\theta) \quad (1)$$

where r is the distance of observer from the sample, a is the number of scattering particles per unit volume and α is the electrical polarizability of the particle.

Refractive index n of the scattering particles can be use as a measure of their polarizability. The specific refraction can be given by

$$\frac{n^2 - 1}{n^2 + 2} = 4/3\pi a\alpha \quad (2)$$

assuming that n ≈ 1 so that $n^2 + 2 \approx 3$, this eq reduces to

$$\alpha = \frac{n^2 - 1}{4\pi a} \quad (3)$$

In the case of a solution we are interested in knowing the difference between the polarizability α of the solution and the polarizability α_0 of the solvent so that

$$\alpha - \alpha_0 = \frac{n^2 - n_0^2}{4\pi a} \quad (4)$$

for a solution having concentration c, the refractive index can be written as Talyor's series viz

$$n = n_0 + c(dn/dc) + \ldots\ldots \quad (5)$$

where n_0 is the refractive index when the concentration c is zero.

Squaring both sides of this eq.

$$n^2 = n_0^2 + 2n_0 c dn/dc + c^2(dn/dc)^2 + \ldots\ldots$$

the last term being small, can be neglected, giving

$$n^2 - n_0^2 = 2n_0 c dn/dc \quad (6)$$

Since the light scattering method yields the mass-average molar mass, hence a may be written as $cN_a/\overline{M}_M$. Combining eq. 4 and 6 and assuming that the polarizability of the solvent, α_0 is negligible, we obtain

$$\alpha = \frac{n_0 (\frac{dn}{dc}) \overline{M}_M}{2\pi N_A} \quad (7)$$

squaring both sides of this equation and substituting for α^2 in Rayleigh eq. 1, we get

$$\frac{I_\theta}{I_0} = \left(\frac{2\pi^2 n_0^2 \left(dn/dc\right)^2}{\lambda^4 N_A}\right)\left(\frac{1 + cos^2\theta}{r^2}\right)\overline{M}_M c \quad (8)$$

which may be written as, $R_\theta = K\overline{M}_M c$ (9)

where $R_\theta = \left(\frac{I_\theta}{I_0}\right)\left(\frac{r^2}{1+ cos^2\ \theta}\right)$ (10)

$$K = \frac{2\pi^2 n_0^2 (\frac{dn}{dc})^2}{N_A \lambda^4} \quad (11)$$

R_θ is called Rayleigh ratio, it represent the intensity ratio corrected for the geometry of the system. K is optical constant which contains the value of wavelength light and information about the refractive index. R_θ is independent of the value of θ. Eq. 9 can be used to calculate the molar mass of polymer.

For non-ideal polymer solutions where there are interactions between the polymer molecules, it is found that

$$\frac{K_c}{R_\theta} = \frac{1}{RT}\frac{d\Pi}{dc} \quad (12)$$

where Π is the osmotic pressure. It may be related that for an ideal solution, $\Pi = cRT/\overline{M}_M$. For non ideal solution,

$$\frac{\Pi}{c} = RT\left(\frac{1}{\overline{M}_M} + B_c\right) \quad \text{(B is second viral coefficient)} \quad (13)$$

From eqs. 11 and 12, $\frac{K_c}{R_\theta} = \frac{1}{\overline{M}_M} + 2Bc$

A graph of K_c/R_θ versus c gives a straight line with slope = 2B and intercept = $1/\overline{M}_M$. This permits the determination of $\overline{M}_M$, the mass-average molar mass of the polymer.

(4) DIFFUSION

The diffusion of a substance across a plane perpendicular to the direction of motion is given by **Fick's first law of diffusion,** viz.,

$$J = - D(dc/dx) \quad (1)$$

where J = dm/dt is the amount of mass diffusing across a plane of unit area per unit time, D is the diffusion coefficient and dc/dx, the concentration gradient, is the change in concentration per unit distance, across the plane.

The diffusion of particles through the solution is due to the decrease in free energy. The driving force F for diffusion is given by

$$F = -d\mu/dx \qquad (\mu = \text{chemical potential of solute}) \quad (2)$$

Since, per molecule, $\mu = \mu_0 + (RT/N_A)\ln c$

hence $$F = \frac{RT}{N_A}\frac{d(\ln c)}{dx} = -\frac{RT}{N_A c}\left(\frac{dc}{dx}\right) \quad (3)$$

The diffusion of the solute in the solution is opposed by the frictional drag due to the solvent given by Stoke's equation, viz.,

$$F = 6\pi\eta r v = 6\pi\eta r(dx/dt) \quad (4)$$

Where *v* is the velocity of the particle of radius *r* through the solution, the particle being assumed to be spherical. Since these two forces must be equal, hence

$$6\pi\eta r(dx/dt) = -\frac{RT}{N_A c}\left(\frac{dc}{dx}\right)$$

or $$c(dx/dt) = -\frac{RT}{6\pi\eta r N_A}\left(\frac{dc}{dx}\right) \quad (5)$$

But, c(dx/dt) = dm/dt which means that all the molecules with total mass *m* at a distance dx from the boundary and boundary and travelling with a velocity *dx/dt* will cross the boundary in time *dt*. Hence, $$dm/dt = -\frac{RT}{6\pi\eta r N_A}\left(\frac{dc}{dx}\right) \quad (6)$$

Comparing eq. 6 with eq. 1, we find that

$$D = \frac{RT}{6\pi\eta r N_A} = \frac{kT}{6\pi\eta r} = \frac{kT}{f} \quad \textbf{(Stokes-Einstein equation)} \quad (7)$$

From the measurement of η and D, the radius of solute particles can be determined. When diffusion measurements are coupled with sedimentation experiments, they give fairly reliable molar masses of the polymer.

CONFORMATION AND CONFIGURATION OF MACROMOLECULES IN SOLUTION

The term **configuration** *implies aspects of structure that can be changed only by breaking bonds and reforming new ones* while the term **conformation of polymer chain** *refers to the spatial arrangement of the different arrangement of the different parts of the macromolecule*.

The **counter length, R_c,** is the length of the macromolecule measured along its backbone from atom to atom. For a polymer of N monomer units each of length *l*, the counter length $R_c = Nl$. It is known that the probability of the ends of the chain lying in the range R to R+dR is given by *f(d)dR* where

$$F(R) = \left(\frac{a}{\pi^{1/2}}\right)^3 4\pi R^2 e^{-a^2R^2}; \quad a^2 = \frac{3}{2Nl^2} \tag{1}$$

where N is the number of bonds and l is the bond length. Using the function defined in eq. 1, the root mean square end-to-end distance of the chain (R_{rms}), the mean end-to-end distance of the chain ($\overline{R}$) and most probable end-to-end distance (R_{mp}).

$$R_{rms} = N^{1/2} l$$

$$\overline{R} = 2/a\pi = \left(\frac{8}{3\pi}\right)^{1/2} N^{1/2} l$$

$$R_{mp} = \left(\frac{2}{3}\right)^{1/2} N^{1/2} l$$

The dissolution of a polymer in a solvent is often a very slow process. As the solvent permeates the polymer network, considerable swelling occurs. In some cases, after initial swelling, the polymer dissolves in the solvent after a considerable period of time. In polymer chemistry we often speak '**good solvent'** and **"poor solvent'**. In a good solvent, there is a stronger interaction between the solvent and the polymer than between the solvent and the polymer than between the solvent and the solvent or between the various segments of the polymer. On the other hand, in a poor solvent, there is stronger interaction between the various segments of the polymer than between the polymer and the solvents. Thus, while in good solvent, the polymer stretches our i.e., uncoils, in solution, in poor solvent the polymer coils upon itself.

ELECTRONICLALLY CONDUCTING POLYMERS

Conducting polymers are macromolecules which in the solid state provide pathways for electronic conduction. They provide pathways for electron (or positive hole) to migrate along a polymer chain and jump from chain to chain. In polymers, the process generally depends on the presence of arrays of 'conjugated', delocalized double bonds, as found in poly(sulfur nitride) or polyacetylene. Doping of such polymers is often required to inject electrons into the delocalized framework or to remove electrons to leave positive holes. This types of system required much on the ordered, crystalline nature of the solid state arrangement as on the molecular structure of polymer.

1. Poly(Sulphur Nitride, $(SN)_x$

This polymer shows the property of electrical conductivity. At low temperature it behaves like superconductor which is anisotropic and probably occurs between the chains. Individual chains occupy a cis-trans planar conformation, with S-N bond lengths intermediate between those of single and double bonds. This suggests that a delocalized bonding arrangement exists along the chain via delocalized half filled π-orbitals which would permit the existence of metallic conduction band. The inter chain packing is such that electronic transmission could occur via orbital overlaps between S-S, N-N or S-N pairs on adjacent chains.

2. Polyacetylene

It exists in cis-trans planar form and trans-trans planar form. This polymer is synthesize by **Shirakawa technique,** which involves the polymerization of acetylene in contact with Ziegler_Natta catalyst. The polymer is metallic in appearance despite its porous structure. If polymerization is carried out at -78 ^{0}C, the polymer exhibits a cis-trans planar conformation and if reaction temperature is 150 ^{0}C, the polymer is generated as the trans-trans form. The electrical conductivity is quite low however if it reduced by alkali metals, radical anions or oxidized by electron acceptors such as AsF_5, SbF_5, iodine and again by electrochemical methods, to give materials which markedly increased conductivity, following doping. The electron added to polyacetylene by doping goes not into the conduction band but into an intermediate electronic state within the band gap. The product of reduction is a radical anion, in which the intergap energy states are occupied by two electrons from one π-band and the other is added by reduction. This state is known as **polaron.** Addition of a second electron to the same site yields a di-anion, called a **bipolaron.**