# The main differences between high and low $M.W_t$. compounds

## 1- Physical differences:

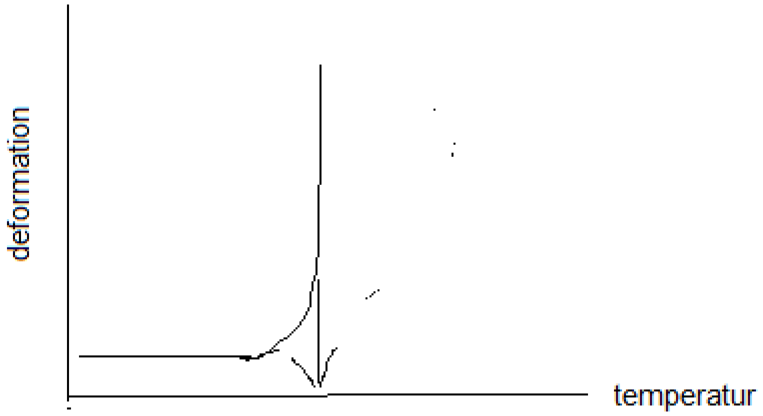
a) High $M.Wt$. compounds have high viscosity in solution or in molten state.

b) Have high degree of asymmetry within the molecule, led to high degree of reversible viscosity.

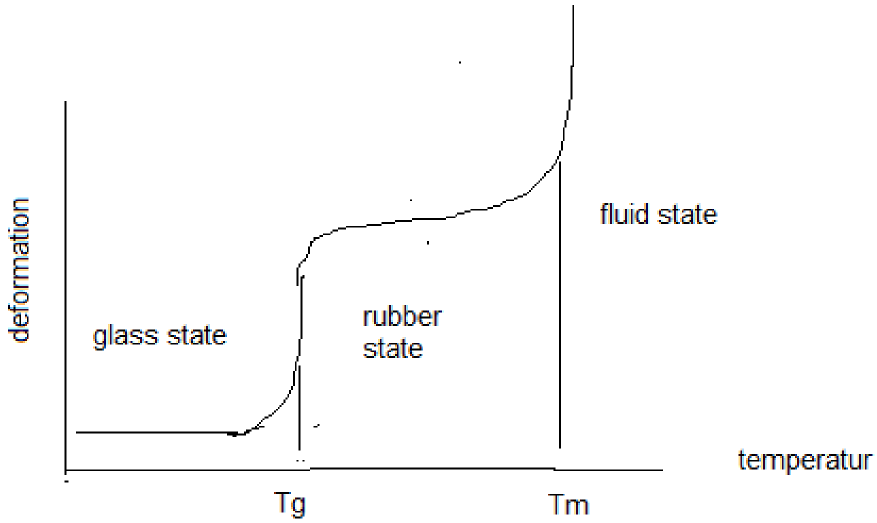
*(The polymer chain deformed when it was put under external stress. It was returned to its original shapes when it was repressed. This is known the flexibility).*

c) The high $M.Wt$. compounds cannot be evaporated, e.g. cannot be found in gas phase.

d) Thermo mechanical behavior: the low $M.Wt$. compounds are melted when it was expressed to heating program. It was melted at melting point temperature, as below:



When the polymer exposed to heating program, it was firstly converts from solid phase (glass state) to rubbery phase (rubber state) at temperature known as ( glass transition temperature Tg ). Continuation heating the rubber state begin to flue and converts to fluid at temperature known as fluid or melting temperature (Tm).



**Tg and Tm are changed according to the M.wt. of the polymer.**

## 2- Chemical differences:

a) The low M.wt. compounds can be oxidized completely when an oxidizing compounds was added to it, while high M.wt. cannot.

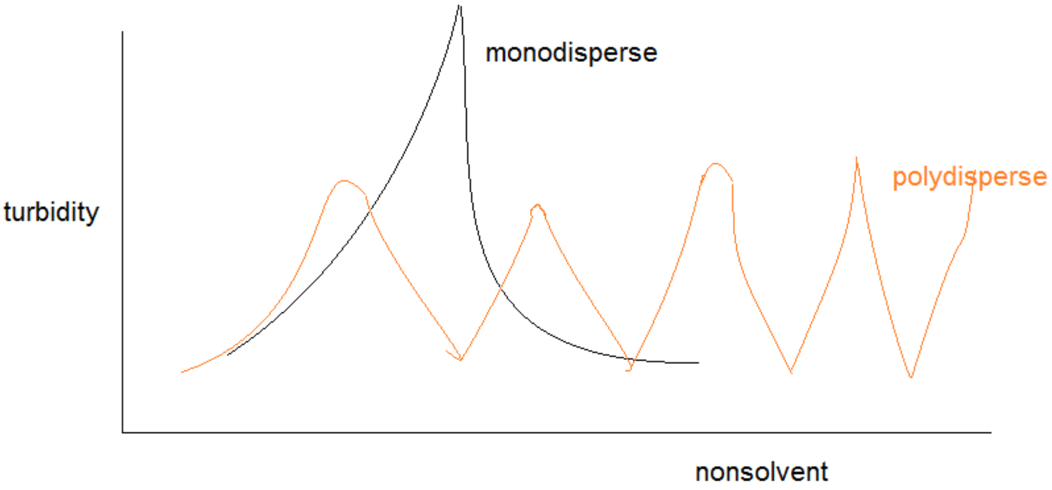
b) Low M.wt. compounds cannot formed copolymers or grafted polymers, but polymers can.

c) Low M.wt. compounds have fixed M.wt., while polymers have M.wt. distribution ( there are different molecules differs in their M.wt. but have the same chemical structure).

If all the polymer molecules have the same M.wt. , the state called monodisperse polymer. In polydisperse polymer there are different distribution of M.wt.

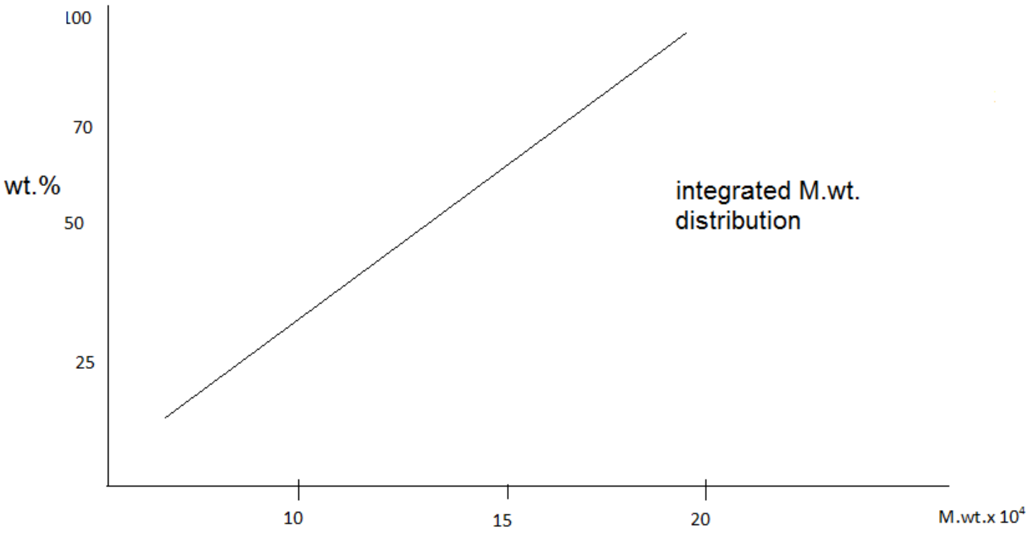
This can be noticed by adding gradually precipitating solvent to a solution of polymer and following the turbidity of the solution continuously.

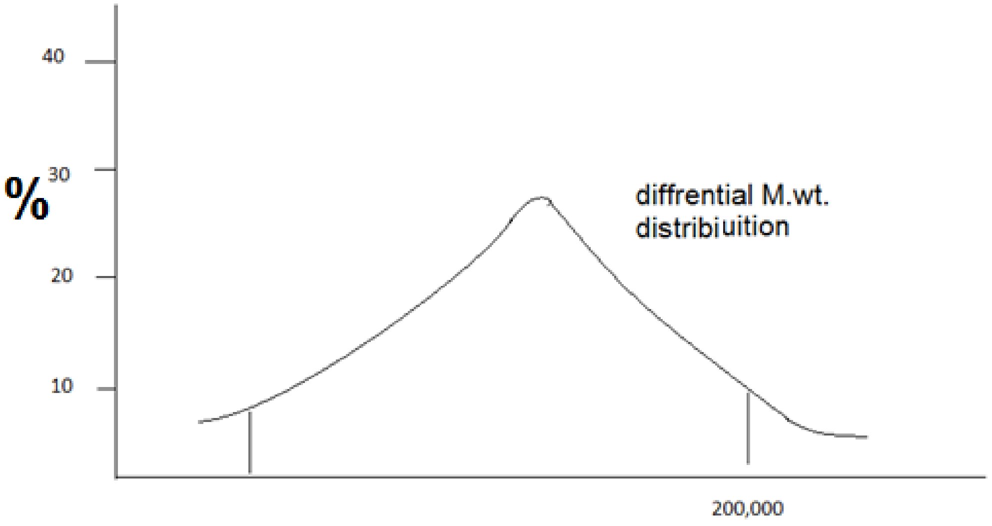
So that the M.wt of the polymer known as the average molecular weight $\overline{M.wt.}$



**Example:** 1g of polystyrene in solution, using methanol as nonsolvent, the separating of different M.wt. are shown below

| | | | | | |
|---|---|---|---|---|---|
| % | 15 | 25 | 30 | 15 | 15 |
| M.wt. | 20x$10^4$ | 16x$10^4$ | 10x$10^4$ | 6x$10^4$ | 4x$10^4$ |





$$Mw = \frac{\Sigma \text{WiMi}}{\Sigma Wi}$$

$$\overline{\text{Mw}} = \frac{10^5(0.15\text{x}2+0.25\text{x}1.6+0.15\text{x}0.6+0.15\text{x}0.4)}{0.15+0.2+0.3+0.15+0.15}$$

$$\overline{\text{Mw}} = 1.06\text{x}10^5$$

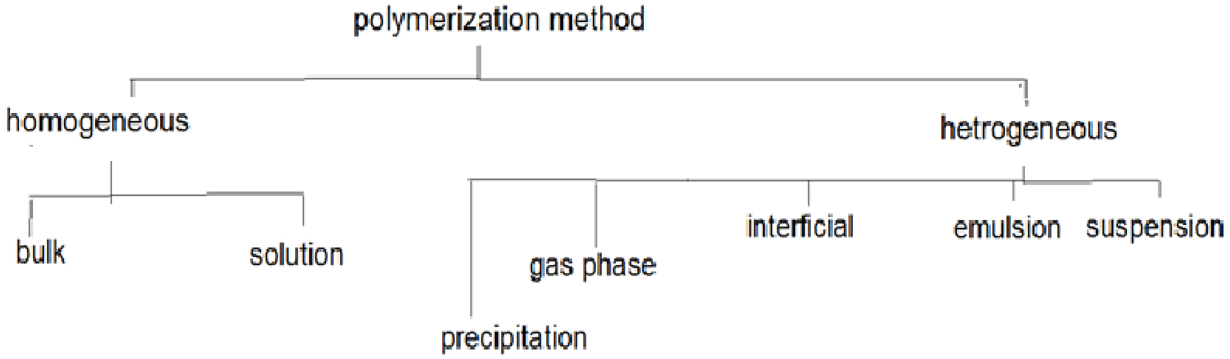
## Polymerization methods and conditions:

Choosing the type of method to prepare the polymer depends on many factors:

1- M.wt. needed.

2- M.wt. distribution.
3- using of polymer.
4-Economic aspects.
5- The system of preparation; batch or continues.

**In general there are two types of polymerization methods or conditions: (Homogeneous methods and Heterogeneous method).**



## 1- Homogeneous methods.

### Bulk polymerization:

It was the simplest method of polymerization. The method include **heating the monomer** (almost liquid) **without solvent** with the presence of initiators until the polymer formed.

The polymerization process is exothermic process. There are **many problems** of this method as:

1-Because there is no solvent, it was very difficult to control the distribution of the heat (heat transfer). Some region in the medium of the polymerization become very hot and the temperature may reach the ceiling temperature and the polymer dissociate. (Ceiling temperature is the temperature at which the polymer started decomposition, depolymerization).

2- If the polymer did not dissolved in the monomer, at 10% conversion, all the unreacted monomer absorbed by the polymer and form a slurry matter, which is very difficult to mix. So that this method is suitable for polymers soluble in their monomers as polystyrene and poly (methacrylate). The process is unsuitable for poly (vinyl chloride) or poly acrylonitrile.

In general the bulk polymerization process is **suitable for condensation polymerization** more than addition polymerization, the reasons are:

1-The addition polymerization is more exothermic than condensation.

2- The high M.wt. in addition was formed in the beginning of the reaction, so the viscosity of the medium was increased at the beginning of the reaction, while in condensation reaction the high M.wt. was formed at the end of the reaction, the viscosity still low until the end.

### Solution polymerization:

Polymerization of vinyl monomer in solution is ***advantageous*** from stand point of heat removal and control (by allowing the solvent to reflux).

The formed polymer is soluble in the used solvent producing low viscous medium which can be mixed very easy.

The ***disadvantageous*** of this method are:

1) The solvent must be selected to avoid the chain transfer to solvent.

2) The solvent is very hard to remove from the medium after complete the polymerization reaction (need evaporation under much reduced pressure).

So that the solution process is mainly applied when the polymer should preferably utilized in solution (the solution of the polymers are required) e.g. Lacquers,and adhesives.

## 2- Heterogeneous polymerization

It occurs when there are **many phases** in the process, e.g. the monomer is in the gas phase and the medium is liquid while the produced polymer is solid.

### Suspension polymerization:

It was polymerization in an **aqueous phase**. The monomer is a dispersed phase and the initiator **dissolved** in the monomer. The resulting polymer is a dispersed solid phase. The dispersion of the monomer as a droplet (0.01- 0.5cm in diameter) is maintained by a combination of agitation and using of water soluble stabilizers.

**The stabilizers** protect the accumulation of the monomer droplets. Some types of stabilizers are: organic or inorganic like hydroxides of various metals and surfactants, or some water soluble polymers like carboxymethyle cellulose (CMC), or poly (vinyl alcohol).

The polymerization take place within the disperse droplets and the produced polymer is look like beads.

The ***disadvantageous*** of this method is the pollution of the polymer with the stabilizers and limited M.wt.

The method is used commercially to prepare **hard glassy vinyl polymers,** such as polystyrene, poly (methyl methaacrylate), poly (vinyl alcohol) and poly acrylonitrile.

## Emulsion polymerization:

The method is **like suspension** method by using water as dispersion medium and very easy in cooling the system.

It was **differ** from suspension in many important respects:

1-the initiator is located in the aqueous phase.

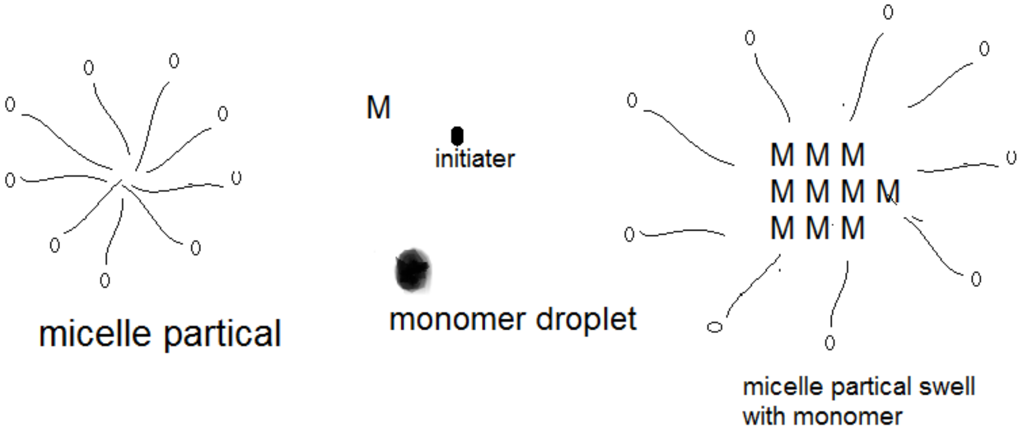
2- the polymer particles or beads are of order of o.1µm in diameter (very smaller than in suspension.

3- The produced polymer have higher M.wt. produced at higher rate than do bulk or suspension system.

The emulsion polymerization mixture consist of water as a **dispersion medium** and **initiator** dissolved in water (e.g. ammonium persulphate or azo compounds). The water contain **emulsifying agent** which was arranged as micelles. The hydrophilic ends of the micelles alined out the micelles while the hydrophobic ends are alined inside the micelles.

The emulsifying agents may be ionic such as alkyl or aryl sulphate or phosphate and sodium loryl sulphate. The non-ionic type of emulsifying agents are hydroxyl ethyl cellulose, poly (vinyl alcohol) or poly (ethylene oxide).

The monomer distribute to three parts, little dissolved in emulsion medium, the second part is also little inter the micelles. The most monomer (third part) is dispersed as droplets in the medium and emulsifying agent was adsorbed on the surface of these droplets.



***The polymerization steps occurs as following:***

1-The free radical formed in the water from the initiator.

2- The free radical inter the micelle particle and initiate the polymerization of the monomer molecules.

3- When all the molecules of the monomer polymerized, another molecule of monomer from the droplet inter the micelle and continue polymerization (the droplet become as storage of the monomer).

4- The termination step did not occur until free radical inter the growing micelle, so a **high M.wt. was formed** by this techniques.

5- The size of the polymer droplets was grow to about 1000µm.

6- Once the polymerization is complete, the polymer can be isolated by evaporation of the water in a spray drier or by coagulation the polymer latex by filtration and drying.

The produced emulsion polymer can also be used without step 6 in case of using in **emulsion paints** or in using as **adhesives**.

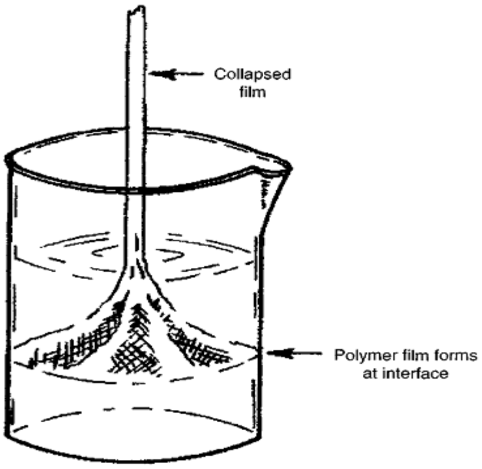
This method was used in **preparation of some vinyl polymers** like polystyrene, poly (vinyl chloride) or styrene butadiene rubber (synthetic rubber).

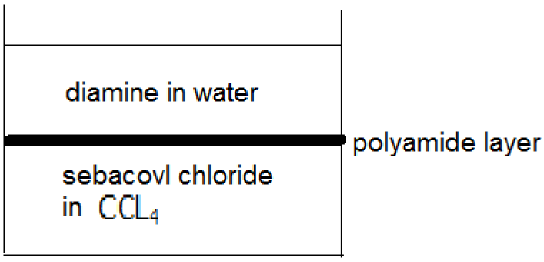
*Emulsion polymerization* can also be carried out by using an aqueous solution of a **hydrophilic monomer**, such as acrylic acid or acrylamide emulsified in a continuous oil phase using an appropriate water – in – oil emulsifier. The usual initiators can be oil or water – soluble.

## Interfacial polymerization:

This method was used in **condensation polymerization**, as in preparation of poly esters or polyamides or polycarbonate. The importance of this method is that can be used at **normal temperature**, but can be used only for rapid reactions only, *[i.e. monomers that are very reactive are capable of reacting rapidly at low temperatures to yield polymers that are of higher molecular weight than would be produced in normal bulk polycondensations]* as in reaction of acid halides with di alcohols or diamines to form polyesters or polyamides *respectively* *[i.e. the best and most widely used reactants are organic diacid chlorides and compounds containing active hydrogens (diamine or diol)]*.

The system of two immiscible solutions, each monomer was dissolved in each solution. One solution is water to dissolve the dialcohol or the diamine monomer [The aqueous phase contains the diamine, diol, or other active hydrogen compound and the acid receptor or base (e.g., NaOH)], the other solution is organic to dissolve the acid halide monomer, the polymerization occur **in between the surfaces of the two solutions**. For example in preparation of polyamide (nylon), hexa methylene diamine was dissolved in water and the sebacoyl chloride was dissolved in carbon tetrachloride. The first solution was added slowly to the second solution in a beaker. The polymer was formed as a layer between the two surfaces of the solutions. **The polymer have high M.wt.** and cab be removed from the medium as a **fiber**.





## Gas phase polymerization:

In this method the monomer is **a gaseous phase** injected to the reactor and initiated by UV light. The polymer was directly formed as **a fog and precipitate**. This process can be used to polymerize some vinyl monomers like ethylene or vinyl chloride.

## Precipitation polymerization:

It is a type of **solution** or **bulk polymerization**. The solvent is the **monomer**. The formed polymer was precipitate from the monomer and can be separated by centrifugation or simple filtration. There is no problem in **heat dissipation** and the polymer have **high molecular weight**.

Precipitation polymerization, also known as **slurry polymerization**, involves solution systems in which the monomer is soluble but the polymer is not. The process involves, essentially, a catalyst preparation step and polymerization at pressures usually less than 50 atm. and low temperatures (less than 100°C). The resultant polymer -which is precipitated- suspended in the liquid hydrocarbon employed as solvent. The polymer is recovered by stripping off the solvent washing off the catalyst, and if necessary, extracting any undesirable polymer components.

The suspension of the polymer in the solvent produces a physical system of low viscosity that is easy to stir. However, problems may arise due to settling of the polymer and the formation of deposits on the stirrer and reactor walls.

# Classification of polymers

## 1- Based on their origin

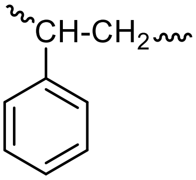
**a) Natural;** i.e. cotton, wool, Protein, DNA, natural rubber …….

**b) Synthetic;** i.e. polyester, polyamide…..

## 2- Based on polymerization reaction type:

### a) Addition polymers

Which are produced via addition of monomer molecule to another to form chain. This repeating unit have the same chemical structure of the monomer, i.e.



polstyrene

$--(CH_2\text{-}CH_2--)_n$

polyethlene

### b) Condensation polymers

Which are produced by connecting two monomers molecules and losing one small molecule from the two monomers. i.e. polyester, polyamide…

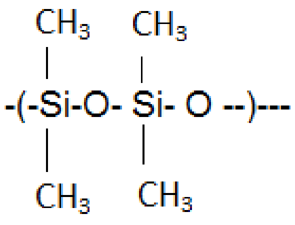
## 3- Organic or Inorganic

The organic polymers consist of pure organic moieties within the polymer chain.

**The inorganic polymers can be classified into three different types as below:**

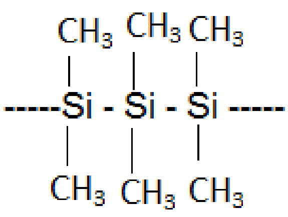
### a) Organic- inorganic (organometallic) polymers.

The backbone is inorganic and the side chain is organic groups



$$-(-\underset{CH_3}{\overset{CH_3}{Si}}-O-\underset{CH_3}{\overset{CH_3}{Si}}-O--)---$$

poly(dimethyle siloxane )



$$-----\underset{CH_3}{\overset{CH_3}{Si}}-\underset{CH_3}{\overset{CH_3}{Si}}-\underset{CH_3}{\overset{CH_3}{Si}}-----$$

poly(dimettyl silane)

### b) Coordination polymers

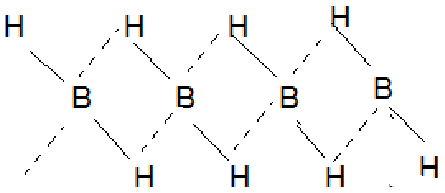
In this type, **the metal ion** was linked or inserted with organic polymeric chain. The bond between the metal and the organic group is a **coordination type**. These polymers known as ***metal chelate polymers***.

poly(vinyl ferrocene)

### c) pure inorganic polymers

The chain consist only from inorganic elements. All the elements in the periodic table can formed polymers except the element in group (IA)

---(- Mg – O – Mg – O -)-- poly(magnesium oxide)



poly(hydrogen boride)

## 4- Classification based on technological aspects:

The polymers can be classified according to their **thermal resistance**.

Tg : When the temperature below it , the material is solid, above Tg the material is flexible, Tg called ( **glass transition temperature**), where above the Tg the chains begin to move around itself.

### a) Thermoplastic polymers or plastic:

$$\mathbf{R.T.} < \mathbf{Tg} < \mathbf{150^{O}C}$$

These polymers are hard at room temperature, softened when heated to elevated temperature and can be deformed to another shape (to desirable shape) many times.  When exposed to another heating it may flow. Cooling the flow, it will change to a paste then to solid.

**Example:** polystyrene, polyethylene, PVC …

**b) Thermosetting polymers:**

$$Tg > 300\,^{O}C$$

Have high thermal resistivity and cannot reformed from shape to another because their chains are **cross linked**. Did not dissolve in any solvents and are considered as an electrical and thermal insulators.

**The thermoplastic polymers can be changed to thermosetting** by using chemical or physical manners. Chemically changing is by adding some chemicals reagents called crosslinking agents.

Physically changing is by exposing to high energy of heat or radiations.

**Example:** phenol- formaldehyde resin, epoxy…

**c) Elastomers or Elastoplast polymers**

$$Tg < R.T.$$

These polymers have some properties like **extensibility** and **resiliency** (**flexibility**)

The chains of these polymers are **linear** and can be reformed **as in thermoplastics**.

**d) Fibers**

$$160\,^{O}C < Tg < 260\,^{O}C$$

These polymers are **crystalline** and have high forces between their molecules. Used in textile industry, their chains are **linear** and **can be arranged** to have high thermal and mechanical stability.