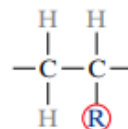*MTN - 208*

*Engineering Polymers and Composites*

*Lecture 2*
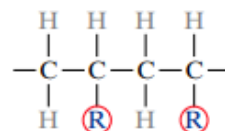
*Prof. Anjan Sil*

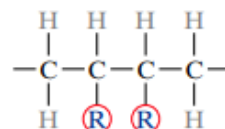*MMED, IIT Roorkee*

## 14.8 MOLECULAR CONFIGURATIONS

For polymers having more than one side atom or group of atoms bonded to the main chain, the regularity and symmetry of the side group arrangement can significantly influence the properties. Consider the repeat unit

$$\begin{array}{c} H \quad H \\ | \quad\; | \\ -C-C- \\ | \quad\; | \\ H \quad \textcircled{R} \end{array}$$

in which R represents an atom or side group other than hydrogen (e.g., Cl, $CH_3$). One arrangement is possible when the R side groups of successive repeat units are bound to alternate carbon atoms as follows:

$$\begin{array}{c} H \quad H \quad H \quad H \\ | \quad\; | \quad\; | \quad\; | \\ -C-C-C-C- \\ | \quad\; | \quad\; | \quad\; | \\ H \quad \textcircled{R} \quad H \quad \textcircled{R} \end{array}$$

This is designated as a head-to-tail configuration.[7] Its complement, the head-to-head configuration, occurs when R groups are bound to adjacent chain atoms:

$$\begin{array}{c} H \quad H \quad H \quad H \\ | \quad\; | \quad\; | \quad\; | \\ -C-C-C-C- \\ | \quad\; | \quad\; | \quad\; | \\ H \quad \textcircled{R} \quad \textcircled{R} \quad H \end{array}$$

In most polymers, the head-to-tail configuration predominates; often a polar repulsion occurs between R groups for the head-to-head configuration.

Isomerism (Section 14.2) is also found in polymer molecules, wherein different atomic configurations are possible for the same composition. Two isomeric subclasses, stereoisomerism and geometrical isomerism, are topics of discussion in the succeeding sections.

## Stereoisomerism

**Stereoisomerism** denotes the situation in which atoms are linked together in the same order (head-to-tail) but differ in their spatial arrangement. For one stereoisomer, all of the R groups are situated on the same side of the chain as follows:
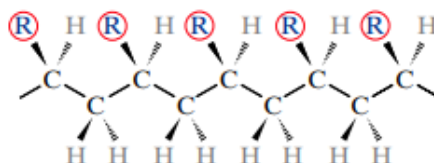
This is called an **isotactic configuration.** This diagram shows the zigzag pattern of the carbon chain atoms. Furthermore, representation of the structural geometry in three dimensions is important, as indicated by the wedge-shaped bonds; solid wedges represent bonds that project out of the plane of the page, and dashed ones represent bonds that project into the page.[8]

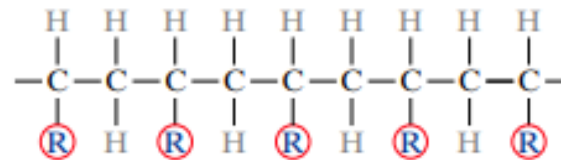In a **syndiotactic configuration,** the R groups alternate sides of the chain:[9]
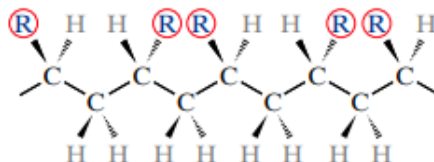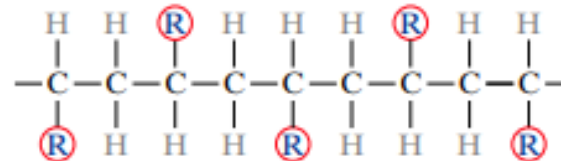
and for random positioning.
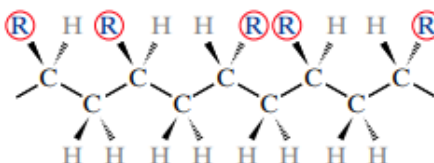
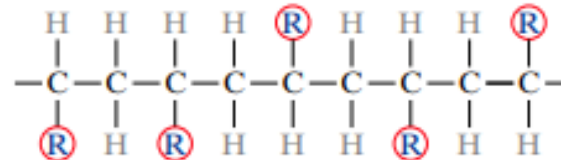the term **atactic configuration** is used.[10]

[8] The isotactic configuration is sometimes represented using the following linear (i.e., nonzigzag) and two-dimensional schematic:



[9] The linear and two-dimensional schematic for syndiotactic is represented as



[10] For atactic the linear and two-dimensional schematic is

Conversion from one stereoisomer to another (e.g., isotactic to syndiotactic) is not possible by a simple rotation about single chain bonds;

these bonds must first be severed, and then, after the appropriate rotation, they are re-formed.

In reality, a specific polymer does not exhibit just one of these configurations; the predominant form depends on the method of synthesis.
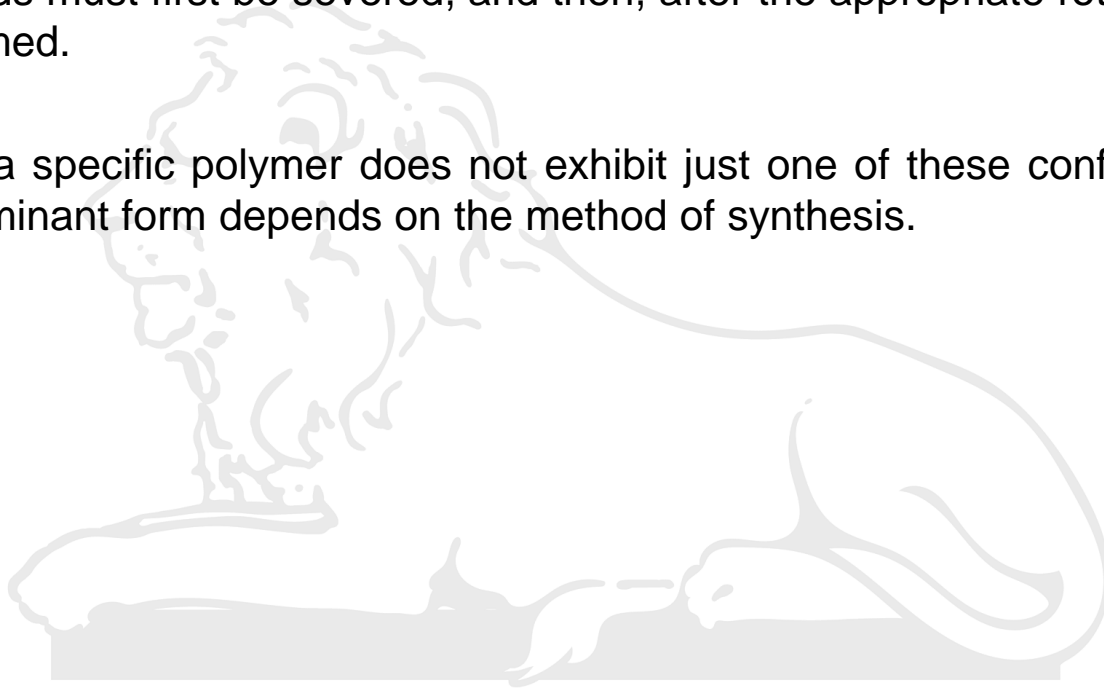
### Geometrical Isomerism

Other important chain configurations, or geometrical isomers, are possible within repeat units having a double bond between chain carbon atoms. Bonded to each of the carbon atoms participating in the double bond is a side group, which may be situated on one side of the chain or its opposite. Consider the isoprene repeat unit having the structure
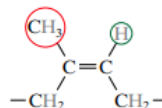
**cis (structure)**

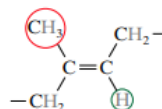in which the $CH_3$ group and the H atom are positioned on the same side of the double bond. This is termed a **cis** structure, and the resulting polymer, *cis*-polyisoprene, is natural rubber. For the alternative isomer

**trans (structure)**

the **trans** structure, the $CH_3$ and H reside on opposite sides of the double bond.[11] *Trans*-polyisoprene, sometimes called gutta percha, has properties that are distinctly different from natural rubber as a result of this configurational alteration. Conversion of trans to cis, or vice versa, is not possible by a simple chain bond rotation because the chain double bond is extremely rigid.

Summarizing the preceding sections, polymer molecules may be characterized in terms of their size, shape, and structure. Molecular size is specified in terms of molecular weight (or degree of polymerization). Molecular shape relates to the degree of chain twisting, coiling, and bending. Molecular structure depends on the manner in which structural units are joined together. Linear, branched, crosslinked,

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[11]For *cis*-isoprene the linear chain representation is as follows:
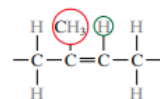


whereas the linear schematic for the trans structure is
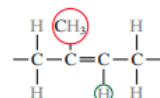
## THERMOPLASTIC AND THERMOSETTING POLYMERS

The response of a polymer to mechanical forces at elevated temperatures is related to its dominant molecular structure. In fact, one classification scheme for these materials is according to behavior with rising temperature.

Thermoplastics (or thermoplastic polymers) and thermosets (or thermosetting polymers) are the two subdivisions.

Thermoplastics soften when heated (and eventually liquefy) and harden when cooled— processes that are totally reversible and may be repeated.

On a molecular level, as the temperature is raised, secondary bonding forces are diminished (by increased molecular motion) so that the relative movement of adjacent chains is facilitated when a stress is applied.

Irreversible degradation results when a molten thermoplastic polymer is raised to too high a temperature. In addition, thermoplastics are relatively soft.

Most linear polymers and those having some branched structures with flexible chains are thermoplastic.

These materials are normally fabricated by the simultaneous application of heat and pressure.

Examples of common thermoplastic polymers include polyethylene, polystyrene, poly(ethylene terephthalate), and poly(vinyl chloride).

**Thermosetting polymers are network polymers.**

They become permanently hard during their formation and do not soften upon heating.

Network polymers have covalent crosslinks between adjacent molecular chains.

During heat treatments, these bonds anchor the chains together to resist the vibrational and rotational chain motions at high temperatures.

Thus, the materials do not soften when heated. Crosslinking is usually extensive, in that 10 to 50% of the chain repeat units are crosslinked.

Only heating to excessive temperatures will cause severance of these crosslink bonds and polymer degradation.

Thermoset polymers are generally harder and stronger than thermoplastics and have better dimensional stability.

Most of the crosslinked and network polymers, which include vulcanized rubbers, epoxies, and phenolics and some polyester resins, are thermosetting.

## COPOLYMERS

Polymer chemists and scientists are continually searching for new materials that can be easily and economically synthesized and fabricated, with improved properties or better property combinations than are offered by the homopolymers previously discussed.

One group of these materials are the copolymers.

Consider a copolymer that is composed of two repeat units as represented by and in Figure 14.9.

Depending on the polymerization process and the relative fractions of these repeat unit types, different sequencing arrangements along the polymer chains are possible.

For one, as depicted in Figure 14.9a, the two different units are randomly dispersed along the chain in what is termed a random copolymer.

For an alternating copolymer, as the name suggests, the two repeat units alternate chain positions, as illustrated in Figure 14.9b.

A block copolymer is one in which identical repeat units are clustered in blocks along the chain (Figure 14.9c).

Finally, homopolymer side branches of one type may be grafted to homopolymer main chains that are composed of a different repeat unit; such a material is termed a graft copolymer (Figure 14.9d).

When calculating the degree of polymerization for a copolymer, the value m in Equation 14.7 is replaced with the average value that is determined from (14.7)

$$\overline{m} = \Sigma \quad f_j m_j$$

In this expression, $f_j$ and $m_j$ are, respectively, the mole fraction and molecular weight of repeat unit $j$ in the polymer chain.
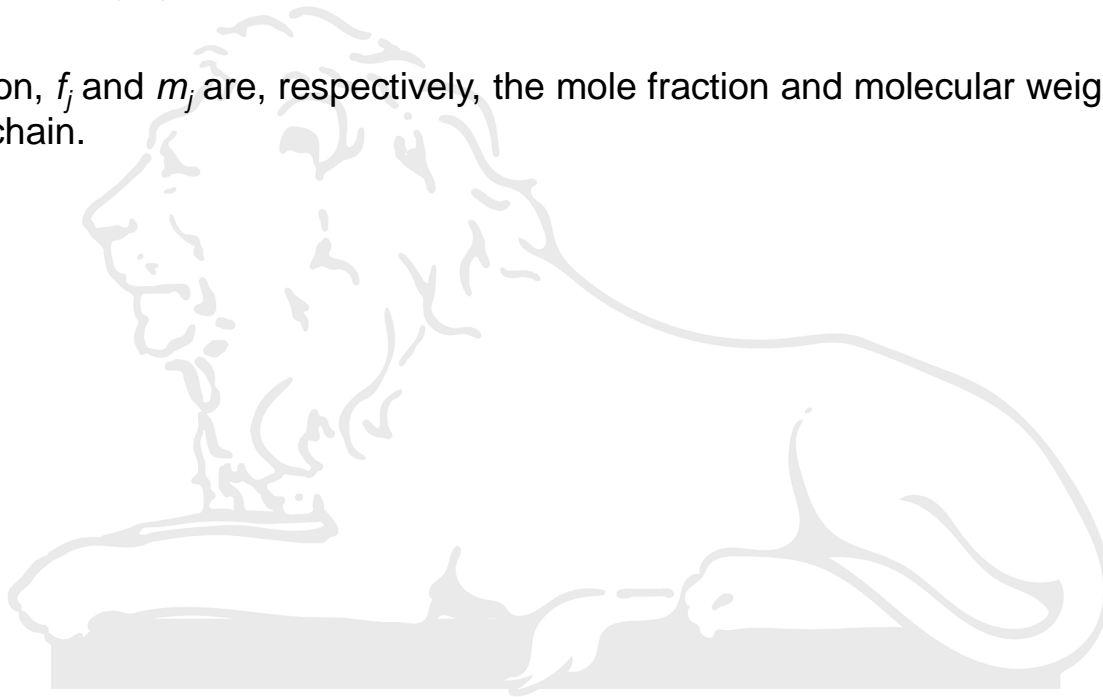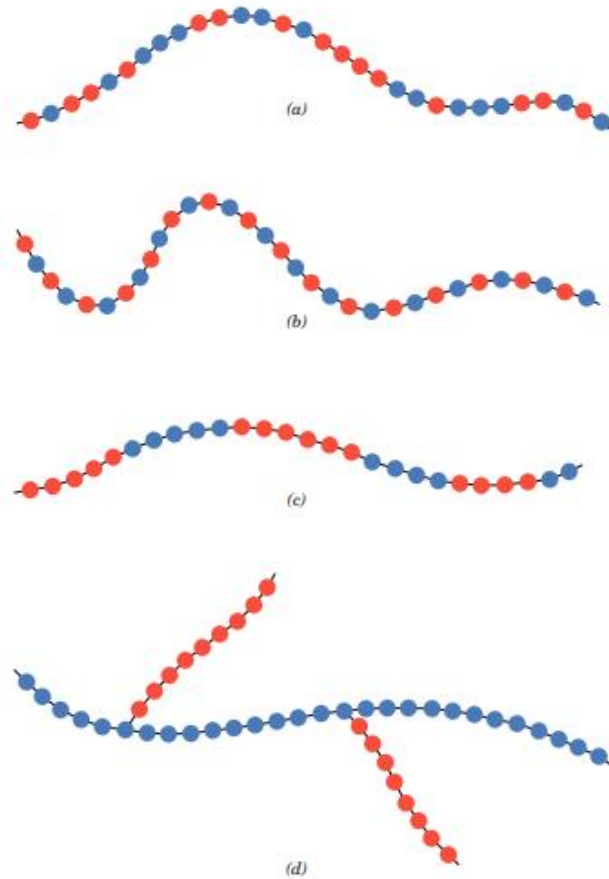
**Figure 14.9** Schematic representations of (*a*) random, (*b*) alternating, (*c*) block, and (*d*) graft copolymers. The two different repeat unit types are designated by blue and red circles.

Synthetic rubbers, discussed in Section 15.16, are often copolymers; chemical repeat units that are employed in some of these rubbers are shown in Table 14.5.

Styrene–butadiene rubber (SBR) is a common random copolymer from which automobile tires are made.

Nitrile rubber (NBR) is another random copolymer composed of acrylonitrile and butadiene.

It is also highly elastic and, in addition, resistant to swelling in organic solvents; gasoline hoses are made of NBR.

Impact-modified polystyrene is a block copolymer that consists of alternating blocks of styrene and butadiene. The rubbery isoprene blocks act to slow cracks propagating through the material.
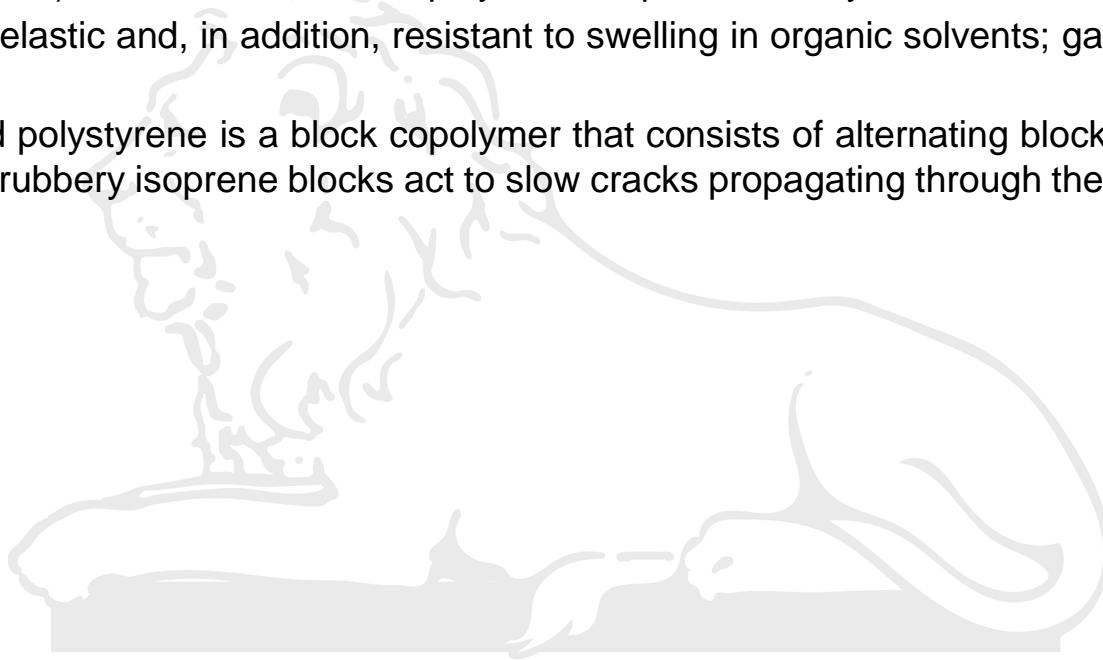
**Table 14.5  Chemical Repeat Units That Are Employed in Copolymer Rubbers**

| Repeat Unit Name | Repeat Unit Structure | Repeat Unit Name | Repeat Unit Structure |
|---|---|---|---|
| *VMSE* Acrylonitrile |  | *VMSE* Isoprene |  |
| **Repeat Units for Rubbers** *VMSE* Styrene |  | *VMSE* Isobutylene |  |
| *VMSE* Butadiene |  | *VMSE* Dimethylsiloxane |  |
| *VMSE* Chloroprene |  | | |

## POLYMER CRYSTALLINITY

The crystalline state may exist in polymeric materials. However, because it involves molecules instead of just atoms or ions, as with metals and ceramics, the atomic arrangements will be more complex for polymers.

We think of polymer crystallinity as the packing of molecular chains to produce an ordered atomic array.

Crystal structures may be specified in terms of unit cells, which are often quite complex.

For example, Figure shows the unit cell for polyethylene and its relationship to the molecular chain structure; this unit cell has orthorhombic geometry.

Of course, the chain molecules also extend beyond the unit cell.
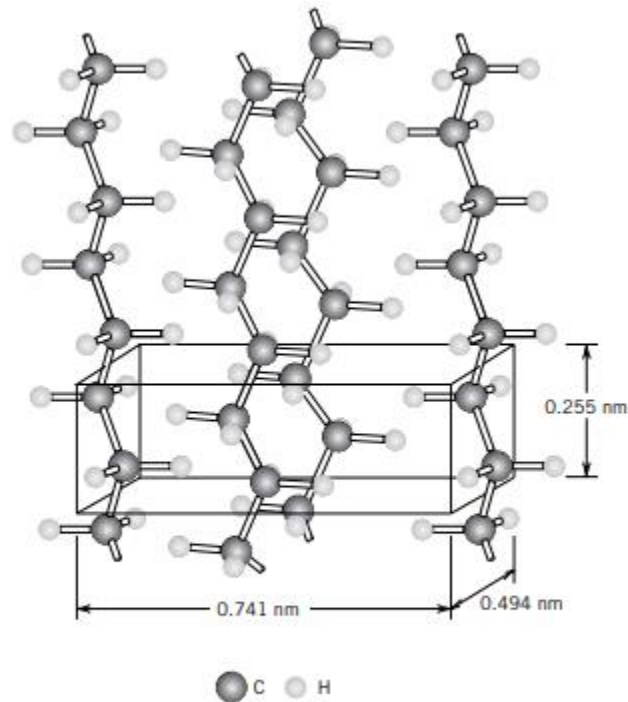
**Figure 14.10** Arrangement of molecular chains in a unit cell for polyethylene. (Adapted from C. W. Bunn, *Chemical Crystallography*, Oxford University Press, Oxford, 1945, p. 233.)

0.255 nm

0.741 nm

0.494 nm

C    H

Molecular substances having small molecules (e.g., water and methane) are normally either totally crystalline (as solids) or totally amorphous (as liquids).

Polymer molecules are often only partially crystalline (or semicrystalline), having crystalline regions dispersed within the remaining amorphous material.

Any chain disorder or misalignment will result in an amorphous region, a condition that is fairly common,

because (i) twisting, (ii) kinking, and (iii) coiling of the chains

prevent the strict ordering of every segment of every chain.

Other structural effects are also influential in determining the extent of crystallinity.
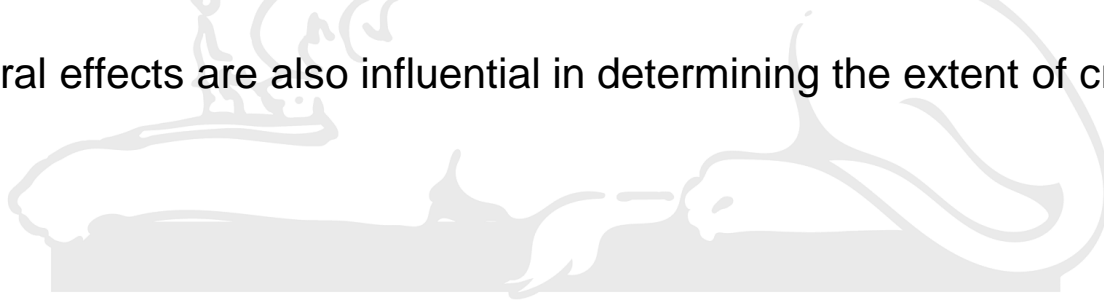
The **degree of crystallinity** may range from completely amorphous to almost entirely (up to about 95%) crystalline; in contrast, metal specimens are almost always entirely crystalline, whereas many ceramics are either totally crystalline or totally noncrystalline.

Semicrystalline polymers are, in a sense, analogous to two phase metal alloys.
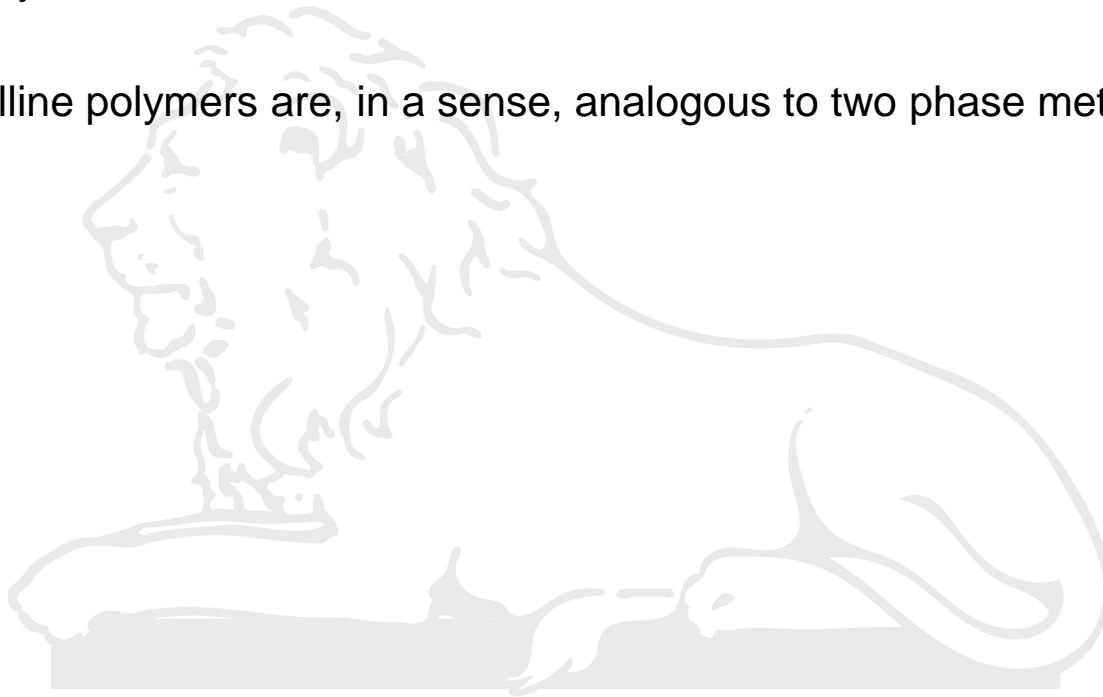
The density of a crystalline polymer will be greater than an amorphous one of the same material and molecular weight, because the chains are more closely packed together for the crystalline structure. The degree of crystallinity by weight may be determined from accurate density measurements, according to

$$\% \text{ crystallinity} = \frac{\rho_c(\rho_s - \rho_a)}{\rho_s(\rho_c - \rho_a)} \times 100 \qquad (14.8)$$

where $\rho_s$ is the density of a specimen for which the percent crystallinity is to be determined, $\rho_a$ is the density of the totally amorphous polymer, and $\rho_c$ is the density of the perfectly crystalline polymer. The values of $\rho_a$ and $\rho_c$ must be measured by other experimental means.

The degree of crystallinity of a polymer depends on

(i) the rate of cooling during solidification as well as

(ii) on (ii) the chain configuration.

During crystallization upon cooling through the melting temperature, the chains, which are highly random and entangled in the viscous liquid, must assume an ordered configuration.

For this to occur, sufficient time must be allowed for the chains to move and align themselves.
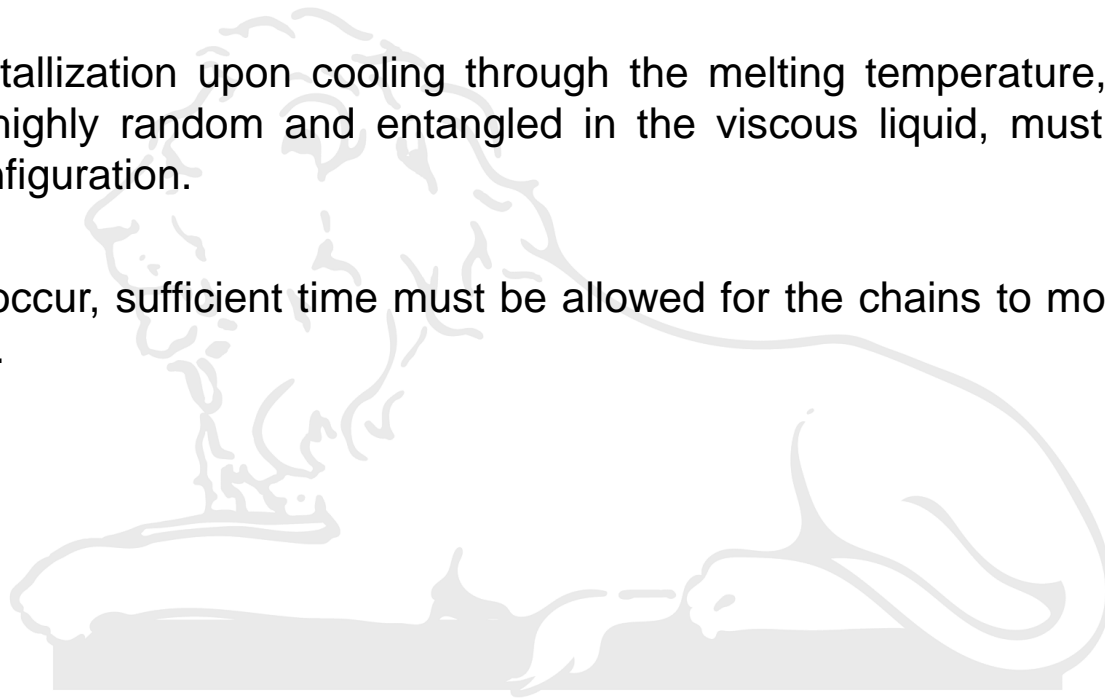
The molecular chemistry as well as chain configuration also influence the ability of a polymer to crystallize.

Crystallization is not favored in polymers that are composed of chemically complex repeat units (e.g., polyisoprene).

On the other hand, crystallization is not easily prevented in chemically simple polymers such as polyethylene and polytetrafluoroethylene, even for very rapid cooling rates.