Polymer Chemistry

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Polymer Science and Technology

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3. Chemical Bonding and Polymer Structure

I. INTRODUCTION

In organic chemistry, the physical state of a homologous series (alkane series with the general formula [C_nH_{2n+2}]) changes as the molecular size increases.

By moving from the low- to the high-molecular-weight end of the molecular spectrum, the physical states change progressively from the gaseous state through liquids of increasing viscosity (decreasing volatility) to low melting solids and ultimately terminate in high-strength solids.

Table 3.1 *Change of State with Molecular Size for the Alkane [C_nH_{2n+2}] Series*

No. of Carbon Atoms	Molecular State
1	Methane — boiling point –162°C
2–4	Natural gas — liquefiable
5–10	Gasoline, diesel fuel — highly volatile, low viscosity liquid
10–10^2	Oil, grease — nonvolatile, high viscosity liquid
10_2–10^3	Wax — low melting solid
10^3–10^6	Solid — high strength

Polymers belong to the high-molecular-weight end of the spectrum.

To study the unusual properties of high polymers, we should investigate the **chemical and structural aspects** of polymers at **three** different levels:

1. The chemical structure (atomic composition) of the monomer (**primary structure**)
2. The single polymer chain (**secondary structure**)
3. Aggregation of polymer chains (**tertiary structure**)

II. CHEMICAL BONDING

The electronic structure of atoms determines the type of bond between the atoms concerned.

Chemical bonds may be classified as *primary* or *secondary* depending on the extent of electron involvement.

Valence electrons are involved in the formation of primary bonds, that are quite strong. Valence electrons are not involved in the formation of secondary bonds, leading to weak bonds.

Primary bonds

- a. Ionic
- b. Covalent
- c. Metallic

Secondary bonds

- a. Dipole forces
- b. Hydrogen-bonding
- c. Induction forces
- d. Van der Waals (dispersion)

Ionic bonds are not common features in polymeric materials. However, divalent ions are known to act as cross-links between carboxyl groups in natural resins. The relatively new class of polymers known as ionomers contain ionic bonds.

Covalent bonds are the predominant bond in polymers. Covalent bonds can be single, double, or triple depending on the number of electron pairs (bond strengths).

Dissociation energy has a direct relationship with the thermal stability of polymers. While atoms are free to rotate about single bonds (flexible), they remain spatially fixed (rigid) for double and triple bonds.

Polar molecules have a small separation of charge (permanent dipole). **Dipoles** interact through coulombic forces, which can become quite significant at molecular distances.

Polar molecules are held together in the solid state by the interaction between oppositely charged ends of the molecules (**dipole-interaction forces** or **dipole–dipole interaction**).

Molecular orientation is generally opposed by thermal agitation (temperature dependent).

In polymers, hydrogen bonding usually occurs between functional groups (in amines, amides, urethanes, urea) in the same or different molecules.

The hydrogen bond plays a vital role in the structure and properties of polymers, particularly proteins.

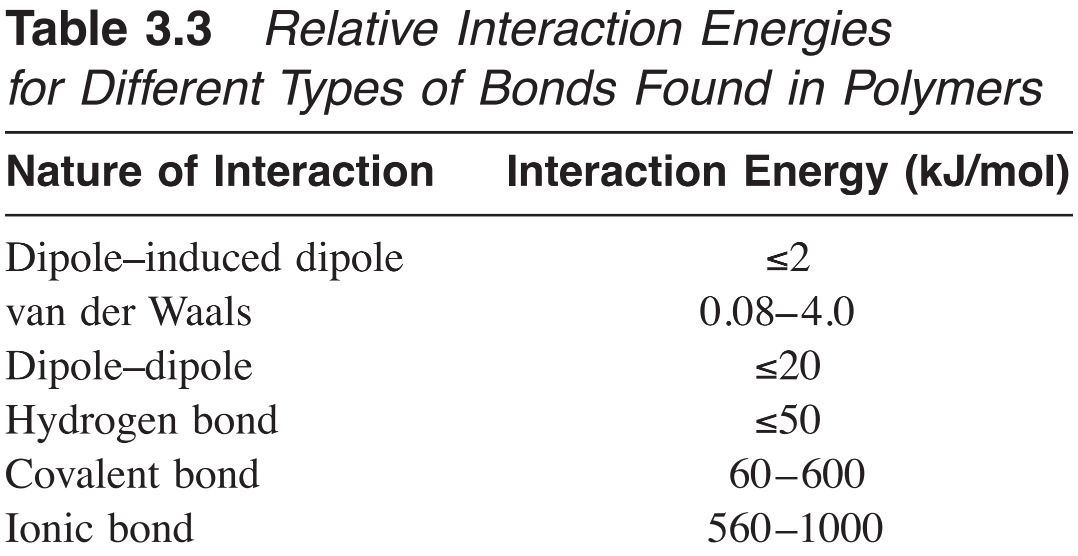


Table 3.3 *Relative Interaction Energies for Different Types of Bonds Found in Polymers*

Nature of Interaction	Interaction Energy (kJ/mol)
Dipole–induced dipole	≤2
van der Waals	0.08–4.0
Dipole–dipole	≤20
Hydrogen bond	≤50
Covalent bond	60–600
Ionic bond	560–1000

III. PRIMARY STRUCTURE

Primary structure refers to the atomic composition and chemical structure of the monomer — the building block of the polymer chain.

The nature of the monomer is fundamental to understanding the structure–property relationship of polymers.

The chemical and electrical properties of a polymer are directly related to the chemistry of the constituent monomers.

The physical and mechanical properties of polymers are largely a consequence of the macromolecular size of the polymer, which in itself is related to the nature of the monomer.

By definition, a polymer is a chain of atoms hooked together by primary valence bonds.

The structure and properties of the resulting polymers depends on the structure of the monomer:

- The nature of bonds in monomers (chemical bonding)
- The type of monomers that are capable of forming polymers (functionality of monomers)
- The mode of linking of monomers (polymerization mechanisms)
- The chemical composition of monomers and their relevant properties

A. POLARITY OF MONOMERS

The chemical composition and atomic arrangement of an organic molecule confer certain properties on the molecule. One such property is the polarity of the molecule.

The degree of polarity (in covalent bonds) varies depending on the electronegativities of the constituent atoms.

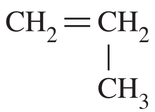
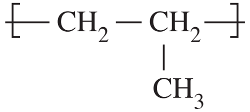
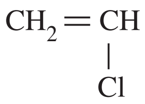
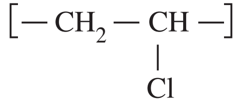
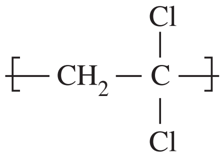
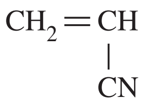
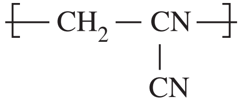
Monomers such as ethylene and propylene are nonpolar. The polar monomers vinyl chloride [CH_2=CHCl] and acrylonitrile [CH_2=CHCN] result in polar polymers. However, the symmetrical monomers vinylidene chloride and vinylidene fluoride lead to nonpolar polymers.

In condensation polymers,–CO.O– (ester), –CO.NH– (amide), –HN–CO–NH– (urea), and –O.CO–NH– (urethane) are polar.

Polarity affects the intermolecular attraction between chain molecules, and thus the regularity and symmetry of polymer structure.

Properties such as the solubility and electrical nature of polymers, which depend on polymer structure, are intimately related to polarity.

Table 3.6 *Polarity of Monomers and Their Associated Polymers*

Monomer	Polarity	Polymer	Polarity
$CH_2{=}CH_2$ Ethylene	Nonpolar	$\left[-CH_2-CH_2-\right]$ Polypropylene	Nonpolar
 $CH_2{=}\underset{CH_3}{\underset{\vert}{CH_2}}$ Propylene	Nonpolar	 $\left[-CH_2-\underset{CH_3}{\underset{\vert}{CH_2}}-\right]$ Polypropylene	Nonpolar
 $CH_2{=}\underset{Cl}{\underset{\vert}{CH}}$ Vinyl chloride	Polar	 $\left[-CH_2-\underset{Cl}{\underset{\vert}{CH}}-\right]$ Poly(vinyl chloride)	Polar
$CH_2{=}CCl_2$ Vinylidene chloride	Nonpolar	 $\left[-CH_2-\overset{Cl}{\overset{\vert}{\underset{Cl}{\underset{\vert}{C}}}}-\right]$ Poly(vinylidene chloride)	Nonpolar
 $CH_2{=}\underset{CN}{\underset{\vert}{CH}}$ Acroylonitrile	Polar	 $\left[-CH_2-\underset{CN}{\underset{\vert}{CN}}-\right]$ Polyacrylonitrile	Polar
$CF_2{=}CF_2$ Tetrafluoroethylene (symmetrical)	Nonpolar	$\left[-CF_2-CF_2-\right]$ Polytetrafluorethylene (Teflon)	Nonpolar

IV. SECONDARY STRUCTURE

To understand polymer properties, the secondary structure (**size** and **shape** of an isolated single molecule) should be considered.

The size of the polymer is related to the molecular weight.

The shape of the polymer molecule (molecular architecture) is influenced by the nature of the repeating unit and the manner in which these units are linked together.

Polymer shape:

- Configuration — Arrangement fixed by primary valence bonds; can be altered only through the breaking or reforming of chemical bonds
- Conformation — Arrangement established by rotation about primary valence bonds

A. CONFIGURATION

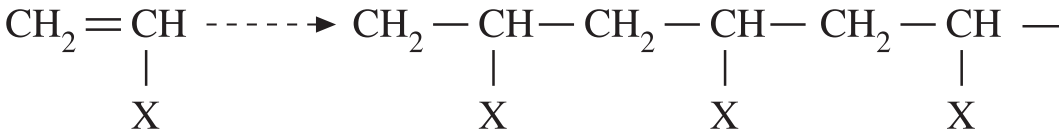
A polymer molecule may be linear, branched, or cross-linked depending on the functionality of the monomers used.

If repeating units along the chain are chemically and sterically regular, then the polymer is said to possess **structural regularity**.

To consider structural regularity, we need to define two terms: ***recurrence regularity*** and ***stereoregularity***.

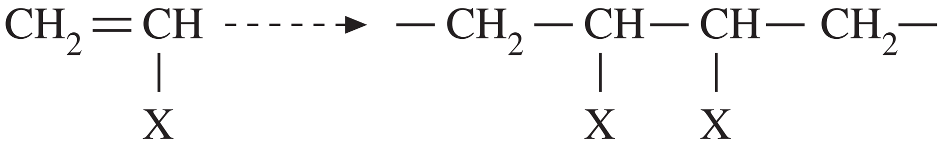
Recurrence regularity refers to the regularity with which the repeating unit occurs along the polymer chain.

- Head-to-tail configuration



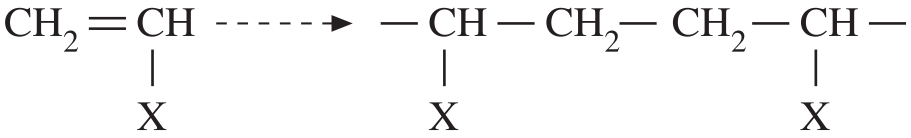
$$CH_2{=}\underset{\underset{X}{|}}{CH} \dashrightarrow CH_2-\underset{\underset{X}{|}}{CH}-CH_2-\underset{\underset{X}{|}}{CH}-CH_2-\underset{\underset{X}{|}}{CH}-$$

- Head-to-head configuration



$$CH_2{=}\underset{\underset{X}{|}}{CH} \dashrightarrow -CH_2-\underset{\underset{X}{|}}{CH}-\underset{\underset{X}{|}}{CH}-CH_2-$$

- Tail-to-tail configuration



$$CH_2{=}\underset{\underset{X}{|}}{CH} \dashrightarrow -\underset{\underset{X}{|}}{CH}-CH_2-CH_2-\underset{\underset{X}{|}}{CH}-$$

The **last two configurations do not appear** in any measurable extent in known polymers.

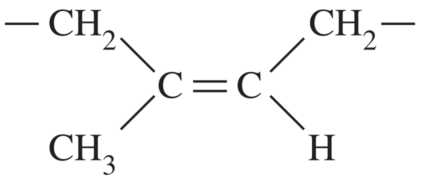
Stereoregularity refers to the spatial properties of a polymer molecule.

1. Diene Polymerization

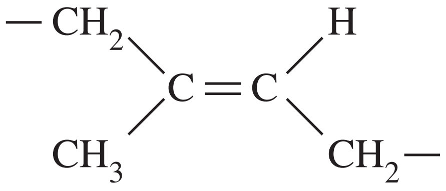
The propagation step in the polymerization of diene monomers (monomers with two double bonds) can proceed by either of two mechanisms: 1,2- and 1,4-additions.

In 1,2-addition the resulting unsaturation is part of the pendant group, while in 1,4-addition the unsaturation is part of the backbone.

For 1,4-addition structure, the backbone has a rigid structure and rotation is not free around it. Therefore, two different configurations, known as ***cis*** and ***trans**,* are possible.



cis-1,4-polyisoprene (natural rubber)



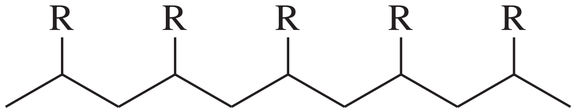
trans-1,4-polyisoprene (gutta-percha)

2. Tacticity

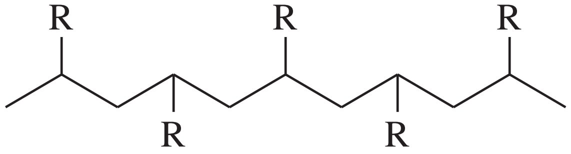
Polymers of monosubstituted olefins [CH_2=CHX] contain a series of asymmetric carbon atoms along the chain.

For this type of polymers, in a planar zigzag form, three arrangements are possible, namely:

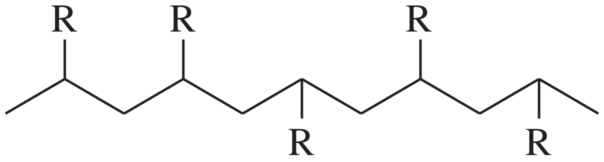
- Isotactic — All the substituent groups, R, lie above (or below) the plane of the main chain.



- Syndiotactic — Substituent groups lie alternately above and below the plane.



- Atactic — Random sequence of position of substituent occurs along the chain.



B. CONFORMATION

In addition to the molecular shape fixed by chemical bonding, variations in the overall shape and size of the polymer chain may occur due to rotation about primary valence bonds (conformation).

A polymer molecule may assume a large or limited number of conformations depending on:

- Steric factors
- Whether the polymer is amorphous or crystalline
- Whether the polymer is in a solution state, molten state, or solid state

Two extreme **shapes** of a polymer chain: **planar zigzag** and completely **random coil**.

In **planar zigzag** conformation, each successive carbon atoms lies in the same plane in the *trans* location in the chain — thus forming a fully extended plane of zigzag arrangement of carbon atoms.

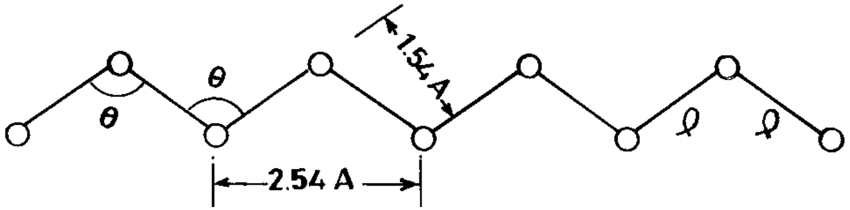


Figure 3.5 *The fully extended all-trans conformation of a carbon–carbon chain.*

It exists in some crystalline polymers or in highly oriented amorphous polymers, for examples, PE, PVC, and polyamides, where the small size of the pendant group does not complicate alignment and packing.

In those polymers with large and bulky side groups like PP and PS (in general, isotactic and syndiotactic polyolefins), it is impossible sterically to accommodate the pendant groups in the planar zigzag.

Consequently, the entire main chain is rotated in the same direction to form either a **right- or left-handed helix**. This occurs exclusively in the crystalline form of stereoregular polymers with bulky side groups.

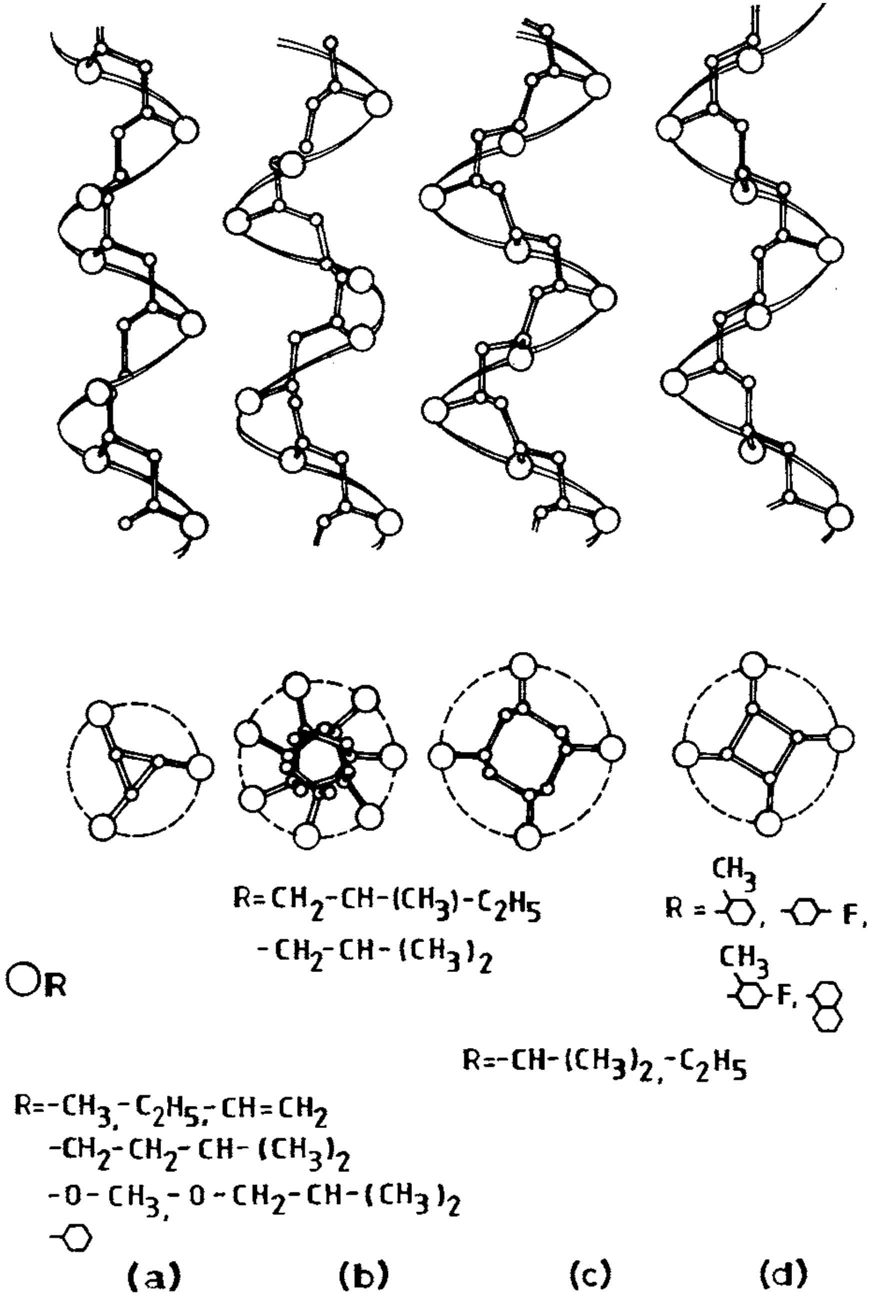


Figure 3.6 *Helical conformations of isotactic vinyl polymers. (From Gaylord, N.G. and Mark, H., Linear and Stereoregular Addition Polymers, Interscience, New York, 1959. With permission.)*

Completely random coil: polymers in solution, in melt, or amorphous in the solid state assume this conformation.

Between these two extremes (planar zigzag and random coil conformation), the number of conformation shapes in the polymer chain can assume to be virtually limitless.

Free rotation about single bonds: there is no completely free rotation, and all bonds have to overcome certain rotational energy barriers whose magnitude depends on such factors as steric hindrance, dipole forces, etc.

The thermal energy of the molecular environment provides the energy required to overcome the rotational energy barrier. Consequently, the **shape** (flexibility) of a polymer molecule is **temperature dependent**.

At sufficiently high temperatures, the polymer chain constantly wiggles, assuming a myriad of random coil conformations.

The **flexibility** of polymer molecules is a function of substituents on the backbone, has a strong influence on polymer properties.

C. MOLECULAR WEIGHT

The terms ***giant molecule***, ***macromolecule***, and ***high polymer*** are used to describe a polymer molecule emphasizing its large size.

Although the same bonding forces (intra- and intermolecular) exist in both low- and high-molecular-weight materials, but unique properties exhibited by polymers. The difference in behavior between polymers and their low-molecular-weight analogs are attributable to their large size and flexible nature.

Important **mechanical properties** (tensile and compressive strengths, elongation at break, modulus, impact strength) and other **properties** (softening point, solution and melt viscosities, solubility) **depend** on **molecular weight** in a definite way.

Optical and electrical properties, color, and density show a **less marked dependence** on molecular weight.

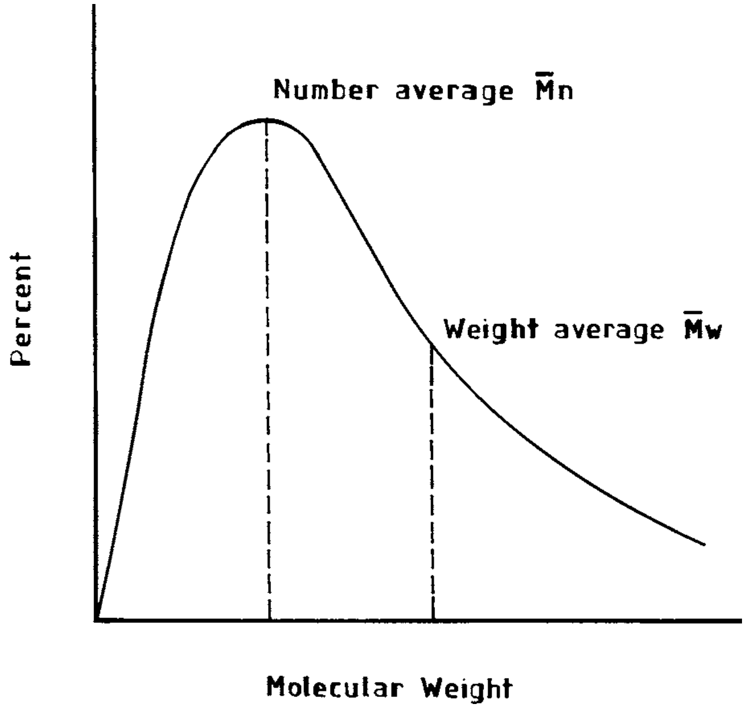
Regardless the polymerization mechanism, the **formation** of polymer is a **purely random** occurrence.

Unlike biological systems, synthetic polymers do not consist of identical molecules, but represent a mixture of many systems each of which has a different molecular weight.

Thus, the **molecular weight distribution** (MWD) curve represents a plot of the percentage (frequency) of a particular species against its molecular weight.

As a result of the existence of different sizes of molecular species in a polymeric material, we **cannot strictly speak** of the molecular weight of a polymer.

Instead we use **molecular weight averages** to express the **size of synthetic polymers**.



Different average molecular weights exist. The most common ones in use are number-average molecular weight, M_n, and weight-average molecular weight, M_w.

Others are the z-average molecular weight, M_z, and viscosity-average molecular weight, M_v.

$$\overline{M}_n - \frac{W}{\sum_{i=1}^{\infty} N_i} = \frac{\sum_{i=1}^{\infty} N_i M_i}{\sum_{i=1}^{\infty} N_i} = \frac{\sum_{i=1}^{\infty} W_i}{\sum_{i=1}^{\infty} W_i / M_i} = \frac{1}{\sum w_i / M_i}$$

$$\overline{M}_w = \sum_{i=1}^{\infty} w_i M_i = \frac{\sum_{i=1}^{\infty} w_i M_i}{W} = \frac{\sum_{i=1}^{\infty} N_i M_i^2}{\sum_{i=1}^{\infty} N_i M_i}$$

$$\overline{M}_z = \frac{\sum_{i=1}^{\infty} N_i M_i^3}{\sum_{i=1}^{\infty} N_i M_i^2} = \frac{\sum_{i=1}^{\infty} w_i M_i^2}{\sum_{i=1}^{\infty} w_i M_i}$$

$$\overline{M}_v = \left[\sum_{i=1}^{\infty} w_i M_i^a\right]^{1/a} = \left[\frac{\sum_{i=1}^{\infty} N_i M_i^{a+1}}{\sum_{i=1}^{\infty} N_i M_i}\right]^{1/a}$$

Where N_i = number of molecules having molecular weight M_i
W = total weight
N = total number of molecules
w_i = weight fraction of molecules having molecular weight M_i
W_i = weight of molecule having molecular weight M_i
a = constant in **Mark–Houwink equation** $\eta = Km^a$ in which the intrinsic viscosity (η) and the molecular weight M are related through constants K and a for given polymer/solvent system; a is at least 0.5 and mostly less than 0.8.

The molecular weight of polymers can be determined by a number of physical and chemical methods:

(1) end group analysis,
(2) measurement of colligative properties,
(3) light scattering,
(4) ultracentrifugation,
(5) dilute solution viscosity, and
(6) gel permeation chromatography (GPC).

The first four methods permit a direct calculation of molecular weight without using calibration. The methods are, in principle, absolute.

The last two methods require proper calibration to obtain the value of molecular weight.

Colligative properties are determined by the following measurements on dilute polymer solutions:

- Vapor pressure lowering
- Boiling point elevation (ebulliometry)
- Freezing point depression (cryoscopy)
- Osmotic pressure (osmometry)

M_n is determined from end-group analysis, colligative property measurements, and GPC.

M_w is determined from light scattering, ultracentrifugation, and GPC.

M_z is determined from GPC.

M_v is determined from measurements of polymer solution viscosity.

V. TERTIARY STRUCTURE

A given polymeric solid material is an aggregate of a large number of polymer molecules.

Depending on the molecular structure, the process of molecular aggregation occurs essentially by either of two possible arrangements of molecules, leading to either a **crystalline** or **amorphous** material.

Irrespective of the type of molecular arrangement, the forces responsible for molecular aggregation are the intermolecular secondary bonding forces.

The overall bonding energies due to secondary bonding forces range from 0.5-10 kcal/mol compared with those of primary bonding forces, which are of the order 50-100 kcal/mol.

When molecules are large enough, the attractive forces resulting from the secondary intermolecular bonding forces may build up to such a level that, in some cases, they become greater than the primary valence forces responsible for intramolecular bonds.

A. SECONDARY BONDING FORCES (COHESIVE ENERGY DENSITY)

Tertiary structure is concerned with the nature of the intermolecular secondary bonding forces and with structural order of the resulting polymer.

The magnitude of these secondary bonding forces, coupled with the high physical entanglement between chains, dictates many polymer properties.

A quantitative measure of the magnitude of secondary bonding forces is the cohesive energy density (CED), which is the total energy per unit volume needed to separate all intermolecular contacts and is given by:

$$\mathrm{CED} = \frac{\Delta E_v}{V_L}$$

where ΔE_v = molar energy of vaporization, V_L = molar volume of the liquid

It can be shown from the Classius–Clapeyron equation that

$$\Delta E_v = \Delta H_v - RT$$

where ΔH_v = molar heat of vaporization, T = absolute temperature (K)

Consequently:

$$\mathrm{CED} = \frac{\Delta E_v}{V_L} = \frac{\Delta H_v - RT}{V_L}$$

For liquids of low molecular weight the energy necessary to separate molecules from one another is evaluated from the heat of evaporation or from the dependence of vapor pressure on temperature.

Since polymers cannot be evaporated, the cohesive energy density is estimated indirectly by dissolution in liquids of known cohesive energy density.

The relation between the cohesive energy density and solubility parameter:

$$\mathrm{CED} = \delta^2$$

where δ = **solubility parameter**. As a first approximation and in the absence of strong interactions such as hydrogen bonding, a polymer δ_2 will dissolve in a solvent δ_1 if

$$\delta_1 - \delta_2 \leq 1.7 - 2.0.$$

B. CRYSTALLINE AND AMORPHOUS STRUCTURE OF POLYMERS

When a polymer is cooled from the melt or concentrated from a dilute solution, molecules are attracted to each other forming a solid mass.

Two arrangements are essentially possible:

1. The molecules vitrify, with the polymer chains randomly coiled and entangled. The resulting solid is amorphous and is hard and glassy.

2. The individual chains are folded and packed in a regular manner characterized by three-dimensional long-range order. The polymer thus formed is said to be crystalline.

Polymers are made up of long molecules; therefore, the concept of crystallinity in polymers must be viewed slightly differently from that in low-molecular-weight substances.

Complete parallel alignment is never achieved in polymeric systems.

Only certain clusters of chain segments are aligned to form crystalline domains. These domains do not have the regular shapes of normal crystals.

They are much smaller in size, contain many more imperfections, and are connected with the disordered amorphous regions by polymer chains that run through both the ordered and the disordered segments. Consequently, no polymer is 100% crystalline.

1. Crystallization Tendency

Secondary bonding forces are responsible for intermolecular bonding in polymers. These forces are effective only at very short molecular distances.

Therefore, to maximize the effect of these forces in the process of aggregation of molecules to form a crystalline solid mass, the molecules must come as close together as possible.

The tendency for a polymer to crystallize, therefore, depends on the magnitude of the inherent intermolecular bonding forces as well as its structural features.

2. Structural Regularity

In the process of association of polymer molecules to form a solid mass, molecules must come as close together as possible.

Any structural features of polymer molecules can impede this process will necessarily detract from crystallinity.

Polyethylene is nonpolar with the intermolecular attraction resulting from the relatively weak van der Waals forces. The chains can assume a planar zigzag conformation.

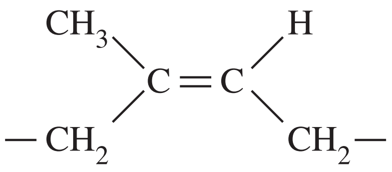
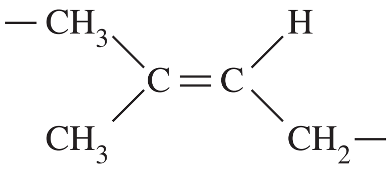
High structural regularity in polyethylene molecules (permits close packing of the chains coupled with the limited chain flexibility) leads to an unexpectedly high melting point (T_m = 135 °C), relatively high rigidity, and low room-temperature solubility. **(HDPE)**

As irregularities are introduced into the structure, as with low-density polyethylene **(LDPE)**, the value of these properties shows a significant reduction. The crystalline melting point of polyethylene is reduced 20 to 25 °C on going from the linear to the branched polymer.

Regularity is not sufficient to ensure crystallizability in polymers. The spatial regularity and packing are important.

In stereoregular polymers, ***trans*** form is more readily packed and crystallizable and has properties of crystalline polymers.

Table 3.8 *Properties of Polyisoprene Isomers*

Isomer	**Structure**	**Properties**
1,4-*cis*=polyisoprene (heavea rubber)		Soft, pliable, easily soluble rubber; has a high retractive force; used for making vehicle tires
1,4-*trans*-polyisoprene (gutta-percha)		Tough, hard; used as golf ball covers

The stereoregularity in monosubstituted vinyl polymers of olefins can occur in three forms of **tacticity**: isotactic, syndiotactic, and atactic.

Isotactic and syndiotactic polymers possess stereoregular structures, and are rigid, **crystallizable**, high melting, and relatively insoluble.

Atactic polymers are soft, low melting, easily soluble, and **amorphous**.

3. Chain Flexibility

During crystallization, the alignment and uniform packing of polymer chains are opposed by thermal agitation, which tends to induce segmental, rotational and vibrational motions.

The potential energy barriers hindering this rotation range from 1-5 kcal/mol, the same order of magnitude as molecular cohesion forces. Polymers with flexible chains are more susceptible to the thermal agitation than those with rigid or stiff chain structure.

The flexibility of chain molecules arises from rotation around saturated chain bonds ($–CH_2–$ units).

- Rapid conformational change due to ease of rotation around single bonds occurs if such groups as (–CO–O–), (–O–CO–O–), and (–C–N–) are introduced into the main chain.

If they are **regular** and/or if there exist considerable intermolecular forces, the materials are crystallizable, relatively high melting, rigid, and soluble with difficulty.

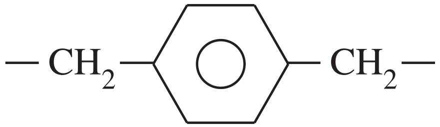
If they occur **irregularly** along the polymer chain, they are amorphous, soft, and rubbery materials.

- Ether and imine bonds, and double bonds in the *cis* form reduce the energy barrier for rotation of the adjacent bonds and “soften” the chain; making polymers less rigid, more rubbery, and more readily soluble than the chain of consecutive carbon–carbon atoms.

If such “**plasticizing**” bonds are irregularly distributed along the polymer chain length, crystallization is inhibited.

- Cyclic structures in the backbone and polar group such as $–SO_2–$, and –CONH– drastically reduce flexibility and enhance crystallizability

Table 3.9 *Effect of Chain Flexibility of Crystalline Melting Point*

Polymer	**Repeating Unit**	**T_m (°C)**
Polyethylene	$—CH_2—CH_2—$	135
Polyoxyethylene	$—CH_2—CH_2—O—$	65
Poly(ethylene suberate)	$—O(CH_2)_2—OCO—(CH_2)_6CO—$	45
Nylon 6,8	$—NH(CH_2)_6NHCO(CH_2)_6CO—$	235
Poly (*p*-xylene)		400

4. Polarity

When molecules come together and aggregate into a crystalline solid, a significant cohesion between neighboring chains is possible.

Polymer molecules with specific groups that are capable of forming strong intermolecular bonding, are crystallizable:

$$-\overset{H}{\overset{|}{N}}-\overset{O}{\overset{\|}{C}}- \text{ (amide); } -\overset{H}{\overset{|}{N}}-\overset{O}{\overset{\|}{C}}-O- \text{ (urethane); and } -\overset{H}{\overset{|}{N}}-\overset{O}{\overset{\|}{C}}-\overset{H}{\overset{|}{N}}- \text{ (urea)}$$

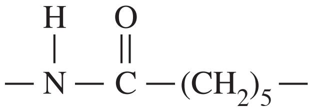
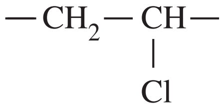
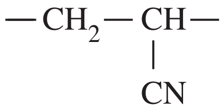
In nylon 6 or 6,6, the regular occurrence of amide linkages leads to a highly crystalline, high melting polymer. Molecules whose backbone contains –O– units or with polar side groups (–CN, –Cl, –F, or $–NO_2$) exhibit polar bonding.

The bonding energies of such dipoles or polarizable units are in the range between hydrogen bonding and van der Waals bonding. If these groups occur regularly along the chain (isotactic and syndiotactic), the resulting polymers are usually crystalline and have higher melting points than polyethylene.

The presence of –O– units in a chain backbone enhances flexibility, but the melting point of polyoxymethylene (180 °C) is higher than that of polyethylene (135 °C)! **Contradict!**

However, the dipole character of the C–O–C group produces polar forces between adjacent chains that act over a longer range and are stronger than van der Waals forces.

Table 3.10 *Effect of Polarity on Crystallizability*

Polymer	**Repeat Unit**	**T_{em} (°C)**
Polyethylene	$-CH_2-CH_2-$	135
Nylon 6	 $-\overset{H}{\overset{\vert}{N}}-\overset{O}{\overset{\Vert}{C}}-(CH_2)_5-$	223
Nylon 6,6	 $-\overset{H}{\overset{\vert}{N}}-(CH_2)_6-\overset{H}{\overset{\vert}{N}}-\overset{O}{\overset{\Vert}{C}}-(CH_2)_4-\overset{O}{\overset{\Vert}{C}}-$	265
Polyoxymethylene	$-CH_2-O-$	180
Poly(vinyl chloride)	 $-CH_2-\underset{\underset{Cl}{\vert}}{CH}-$	273
Polyacrylonitrile	 $-CH_2-\underset{\underset{CN}{\vert}}{CH}-$	317

5. Bulky Substituents

The vibrational and rotational mobility of intrinsically flexible chains can be inhibited by bulky substituents; the degree of stiffening depends on the size, shape, and mutual interaction of the substituents.

Vinyl polymers with small substituents such as polypropylene [–CH_3] and polystyrene [–C_6H_5] can crystallize if these pendant groups are spaced regularly on the polymer chain as in their isotactic and syndiotactic forms.

In their atactic forms, the randomly disposed pendant groups prevent the close packing of the chains into crystalline lattice, therefore, they are amorphous.

Large or bulky substituents increase the average distance between chains and prevent the effective and favorable utilization of the intermolecular bonding forces.

Polymers like poly(methyl acrylate) and poly(vinyl acetate) with large pendant groups –CO–O–CH_3 and O–OC–CH_3, respectively, cannot crystallize even if the pendant groups are spaced regularly (isotactic and syndiotactic forms).

For polyolefins: polyethylene, polypropylene, poly(1-butene), and poly(1-pentene), the melting point shows a maximum for polypropylene.

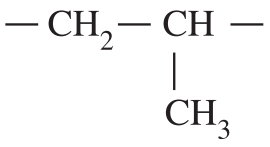
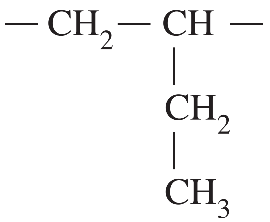
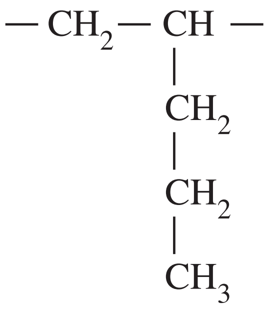
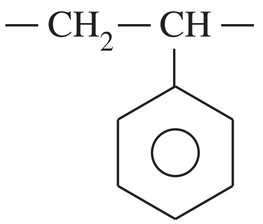
A large pendant group in close proximity of the main chain stiffens the chain.

When the size of the pendant group increases, the packing distance between the chains is increased, the forces of interaction between chains and also melting point decreased.

The presence of an aromatic side group in polystyrene considerably stiffens the chain, which has a stable helix form in the solid state. The helices pack efficiently allow greater interchain interaction.

Note: **Stereo-regularity**, **chain flexibility**, **polarity**, and **steric factors** have profound influence on **crystallizability** and **melting points**, and play an important role in the **thermal** and **mechanical** behavior of polymers.

Table 3.11 *Stiffening of Polymer Chains by Substituents*

Polymer	**Repeat Unit**	**T_m (°C)**
Polyethylene	$-CH_2-CH_2-$	135
Polypropylene	 $-CH_2-\underset{CH_3}{\underset{\vert}{CH}}-$	176
Poly(1-butene)	 $-CH_2-\underset{\underset{\underset{CH_3}{\vert}}{CH_2}}{\underset{\vert}{CH}}-$	125
Poly(1-pentene)	 $-CH_2-\underset{\underset{\underset{\underset{\underset{CH_3}{\vert}}{CH_2}}{\vert}}{CH_2}}{\underset{\vert}{CH}}-$	75
Polystyrene		240

C. MORPHOLOGY OF CRYSTALLINE POLYMERS

Most polymers are partially crystalline. X-ray diffraction patterns of some polymers showed sharp features, associated with regions of three-dimensional order, superimposed on a diffuse background characteristic of amorphous (liquid-like substances).

In fact, polymers are semi-crystalline, consisting of small, relatively ordered regions — the crystallites embedded in an otherwise amorphous matrix.

The “**fringed micelle**” model: polymer chains are very long and they passed successively through the crystallites and amorphous regions. The chains were thought to run parallel to the longer direction of the crystallites.

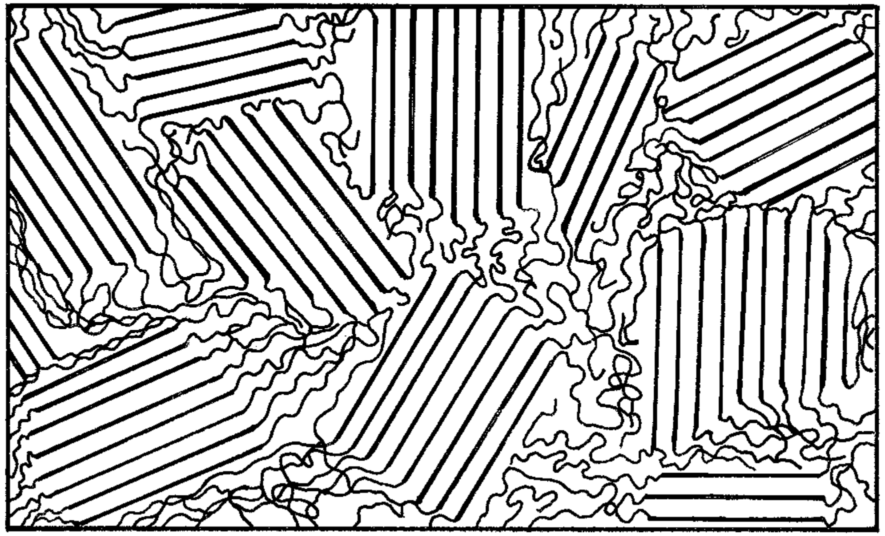


Figure 3.10 *Fringed micelle model. (From Bryant, W.W.D., J. Polym. Sci., 2, 547, 1947. With permission.)*

The **morphology** of crystalline polymers — that is, the **size**, **shape**, and relative **magnitude of crystallites** — is rather complex and **depends** on **growth conditions** such as **solvent type**, **temperature**, and **growth rate,** and even **polymer molecular weight**.

In polymer crystalline morphology, molecular packing concerns how the polymer chains (with an extended conformation of either planar zigzag or helix) are packed into the unit cell.

1. Crystal Structure of Polymers

The fully extended planar zigzag (*trans* conformation) is the minimum energy conformation for an isolated section of polyethylene or paraffin hydrocarbon. The energy of the *trans* conformation is about 800 cal/mol less than that of the gauche form.

Consequently, the *trans* form is favored in polymer crystal structures. Typical polymers that exhibit this *trans* form include polyethylene, poly(vinyl alcohol), syndiotactic forms of poly(vinyl chloride) and poly(1,2-butadiene), most polyamides, and cellulose.

Degree of Crystallinity

Polymers, by virtue of their large size and in contrast to low-molecular-weight materials, are incapable of 100% crystallinity.

The term *semicrystalline* is frequently used to describe crystalline polymers. They are a two-phase system with a distinct demarcation between the crystalline and amorphous material.

To estimate the degree of crystallinity, the actual or measured property of the polymer (P_m) should be determined by using the relevant properties of the crystalline (P_c) and amorphous (P_a) components individually:

$$p_m = \phi \, p_c + (1 - \phi) \, p_a \qquad \phi = \frac{p_a - p_m}{p_a - p_c}$$

Material properties: **specific volume**, **specific heat**, **enthalpy**, and **electrical resistivity**.

2. Morphology of Polymer Single Crystals Grown from Solution

For a long time, it was believed that, because of the molecular entanglements of polymer chains in solution, it would be impossible to produce polymer single crystals. The first report of the growth of polymer single crystals from dilute solution was in 1953.

Growth of polymer single crystals requires crystallization from dilute solutions at relatively high temperatures by cooling from a temperature above the crystalline melting point.

Different **morphologies** result depending on **polymer type** and **growth conditions**.

a. Lamellae

All polymer single crystals have the same general appearance. Under an electron microscope, they appear as thin, flat platelets that are 100 to 120 Å thick and several microns in lateral dimensions.

Growth of the crystal normal to lamellar surface occurs by the formation of additional lamellae of the same thickness as the basal lamellae; thick crystals are usually multilamellar.

b. Chain Folding

Figure 3.16 is an electron micrograph of crystals of PE obtained by cooling a dilute solution (0.1%, in tetrachloroethylene). Such electron microscopy and diffraction studies have confirmed not only the lamellar nature of single crystals, but have also revealed that the polymer molecules are oriented normal to the lamellar surface.

Since polymer molecules are generally 1000 to 10,000 Å long and lamellae are only 100 Å thick, it follows that chains must fold repeatedly on themselves. For PE, only about five chain carbon atoms are required for the chain to fold on itself.

The regular folding of chains defines as *fold plane,* while the thickness of the lamella is regarded as the *fold period*.

Chain ends may either terminate within the crystal, forming a defect, or be excluded from the crystal, forming cilia.

Irregular folding and branch points can also occur.

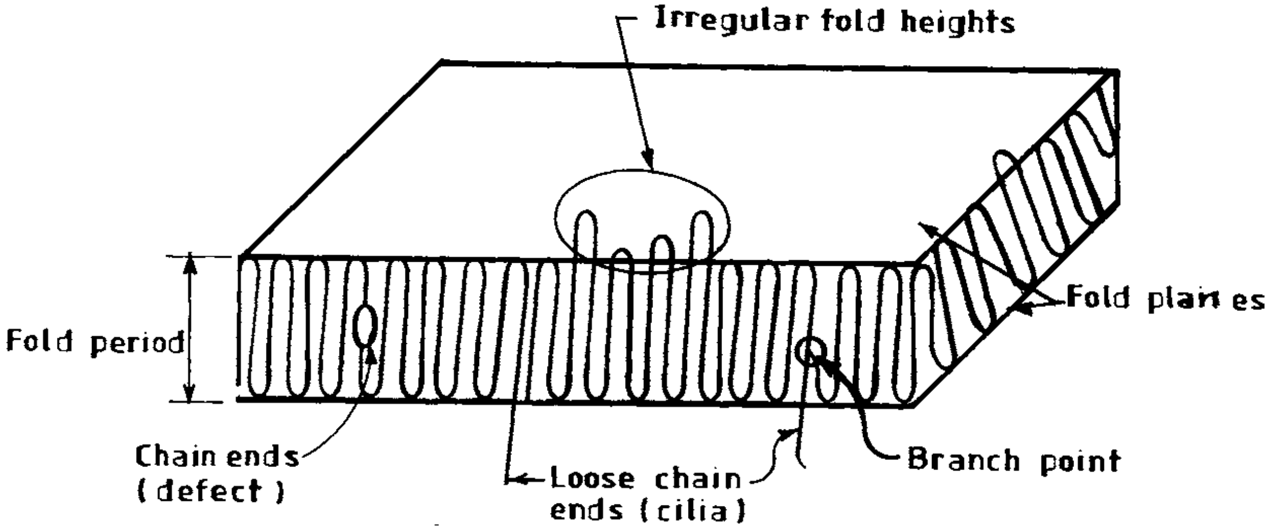


Figure 3.16 *Schematic diagram of chain folding showing conformational imperfections.*

Figure 3.17 represents the top surface of an idealized model of a diamond-shaped PE single crystal as seen along the (001) (c axis).

The curved lines, which represent the chain folds, terminate on solid lines representing the plane of zigzag.

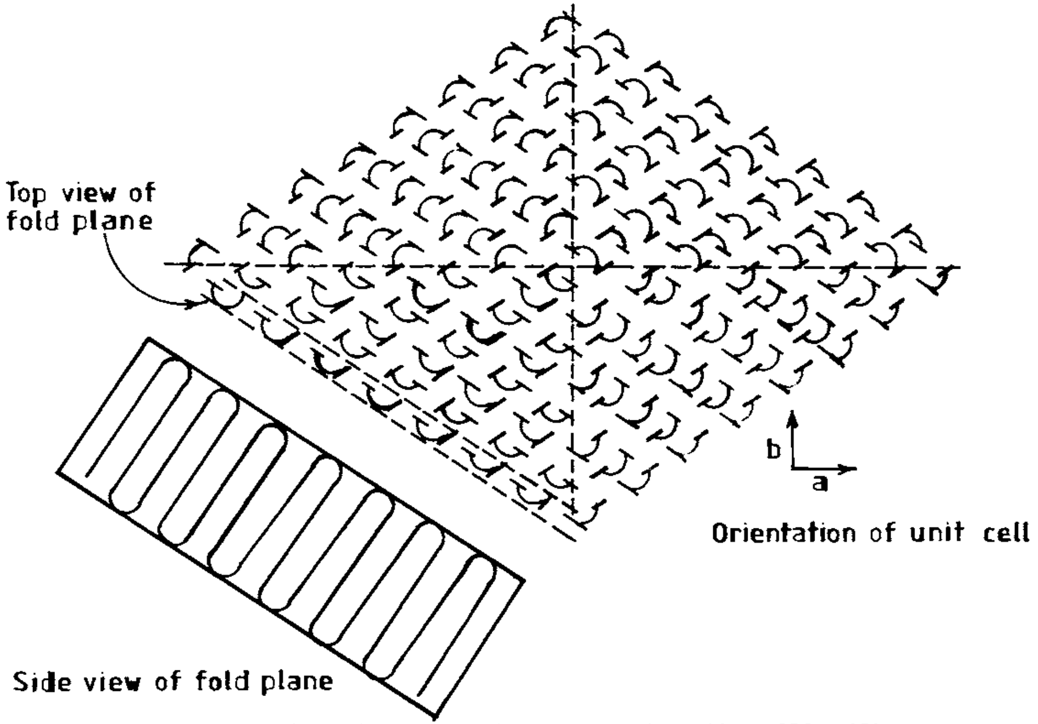


Figure 3.17 *Fold packing in a polyethylene single crystal. (From Reneker, D.H. and Geil, P.H., J. Appl. Phys., 31, 1916, 1960. With permission.)*

c. Hollow Pyramidal Structure

Crystals of PE are not simply flat lamellae. Experimental evidence has shown that they may exist in solution as hollow pyramids.

The hollow pyramidal structure is due to the packing of the folded chains in which successive planes of folded molecules are displaced from their neighbors by an integral of repeat distances.

In some cases, the fold and fold period are regular, and the displacement of adjacent fold planes is uniform, resulting the formation of a planar pyramid.

In other cases, the direction of displacement is reversed periodically, and corrugated pyramids are formed.

3. Morphology of Polymers Crystallized from the Melt

The most prominent structural feature of polymers crystallized from the melt is the **spherulite**.

The spherulite is not a single crystal, but an extremely complex spherical aggregate of lamellae ranging in size from about 0.1 μ to possibly a few millimeters in diameter.

Under a **polarizing microscope**, spherulites show characteristic dark Maltese cross patterns arising from the birefringent effects associated with the molecular orientation of lamellae morphology.

When a sample of a crystallizable polymer like PE, nylon 6,6, or poly(ethylene terephthalate) is heated above its melting temperature and then supercooled by about 10 to 15°C, spherulite growth is indicated at several centers.

In the case of homogenous nucleation, these centers arise spontaneously in the melt, while for heterogeneous nucleation the nucleation center is a foreign body.

During growth, spherulites expand radially at a constant linear rate until the growth fronts from neighboring spherulites impinge.

Electron microscopy and electron diffraction studies have revealed that for almost all polymers, spherulites are composed of lamellar structure. Each lamella is a flat ribbon, and, like in simple crystals, chains that are folded are oriented perpendicular to the surface of the lamella.

Spherulites represent the crystalline portion of a sample growing at the expense of the noncrystallizable material.

The amorphous regions therefore constitute the residual elements of disorder resulting from the noncrystallizable material in the original melt — which includes catalyst residues, nonstereoregular chains (e.g., atactic chain segments), short-chain components, plasticizer molecules, and chain ends (low-molecular-weight chains) — is unable to disentangle and rearrange itself into the ordered arrays required in the crystalline state.

VI. CRYSTALLINITY AND POLYMER PROPERTIES

Crystallinity is important in determining **optical properties** because the **refractive index** of the crystalline region is always higher than that of the amorphous component irrespective of whether the amorphous component is in the glassy or rubbery state.

This difference in refractive indices of the component phases leads to high scattering and consequently, the **translucency** or **haziness** of **semicrystalline** polymers.

For a purely **amorphous** polymer, this does not occur, and hence amorphous polymers are usually **transparent**.

State	Polymer Properties
1	Polymer is in the melt form and therefore completely amorphous.
2	As a result of rapid cooling, polymer molecules are unable to align themselves for crystallization. Polymer is therefore amorphous, glassy, and transparent.
3	At 100°C which is higher than the T_g of the polymer, some molecular (segmental) mobility of polymer is now possible. Given sufficient time at this temperature, molecular alignment occurs for crystallization to take place. Polymer is now semicrystalline since crystallization cannot be 100%. The differing refractive indices of the amorphous and crystalline components result in translucency.
4	When cooled to this state, polymer retains its semicrystalline nature and hence its translucency.

Polymer Nomenclature

The IUPAC has specific guidelines for the nomenclature of polymers. Common names and trade names are also frequently used.

Simple **vinyl polymers** are named by attaching the prefix ***poly*** to the monomer name. For example, the polymer made from styrene becomes polystyrene.

When the monomer name consists of more than one word or is preceded by a letter or a number, the monomer is enclosed in parenthesis with the prefix *poly.* Thus polymers derived from vinyl chloride or 4-chlorostyrene are designated poly(vinyl chloride) and poly(4-chlorostyrene), respectively.

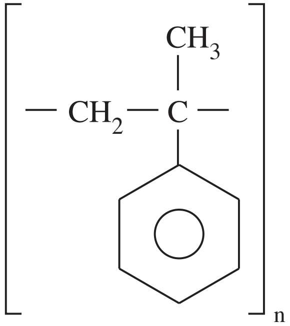
Diene polymerization may involve either or both of the double bonds. Geometric and structural isomers of butadiene, for example, are indicated by using appropriate prefixes — *cis* or *trans*; 1,2 or 1,4 — before *poly*, as in *cis*-1,2-poly(1,3-butadiene).

Tacticity of the polymer may be indicated by using the prefix *i* (isotactic), *s* (syndiotactic), or *a* (atactic) before *poly,* such as *s*-polystyrene.

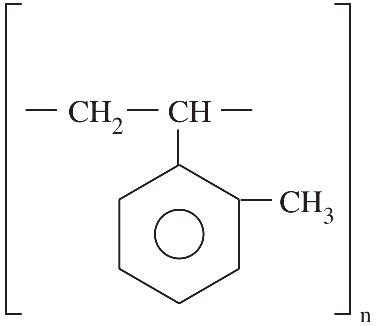
Copolymers are identified by separating the monomers involved within parentheses by either *alt* (alternating), *b* (block), *g* (graft), or *co* (random), as in poly(styrene-*g*-butadiene).

When side groups are attached to the main chain, some ambiguity could result from naming the polymers. For example, poly(methylstyrene) is an appropriate designation for any of the following structures.

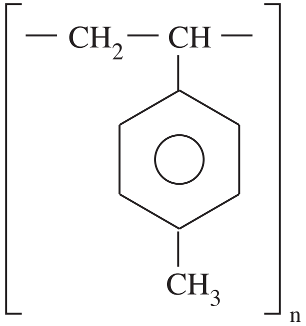
To avoid such ambiguity, these structures are designated poly(α-methylstyrene) (1), poly(*o*-methylstyrene) (2), and poly(*p*-methylstyrene) (3), respectively.



(1)



(2)

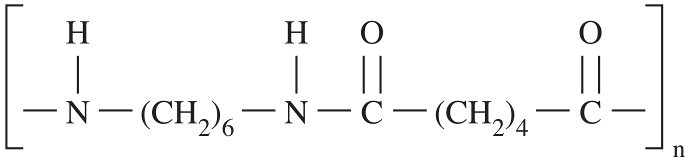


(3)

The nomenclature of **step-reaction** polymers is more complicated. These polymers are usually named according to the source or initial monomer(s) and the type of reaction involved in the synthesis.

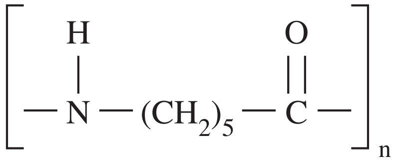
For example, nylon 6,6 (4) is usually designated poly(hexamethylene adipamide), indicating an amidation reaction between hexamethylenediamine and adipic acid.

Nylon 6 is called either poly(6-hexanoamide) or poly(ε-caprolactam). The former name indicates the structural and derivative method, while the latter is more commonly used and based on the source of the monomer.



$$\left[-\overset{H}{\overset{|}{N}}-(CH_2)_6-\overset{H}{\overset{|}{N}}-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-\right]_n$$

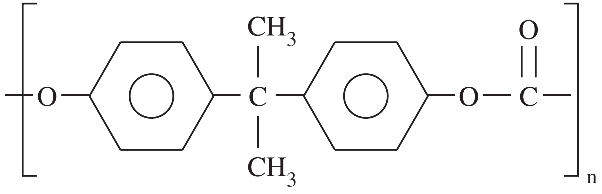
(4)



$$\left[-\overset{H}{\overset{|}{N}}-(CH_2)_5-\overset{O}{\overset{\|}{C}}-\right]_n$$

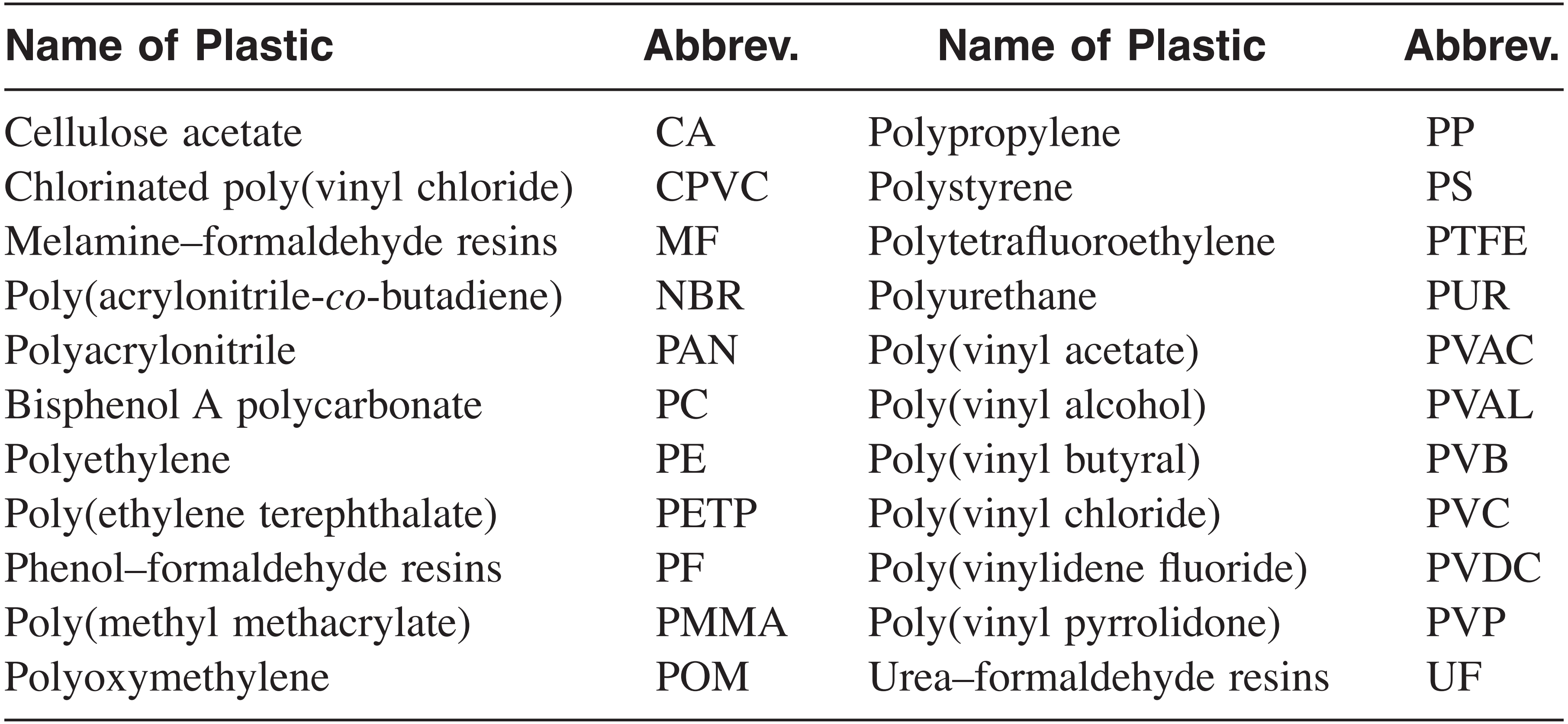
(5)

Some polymers are referred to almost exclusively by their **common names** instead of the more appropriate chemical names. An example is **polycarbonate** in place of poly(2,2-bis(4-hydroxyphenyl) propane) (6).



(6)

The following table lists the internationally accepted abbreviations for some common commercial polymers.



Name of Plastic	Abbrev.	Name of Plastic	Abbrev.
Cellulose acetate	CA	Polypropylene	PP
Chlorinated poly(vinyl chloride)	CPVC	Polystyrene	PS
Melamine–formaldehyde resins	MF	Polytetrafluoroethylene	PTFE
Poly(acrylonitrile-*co*-butadiene)	NBR	Polyurethane	PUR
Polyacrylonitrile	PAN	Poly(vinyl acetate)	PVAC
Bisphenol A polycarbonate	PC	Poly(vinyl alcohol)	PVAL
Polyethylene	PE	Poly(vinyl butyral)	PVB
Poly(ethylene terephthalate)	PETP	Poly(vinyl chloride)	PVC
Phenol–formaldehyde resins	PF	Poly(vinylidene fluoride)	PVDC
Poly(methyl methacrylate)	PMMA	Poly(vinyl pyrrolidone)	PVP
Polyoxymethylene	POM	Urea–formaldehyde resins	UF