

**POLYMER: CLASSIFICATION, METHODS, PROPERTIES, AND THEIR CHARACTERIZATION**

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**INTRODUCTION**

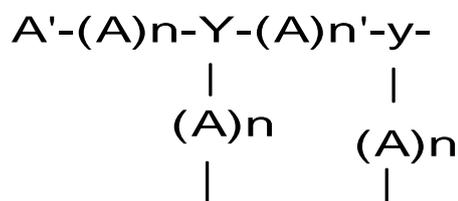
Polymers are known as macromolecules, are very large molecules consisting of many repeating units and are formed by a process called polymerization, which links together small molecules known as monomers. The monomers can be linked together in various ways to give rise to linear polymer(Fig.1a),branched polymer(Fig.1b) ,or cross linked polymers(Fig.1c).In these representation A is a monomer and A' and A'' are the terminal groups. The quantity x is known as the degree of polymerization, usually denoted as DP and the molecular weight of the polymer is the product of the degree of polymerization

and the Molecular weight of the repeat unit.

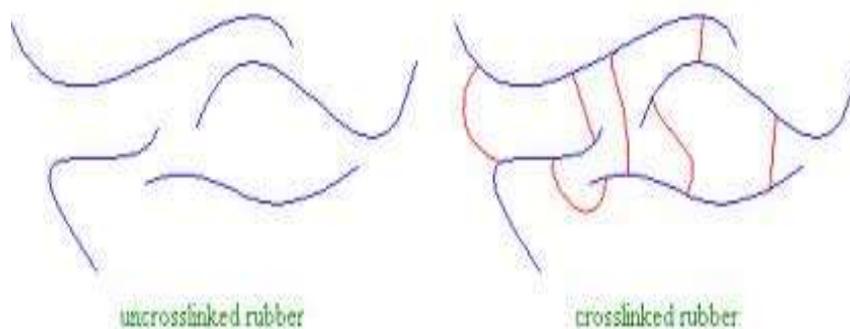
(a) Linear  $A'-(A)_x-A''$  X= degree of polymerization DP

A' and A''= terminal groups

(b) Branched



(c) Cross-linked



**Fig.1 various polymer types: (a) linear polymer, (b) branched polymer, (c) cross linked polymer.**

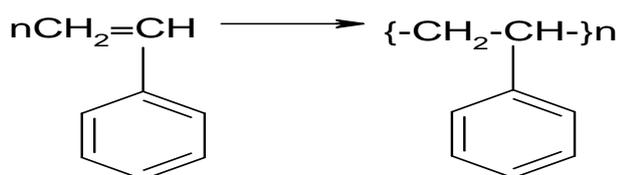
Linear and branched polymers are known as thermoplastic materials because they flow when heated and can thus be fabricated by application of heat and pressure. They are soluble in certain solvents. Cross linked polymers are known as thermosetting materials, and unlike thermoplastic materials they do not flow when heated and thus cannot be fabricated by application of heat and pressure. Because all polymer chains are interconnected by covalent crosslink's, they cannot dissolve and can only swell to the extent allowed by the crosslink density.

## II. POLYMER CLASSIFICATION

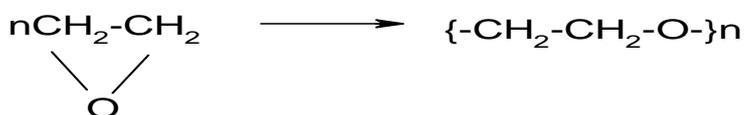
### POLYMERS ARE CLASSIFIED ACCORDING TO THE METHOD OF POLYMERIZATION

- i . Addition polymers
- ii. Condensation polymers

In addition polymers the molecular formula of the monomer is the same as the repeating unit of the polymer, and such polymers are prepared by the polymerization of monomer that contain one or more double or triple bonds or by

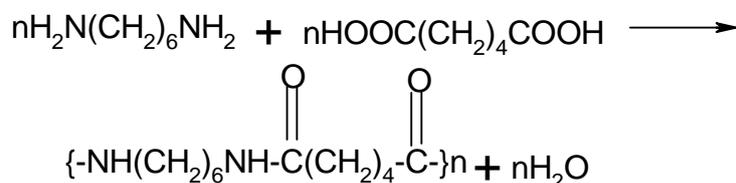


or



**The ring opening of cyclic structures.**

Condensation polymers are formed by successive reactions of functional groups, and because a small molecule by product forms the repeating unit of the polymer has fewer atoms than the monomers, such as in formation of polyurethanes, polyureas and polyacetals.

**POLYMERS ARE CLASSIFIED ACCORDING TO THE POLYMERIZATION MECHANISM**

- (A) Chain polymerization
- (B) step-growth polymerization

In this scheme addition polymerizations are included in chain polymerization, and condensation polymerizations are included in step-growth polymerizations.

**All chain polymerizations are characterized by the following features.**

1. Discrete initiation, propagation, and termination steps
2. Rapid preferential growth of each polymer chain once started
3. Monomer concentration that decreases steadily as polymerization proceeds.

**All step-growth polymerizations are characterized by the following features.**

1. No discrete initiation propagation and termination steps and any two molecular species can react.
2. Polymer molecular weight rises steadily throughout the reaction.
3. Monomer disappears early in the reaction.

**A. Chain polymerization**

Chain polymerization can be divided into the following four types according to the nature of the active center.

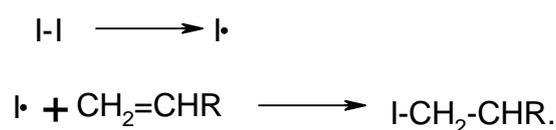
1. Free radical
2. Anionic
3. Cationic
4. Ziegler-Natta

## 1. Free Radical Polymerization

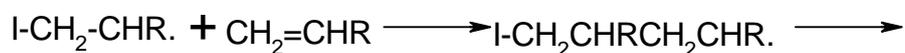
A free radical is species bearing an odd number of electrons and hence has an unpaired electron. Because unstabilised free radicals are extremely reactive molecules, initiation in free radical polymerization involves first the generation of free radicals, which then react with the vinyl monomer in an initiation reaction.

Free radicals can be generated in many ways, but the most common involves hemolytic decomposition of covalent bonds having bond energies of about 30-40kcal/mole, for example A free radical polymerization process can be schematically represented as follows:

### Initiation



### Propagation



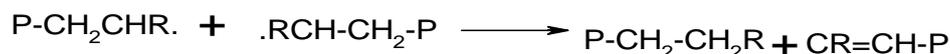
### To high polymer

Termination:-Free radical polymerizations terminate by two facile reactions: coupling and disproportionation. In addition to termination reactions chain transfer reactions can also take place.

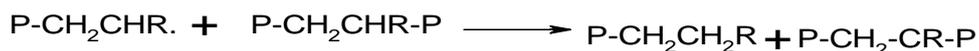
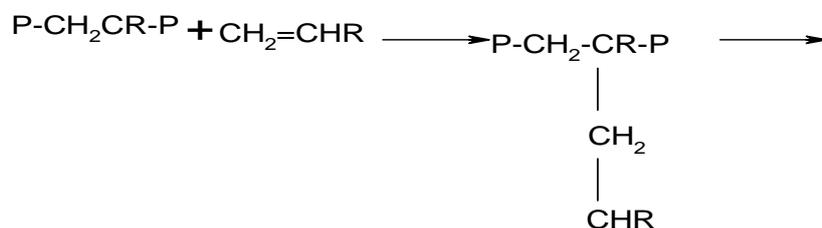
### Coupling



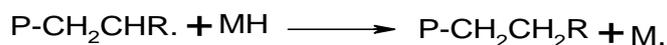
### Disproportionation



Chain Transfer:-Chain transfer involves abstraction of a hydrogen from another molecule by the growing polymer chain. When the hydrogen is abstracted from another polymer chain, branches are created when that radical initiates monomer molecules.

**Abstraction****Branching****Branch growth**

Hydrogen abstraction from a small molecule can also take place.

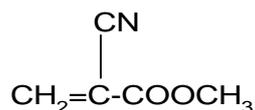


When the radical M. is capable of initiating monomer, MH is known as a chain transfer agent.

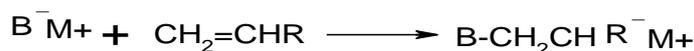
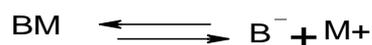
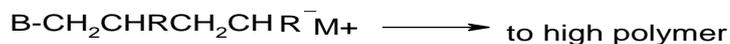
**2. Anionic Polymerizations**

Unlike free radical polymerizations, where the growing chain end is neutral, in anionic polymerizations the growing chain end is an anion and is thus associated with a positive counter ion.

Only monomers that contain an electron-withdrawing substituent on the double bond and can stabilize an anion will undergo anionic polymerizations. An example of a highly activated monomer is methyl cyanoacrylate, which contains two electron-withdrawing groups on one carbon, and even water is sufficiently basic to initiate polymerization.



Anionic polymerizations are commonly initiated with organic bases. Such as organometallic compounds, or with electron-transfer agents. Using base initiation as an example, initiation and propagation occur as follows.

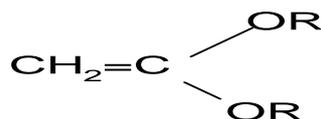
**Initiation****Propagation**

Because there are no chain transfer reactions, high molecular weight, unbranched polymers are formed

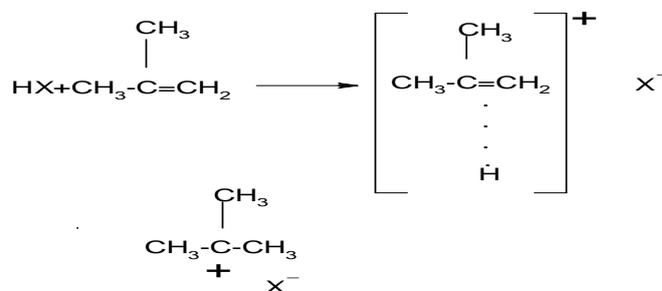
**3. Cationic Polymerizations**

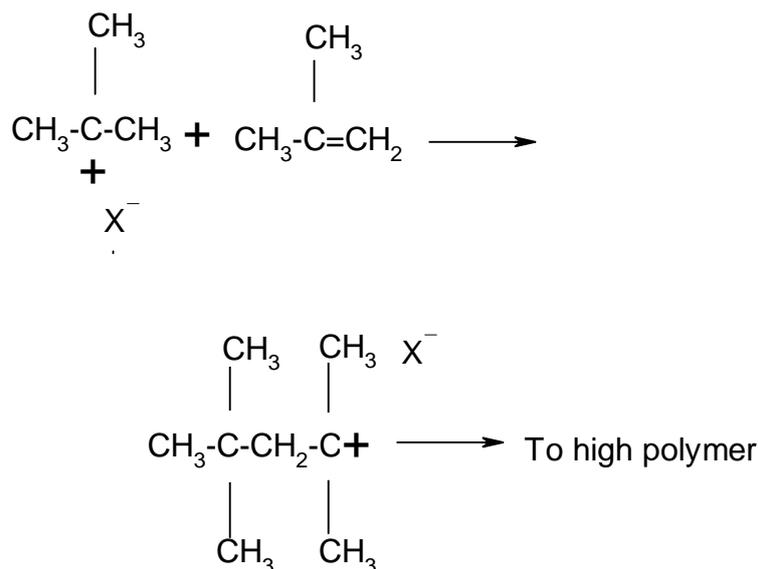
These are also ionic polymerizations but differ from anionic polymerizations in that the active chain end is a cation and the associated counter ion is a negative species.

Only monomers that contain an electron-donating substituent on the double bond that is capable of stabilizing a cation will undergo cationic polymerizations. Examples of a highly activated monomer are ketene acetals, which contain two electron donors on a double bond.



Cationic polymerizations are commonly initiated with acids, either protonic or Lewis. Using a protonic acid as an example, initiation and propagation occur as follows:

**Initiation**

**Propagation**

Because there is a strong driving force to form the most stable carbonium ion, rearrangement reactions can take place during propagation.

**4. Ziegler-Natta Polymerizations**

The combination of metal alkyls and transition metal compounds are known as Ziegler-Natta catalyst systems. Of particular importance are aluminum alkyls, such as aluminum triisobutyl and titanium, or vanadium halides, such as  $\text{TiCl}_4$ ,  $\text{VCl}_4$ ,  $\text{TiCl}_3$ , or  $\text{VCl}_3$ .

These catalyst systems are not only capable of polymerizing olefins, such as ethylene or propylene, at essentially atmospheric pressure to very high molecular weight polymers, but are also capable of producing stereo regular polymers.

**B. Step-Growth Polymerizations**

Unlike chain polymerizations, step-growth polymerizations do not have discrete initiation, propagation, and termination steps and any two species in the reaction mixture can react by a specific reaction between two appropriate functional groups.

To be useful in the synthesis of high molecular weight polymers the condensation reaction must precede in extremely high yields, illustrated by the Carothers equation:  $DP = 1/(1-P)$

Where DP is the degree of polymerization and p is the percent conversion of functional groups (yield).

According to this equation a DP of 20 requires that 95% of the functional groups react and a DP of 50 requires a 98% conversion. Because most condensation polymers are not useful unless the DP is at least 50, it is clear that only reactions that proceed in extremely high conversions can be used.

## POLYMERS ARE CLASSIFIED ACCORDING TO THE MONOMERS

i .Homopolymers

ii.Co-polymers

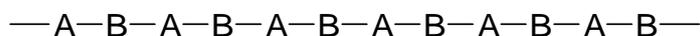
Homopolymers consist of single monomer example-polyethylene, polyvinylpyrrolidone and naturally occurring homopolymers are cellulose, rubber.

A co-polymer is a polymer chain that contains two or more constituent monomers example-protein. Depending on the arrangement of the monomers in the co-polymer, various types of co-polymers can be identified .Using A and B to denote two different monomers; these can be depicted as follows.

Random co-polymer-The two repeat unit follows no particular sequence in chain example:-  
Random co-polymers of propylene (A) & ethylene (B).



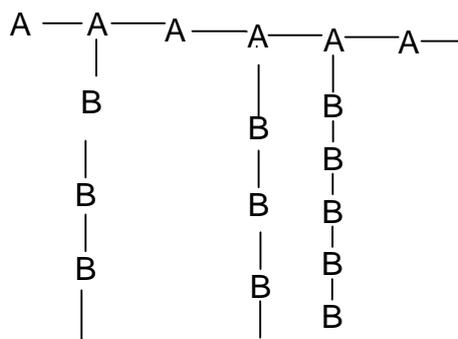
Alternating co-polymer-The two units alternate in chain example:- polypropylene sulfone made by co-polymerization of propylene & sulfur dioxide.



Block co-polymer-It contains long sequences of the monomers example:-fecal softener POLOXALKOL is a block co-polymer of ethylene oxide & propylene oxide.



Graft co-polymer-It contains long sequences of one monomer in which branching occurs at various points by the long chain of second monomer.



## POLYMERS ARE CLASSIFIED ACCORDING TO THE THERMOSTABILITY

- i. Thermoplastic
- ii. Thermosetting

Thermoplastic materials can flow when heated & can thus be fabricated by application of heat and pressure.

Thermosetting material do not flow. Since these polymers are interconnected, by covalent crosslink's they cannot dissolve but can only swell to the extent allowed by the crosslink's divisibly.

## III. POLYMERIZATION METHODS

### A. Polymerization Methods for Chain Polymerizations

#### 1. Bulk Polymerization

This method involves the polymerization of neat monomers and two situations can arise. In one the polymer is not soluble in the monomer, so solid polymer precipitates as the polymerization process takes place. In the other the polymer is soluble in the monomer, so the viscosity of the polymer mass increases with time until it is completely converted to solid polymer. An example of the former situation is the polymerization of acrylonitrile; an example of the latter situation is the polymerization of styrene or methyl methacrylate.

#### 2. Solution Polymerization

In this method the monomer or monomers are dissolved in a suitable solvent and then polymerized. The chosen solvent should be a solvent for both monomer and polymer. Because the end-product is a solution of the polymer in the solvent, stirring throughout the polymerization process is possible; thus, heat evolution can be controlled by means of

external cooling. The concentration of the monomer in the solvent should be adjusted to avoid an excessively viscous final solution.

### 3.Suspension Polymerization

In the method the monomer is dispersed in a dispersing medium, and polymerization occurs in the monomer droplets suspended in the dispersing medium. Although no aqueous media can be used, water is used almost exclusively as the dispersing medium. Clearly, when water is used as the dispersing medium, water-soluble monomers can not be used unless a salting out procedure is used.

Suspension polymerizations are used with free radical polymerizations where the initiator is dissolved in the monomer, which is then dispersed in water using a suspending agent. Polymerization is initiated in the monomer droplets dispersed in the aqueous medium. Polymers obtained by this polymerization method are spheres, typically between 0.01-0.5cm in diameter.

### 4.Emulsion Polymerization

Experimentally, this polymerization procedure is identical to suspension polymerizations, but differs in that the initiator is insoluble in the monomer and soluble in water. Because of this difference, the kinetics of the polymerization process is distinctly different. Polymer particles produced by this method are typically 0.1 $\mu$ m in diameter.

When a water-insoluble monomer is dispersed in water that also contains a water-soluble initiator and an emulsifying agent, the various species shown in figure 2 are present in the polymerization system

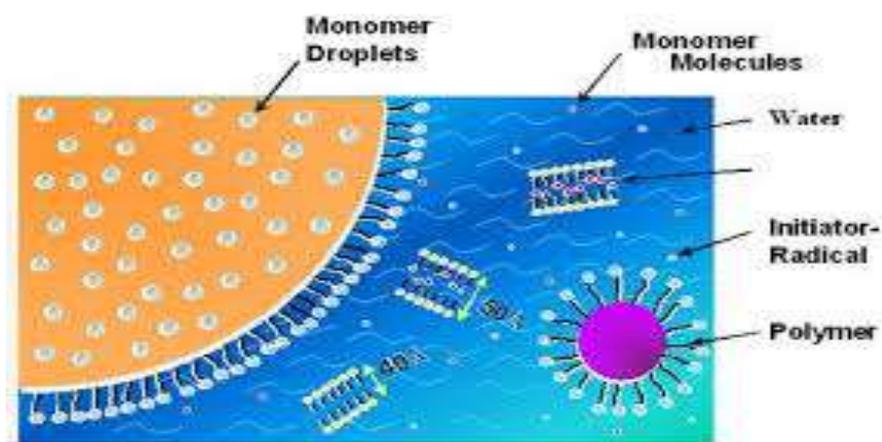


Fig. 2 Simplified representation of an emulsion polymerization system.

A small portion of the emulsifier molecules are dissolved in water, but the bulk aggregate to form colloidal clusters also known as micelles, where the emulsifier molecules arrange their hydrocarbon portions towards the interior and the hydrophilic ends towards the outside.

A small portion of the monomer molecules dissolve in water and a somewhat larger, but still very small portion of the monomer molecules dissolve in the hydrocarbon portion of the micelles. However, the bulk of the monomer is present as dispersed monomer droplets, stabilized by the emulsifier. Typically; the size of these monomer droplets is about 10,000Å at a concentration of about  $10^{10}$  monomer droplets/cc. This concentration is significantly smaller than that of the micelles which are present at a concentration of about  $10^{18}$ /cc. Because the concentration of the monomer dissolved in the aqueous phase is extremely low and because the initiator is not soluble in the monomer droplets, polymerization takes place almost exclusively in the micelles which serve as the meeting place for the water soluble initiator and water insoluble monomer.

As polymerization precedes the size of the micelles increases by addition of monomer from the monomer droplets and as the active micelles grow in size, they absorb emulsifier molecules from the solution.

When the emulsifier concentration in solution falls below the critical micelle concentration the inactive micelles become unstable and dissolve. At this point, the active micelles are no longer considered micelles, but are in reality monomer swollen polymer particles and all of the emulsifier molecules have adsorbed on the polymer particles.

As polymerization continues in polymer particle, monomer from monomer droplet diffuse into the polymer particles & size of monomer droplets decreases while size of polymer particle increases.

In this method polymerization starts when a free radical diffuses into a micelle & initiates the polymerization process.

There are two very important consequences of this unique polymerization process.

\*First due to lower frequency of termination, chain growth can continue for longer period of time & hence polymers prepared have very high molecular weight.

\*In conventional free radical polymerization the propagation rate is described by.

$$r_p = k_p [M][M.]$$

where as in emulsion polymerization the rate is described by.

$$r_p = k_p [M] [N/2]$$

[M]= concentration of monomer,

[M.]=concentration of radical chain ends,

N= number of micelles.

## B. Polymerization Methods for Step-Growth Polymerization

### 1. Bulk Polymerization

Because step-growth polymerizations are not exothermic, heat dissipation is not a problem, and bulk polymerization is an excellent method for producing polymers by a step-growth polymerization.

### 2.Solution Polymerization

This is also an excellent polymerization method. Because of the critical importance of exact stoichiometry for achievement of high molecular weight, the solvent must be purified to remove impurities that might react with monomer functional groups.

### 3.Interfacial Polycondensation

This is a specialized method using two mutually immiscible solvents, each containing one monomer and where the polycondensation reaction occurs at the interface between the two solvents. The method can only be applied to very rapid reactions such as the reaction between an acid chloride and an amine. Thus, polyamides can be readily formed by this process by placing the amine in water and the diacid chloride in carbon tetrachloride.

## IV. POLYMER PROPERTIES

### A. Molecular Weight and Molecular Weight Distribution

Because polymerization is a random process, molecules within a given polymer mass will have different molecular weight, and for this reason molecular weights of polymers are described in terms of average molecular weights.

Common molecular weights are the number average molecular weight,  $\overline{M}_n$

The weight average molecular weight,  $\overline{M_w}$

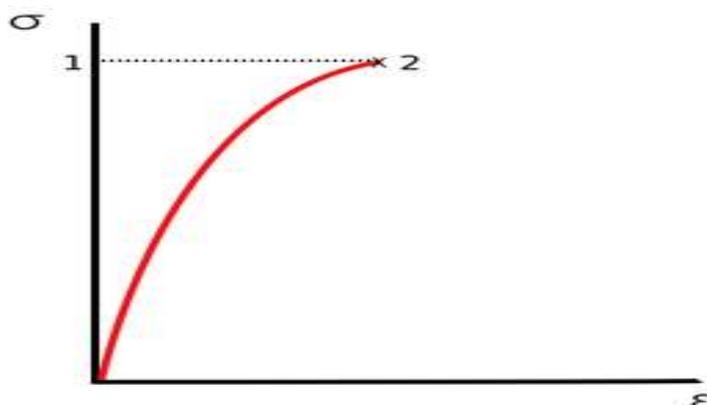
And viscosity average molecular weight,  $\overline{M_v}$

These averages are defined as follows.

The ratio of  $\overline{M_w}/\overline{M_n}$  also known as the polydispersity index, indicates broadness of molecular weight distribution, and for  $\overline{M_w}/\overline{M_n} = 1$  the polymer is monodispersed; that is, all polymer molecules within a polymer mass have the same molecular weight.

Knowledge of molecular weight and molecular weight distribution of polymers is important because there is a definite relationship between polymer molecular weight and polymer properties. Thus, at very low molecular weights the polymer has essentially no useful mechanical properties, but as the molecular weight rises, the magnitude of the mechanical property of interest also rises.

This effect is illustrated in figure 3 which shows the increase of tensile strength of polystyrene with increasing number average molecular weight.



**Fig.3 Plot of tensile strength against number average molecular weight for polystyrene.**

The relationship between property and  $\overline{M_n}$  can in general be represented as

$$\text{Property} = a + b/\overline{M_n}$$

**Where a and b are constants.**

#### B. Polymer Hydrophobicity

When a polymer is placed in an aqueous environment, it will gradually absorb water, and the amount of absorbed water is determined by the polymer structure. Because use of a

polymeric controlled release device exposes the polymer to an aqueous environment, its interaction with water is of considerable importance.

According to the nature of polymer-water interaction, polymers can be broadly classified into hydrophobic polymers, hydrophilic polymers, water-soluble polymers, and hydrogels.

### **1. Hydrophobic Polymers**

These polymers are essentially water impermeable and, when placed in an aqueous environment, will absorb very little water. The amount of absorbed water should be less than 5wt%.

Structural parameters are:-chain stiffness

- High degree of crystalline
- Presence of highly hydrophobic groups where C-H bonds have been replaced by C-F bonds.

### **2. Hydrophilic Polymers**

These are polymers that absorb more than 5wt% water.

Structural parameters are.

- chain flexibility
- absence of crystal
- presence of certain group such as amino,carboxyl,andhydroxyl, etc.

### **3. Water-Soluble Polymers**

Some polymers are freely soluble in water, even though they are of very high molecular weight. Examples of such polymers include poly(vinyl alcohol),poly(acrylic acid),poly(N-vinyl pyrrolidone),poly(acrylamide) and poly(ethylene oxide).

### **4. Hydro gels**

These are highly hydrophilic or water-soluble polymers that have been cross linked by means of covalent bonds. The polymer cannot dissolve due to the covalent crosslink's.

#### **C. Glass Transition Temperature**

At low enough temperatures, all amorphous polymers exist in a glassy state where no large-scale molecular motion can take place, and while in the glassy state, polymers are characterized by their hardness, stiffness, and brittleness. As the temperature is raised,

polymers undergo a transition, known as the glass transition temperature,  $T_g$ , where they change from a glass to a rubbery elastomer or flexible plastic.

As a consequence of this transition, the polymer undergoes an abrupt change in properties. Among these are.

- \*coefficient of expansion, permeability,
- \*heat content,
- \* Refractive index, and
- \* Hardness.

Thus in designing a controlled-release device, it must be known whether at use, the polymer will be above or below its glass transition temperature.

#### **D. Crystalline**

Polymers that have a regular structure are able to achieve a regular packing of polymer chains and crystallize. The driving force for crystallization is a closer packing of polymer chains with consequent enhancement of intermolecular attractions. A few polymers, among these polyethylenes, can be prepared as single crystals. Because crystalline regions act as crosslink's for the regions and for this reason stiffen and toughen the polymer and reduce swelling in solvents.

Furthermore, because crystalline regions are impermeable to diffusing molecules, an enhancement of crystalline results in a decrease in polymer permeability. Crystalline regions are also essentially impermeable to water, so the rate of polymer hydrolysis in crystalline regions is significantly reduced.

### **V. POLYMER CHARACTERIZATION**

#### **A. Molecular Weight**

Various methods for determining molecular weight:

##### **1. Osmometry**

It determines number average molecular weight ( $\overline{M}_n$ ). Osmotic measurements use a semipermeable membrane through which solvent molecule pass freely but polymer molecules are excluded, as a result a osmotic pressure driving solvent into polymer solution is developed.  $\frac{\pi}{c} \cong RT/\overline{M}_n$

## 2. Light Scattering

Scattering of light by liquids can be related to local fluctuations in density due to thermal motions of molecules. From measurements of light scattering of dilute polymer solutions it is possible to derive the weight average molecular weight  $\overline{M_w}$ .

## 3. Viscometry

Viscometry is a relative method and requires calibration with samples of polymer of known molecular weight. As polymer molecular weight increases so does the viscosity of its solution. Viscosity can be measured by various viscometers, shown in Figure 4. By this we get relative viscosity and specific viscosity.

$$\eta_r = t/t_0 \quad \eta_{sp} = \eta_r - 1$$

$t_0$  = flow time of pure solvent,  $t$  = flow time of polymer solution

A viscosity average molecular weight,  $\overline{M_v}$ , can be obtained by measuring reduced viscosity  $\eta_{red} = \eta_{sp}/c$

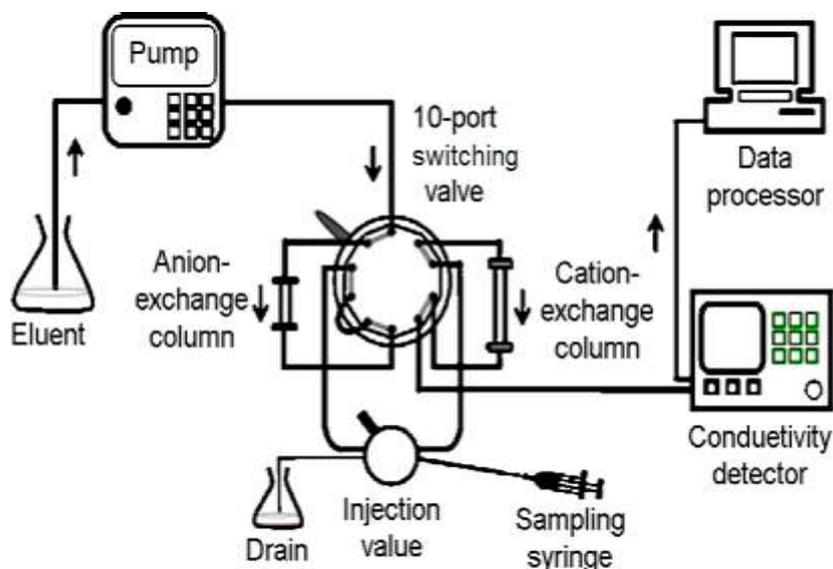


Fig. 4 Capillary viscometers Ostwald, Fenske, Ubbelohde

## 4. Gel Permeation Chromatography

Gel permeation chromatography is a procedure whereby polymer molecules are separated according to their size. In this procedure a dilute polymer solution is pumped through a series of columns containing porous beads with different pore sizes but about of the same dimension as the polymer molecules. Then, the smallest polymer molecules will be able to penetrate all pores, the largest polymer molecules will not be able to penetrate any pores, and intermediate size polymer molecules will penetrate some pores but not penetrate others. Therefore, on the average, the smallest molecules will take the longest path through the columns, and the largest molecules will take the shortest paths through the columns flowing only through the interstitial volumes. Therefore, the highest molecular weight species will emerge first and the lowest molecular weight species will emerge last.

A schematic diagram of a typical apparatus is shown in figure 5. Typical detectors are a differential refracto meters, U. V. or IR detectors. Molecular weights can be determined only if the method is first calibrated with polymer samples having known molecular weights and a plot of molecular weight versus retention times constructed. With this arrangement absolute molecular weights and molecular weight distributions can be determined.



**Fig. 5 Schematic diagram of a gel permeation chromatography apparatus.**

## B. Thermal Analysis

The most commonly used method for the thermal analysis of polymers is.

- Thermo gravimetric analysis (TGA),
- Differential scanning calorimetry (DSC),
- Thermomechanical analysis (TMA).

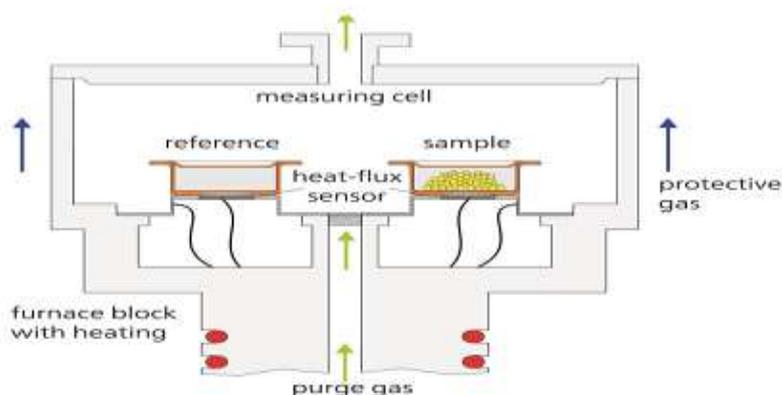
### 1. Thermo gravimetric Analysis

The method used a thermo balance that is capable of continuously and very accurately measuring the weight of a sample contained in a pan. The pan is placed in a furnace and the temperature of the furnace slowly raised, usually at 5<sup>o</sup> to 10<sup>o</sup>c/min.

The technique is used to determine thermal stability of polymers and the upper limit of thermal stability is usually taken as the temperature at which weight loss of the sample begins. However, the method only measures loss of volatile degradation products from the polymer and is unable to detect chain cleavages that produce degradation fragments that are too large for volatilization.

## 2. Differential Scanning Calorimetry (DSC)

This is an extremely useful technique for measuring glass transition temperature, crystalline melting point, heats of fusion, and heats of crystallization. The principle on which DSC operates is shown in figure 6.

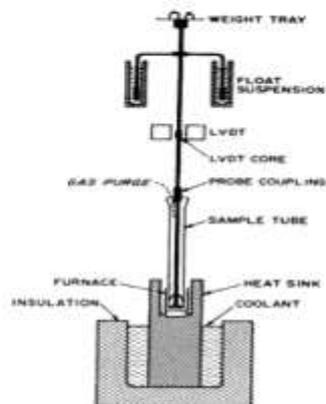


**Fig.6 Schematic of differential calorimetry sample holder.**

The sample and a reference substance, which does not undergo a thermal transition in the temperature range of interest, are placed in two small metal containers and heated by individual electric heaters. The temperature of both samples, monitored by thermocouples, is then gradually raised in such a manner that the temperature of sample and reference remain the same. Then, if the sample suddenly absorbs heat, its heater will supply additional heating to maintain its temperature equal to the reference and if the sample suddenly evolves heat the heater will supply less heat. In this way, transition temperatures can be very accurately measured by monitoring the electric current going to the heaters.

## 3. Thermo mechanical Analysis (TMA)

This technique measures deformation of a substance under a no oscillatory load as a function of the temperature of the sample, which is placed on a platform and contacted with a probe. The probe assembly includes a weight tray that permits a choice of loading on the sample. The probe is connected to the armature of a linear differential transformer that can accurately measure the movement of the probe. A schematic of a typical TMA apparatus is shown in figure 7.



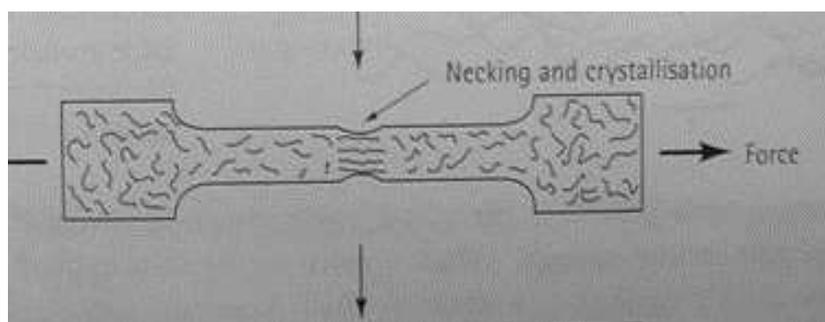
**Fig. 7 Typical thermomechanical apparatus.**

TMA can conveniently measure transitions from a glassy to a rubbery polymer and can also measure softening temperatures.

### C. Mechanical Properties

Mechanical properties of a polymer are most conveniently determined by measuring their stress-strain relationship. Stress is the stretching force applied to the sample, and strain is the elongation of the sample under a given stress. Stress-strain relationships in polymers are time-dependent.

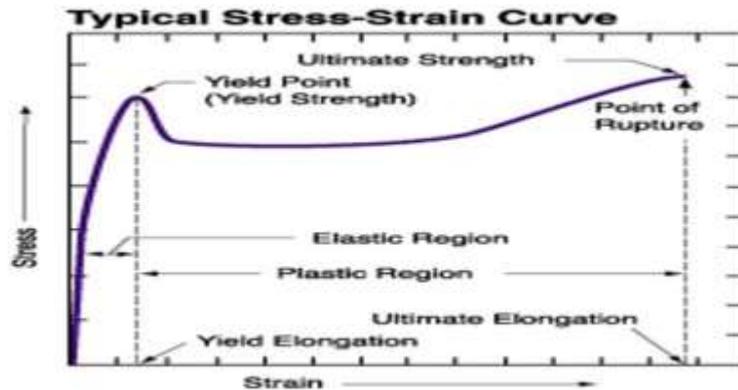
Stress-strain measurements in polymers are usually performed on dumbbell-shaped specimens as shown in figure 8.



**Fig. 8 Typical shape of a flat polymer sample used for stress-strain tests.**

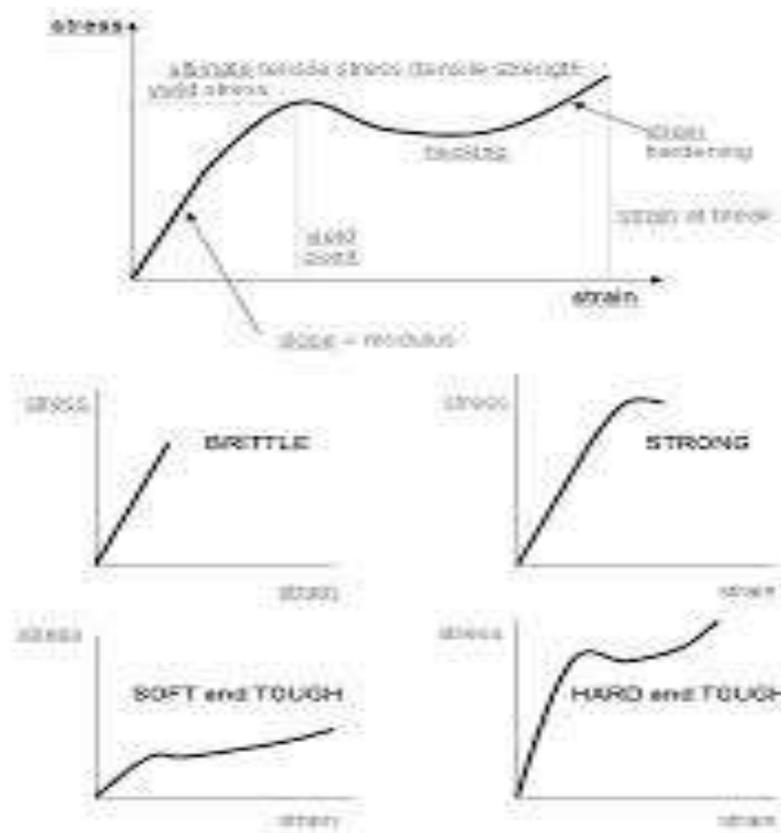
The specimen is clamped in a tester, such as an Instron tester, that is capable of extending the specimen at a chosen constant rate and measuring the force that the specimen exerts on a load

cell. A typical stress-strain curve for a thermoplastic material, such as polyethylene, is shown in figure 9.



**Fig. 9** Stress-strain curve for a thermoplastic material such as polyethylene.

In the initial phase, application of stress causes a moderate elongation to the yield point, after which significant elongation takes place without greatly increased stress. Elongation then continues until the specimen breaks.



**Fig. 10** illustrates the stress-strain behavior of five typical materials

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