Polymeric Materials

Instructor : Prof. Bishakh Bhattacharya
Dept. of Mechanical Engineering
IIT Kanpur
India

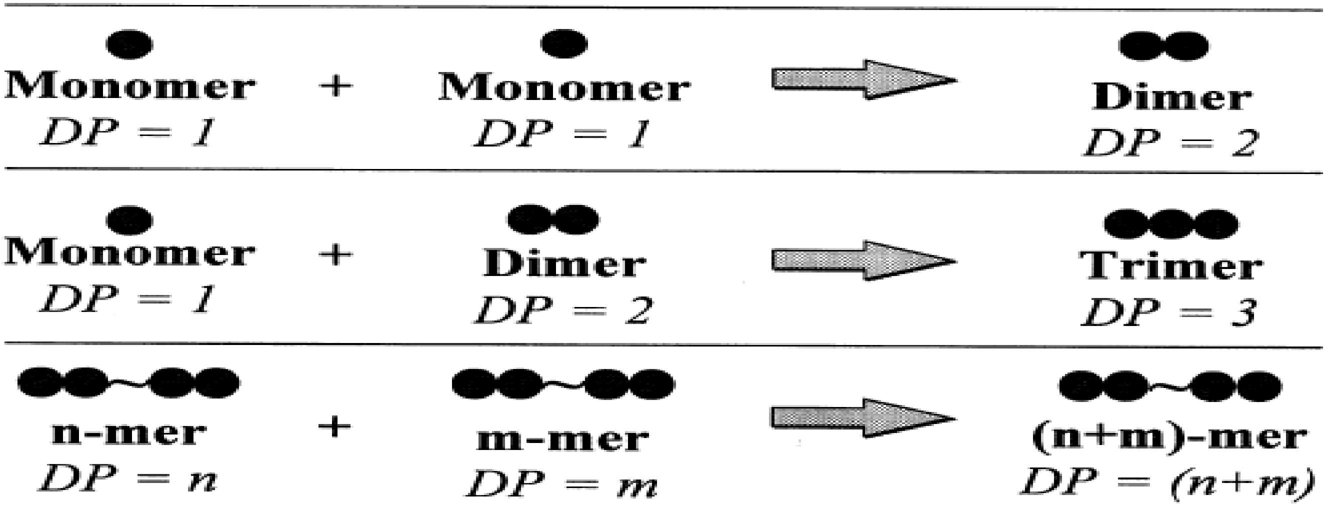
E-mail : *bishakh@iitk.ac.in*

Smart Materials Structures and Systems
Laboratory
IIT Kanpur

Contents

Polymer Basics

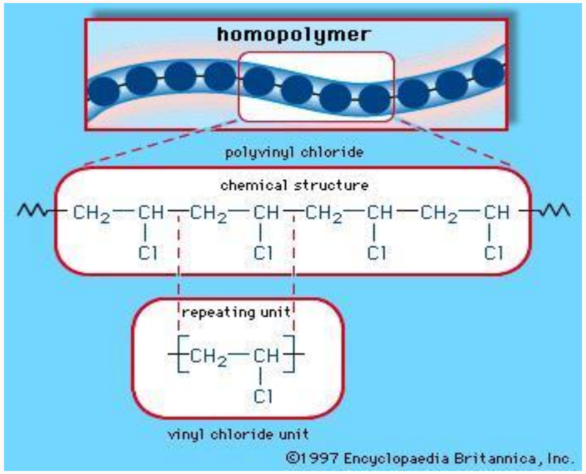
- poly = many
  mer = parts
- degree of polymerization = DP



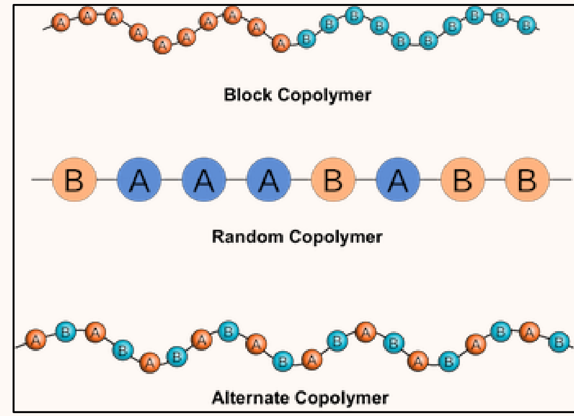
A macromolecule where each unit could either be an atom like Sulfur in Polysulfide or group of atoms.

Chemistry of Polymer molecules

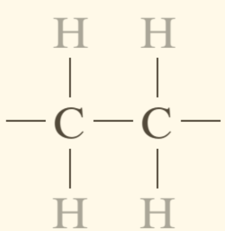
- When all the mers are the same, the molecule is called a **Homo-polymer**.



- When there is more than one type of mer present, the molecule is a **Co-polymer.**

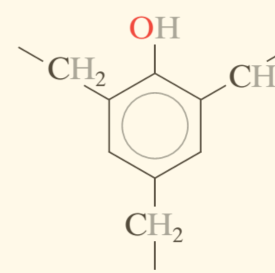


- Mer units that have **2 active bonds** to connect with **other mers** are called bi-functional.



Polyethylene

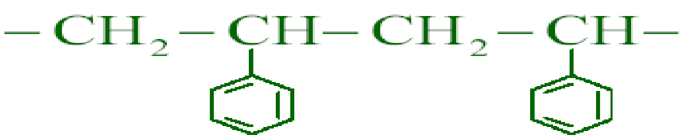
- Mer units that have **3 active bonds** to connect with other mers are called tri-functional. They form 3-D molecular network structures.



Phenol-formaldehyde (Bakelite)

Typical Examples

$$-CH_2-CH_2-CH_2-CH_2-$$ Poly(ethylene)

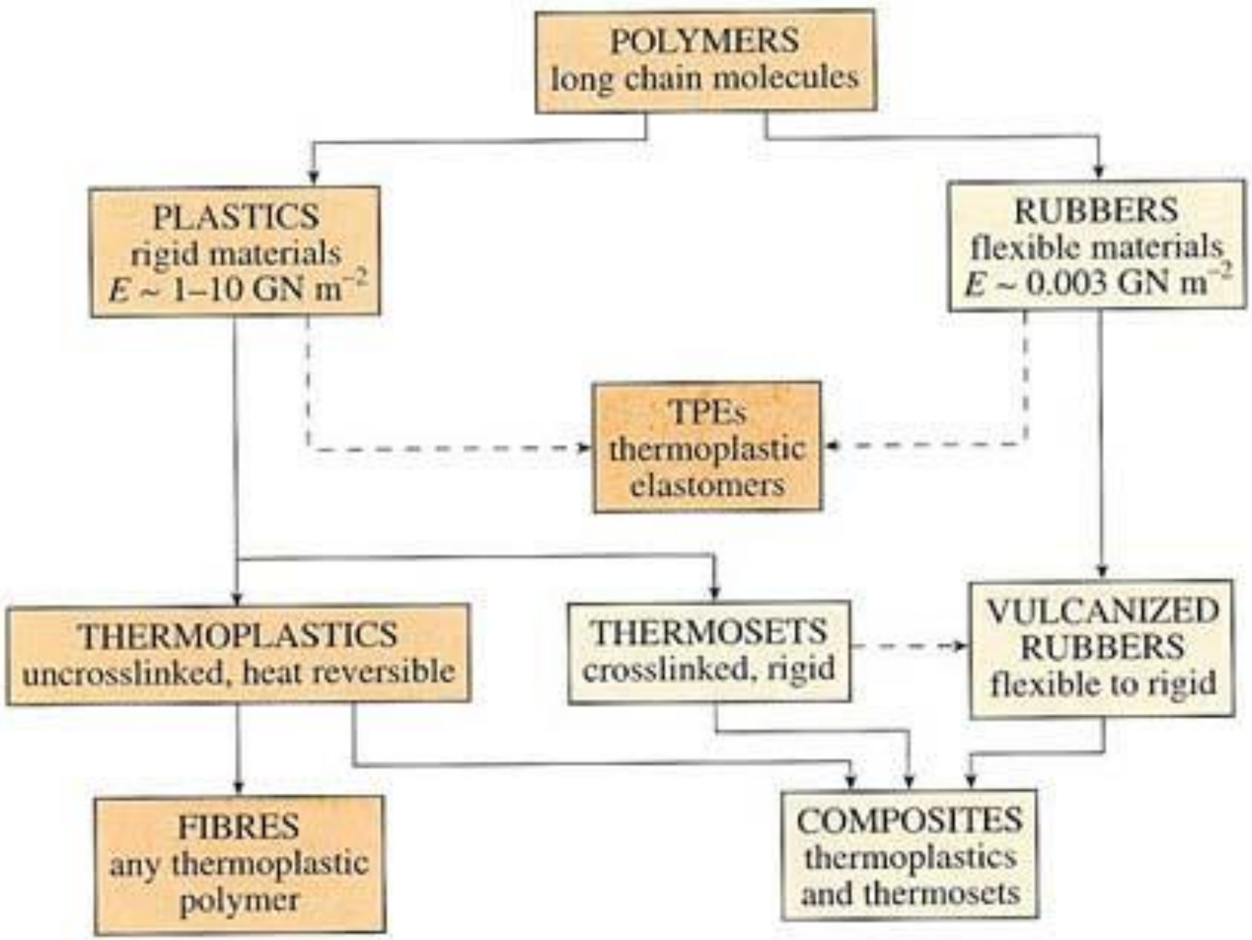


Poly(styrene)

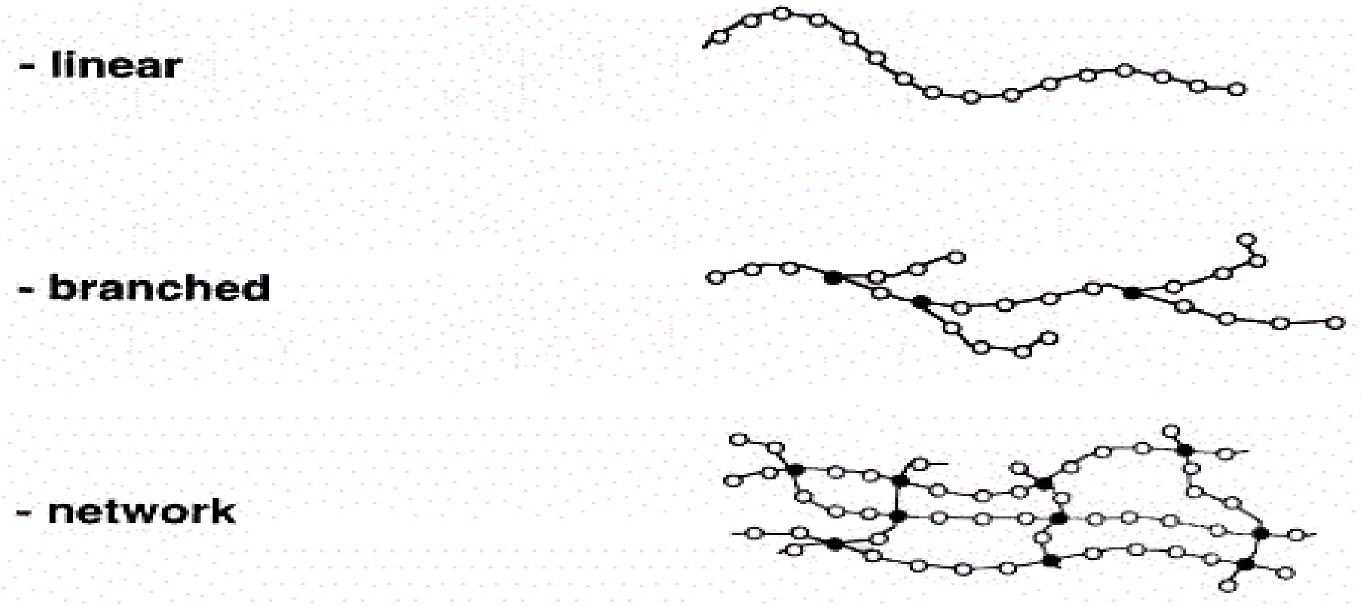
$$-CH_2-\underset{\displaystyle Cl}{\underset{|}{CH}}-CH_2-\underset{\displaystyle Cl}{\underset{|}{CH}}-$$ Poly(vinyl chloride)

Number of monomer units in the chain $N >> 1$.

Classifications of Polymers



Polymer Configuration



Linear Structure: Soluble and Fusible

Branched Structure: More Soluble and Fusible

Networked Structure: Insoluble and Infusible

Structural Isomerism

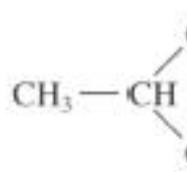
C_1 CH_4 methane

C_2 CH_3-CH_3 ethane

C_3 $CH_3-CH_2-CH_3$ propane

C_4 $CH_3-CH_2-CH_2-CH_3$

n-butane

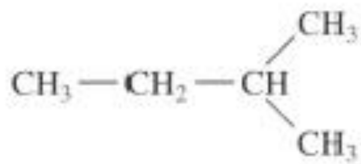


iso-butane

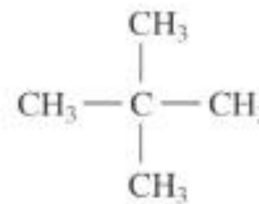
C_4H_{10}

C_5 $CH_3-CH_2-CH_2-CH_2-CH_3$

n-pentane



iso-pentane

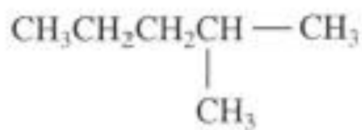


neo-pentane

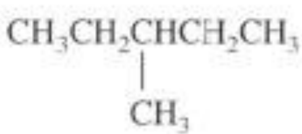
C_5H_{12}

C_6 $CH_3-CH_2CH_2CH_2CH_2-CH_3$

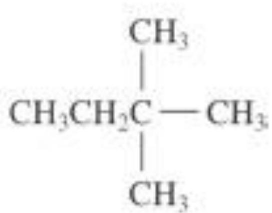
n-hexane



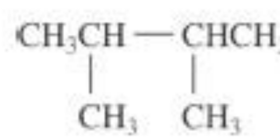
2-methylpentane



3-methylpentane



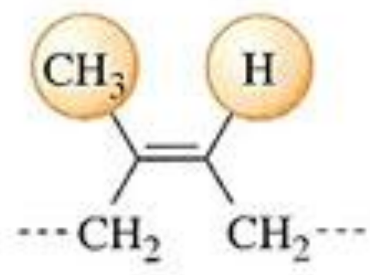
2,2-dimethylbutane



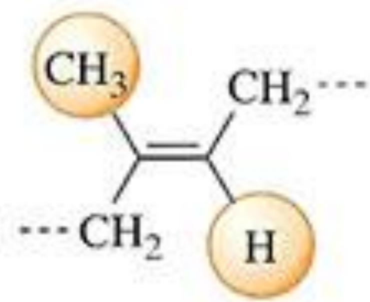
2,3-dimethylbutane

C_6H_{14}

Geometric Isomerism

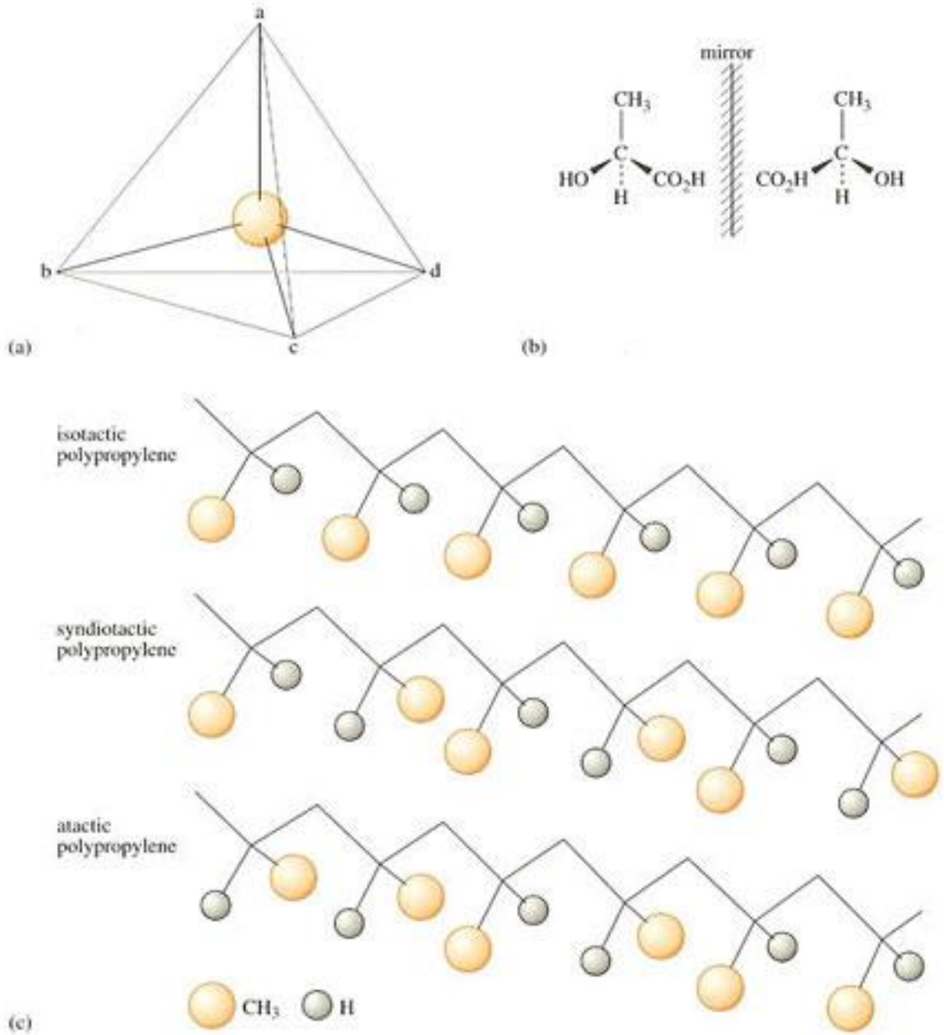


cis- polyisoprene



trans- polyisoprene

Stereo-isomerism



Another Classification

Polymers can be classified according to their **thermo physical behavior**.

Those which soften and flow upon heating are termed **thermoplastic;** those which do not are called **thermoset** polymers**.**

Thermoplastics may remain soluble and fusible under many cycles of heating and cooling**.**

Thermosets can be obtained in soluble or fusible stage in early or intermediate stage but once they get cured they will be infusible and insoluble**.**

Characteristics of Thermoplastic polymers:

•Linear or branched structure
•Polymer melts and flows upon heating
•Heat sensitive properties
•Individual polymer molecules are held together by weak Secondary forces:

- **Van der Waals forces**
- **Hydrogen bonds**
- **Dipole-dipole interactions**

Examples:

•Polypropylene
•Nylon
•Polymethyl methacrylate
•Polyethylene
•Polystyrene

Characteristics of Thermoset polymers:

- Upon application of heat, liquid resin becomes rigid via <u>Vitrification</u> process
- End polymer is less temperature sensitive than thermoplastics
- Cross linked network structure (formed from chemical bonds) exists throughout
- Cross linking provides thermal stability such that polymer will not melt or flow upon heating.

Examples

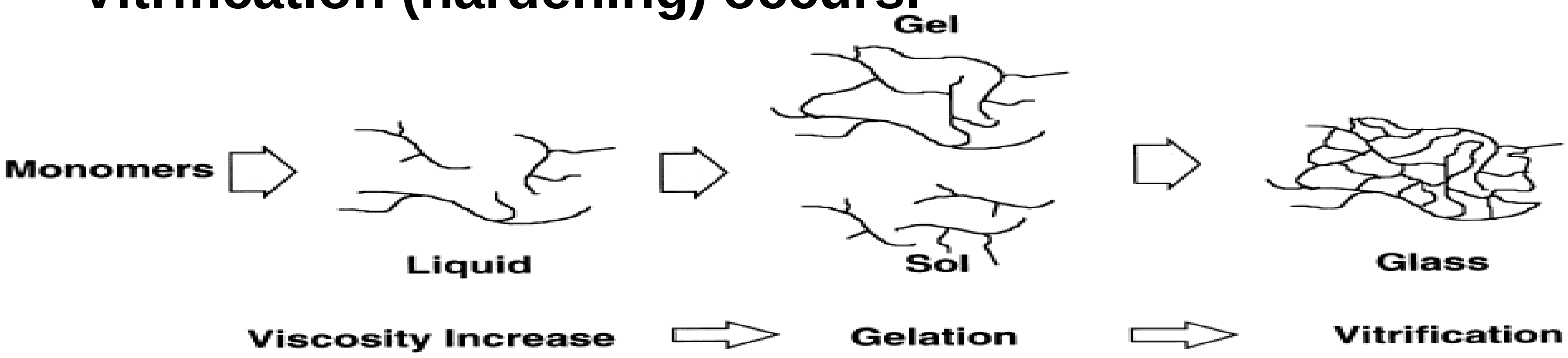
- Epoxy
- Unsaturated polyesters
- Vinyl esters
- Phenol formaldehyde
- Urethane

CURING of THERMOSETS

Viscosity of the system rises until Gelation occurs.

At this point, two phases exist: a **gel phase** and a **sol phase. The gel phase is the networked gelled part; the sol phase can be extracted with solvents.**

The amount of sol phase present decreases as the reaction progresses further. **Upon further reaction, Vitrification (hardening) occurs.**



Advantages and Disadvantages of Thermoplastics

Advantages of thermoplastics:

- **Unlimited shelf life -- won't undergo polymerization during storage or in processing unit**
- **Easy to handle (no tackiness)**
- **Recyclable -- they undergo melt and solidify cycles**
- **Easy to repair by welding, solvent bonding, etc.**
- **Postformable**

Disadvantages of thermoplastics:

Thermoplastics are prone to creep

Poor melt flow characteristics

Advantages & Disadvantages of Thermosets

Advantages of thermosets:

- **Low resin viscosity**
- **Good fiber wet-out**
- **Excellent thermal stability once polymerized**
- **Chemically resistant**
- **Creep resistant**

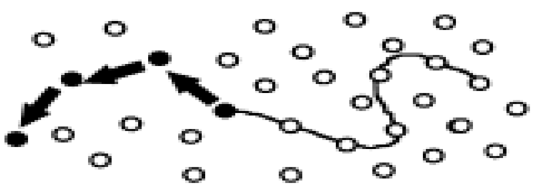
Disadvantages of thermosets:

- **Brittle**
- **Non-recyclable via standard techniques**
- **Must mold polymer in shape of final part--not postformable**

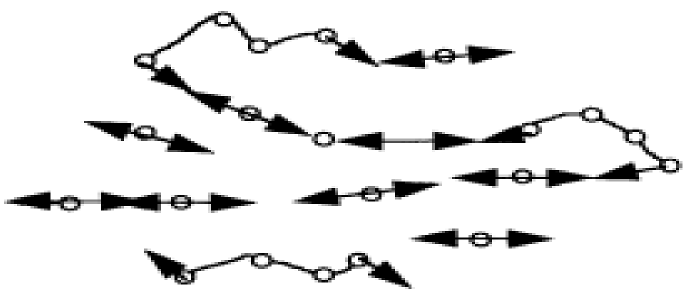
Classification Based on Polymerization Reactions

There are two fundamental polymerization reactions: **Chain polymerization** and **Step polymerization.**
This classification is of particular importance to thermosetting systems which polymerize *in situ* when used in processes.

Chain Polymerization



Step Polymerization



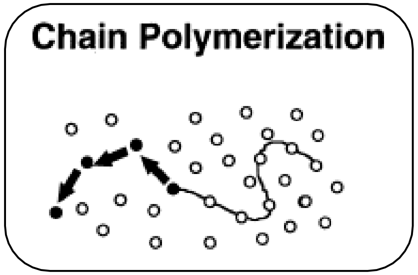
Polymerization reaction

1. Chain (addition) Polymerization
   - Monomer units are attached one at a time in chainlike fashion to form a linear macromolecule.
   - Characterized by the presence of a few active sites which react and propagate through a sea of monomers.
   - Distinct stages:
     - ✓ Initiator decomposition

       $$\mathbf{I}\ (\text{catalyst}) \longrightarrow \mathbf{2R^*}\ ,\ R^* = \text{active initiator}$$

     - ✓ Chain initiation

       $$\mathbf{R^* + M \longrightarrow RM_1^*}\ ,\ M = \text{monomer unit}$$



     - ✓ **Chain propagation** (linear growth - sequential addition)

       $$\mathbf{RM_1^* + M \longrightarrow RM_2^*}$$

       $$\mathbf{RM_{n-1}^* + M \longrightarrow RM_n^*}$$

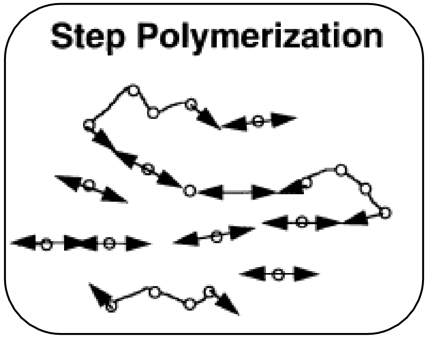
     - ✓ **Chain termination**

       $$\mathbf{RM_n^* + RM_m^* \longrightarrow R - M_{m+n} - R}$$

   - Used in the **synthesis of thermoplastics.**

Polymerization reaction

2. Step (condensation) Polymerization



- Involve more than one monomer species.
- Monomers can react with any nearby monomer.
- No special activation is needed to allow a monomer to react.
- A small molecular weight **byproduct** such as water that is **eliminated** (or condensed).

Typical reaction

1st Step: HO-R-OH + HOOC-R-COOH $\longrightarrow$ HO-ROOC-R-COOH + H_2O

2nd Step: HO-ROOC-R-COOH +HO-R-OH $\longrightarrow$ HO-ROOC-R-COOR-OH + H_2O

$$\Sigma M_n + \Sigma M_m \longrightarrow \Sigma M_{m+n} + H_2O$$

- The **thermosetting** polyesters, phenol-formaldehyde, the nylons, and the polycarbonates are produced by condensation polymerization.

Chain (or Addition) Polymerization

Chain polymerization is characterized by the presence of a few active sites which react and propagate through a sea of monomers. Polymerization may occur by any of three mechanisms:

- **free radical**
- **cationic**
- **anionic**

Vinyl monomers frequently undergo chain polymerization. Polymers formed via this process include:

- **Polyethylene**
- **Polystyrene**
- **Polypropylene**
- **Polymethyl methacrylate**

Step Polymerization

In a step reaction mechanism, monomers can react with any nearby monomer. In contrast to chain polymerization, <u>no special activation</u> is needed to allow a monomer to react.

Frequently these reactions are **Copolymerizations,** where two types of monomer are present and each reacts only with the other (and not with monomers like itself)

This type of polymerization is also called condensation polymerization because water is often liberated when the polymer bonds form.

Step Polymerization vs Chain Polymerization

Any two molecular species present can react - Reaction occurs only at active centers by adding repeating units one at a time to the chain

Monomer disappears early in the reaction - Monomer concentration decreases steadily throughout the reaction

Polymer molecular weight rises steadily throughout the reaction- High polymer is formed at once--polymer molecular weight changes little

At any stage all molecular species are present in a calculable distribution- Reaction mixture contains only monomer, high polymer, and a minuscule number of growing chains

Molecular Weight

- The molecular weight distribution is **important in thermoplastics**.
- In **thermosets**, a gelled network of essentially **infinite molecular weight** is formed, so the idea of a "molecular weight distribution" is **non-sensical**.

Two ways:-

a) Number average molecular weight (M_n): **Total weight of all the polymer molecules in a sample, divided by the total number of polymer molecules in a sample.**

Number average molecular weight, $\overline{M_n} = \frac{\sum M_i N_i}{\sum N_i} = \sum x_i M_i$

Where, $\mathbf{M_i}$ = molecular weight of i_{th} polymer chain or represents the mean (middle) molecular weight of size range i ;

$\mathbf{N_i}$ = number of chains of that molecular weight.

$\boldsymbol{x_i}$ = fraction of the total number of chains within the corresponding size range

b) Weighted average molecular weight (M_w): **It's based on the fact that a bigger molecule contains more of the total mass of the polymer sample than the smaller molecules do.**

Weighted average molecular weight, $\overline{M_w} = \frac{\sum M_i^2 N_i}{\sum M_i N_i} = \sum w_i M_i$

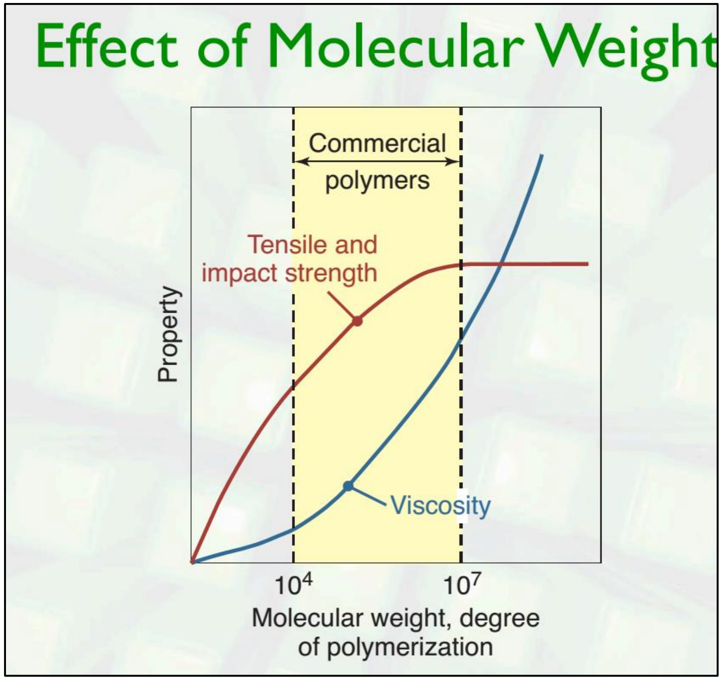
More appropriate

$\boldsymbol{w_i}$ = fraction of the total number of chains within the corresponding size range

Degree of Polymerization

$$DP = \frac{\overline{M}_n}{m}$$

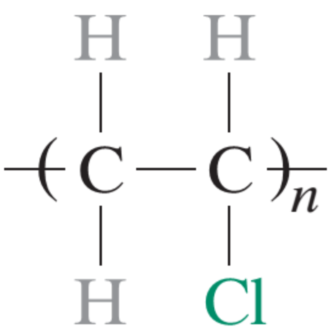
where, $\overline{M_n}$ = Number average molecular weight
m = repeat unit molecular weight (no. of atoms x atomic wt.)



Reference: Kalpakjian, Schmid - Manufacturing Processes for Engineering Materials, 5th ed.

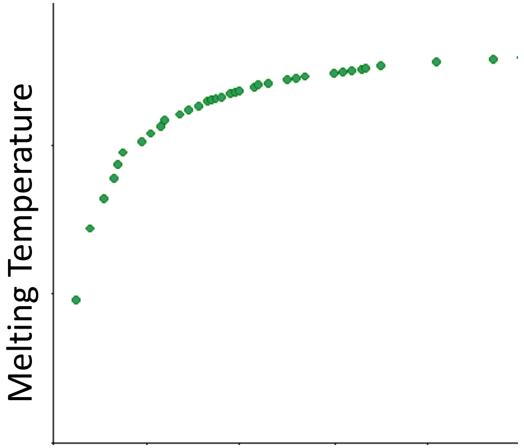
Example: Suppose for **Polyvinyl chloride**, $\overline{M}_n$ = 21,150 g/mol
Then, repeat unit molecular weight, m = 2 x 12 + 3 x 1 + 1 x 35
= 62 g/mol

DP = $\frac{21,150}{62} = 341$



PVC

Repeat unit contains – 2 carbon, 3 hydrogen and 1 chlorine atom

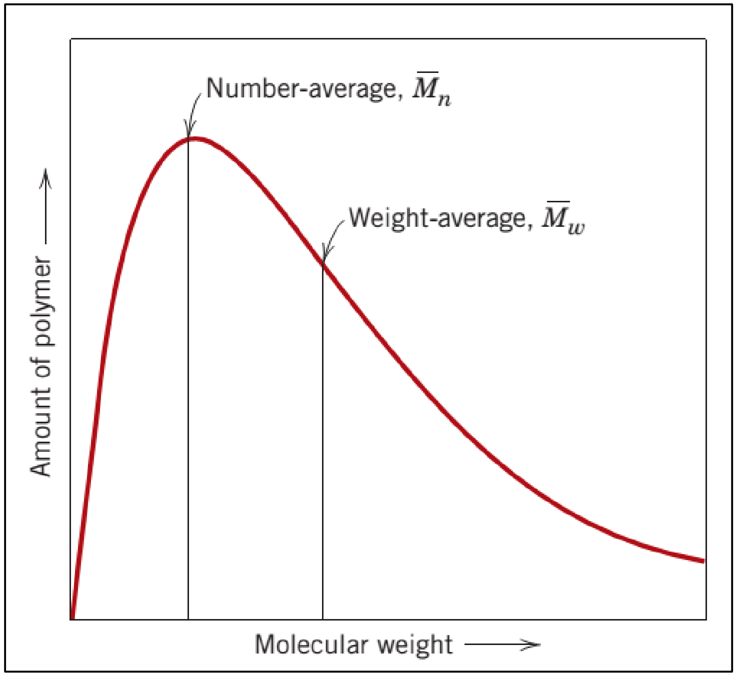


Smart Materials Structures and Systems Laboratory
IIT Kanpur

Polydispersity Index

Polydispersity index,PI = $\frac{\overline{M_w}}{\overline{M_n}}$

- The larger the polydispersity index, the broader the molecular weight.
- Monodisperse polymer, where all the chain lengths are equal (such as a protein) has an PI = 1.
- Step polymerization reactions typically yield values of PI ≈ 2.0
- Chain polymerization reactions yield values between PI = 1.5 - 20.



Distribution of molecular weights for a typical polymer

Reference: W.D Callister, 7 Ed.

Example

No. of molecules (N_i)	Mass of each molecule (M_i) (g/mol)	Total mass of each type of molecule, (N_iM_i) in g/mol	$M_i^2 N_i$
1	800,000	800,000	6.4 x 10^{11}
3	750,000	2250,000	16.8 x 10^{11}
5	700,000	3500,000	24.5 x 10^{11}
8	650,000	5200,000	33.8 x 10^{11}
10	600,000	6000,000	36 x 10^{11}
13	550,000	7150,000	39.3 x 10^{11}
20	500,000	10,000,000	50 x 10^{11}
13	450,000	5850,000	26.3 x 10^{11}
10	400,000	4000,000	16 x 10^{11}
8	350,000	2800,000	98 x 10^{11}
5	300,000	1500,000	4.5 x 10^{11}
3	250,000	750,000	18.75 x 10^{11}
1	200,000	200,000	0.4x 10^{11}
$\sum N_i = 100$		$\sum M_i N_i$ = 50,000,000 (Total mass)	$\sum M_i^2 N_i$ = 370.75 x 10^{11}

Number average molecular weight, $\overline{M_n} = \frac{\sum M_i N_i}{\sum N_i}$

$= \frac{50,000,000}{100}$ = 500,000 g/mol

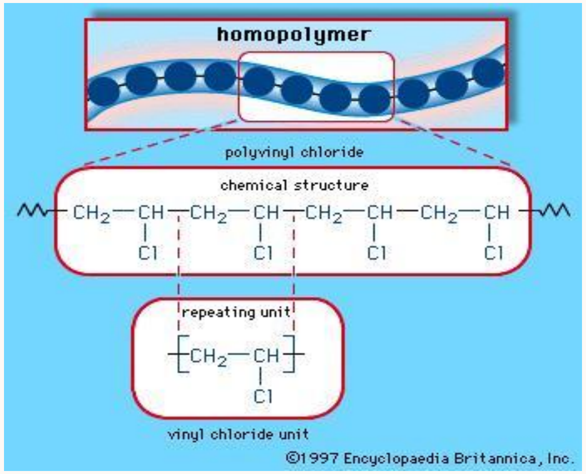
Weighted average molecular weight, $\overline{M_w} = \frac{\sum M_i^2 N_i}{\sum M_i N_i}$

$= \frac{370.75 \text{ x } 1011}{50,000,000} = 741,500$ g/mol

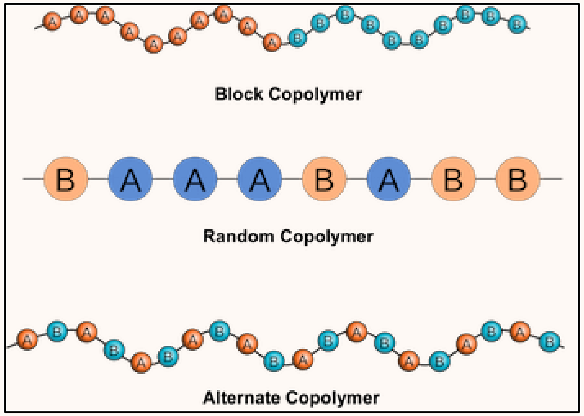
Polydispersity index, PI = $\frac{\overline{M_w}}{\overline{M_n}} = 1.48$

Chemistry of Polymer molecules

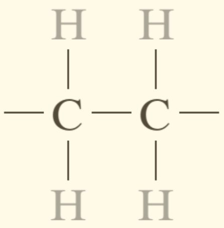
- When all the mers are the same, the molecule is called a **Homo-polymer**.



- When there is more than one type of mer present, the molecule is a **Co-polymer.**

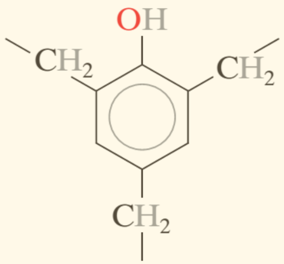


- Mer units that have **2 active bonds** to connect with **other mers** are called bi-functional.



Polyethylene

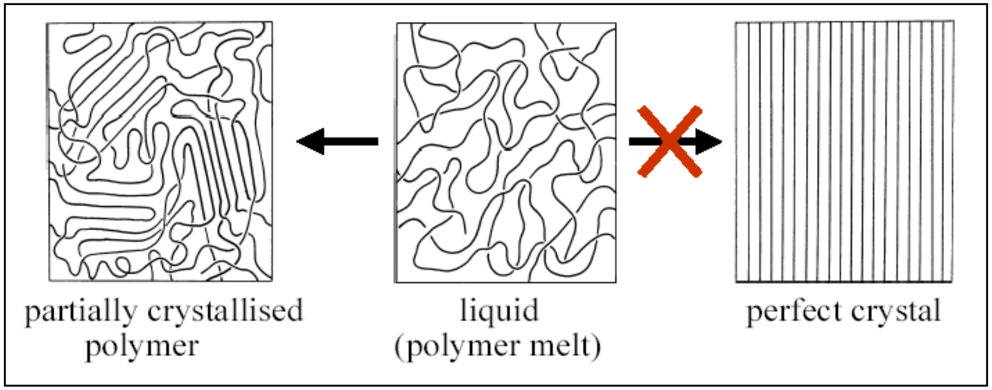
- Mer units that have **3 active bonds** to connect with other mers are called tri-functional. They form 3-D molecular network structures.



Phenol-formaldehyde (Bakelite)

Possible Physical States for Polymer Materials

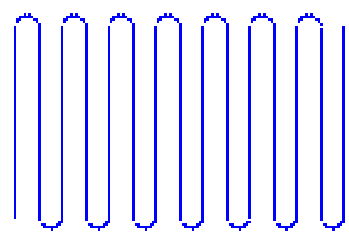
Traditional classification of physical states (gases, liquids, crystals) is not informative for polymer materials.

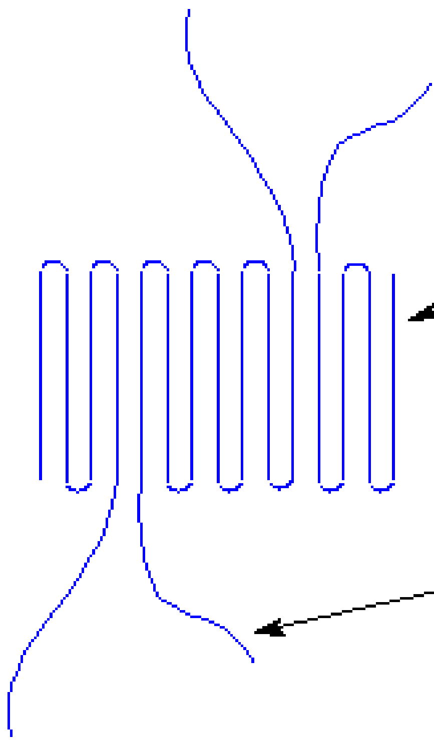


Classification of polymer materials:-

- Partially crystalline state
- Viscoelastic State
- Highly elastic state (e.g. Rubbers)
- Glassy state (e.g. Organic glasses from poly(styrene), poly(methylmethacrylate), poly(vinyl chloride))

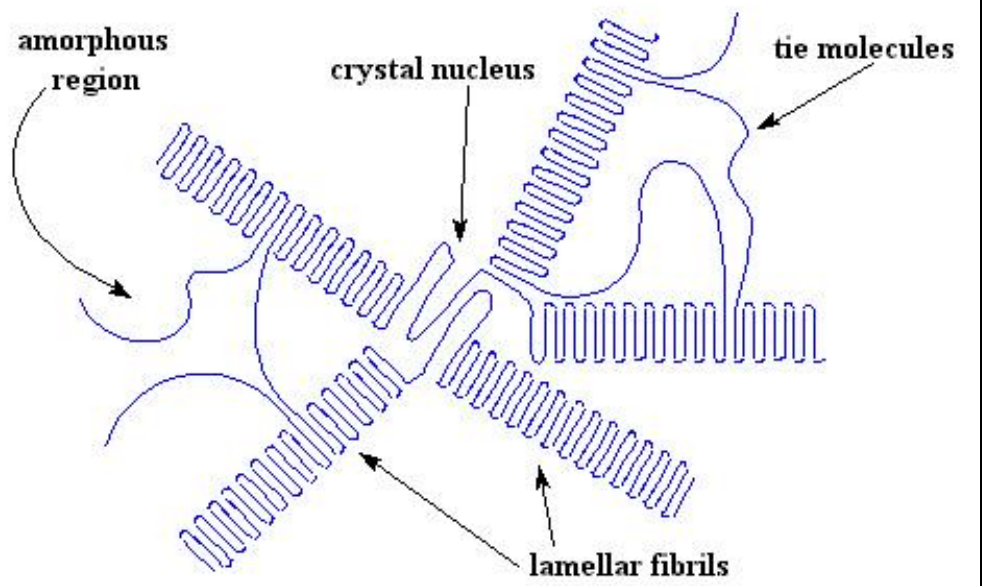
Most polymers don't stretch out fully, like this. Instead, they fold back on themselves after going straight for a short distance, like this.





Sometimes a polymer chain is indecisive, and part of it is in the crystalline lamella, but part of it stays outside the lamella, in the amorphous region.

- ✓ Lamella grow like the spokes of a bicycle wheel from a central nucleus.
- ✓ The whole assembly is called a *Spherulite*. In a sample of a crystalline polymer weighing only a few grams, there are many billions of Spherulites.



a polymer crystalline spherulite

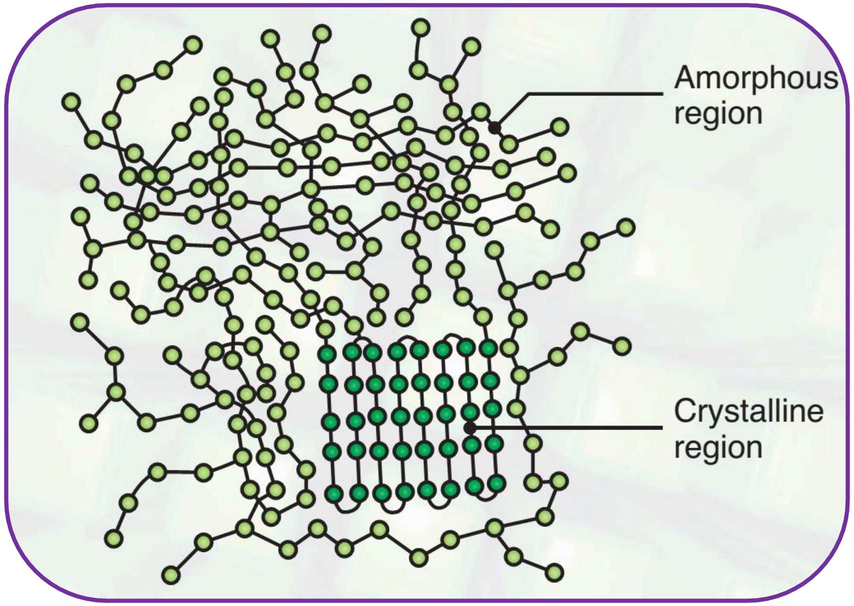
Crystallinity

Crystalline region: Orderly arrangement of molecular chains.

✓ **High crystallinity** means - **higher density**, **more strength**, **higher resistance** to both dissolution and softening by heating.

Degree of crystallinity in Polymers

- Ranges from completely amorphous to about 95% crystalline.
- Metal specimens are almost always entirely crystalline.
- Ceramics are either totally crystalline or totally non-crystalline.



For same material & molecular weight

$$\rho_{crystalline\ polymer} > \rho_{amorphous\ polymer}$$

(due to close packing)

Remember: No polymer is 100% crystalline

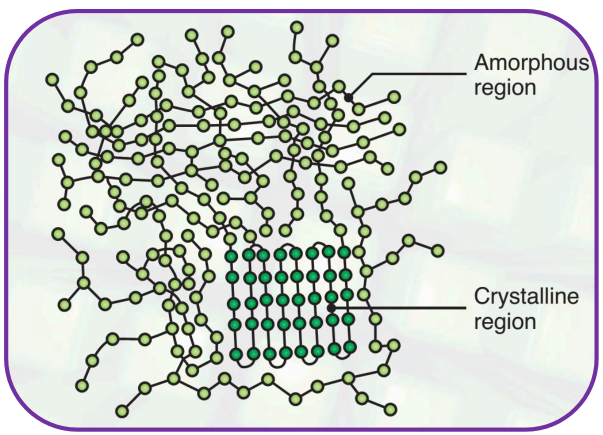
Reference: Kalpakjian, Schmid - Manufacturing Processes for Engineering Materials, 5th ed.

Crystallinity dependence

Degree of crystallinity is affected by:-

- ✓ **Rate of cooling during solidification**
  - ➢ More the rapid cooling – lesser the time for alignment – poorer the crystallinity.

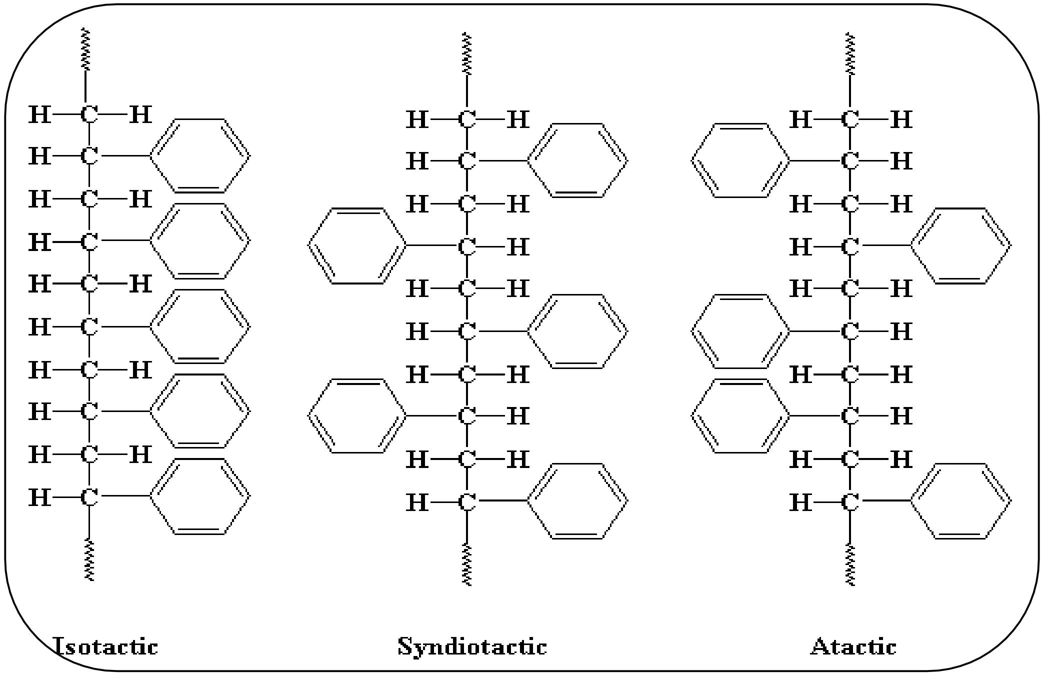
- ✓ **Chain configuration**
  - ➢ More the side branching & cross linking - **more the restriction** to prevent the **chain alignment** – **lesser** the **crystallinity** .
  - ➢ Thus, linear polymer have high degree of crystallinity.
  - ➢ Most network and crosslinked polymers are almost totally amorphous.



Reference: Kalpakjian, Schmid - Manufacturing Processes for Engineering Materials, 5th ed.

Tacticity in Polymers

- ✓ Different atomic configurations for the same composition.
- ✓ Tacticity is the way pendant groups are arranged along the backbone chain of a polymer.
- ✓ Isotactic & Syndiotactic – **regular geometry facilitates** fitting of adjacent chain, thus **more crystalline.**
- ✓ Atactic – Poorly Crystalline due to irregularity of side group.
- ✓ Also, larger the side-bonded groups of atoms - the less is the tendency for crystallization.



Stereoisomers

Some Highly Crystalline Polymers:

- ✓ Polypropylene
- ✓ Syndiotactic polystyrene
- ✓ Nylon
- ✓ Kevlar and Nomex

Some Highly Amorphous Polymers

- ✓ Poly(methyl-methacrylate), PMMA
- ✓ Atactic polystyrene
- ✓ Polycarbonate
- ✓ Polyisoprene

% Crystallinity

$$\% \, Crystallinity = \frac{\rho_c(\rho_s - \rho_a)}{\rho_s(\rho_c - \rho_a)} \text{ x } 100$$

where, ρ_s : Density of specimen

ρ_a : Density of the totally amorphous polymer,

ρ_c : Density of the perfectly crystalline polymer

The values of ρ_s, ρ_a and ρ_c are measured by experimental means.