Polymeric Structure

Contents

- ✓ Concept of molecular weight
- ✓ Chemistry of polymers
- ✓ % Crystallinity
- ✓ Tacticity in polymers

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, $\overline{M_n} = \dfrac{\sum M_i N_i}{\sum N_i}$

Where, $\mathbf{M_i}$ = molecular weight of i_{th} polymer chain;
$\mathbf{N_i}$ = number of chains of that molecular weight.

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, $\overline{M_w} = \dfrac{\sum M_i^2 N_i}{\sum M_i N_i}$

More appropriate

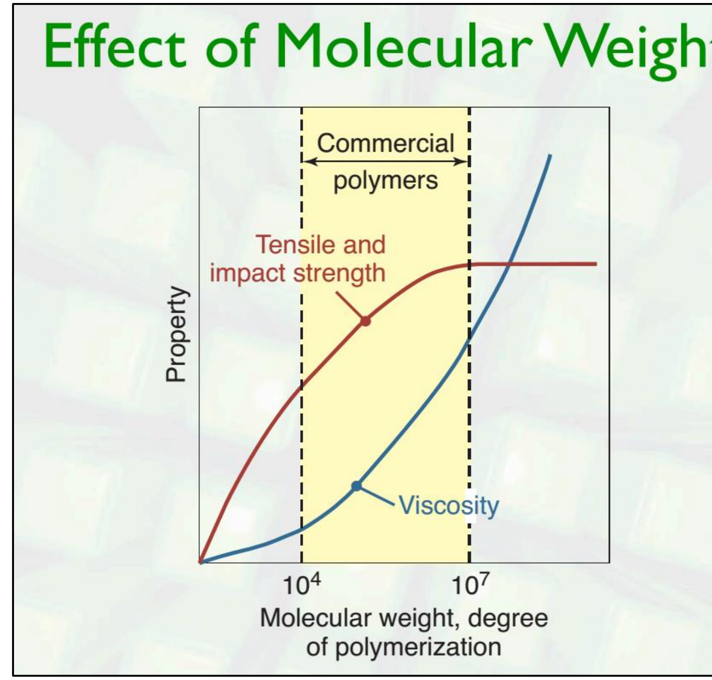
Degree of Polymerization

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

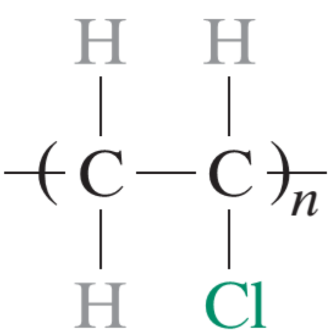
where, $\overline{M_n}$ = Number average molecular weight
m = repeat unit molecular weight (no. of atoms x atomic wt.)

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

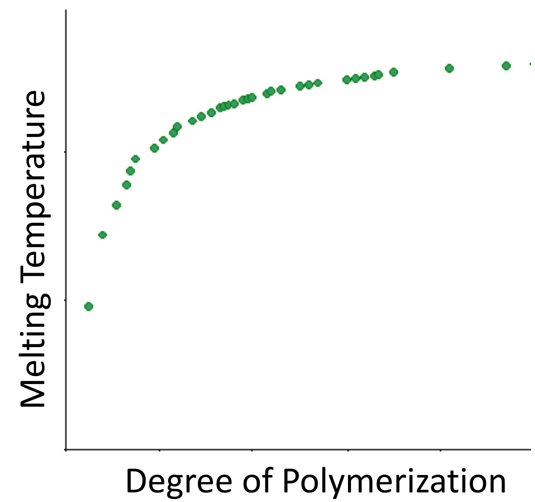


Reference: Kalpakjian, Schmid - Manufacturing Processes for Engineering Materials, 5th ed.



PVC

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



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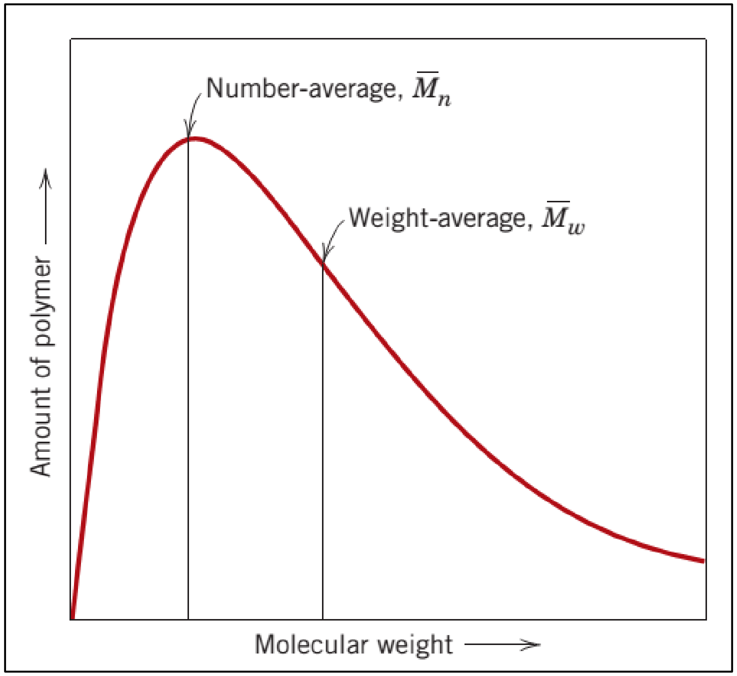
Polydispersity Index

Polydispersity index, PI = $\dfrac{M_w}{M_n}$

- 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

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

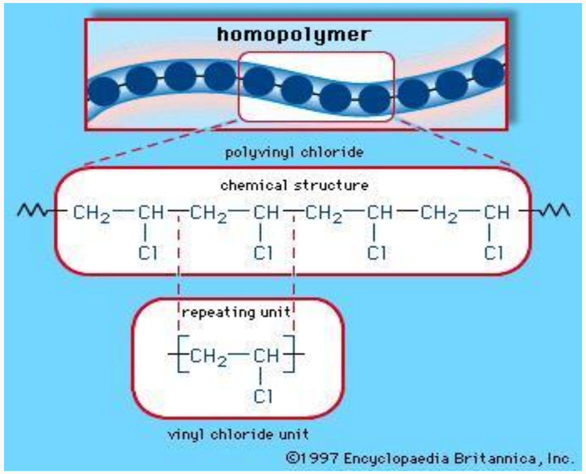
Weighted average molecular weight, $\overline{M_w} = \frac{\sum M_i^2 N_i}{\sum M_i N_i}$

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

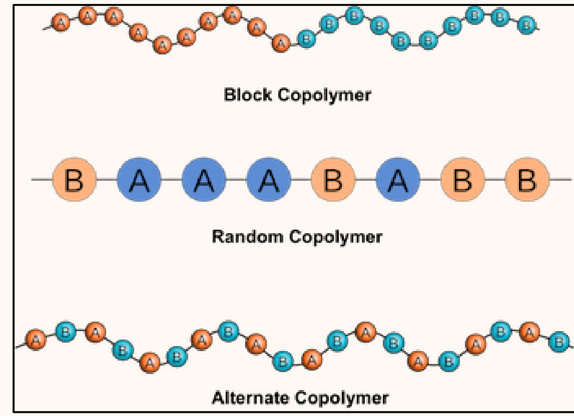
Polydispersity index, PI = $\frac{M_w}{M_n} = 1.48$

Chemistry of Polymer molecules

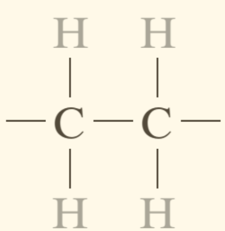
- When all the mers are the same, the molecule is called a **Homo-polymer**.



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

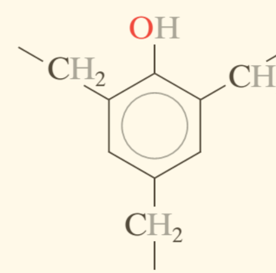


- Mer units that have **2 active bonds** to connect with **other mers** are called bi-functional.



Polyethylene

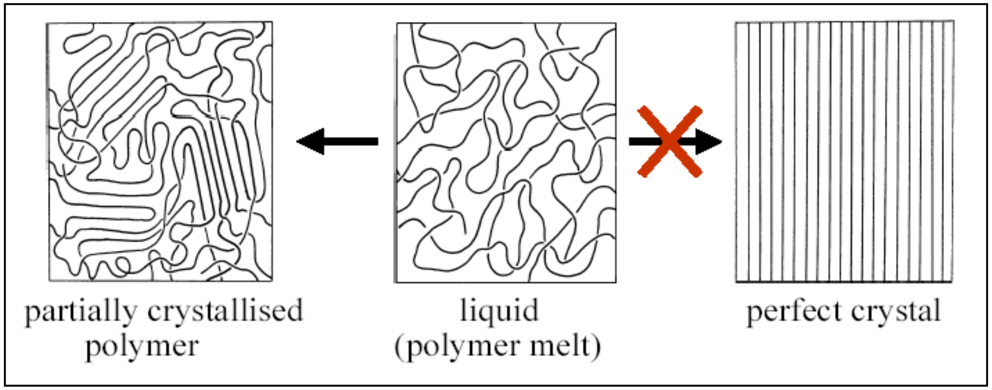
- Mer units that have **3 active bonds** to connect with other mers are called tri-functional. They form 3-D molecular network structures.



Phenol-formaldehyde (Bakelite)

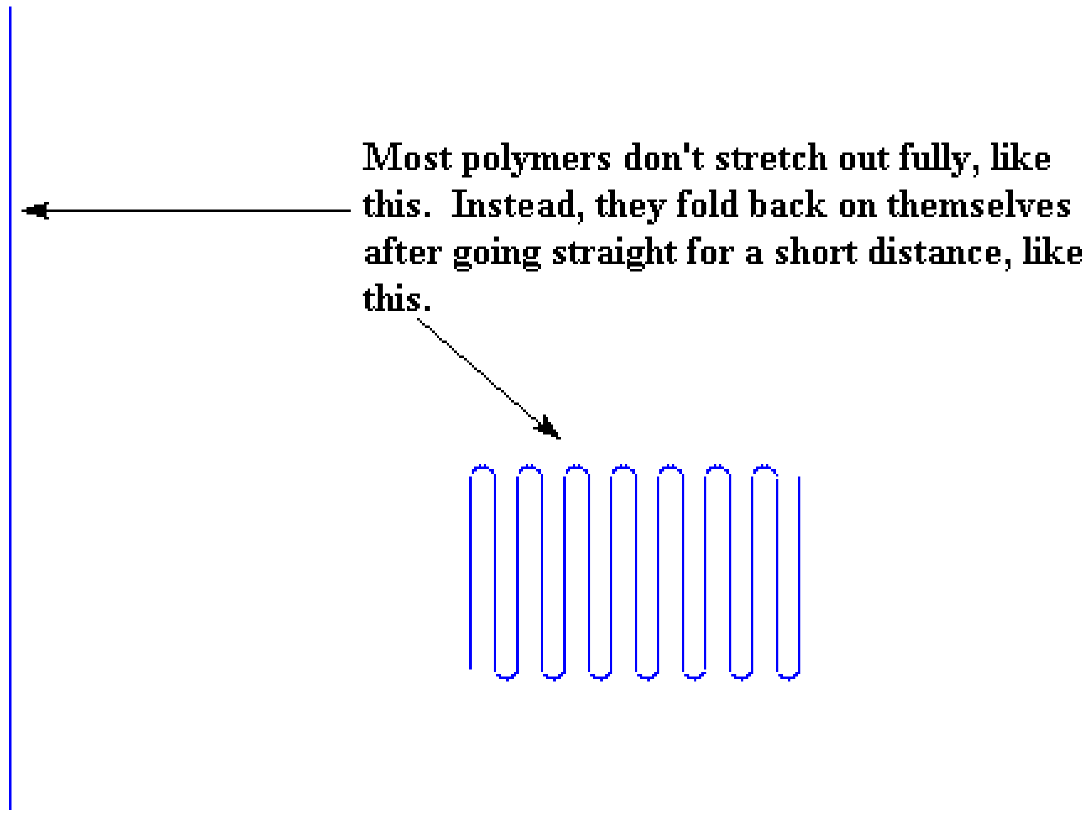
Possible Physical States for Polymer Materials

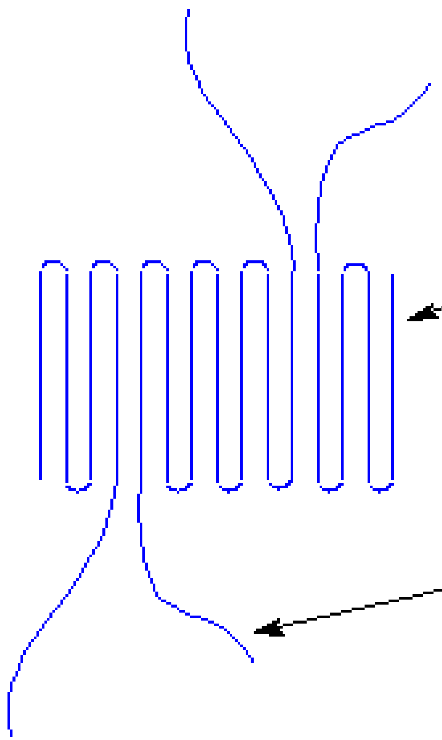
Traditional classification of physical states (gases, liquids, crystals) is not informative for polymer materials.



Classification of polymer materials:-

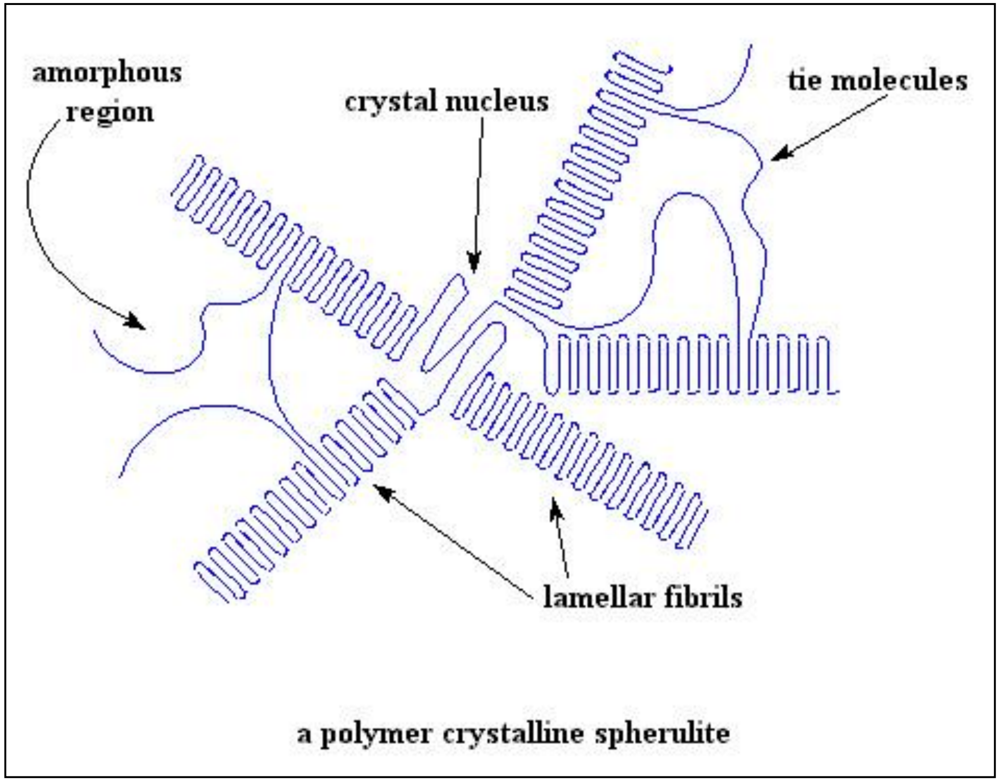
- Partially crystalline state
- Viscoelastic State (polymer melt)
- Highly elastic state (e.g. Rubbers)
- Glassy state (e.g. Organic glasses from poly(styrene), poly(methylmethacrylate), poly(vinyl chloride))


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.



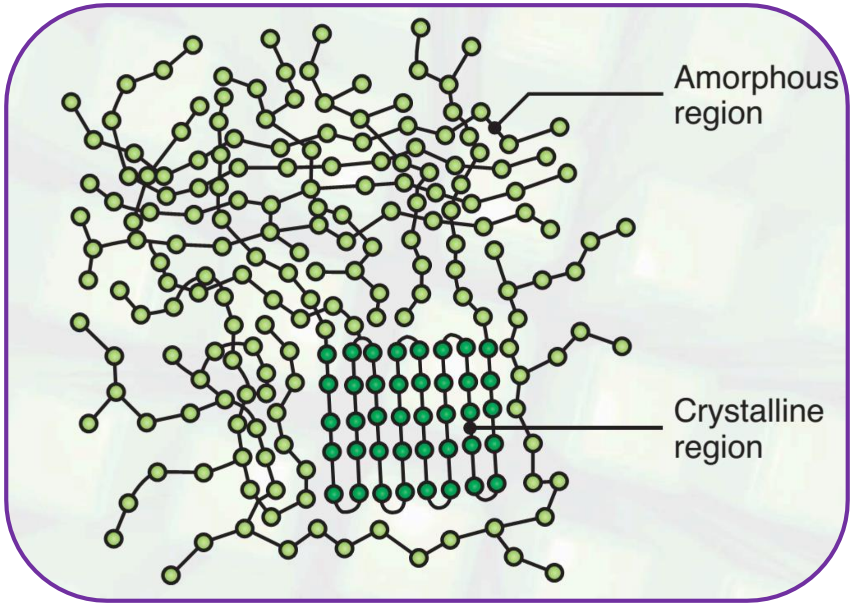
Crystallinity

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

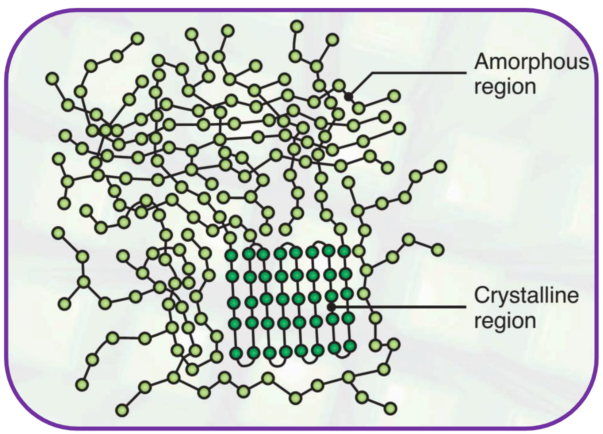
Reference: Kalpakjian, Schmid - Manufacturing Processes for Engineering Materials, 5th ed.

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.



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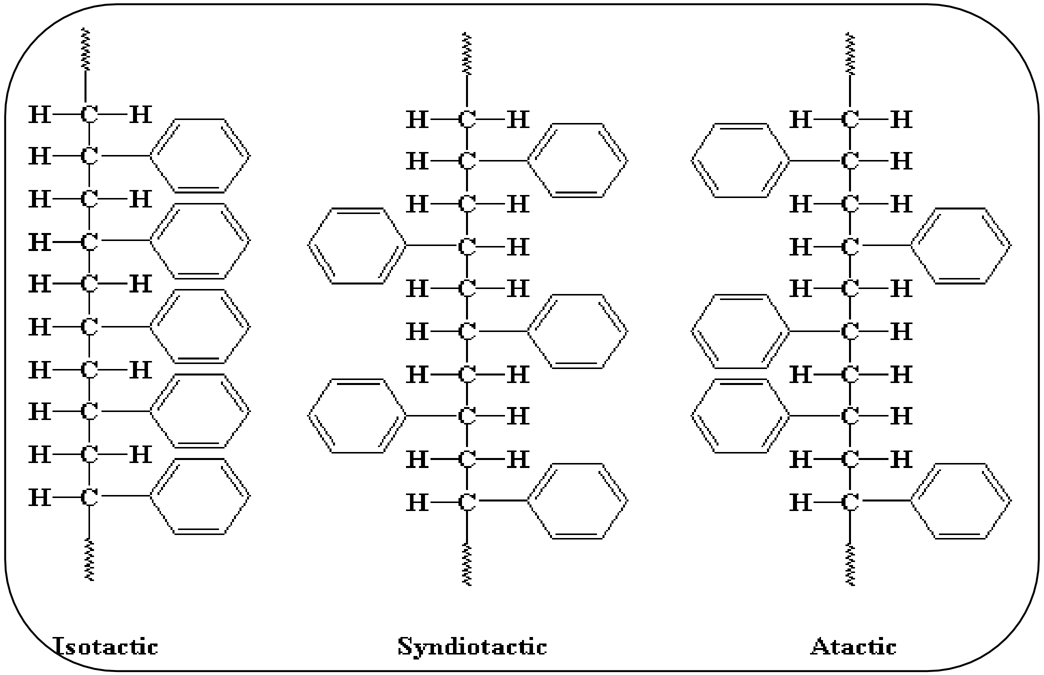
Tacticity in Polymers

- ✓ 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.

In the **next lecture**, we will learn about:

- ✓ Glass Transition temperature (T_g)
- ✓ Experimental methods to determine T_g
- ✓ Factors affecting T_g

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