Chapter 3

Chemical Bonding and Polymer Structure

I. INTRODUCTION

You will recall from your elementary organic chemistry that the physical state of members of a homologous series changes as the molecular size increases. Table 3.1 briefly outlines this for members of the alkane series with the general formula $[C_nH_{2n+2}]$. From Table 3.1, it is obvious that moving from the low- to the high-molecular-weight end of the molecular spectrum, members of the series change progressively from the gaseous state through liquids of increasing viscosity (decreasing volatility) to low melting solids and ultimately terminate in high-strength solids. Polymers belong to the high-molecular-weight end of the spectrum. In the following discussion, we will attempt to illustrate how the unusual properties of high polymers are developed. To do this, it will be convenient to consider 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 level)
3. Aggregation of polymer chains (tertiary structure)

But before we proceed into extensive discussion of these aspects, we must first consider the molecular forces operative in polymers. After all, this is fundamental to understanding polymer structures.

II. CHEMICAL BONDING

The electronic structure of atoms determines the type of bond between the atoms concerned. As we said earlier, 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. This results in a substantial lowering of the potential energies. Consequently, primary bonds are quite strong. On the other hand, valence electrons are not involved in the formation of secondary bonds — leading to weak bonds. Primary and secondary bonds can be further subdivided:

1. Primary bonds
   a. Ionic
   b. Covalent
   c. Metallic
2. Secondary bonds
   a. Dipole
   b. Hydrogen
   c. Induction
   d. van der Waals (dispersion)

We now discuss briefly some of these bonds that occur in polymers.

A. THE IONIC BOND

The so-called inert gases — Ne, Ar, and Kr — have completely filled s and p outermost orbitals, resulting in a spherical distribution of electrons. The inertness of these elements (gases) suggests that their electronic configuration confers stability. It is indeed observed that all elements seek to achieve this stable inert gas electronic configuration. They do this by either losing, gaining, or sharing electrons.

The mutual satisfaction of the need to attain the inert gas electronic configuration by those elements that lose electrons (electropositive elements) and those that gain electrons (electronegative elements) leads to the ionic bond. To illustrate this, consider sodium chloride [NaCl]. Sodium (with low ionization energy) can easily lose the outermost 3s electron to achieve the stable inert gas configuration. Chlorine,

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

on the other hand (with large electron affinity), can achieve a stable electronic configuration by gaining an extra electron. The loss of an electron by sodium results in a positively charged sodium ion, while the gain of an extra electron by the chlorine atom results in a negatively charged chloride ion:

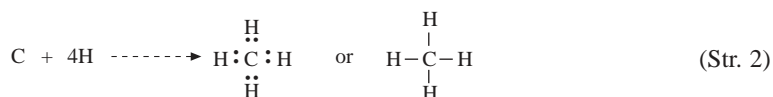$$Na + Cl \rightarrow Na^+ + Cl^- \tag{Str. 1}$$

The bonding force in sodium chloride is a result of the electrostatic attraction between the two ions.

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, as will be discussed later.

B. THE COVALENT BOND

In the previous section, we saw that the stable inert gas electronic configuration can be achieved by electropositive elements through ionization. For elements in the central portion of the periodic table, ionic bonding is impossible because a large amount of energy would be required to ionize the valence electrons. However, stable electronic configuration can be attained by the sharing of valence electrons. Bonds formed by electron sharing are called *covalent* bonds. Consider the formation of methane from hydrogen and carbon. The carbon atom has four unpaired electrons in its outer electron shell, while hydrogen has one electron. By sharing electrons, one from each atom per bond, a stable octet is obtained for the carbon atom and a stable pair for each hydrogen atom. The result is the methane molecule:

$$C \;+\; 4H \;\dashrightarrow\; H\!:\!\overset{\displaystyle H}{\underset{\displaystyle H}{\overset{\bullet\bullet}{\underset{\bullet\bullet}{C}}}}\!:\!H \quad \text{or} \quad H-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-H \tag{Str. 2}$$

This is the predominant bond in polymers. Covalent bonds can be single, double, or triple depending on the number of electron pairs. Typical values of bond strengths, expressed as dissociation energy, for covalent bonds that commonly occur in polymers are summarized in Table 3.2.

Recall that dissociation energy is that required to break the bond. It has a direct relationship with the thermal stability of polymers. Note also that while atoms are free to rotate about single bonds (flexible), they remain spatially fixed (rigid) for double and triple bonds.

C. DIPOLE FORCES

Molecules are electrically neutral, but will have a permanent dipole if the centers of the positive and negative charges do not coincide; this arises if the electrons shared by two atoms spend more time on one of the atoms due to differences in electronegativity. This can be illustrated by considering a diatomic molecule such as hydrogen chloride, HCl. Because chlorine is more electronegative than hydrogen, the shared pair of electrons between the chlorine atom and the hydrogen atom is drawn closer to the chlorine atom. Consequently, the chlorine atom has net negative charge while the hydrogen atom has a net positive charge:

Table 3.2 *Properties of Some Primary Covalent Bonds in Polymers*

Type of bond	Bond length in Å	Average dissociation energy (kcal/mol)	Type of bond	Bond length in Å	Average dissociation energy (kcal/mol)
C–C	1.54	83	C=S	1.71	124
C=C	1.34	147	C–Cl	1.77	79
C≡C	1.20	194	N–H	1.01	93
C–H	1.09	99	N–O	1.15	57
C–O	1.43	84	N–Si	1.74	—
C=O	1.23	171	O–H	0.96	111
C–N	1.47	70	O–O	1.48	33
C=N	1.27	147	O–Si	1.64	88
C≡N	1.16	213	S–S	2.04	51
C–S	1.81	62	S–H	1.35	81
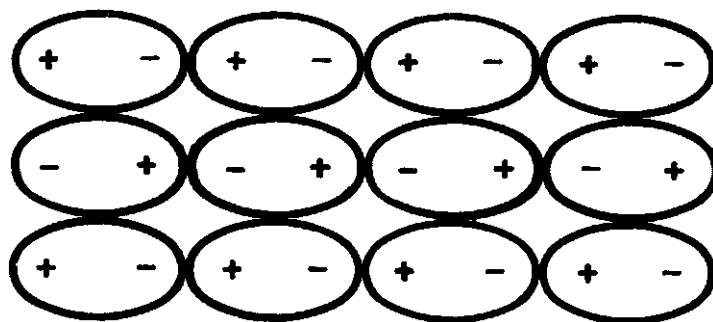
Figure 3.1 *Dipole–dipole interaction between polar molecules.*

$$\underset{H}{\delta+} \dashrightarrow \underset{Cl}{\delta-}$$
(Str. 3)

Any diatomic molecule in which there is a separation of positive and negative charge is said to be polar. As we shall see in Section III.A, in molecules containing more than two atoms the polarity of the molecule is determined by the bond angles. Polar molecules therefore have a small separation of charge, and this sets up a 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. The interaction forces between these molecules are called dipole-interaction forces or dipole–dipole interaction (Figure 3.1). This type of molecular orientation is generally opposed by thermal agitation. Consequently, the dipole–dipole interaction is temperature dependent. As we shall see later, dipole forces play a significant role in determining the tertiary structure and, hence, properties of some polymers.

D. HYDROGEN BOND

A particularly important kind of dipole interaction is the hydrogen bond. This is the bond between a positively charged hydrogen atom and a small electronegative atom like F, O, or N. The anomalous properties of water, for example, are associated with the hydrogen bonding between water molecules (Figure 3.2). The difference in electronegativities between hydrogen (2.1) and oxygen (3.5) causes the bonding electrons in H_2O to shift markedly to the oxygen atom so that the hydrogens behave essentially as bare protons. Hydrogen bonding is limited primarily to compounds containing F, N, and O because the small size of hydrogen permits these atoms to approach the hydrogen atom in another molecule very closely. For example, in spite of the similarity in electronegativities between Cl and N (3.0 for both), HCl with the larger chlorine atoms shows hardly any tendency to form hydrogen bonds.
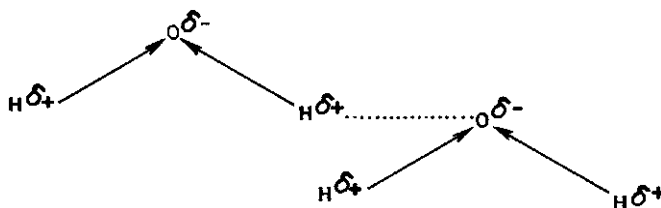
Figure 3.2 *Hydrogen bonding between two water molecules.*

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

Hydrogen bonds are relatively stronger than dipole bonds due to the small size of the hydrogen ion (Table 3.3). In polymers, hydrogen bonding usually occurs between functional groups in the same or different molecules. The hydrogen is generally part of such groups as carboxyl, hydroxyl, amine, or amide, while the other atom in the hydrogen bond is frequently oxygen (in carbonyl, ethers, or hydroxyls) or nitrogen (in amines, amides, urethanes, urea). The hydrogen bond plays a vital role in the structure and properties of polymers, particularly proteins.

E. INDUCTION FORCES

Every dipole has an electric field associated with it. This electric field is capable of inducing relative displacements of the electrons and nuclei in neighboring molecules. The result is that the surrounding molecules become polarized, i.e., possess induced dipoles. Intermolecular forces, called induction forces, exist between the permanent and induced dipole. Induction forces are weak and temperature independent. The ease with which molecules can be polarized — referred to as polarizability — varies.

F. VAN DER WAALS (DISPERSION) FORCES

From the above, it would be expected that the gases He, Ne, Ar, and Kr are incapable of forming any type of bonds (ionic, covalent, or metallic). In fact, these so-called inert gases derive the name from that usual stability (considerable reluctance to undergo reactions). However, at sufficiently low temperature these gases are known to condense to form solids. Similarly, molecules such as methane [CH_4], carbon dioxide [CO_2], and hydrogen [H_2] have all the valency requirements fulfilled and should, in principle, be incapable of forming bonds. Yet, these also solidify at sufficiently low temperatures. It is therefore apparent that some form of intermolecular force exists in these materials.

Electrons are usually in constant motion about their nuclei. At any particular instant, the centers of negative charge of the electrons cloud may not coincide with those of the nuclei. Consequently, instantaneous (fluctuating) dipoles exist even in nonpolar materials. If the orientations of fluctuating dipoles in neighboring molecules are in proper alignment, intermolecular attractions occur. These attractive forces are referred to as van der Waals (dispersion) forces. Van der Waals forces are present in all molecules and, as we shall see later, they contribute significantly to the bonding in polymers. Table 3.3 shows the relative magnitudes of the different interaction energies, while typical melting points for various compounds are shown in Table 3.4.

Table 3.4 *Typical Melting Temperatures for Some Substances with Different Types of Chemical Bonding*

Type of Bond	Substance	Melting Temperature (°C)
Ionic	Na F	988
	NaCl	801
	Na Br	740
	Na I	660
	NaO	2640
	CaO	2570
	Sr O	2430
	Ba O	1923
	Al_2O_3	3500
Covalent	Ge	958
	GaAs	1238
	Si	1420
	SiC	2600
	Diamond	3550
Metallic	Na	98
	Al	660
	Cu	1083
	Fe	1535
	W	3370
Van der Waals	Ne	–249
	Ar	–189
	CH_4	–184
	Kr	–157
	CL_2	–103
Hydrogen	HF	–92
	H_2O	0

Example 3.1: Explain the trend in the melting points of the following:

Compound/Element	Melting Point
KF	46
Na	97.5
F_2	–219.6
Polyethylene	135

Solution:

Compound/Element	Chemical Bonding	Bond Type
KF	Ionic	Primary
Na	Metallic	Primary
F_2	van der Waals	Secondary
Polyethylene (PE)	van der Waals	Secondary

Primary bonds are stronger than secondary bonds. Within the primary bonds ionic bonds are generally stronger than metallic bonds, particularly for univalent metals. Both fluorine and PE molecules are held by van der Waals forces. In the case of fluorine molecules, these forces are readily overcome by thermal agitation and, consequently, fluorine is a gas at room temperature. However, because of the macro-molecular sizes of PE molecules, in the aggregate the van der Waals forces become very large. This, coupled with extensive physical entanglements, results in a high melting point.

III. PRIMARY STRUCTURE

Primary structure refers to the atomic composition and chemical structure of the monomer — the building block of the polymer chain. An appreciation of 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, on the other hand, 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. Therefore, basic to understanding the structure of the monomer vis-á-vis the structure and properties of the resulting polymer is a fundamental understanding of:

- 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 the properties conferred on monomers as a result of their chemical composition

We have discussed chemical bonding, monomer functionality, and polymerization mechanisms in previous sections. Our attention now focuses on the chemical composition of monomers.

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. We now discuss this briefly.

The ionic compound sodium chloride is formed by an electron transfer from sodium (leaving behind a positively charged ion) to chlorine (leaving a negatively charged chloride ion). A diatomic molecule with such a pair of equal but opposite charges possesses a permanent dipole moment and is said to be *polar*. Sodium chloride, like all ionic substances where complete charge transfer has occurred, is highly polar. This polarity is responsible for the electrostatic attraction between adjacent ions in solid sodium chloride.

Covalent molecules, on the other hand, are formed by the sharing of electrons between the constituent atoms. In a diatomic molecule formed from two *like* atoms (e.g., H_2), the electron pair linking the two atoms is equally shared and the molecule is said to be *nonpolar*. But when molecules are formed from two unlike atoms (e.g., hydrogen fluoride, HF), the distribution of the electron cloud is concentrated on the more electronegative atoms (fluorine, in this case). Here again, as in ionic compounds, there is a separation of positive and negative charge and the molecule is said to be polar. However, since no complete charge transfer has taken place in this case, the polarity (of covalent molecules) is less than that of ionic compounds Even among covalent molecules, the degree of polarity varies depending on the electronegativities (electron-attracting ability) of the constituent atoms. The electronegativities of atoms commonly occurring in organic molecules are shown in Table 3.5. It is evident from the table that groups like C–Cl, C–F, –CO–, –CN, and –OH are polar.

In a polyatomic molecule, the polarity is a vector sum of all the dipole moments of the groups within the molecule. This depends on the spatial distribution (symmetry) of the groups within the molecule. To illustrate this, let us consider two triatomic molecules: water [H_2O] and carbon dioxide [CO_2]. Both the OH and CO groups are polar. But while the H_2O molecule is polar, CO_2 is a nonpolar molecule. The structure of CO_2 is linear, resulting in a cancellation of the dipole moments. However, H_2O has a triangular structure and, consequently, possesses an overall dipole moment (Figure 3.3).

Carbon tetrachloride, CCl_4, is another molecule that is nonpolar even though it has four polar C–Cl bonds. The nonpolar nature of CCl_4 is due to the symmetrical distribution of the four chlorines around the carbon atom. Replacement of one of the chlorine atoms by hydrogen destroys symmetry. The resulting

Table 3.5 *Electronegativities of Some Elements*

Atom	H	C	N	O	F	Sl	S	Cl
Electronegativity	2.1	2.5	3.0	3.5	4.0	1.8	2.5	3.0

From Pauling, L., *The Nature of the Chemical Bond,* Cornell University Press, Ithaca, NY, 1960. With permission.
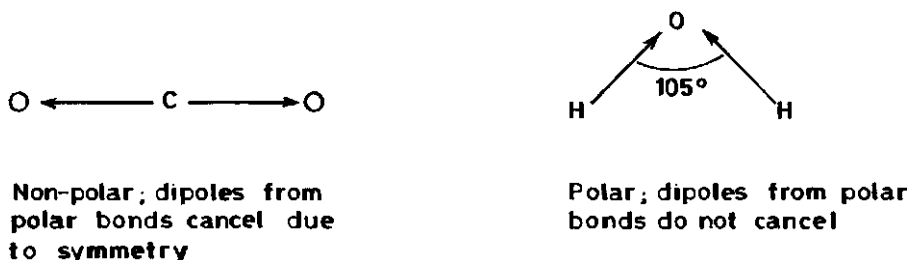
Figure 3.3 *Effect of symmetry on polarity of molecules.*

molecule, chloroform [CHCCl$_3$], is polar. Monomers such as ethylene and propylene are nonpolar, and so are the polymers derived from them. On the other hand, 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 (Table 3.6). The characteristic interunit linkages in condensation polymers, for example, –CO.O– (ester), –CO.NH– (amide), –HN–CO–NH– (urea), and –O.CO–NH– (urethane) are polar. Polarity, as we shall see later, affects the intermolecular attraction between chain molecules, and thus the regularity and symmetry of polymer structure. Naturally, properties such as the solubility and electrical nature of polymers, which depend on polymer structure, are intimately related to polarity.

IV.   SECONDARY STRUCTURE

To be able to understand polymer properties, we must be able to develop a physical picture of what these long molecules are really like. This is what we refer to as the secondary structure, i.e., the size and shape of an isolated single molecule. The size of the polymer is best discussed in terms of molecular weight. The shape of the polymer molecule (molecular architecture) will be influenced naturally by the nature of the repeating unit and the manner in which these units are linked together. It is therefore convenient to consider polymer shape in two contexts:
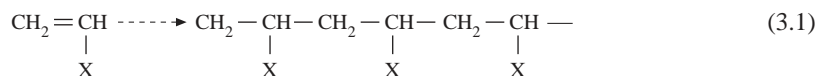
- Configuration — Arrangement fixed by primary valence bonds; can be altered only through the breaking or reforming of chemical bonds
- Conformation — Arrangement established by rotation about primary valence bonds

A. CONFIGURATION

As we saw earlier, a polymer molecule may be linear, branched, or cross-linked depending on the functionality of the monomers used. But let us look more closely at the polymer chain. 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. This may be illustrated by examining the polymers resulting from monosubstituted vinyl monomers. Here there are three possible arrangements:
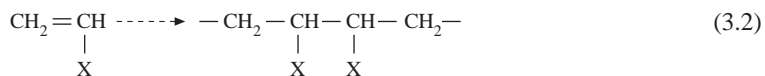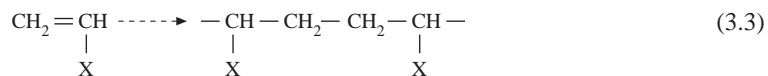
- Head-to-tail configuration

$$\text{CH}_2\!=\!\underset{\underset{\text{X}}{|}}{\text{CH}} \text{ -----} \blacktriangleright \text{ CH}_2-\underset{\underset{\text{X}}{|}}{\text{CH}}-\text{CH}_2-\underset{\underset{\text{X}}{|}}{\text{CH}}-\text{CH}_2-\underset{\underset{\text{X}}{|}}{\text{CH}}- \qquad (3.1)$$

- Head-to-head configuration

$$\text{CH}_2\!=\!\underset{\underset{\text{X}}{|}}{\text{CH}} \text{ -----} \blacktriangleright -\text{CH}_2-\underset{\underset{\text{X}}{|}}{\text{CH}}-\underset{\underset{\text{X}}{|}}{\text{CH}}-\text{CH}_2- \qquad (3.2)$$

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
$CH_2\!=\!CH_2$ $\mid$ CH_3 Propylene	Nonpolar	$\left[\!-CH_2-CH_2-\right]$ $\mid$ CH_3 Polypropylene	Nonpolar
$CH_2\!=\!CH$ $\mid$ Cl Vinyl chloride	Polar	$\left[-CH_2-CH-\right]$ $\mid$ Cl Poly(vinyl chloride)	Polar
$CH_2\!=\!CCl_2$ Vinylidene chloride	Nonpolar	Cl $\mid$ $\left[\!-CH_2-C-\right]$ $\mid$ Cl Poly(vinylidene chloride)	Nonpolar
$CH_2\!=\!CH$ $\mid$ CN Acroylonitrile	Polar	$\left[\!-CH_2-CN-\right]$ $\mid$ CN Polyacrylonitrile	Polar
$CF_2\!=\!CF_2$ Tetrafluoroethylene (symmetrical)	Nonpolar	$\left[\!-CF_2-CF_2-\right]$ Polytetrafluorethylene (Teflon)	Nonpolar

- Tail-to-tail configuration

$$CH_2\!=\!CH \;\cdots\!\!\rightarrow\; -CH-CH_2-CH_2-CH- \qquad (3.3)$$
$$\quad\;\; \underset{X}{\mid} \qquad\qquad\quad \underset{X}{\mid} \qquad\qquad \underset{X}{\mid}$$

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

Stereoregularity refers to the spatial properties of a polymer molecule. To discuss this, let us consider two examples.

1. Diene Polymerization

You will recall that 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 polymer unsaturation is part of the pendant group, while in 1,4 addition the unsaturation is part of the backbone. In the latter case, the backbone has a rigid structure and rotation is not free around it. Therefore, two different configurations, known as *cis* and *trans,* are possible. For example, 1,4-polyisoprene:

$$\text{—CH}_2 \diagdown \text{C}=\text{C} \diagup \text{CH}_2\text{—}$$
$$\text{CH}_3 \diagup \qquad \diagdown \text{H}$$

(Str. 4)

cis-1,4-polyisoprene (natural rubber)

$$\text{—CH}_2 \diagdown \text{C}=\text{C} \diagup \text{H}$$
$$\text{CH}_3 \diagup \qquad \diagdown \text{CH}_2\text{—}$$

(Str. 5)

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

2. Tacticity

Polymers of monosubstituted olefins [CH₂› CHXl 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, on the vinyl polymer lie above (or below) the plane of the main chain.

(Str. 6)

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

(Str. 7)
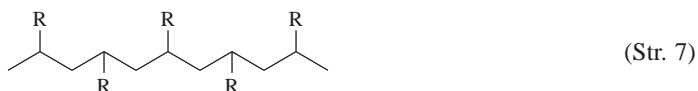
- Atactic — Random sequence of position of substituent occurs along the chain.

(Str. 8)
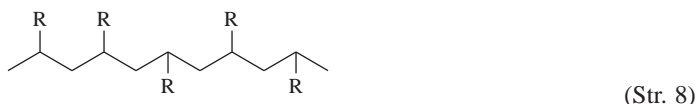
B. CONFORMATION

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

To amplify the discussion, let us consider the possible arrangements of a single isolated polymer chain in dilute solution. We start with a short segment of the chain consisting of four carbon atoms (Figure 3.4).
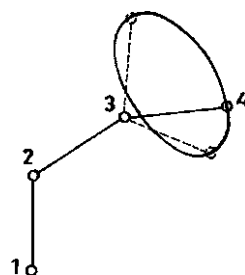
Figure 3.4 *A segment of polymer chain showing four successive chain atoms; the first three of these define a plane, and the fourth can lie anywhere on the indicated circle which is perpendicular to and dissected by the plane.*
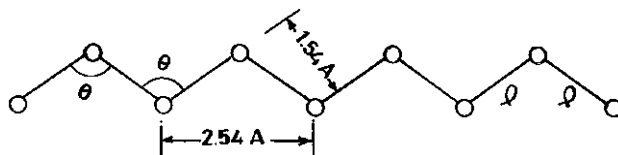
Figure 3.5 *The fully extended all-trans conformation of a carbon–carbon chain.*

We define a plane by three of the carbon atoms in this segment and allow free rotation about the carbon–carbon bond. In this case, the fourth carbon atom can be anywhere on the circle indicated in the figure. Because of steric hindrance, some positions will certainly be more probable than others. Each successive carbon atom on the chain can similarly take any of the several positions in a circle based, randomly, on the position of the preceding atom. For a chain consisting of thousands of carbon atoms, it can thus be seen that the number of conformations is literally infinite. One of these conformations of particular interest is that in which each successive carbon atoms lies in the same plane in the *trans* location with respect to earlier carbon atoms in the chain — thus forming a fully extended plane of zigzag arrangement of carbon atoms (Figure 3.5).

This represents one of the two extreme shapes of a polymer chain, the other being the completely random coil. The planar zigzag conformation exists in some crystalline polymers or in highly oriented amorphous polymers. Typical examples are simple molecules like 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).

The other extreme of the conformation spectrum that may be assumed by the polymer chain is the completely random coil. Polymers that are 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 that a polymer chain can assume is virtually limitless. This, of course, assumes that there is free rotation about single bonds. In practice, however, there is no such thing as completely free rotation. All bonds have to overcome certain rotational energy barriers whose magnitude depends on such factors as steric hindrance, dipole forces, etc. (Figure 3.7).

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. As we shall see later, the flexibility of polymer molecules, which 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 to emphasize its large size. We noted earlier that the same bonding forces (intra- and intermolecular) operate in both low- and high-molecular-weight materials. However, the unique properties exhibited by polymers and 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. At very low molecular weights, hardly any strength, for example, is developed. Beyond this MW or DP, there is a steep rise in the performance until a certain level, beyond which the properties change very little with increase in molecular weight. Finally, an asymptotic value is reached (Figure 3.8). The curve in Figure 3.8 is general for all polymers. Differences exist only in numerical details. Optical and electrical properties, color, and density show a less marked dependence on molecular weight.
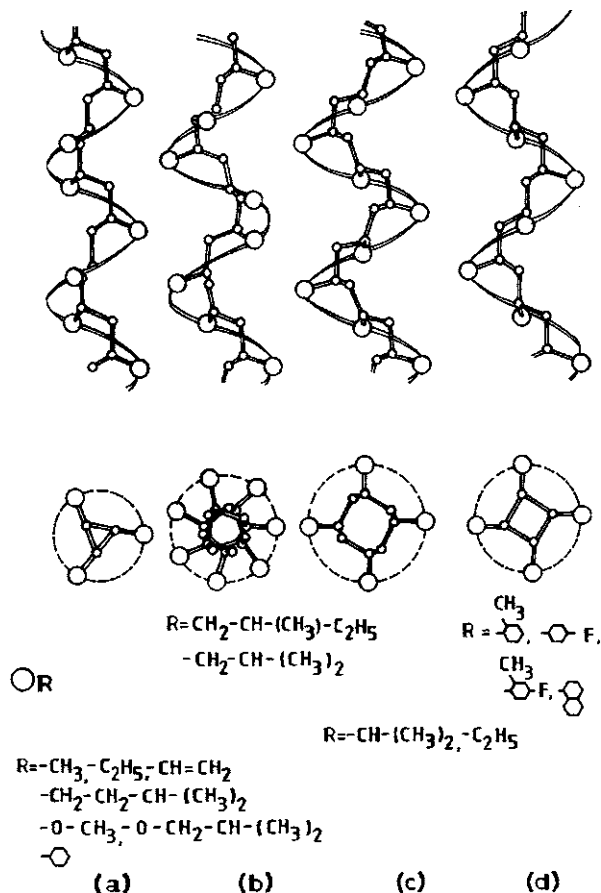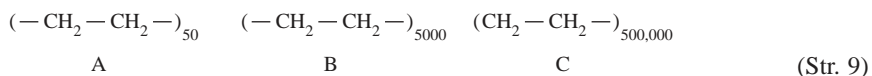
Figure 3.6 *Helical conformations of isotactic vinyl polymers. (From Gaylord, N.G. and Mark, H., Linear and Stereoregular Addition Polymers, Interscience, New York, 1959. With permission.)*

Example 3.2: Which of the following materials will be most suitable for the manufacture of thermoplastic sewage pipe? Explain your answer very briefly.

$$(-CH_2-CH_2-)_{50} \qquad (-CH_2-CH_2-)_{5000} \qquad (CH_2-CH_2-)_{500,000}$$

$$A \qquad\qquad\qquad B \qquad\qquad\qquad C \qquad\qquad\qquad\qquad \text{(Str. 9)}$$

Solution:

Material	Molecular Weight
A	1.4×10^3
B	1.4×10^5
C	1.4×10^7

Material B will be most suitable. The molecular weight of A is too low, and the material will not have developed the physical properties necessary to sustain the mechanical properties that a plastic pipe must withstand. On the other hand, the molecular weight of material C is relatively too high to permit easy processing.
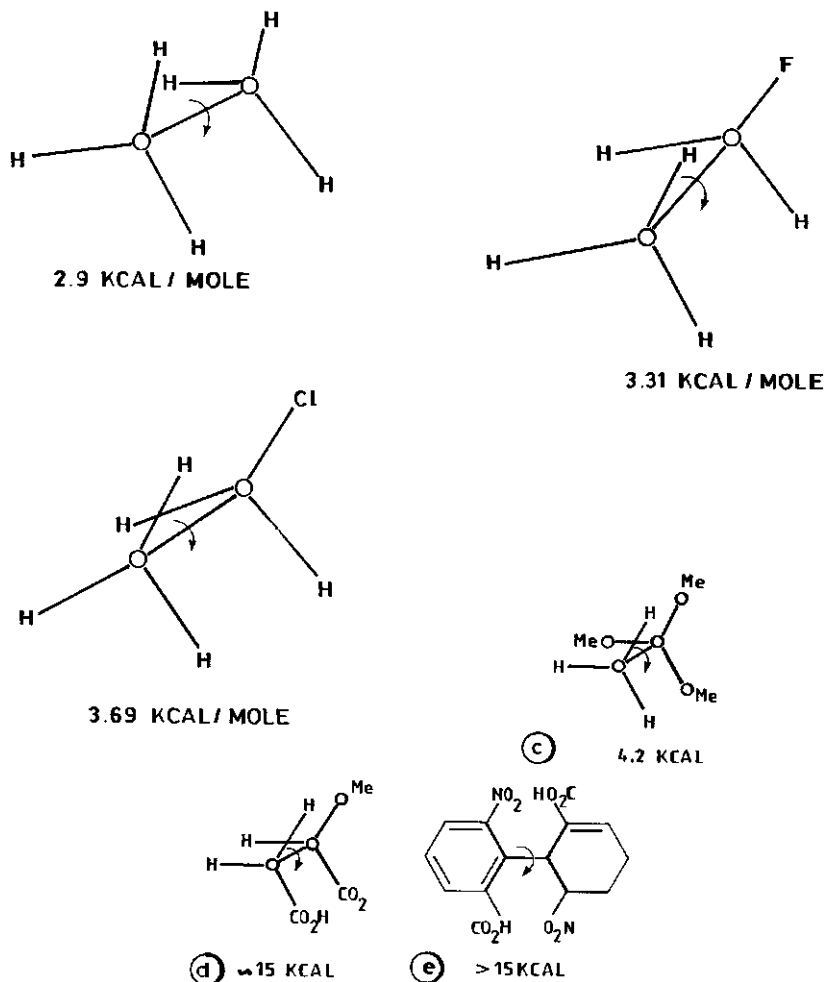

2.9 KCAL / MOLE

3.31 KCAL / MOLE

3.69 KCAL/ MOLE

(c) **4.2 KCAL**

(d) ~15 KCAL

(e) > 15KCAL

Figure 3.7   *Rotational energy as a function of substitution and interaction of substituent groups.*

We also noted earlier that irrespective of the polymerization mechanism, the formation of polymer is a purely random occurrence. Consequently, 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. In order to characterize polymers, therefore, we use the molecular weight distribution (MWD) curve, which represents a plot of the percentage (frequency) of a particular species against its molecular weight (Figure 3.9).

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, $\overline{M}_n$, and weight-average molecular weight, $\overline{M}_w$. Others are the z-average molecular weight, $\overline{M}_z$, and viscosity-average molecular weight, $\overline{M}_v$. Below are the relevant formulas for computing these average molecular weights (Equations 3.4–3.7).

$$\overline{M}_n - \frac{W}{\sum\limits_{i=1}^{\infty} N_i} = \frac{\sum\limits_{i=1}^{\infty} N_i M_i}{\sum\limits_{i=1}^{\infty} N_i} = \frac{\sum\limits_{i=1}^{\infty} W_i}{\sum\limits_{i=1}^{\infty} W_i/M_i} = \frac{1}{\sum w_i/M_i} \tag{3.4}$$

$$\overline{M}_w = \sum_{i=1}^{\infty} w_i M_i = \frac{\sum_{i=1}^{\infty} w_i M_i}{W} = \frac{\sum_{i=1}^{\infty} N_i M_i^2}{\sum_{i=1}^{\infty} N_i M_i} \qquad (3.5)$$

$$\overline{M}_v = \left[\sum_{i=1}^{\infty} w_i M_i^a \right]^{1/a} = \left[\frac{\sum_{i=1}^{\infty} N_i M_i^{a+1}}{\sum_{i=1}^{\infty} N_i M_i} \right]^{1/a} \qquad (3.6)$$

$$\overline{M}_z = \frac{\sum_{i=1}^{\infty} N_i M_i^3}{\sum_{i=1}^{\infty} N_i M_i^2} = \frac{\sum_{i=1}^{\infty} w_i M_i^2}{\sum_{i=1}^{\infty} w_i M_i} \qquad (3.7)$$

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 (η) 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.
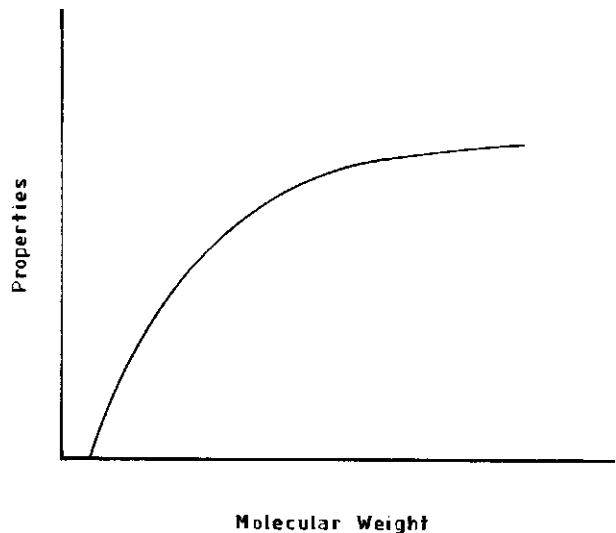

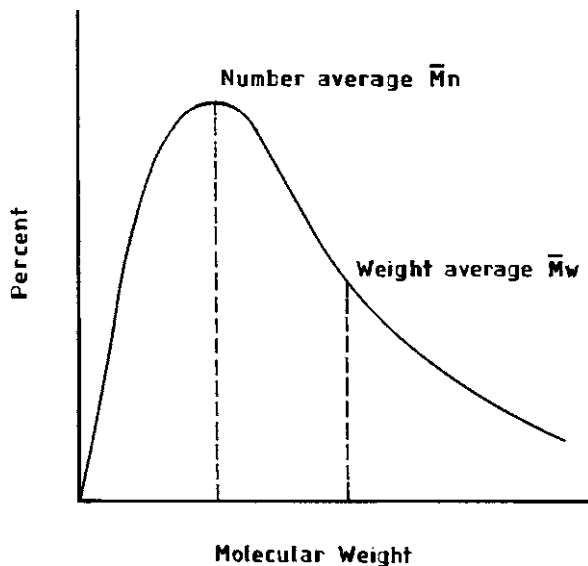**Figure 3.8** *Change of physical properties with molecular weight.*

Figure 3.9 *Molecular weight distribution curve.*

Example 3.3: The following data were obtained in a determination of the average molecular weight of a polymer.

Molecular Weight	Weight (g)
60,000	1.0
40,000	2.0
20,000	5.0
10,000	2.5

a. Compute the number average and the weight average-molecular weights, $\overline{M}_n$ and $\overline{M}_w$.

b. What is the polydispersity of the polymer and how many molecules are in 1 gram of polymer?

Solution:

a. $\dfrac{\sum W_i}{\sum W_i/M_i}$ where W_i = weight species i.

$$\overline{M}_n = \frac{1+2+5+2.5}{1/60\times10^3 + 2/40\times10^3 + 5/20\times10^3 + 2.5/10^4}$$

$$= 18,600 \text{ g/mol}$$

$$\overline{M}_w = \sum w_i M_i; \quad w_i = \frac{W_i}{W} = \text{weight fraction of species i}$$

$$= \frac{10^4}{10.5}\left[6 + 2\times4 + 5\times2 + 2.51\right]$$

$$= 25,200 \text{ g/mol}$$

b. Polydispersity $= \overline{M}_w/\overline{M}_n = \dfrac{25,200}{18,600} = 1.35$

$$\text{Molecules/g} = N_I/\overline{M}_n = \frac{6.02 \times 10^{23}}{18,600} = 3.25 \times 10^{19}$$

The molecular weight of polymers can be determined by a number of physical and chemical methods. These include (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 the need to resort to calibration by another method; that is, 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)

The number-average weight, $\overline{M}_n$, is observed from end-group analysis, colligative property measurements, and gel permeation chromotography. The weight-average molecular weight, $\overline{M}_w$, is determined from light scattering, ultracentrifugation and gel permeation chromatography. z-average molecular weight, $\overline{M}_z$, is determined from GPC, while viscosity-average molecular weight, $\overline{M}_v$, can be 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. However, 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 to 10 kcal/mol compared with those of primary bonding forces, which are of the order 50 to 100 kcal/mol. But 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. The magnitude of these secondary bonding forces, coupled with the high physical entanglement between chains, dictates many polymer properties. Tertiary structure is concerned with the nature of the intermolecular secondary bonding forces and with structural order of the resulting polymer.

A. SECONDARY BONDING FORCES (COHESIVE ENERGY DENSITY)

As we said earlier, secondary bonds consist of dipole, induction, van der Waals, and hydrogen bonds. Dipole forces result from the attraction between permanent dipoles associated with polar groups. Induction forces arise from the attraction between permanent and induced dipoles, while van der Waals (dispersion) forces originate from the time-varying perturbations of the electronic clouds of neighboring atoms. Hydrogen bonds are very important in determining the properties of such polymers as polyamides, polyurethanes, and polyureas. In general, the magnitude of the bond energies decreases from hydrogen bond to dipole bond to van der Waals (dispersion) forces.

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:

$$CED = \frac{\Delta E_v}{V_L} \tag{3.8}$$

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

It can be shown from the Classius–Clapeyron equation that

$$\Delta E_v = \Delta H_v - RT \tag{3.9}$$

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

Consequently,

$$CED = \frac{\Delta E_v}{V_L} = \frac{\Delta H_v - RT}{V_L} \qquad (3.10)$$

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. To do this, we employ the relation between the cohesive energy density and solubility parameter (Equation 3.11).

$$CED = \delta^2 \qquad (3.11)$$

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

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

Values of solubility parameters and cohesive energy of some polymers are given in Table 3.7. The value of E_{coh} is also dependent on the molar volume. For polymers the appropriate volume is that occupied by each repeat unit in the solid state. Thus E_{coh} represents the cohesive energy per repeat unit volume, V_R. These simple relations as stated before, however, are not exact; stronger interactions change the validity of Equation 3.11. However, significant practical predictions can be made from the values in Table 3.7, such as what solvents will dissolve a given polymer.

Table 3.7 *Cohesive Energy of Polymers*

	d (cal$^{1/2}$/cm$^{3/2}$)		V_R	E_{coh} (from δ) (cal/mol)	
Polymers	**From**	**To**	**(cm³/mol)**	**From**	**To**
Polyethylene	7.7	8.35	32.9	1,950	2,290
Polypropene	8.3	9.2	49.1	3,300	4,160
Polyisobutene	7.8	8.1	66.8	4,060	4,300
Polyvinylchloride	9.4	10.8	45.2	3,990	5,270
Polyvinylidene chloride	9.9				
Polyvinyl bromide	9.5		63.8	4,850	
Polyvinylfluoroethylene	6.2		50.0	1,920	
Polychlorotrifluoroethylene	7.2	7.9	61.8	3,200	3,860
Polyvinyl alcohol	12.6	14.2	35.0	5,560	7,060
Polyvinyl acetate	9.35	11.05	72.2	6,310	8,820
Polyvinyl propionate	8.8		90.2	6,900	
Polystyrene	8.5	9.3	98.0	7,080	8,400
Polymethyl acrylate	9.7	10.4	70.1	6,600	7,500
Polyethyl acrylate	9.2	9.4	86.6	7,330	7,650
Polypropyl acrylate	9.05		103.0	8,440	
Polybutyl acrylate	8.8	9.1	119.5	9,360	9,900
Polyisobutyl acrylate	8.7	11.0	114.2	9,020	14,420
Poly-2,2,3,3,4,4,4, heptafluorobutyl acrylate	6.7		148.0	6,640	
Polymethyl methacrylate	9.1	19.8	86.5	7,160	14,170
Polyethyl methacrylate	8.9	9.15	102.4	8,110	8,570
Polybutyl methacrylate	8.7	9.0	137.2	10,380	11,110
Polyisobutyl methacrylate	8.2	10.5	135.7	9,120	14,960
Poly-*tert*,butyl methacrylate	8.3		138.9		9,570
Polyethoxyethyl methacrylate	9.0	9.9	145.6	11,790	15,270

Table 3.7 (continued)   *Cohesive Energy of Polymers*

Polymers	d (cal$^{1/2}$/cm$^{3/2}$) From	To	V_R (cm³/mol)	E_{coh} (from δ) (cal/mol) From	To
Polybenzyl methacrylate	9.8	10.0	152.0	14,600	15,200
Polyacrylonitrile	12.5	15.4	44.8	7,000	10,620
Polymethacrylonitrile	10.7		63.9	7,320	
Poly-*a*-cyanomethyl	14.0	14.5	82.1	16,090	17,260
Polybutadiene	0.1	8.6	60.7	3,900	4,490
Polyisoprene	7.9	10.0	75.7	4,730	7,570
Polychloroprene	8.2	9.25	71.3	4,790	6,100
Polyepichlorohydrin	9.4		69.7	6,160	
Polyethylene terephthalate	9.7	10.7	143.2	13,470	16,390
Polyhexamethylene adipamide	13.6		208.3		138,500
Poly(δ-aminocaprylic acid)	12.7		135.9		21,920
Polyformaldehyde	10.2	11.0	25.0	2,600	3,030
Polytetramethylene oxide	8.3	8.55	74.3	5,120	5,430
Polyethylene sulfide	9.0	9.4	47.9	3,880	1,230
Polypropylene oxide	7.5	9.9	57.6	3,240	5,650
Polystyrene sulfide	9.3		115.8		10,020
Polydimethyl siloxane	7.3	7.6	75.6	4,030	4,300

From Van Krevelen, D.W., *Properties of Polymers,* Elsevier, Amsterdam, 1972. With permission.

Example 3.4: The table below shows the density and enthalpy of vaporization [ΔH_{vap}] of two solvents: methylethyl ketone and acetone.

Solvent	Density (g/cm³)	ΔHv· (cal/g)
Methylethyl ketone	0.8	106
Acetone	0.8	125

Which is a better solvent for polystyrene at room temperature? The CED for polystyrene is 75 cal/cm³. Assume room temperature is 27°C.

Solution: Basis = 1 g of solvent*

$$CED = \frac{\Delta H_{v'} - RT}{V_L} = \frac{\Delta H_{v\cdot} - RT}{1/\rho_{sol}}$$

$$= \rho_{sol}\left(\Delta H_v - RT\right)$$

where ρ_{sol} = density of solvent. In the SI system

$$R = 8.303 \times 10^3 \ \frac{Nm}{(K)kg\ mol}$$

$$= 8.303 \times 10^3 = J/(K)\,(kg\ mol)$$

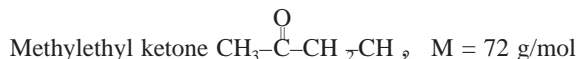* Units of ΔHv are in cal/g; therefore, the units of the term RT must be consistent with this.

$$R = 1.984 \text{ cal}/(K)(g \text{ mol})$$

$$= 1.984 \text{ cal}/(g); \quad T = 27 + 273 = 300 \text{ K}$$

Recall 1 cal = 4.184 J, 1 kg mol = 10^3 g mol.

$$RT = (1.984/M) \times 300 \text{ cal/g} = 595.2/M \text{ cal/g}$$

where M = molecular weight of solvent.

$$\text{Acetone } CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 \quad M = 58 \text{ g/g mol}$$

$$\text{Methylethyl ketone } CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2CH_3 \quad M = 72 \text{ g/mol}$$

Methylethyl ketone:

$$CED = 0.8 \left(g/cm^3\right)\left(106 - \frac{595.2}{72} \text{ cal}\right)$$

$$= 0.8 [106 - 8.27] \text{ cal}/cm^3$$

$$= 78.18 \text{ cal}/cm^3$$

Acetone:

$$CED = 0.8 \left(g/cm^3\right)\left(125 - \frac{595.2}{58} \text{ cal}\right)$$

$$= 0.8 [125 - 10.26]$$

$$= 91.79 \text{ cal}/cm^3$$

Since the CED of methylethyl ketone is closer to that of polystyrene than that of acetone, methylethyl ketone should be a better solvent for polystyrene than acetone.

B. CRYSTALLINE AND AMORPHOUS STRUCTURE OF POLYMERS

As discussed earlier, when a polymer is cooled from the melt or concentrated from a dilute solution, molecules are attracted to each other forming a solid mass. In doing so, two arrangements are essentially possible:
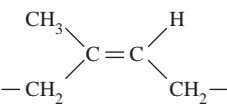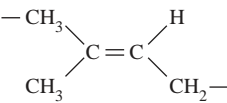
- In the first case, the molecules vitrify, with the polymer chains randomly coiled and entangled. The resulting solid is amorphous and is hard and glassy.
- In the second case, the individual chains are folded and packed in a regular manner characterized by three-dimensional long-range order. The polymer thus formed is said to be crystalline.

We must recall, however, that 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, as we shall see shortly, 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, as we saw earlier, are responsible for intermolecular bonding in polymers. You will recall also that 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. Let us now discuss these in further detail.

Table 3.8 *Properties of Polyisoprene Isomers*

Isomer	Structure	Properties
1,4-*cis*=polyisoprene (heavea rubber)	CH_3, H, $C=C$, $-CH_2$, CH_2-	Soft, pliable, easily soluble rubber; has a high retractive force; used for making vehicle tires
1,4-*trans*-polyisoprene (gutta-percha)	$-CH_3$, H, $C=C$, CH_3, CH_2-	Tough, hard; used as golf ball covers

2. Structural Regularity

We have just said that in the process of association of polymer molecules to form a solid mass, molecules must come as close together as possible. It follows that any structural features of polymer molecules that can impede this process will necessarily detract from crystallinity. Polyethylene is perhaps the simplest molecule to consider in this case. Polyethylene is nonpolar, and the intermolecular attraction is due to the relatively weak van der Waals forces. The chains can readily assume a planar zigzag conformation characterized by a sequence of *trans* bonds and can therefore produce short identity periods along the polymer chain length. The rotation around the C–C bond is inhibited by an energy barrier of about 2.7 kcal/mol of bonds. Thus, even though polyethylene molecules are held together by weak van der Waals forces, the high structural regularity that 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. However, 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, for example, is reduced 20 to 25°C on going from the linear to the branched polymer.

Regularity per se is not sufficient to ensure crystallizability in polymers. The spatial regularity and packing are important. To illustrate this, let us consider two examples of stereoregular polymers. Table 3.8 shows the properties of two isomers: *cis*- and *trans*-polyisoprene. It is obvious from the table that the stereoregular *trans* form is more readily packed and crystallizable and has properties of crystalline polymers.

The second example is the stereoregularity displayed by monosubstituted vinyl polymers of olefins. As we saw earlier, these types of polymers can occur in three forms of tacticity: isotactic, syndiotactic, and atactic. Isotactic and syndiotactic polymers possess stereoregular structures. Generally these polymers are rigid, crystallizable, high melting, and relatively insoluble. On the other hand, atactic polymers are soft, low melting, easily soluble, and amorphous.

3. Chain Flexibility

In the preceding discussion, we consistently emphasized that close alignment of polymer molecules is a vital prerequisite for the effective utilization of the intermolecular bonding forces. During crystallization, this alignment and uniform packing of 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 to 5 kcal/mol, the same order of magnitude as molecular cohesion forces. It is to be expected, therefore, that those polymers whose chains are flexible will be more susceptible to this thermal agitation than those with rigid or stiff chain structure.

The flexibility of chain molecules arises from rotation around saturated chain bonds. With a chain of –CH$_2$– units as a basis, it is interesting to consider how variations on this unit will affect rotation of adjacent units and, hence, chain flexibility. Studies of this type have led to the following general conclusions:

- 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. However, if they occur irregularly along the polymer chain, they are amorphous, soft, and rubbery materials.

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$_2$)$_6$CO—	45
Nylon 6,8	—NH(CH$_2$)$_6$NHCO(CH$_2$)$_6$CO—	235
Poly (p-xylene)	—CH$_2$—⬡—CH$_2$—	400

- 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 by making polymers less rigid, more rubbery, and more readily soluble than the corresponding 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 illustrates the effect of these factors on crystalline melting point.

4. Polarity

When molecules come together and aggregate into a crystalline solid, a significant cohesion between neighboring chains is possible. Consequently, polymer molecules with specific groups that are capable of forming strong intermolecular bonding, particularly if these groups occur regularly without imposing valence strains on the chains, are crystallizable. You will recall from our earlier discussion that such groups as

$$\underset{H}{\overset{H}{|}}\,\underset{}{\overset{O}{||}}$$
–N–C– (amide); –N–C–O– (urethane); and –N–C–N– (urea) (Str. 10)
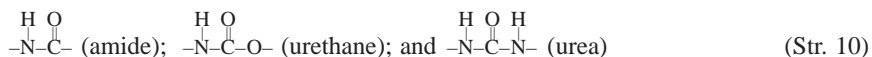
provide sites for hydrogen bonding whose energy ranges from 5 to 10 kal/mol. In nylon 6 or 6,6, for example, the regular occurrence of amide linkages leads to a highly crystalline, high melting polymer.

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 (Table 3.10).

Table 3.10 *Effect of Polarity on Crystallizability*

Polymer	Repeat Unit	T_{em} (°C)
Polyethylene	$-CH_2-CH_2-$	135
Nylon 6	$\begin{array}{c} \text{H} \quad\text{O} \\ \mid \quad\; \mid\mid \\ -N-C-(CH_2)_5- \end{array}$	223
Nylon 6,6	$\begin{array}{c} \text{H} \qquad\qquad \text{H} \quad\text{O} \qquad\qquad \text{O} \\ \mid \qquad\qquad\; \mid \quad\; \mid\mid \qquad\qquad \mid\mid \\ -N-(CH_2)_6-N-C-(CH_2)_4-C- \end{array}$	265
Polyoxymethylene	$-CH_2-O-$	180
Poly(vinyl chloride)	$\begin{array}{c} -CH_2-CH- \\ \mid \\ Cl \end{array}$	273
Polyacrylonitrile	$\begin{array}{c} -CH_2-CH- \\ \mid \\ CN \end{array}$	317

Given our earlier argument that the presence of –O– units in a chain backbone enhances flexibility, the fact that the melting point of polyoxymethylene (180°C) is higher than that of polyethylene (135°C) (Table 3.10) seems contradictory. 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. Thus, for polyoxymethylene the induced flexibility is more than offset by the increased bonding forces resulting from polarity.
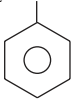
5. Bulky Substituents

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. For example, vinyl polymers with small substituents such as polypropylene [–CH$_3$] and polystyrene [–C$_6$H$_5$] 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. The atactic forms of these polymers are therefore amorphous. Large or bulky substituents, on the other hand, increase the average distance between chains and, as such, prevent the effective and favorable utilization of the intermolecular bonding forces. Thus

polymers like poly(methyl acrylate) and poly(vinyl acetate) with large pendant groups $-\overset{\displaystyle O}{\overset{\|}{C}}-O-CH_3$ and $O-\overset{\displaystyle O}{\overset{\|}{C}}-CH_3$ respectively, cannot crystallize even if the pendant groups are spaced regularly (isotactic and

syndiotactic forms). Table 3.11 shows the change in the crystalline melting point with increased length of the polymer side chain. Note that for the 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. However, when the size of the pendant group is such that the packing distance between the chains in the solid state is increased, the forces of interaction between chains decrease and so does the melting point. 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 to allow greater interchain interaction.

The above discussion clearly indicates that stereo regularity, chain flexibility, polarity, and other steric factors have profound influence on crystallizability and melting points and, hence, as we shall see later, play an important role in the thermal and mechanical behavior of polymers.

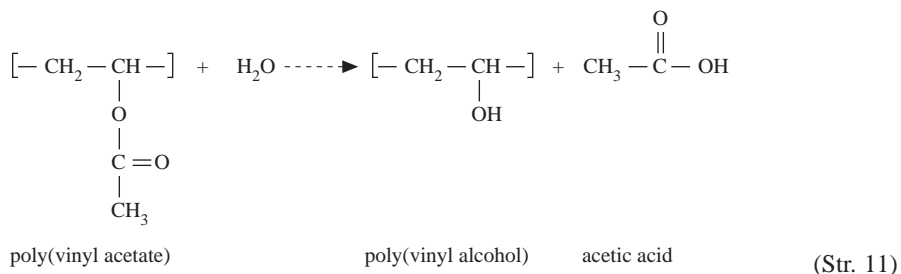**Table 3.11**   *Stiffening of Polymer Chains by Substituents*

Polymer	Repeat Unit	T_m (°C)
Polyethylene	$-CH_2-CH_2-$	135
Polypropylene	$-CH_2-CH-$ $\quad\quad\quad\mid$ $\quad\quad\quad CH_3$	176
Poly(1-butene)	$-CH_2-CH-$ $\quad\quad\quad\mid$ $\quad\quad\quad CH_2$ $\quad\quad\quad\mid$ $\quad\quad\quad CH_3$	125
Poly(1-pentene)	$-CH_2-CH-$ $\quad\quad\quad\mid$ $\quad\quad\quad CH_2$ $\quad\quad\quad\mid$ $\quad\quad\quad CH_2$ $\quad\quad\quad\mid$ $\quad\quad\quad CH_3$	75
Polystyrene	$-CH_2-CH-$ phenyl	240

Example 3.5: Explain the following observations.

a. Atactic polystyrene can be oriented (have its chain aligned by stretching at a temperature above its T_g, but does not crystallize; rubber on the other hand, both crystallizes and becomes oriented when it is stretched.

b. Poly(vinyl alcohol) is made by the hydrolysis of poly(vinyl acetate) because vinyl alcohol monomer is unstable. The extent of reaction may be controlled to yield polymers with anywhere from 0 to 100% of the original acetate groups hydrolyzed. At room temperature, pure poly(vinyl acetate), i.e., 0% hydrolysis, is insoluble in water. However, as the extent of hydrolysis is increased, the polymers become more water soluble up to 87% hydrolysis, after which further hydrolysis decreases water solubility.

c. Toluene and xylene have approximately the same cohesive energy density (CED), but xylene is a more convenient solvent for polyethylene.

Solution:

a. Atactic polystyrene has an irregular structure and therefore will not crystallize when oriented. Natural rubber (*cis*-1,4-polyisoprene) has a relatively small pendant group and as such is crystallizable.

$$[-CH_2-CH-] \;+\; H_2O \;\text{-----}\blacktriangleright\; [-CH_2-CH-] \;+\; CH_3-\overset{\displaystyle O}{\overset{\displaystyle \|}{C}}-OH$$

poly(vinyl acetate) poly(vinyl alcohol) acetic acid (Str. 11)

As the hydroxyl group becomes available following the hydrolysis, there is a corresponding increase in the water solubility of the product, poly(vinyl alcohol), as a result of intermolecular hydrogen bond formation. At an advanced stage of hydrolysis the CED of poly(vinyl alcohol) increases to such an extent that water solubility decreases, from the arguments in Section V.A.

c. Toluene has a boiling point of about 111°C, while xylene has a boiling point of 138 to 144°C. As a result of the highly crystalline nature of polyethylene it will dissolve in solvents only at temperatures close to its melting point (about 135°C). When the boiling points of toluene and xylene are compared, xylene is obviously a preferable solvent for polyethylene.

C. MORPHOLOGY OF CRYSTALLINE POLYMERS

Most polymers are partially crystalline. Evidence for this emerged in the 1920s from X-ray diffraction studies. X-ray diffraction patterns of some polymers, in contrast to those of simple crystalline solids, showed sharp features, associated with regions of three-dimensional order, superimposed on a diffuse background characteristic of amorphous, liquidlike substances. The interpretation of these patterns was that polymers are semicrystalline, consisting of small, relatively ordered regions — the crystallites embedded in an otherwise amorphous matrix. This interpretation led to the "fringed micelle" model of crystalline polymers. The fringed micelle concept, which enjoyed popularity for many years, held that, since polymer chains are very long, they passed successively through the crystallites and amorphous regions (Figure 3.10). The chains were thought to run parallel to the longer direction of the crystallites. Although the fringed micelle model of polymer morphology seemed to explain many of the properties of semicrystalline polymers, it has now been abandoned in favor of more ordered and complex models. This change is partly as a result of developments in the field of electron microscopy.

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 media, temperature, and growth rate. In discussing polymer crystalline morphology, our initial focus is on molecular packing. This concerns how the polymer chains (with an extended conformation of either planar zigzag or helix) are packed into the unit cell, which is the fundamental element of a crystal structure. This is followed by discussion of the morphologic features of the polymer single crystal and those of polymers crystallized from the melt.

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. Note that *trans* conformation is different from the *trans* configuration discussed in Section IV.A.

In some cases, however, steric hindrance causes the main chain to assume a minimum energy conformation other than the *trans* form. Some of these variations may be mere distortions of the fully extended planar zigzag conformation, as in most polyesters, polyisoprenes, and polychloroprene. In other
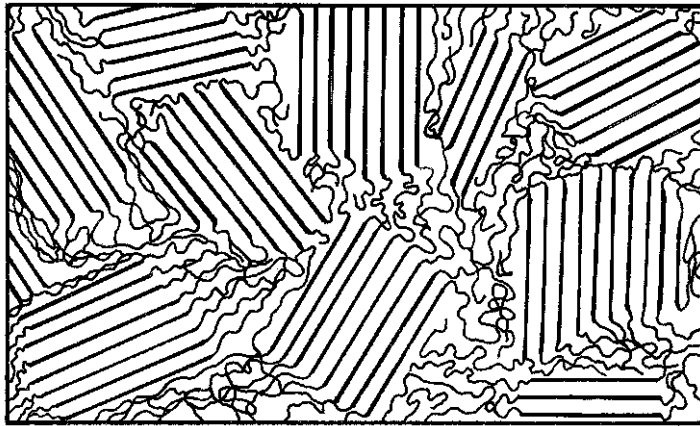
Figure 3.10 *Fringed micelle model. (From Bryant, W.W.D., J. Polym. Sci., 2, 547, 1947. With permission.)*

cases, in order to relieve the strain due to the presence of bulky substituents, the main chain rotates and assumes the helical conformation in the crystalline phase. This is the case for most isotactic polymers and 1,1 disubstituted ethylenes.

a. Polyethylene

The unit cell in polyethylene is a parallelepiped with a rectangular cross-section and lattice parameters: a = 7.41 Å; b = 4.94 Å; and c = 2.55 Å (orthorhombic crystal system) (Figure 3.11). By convention, the polymer chains, in passing through the unit cell, lie parallel to the lattice translation vector c. The lattice parameter c (magnitude of c) depends on the crystallographic repeat unit (Bravais lattice or crystal system). In polyethylene, the crystallographic repeat unit contains one chemical repeat unit. The packing of the repeat units in the unit cell is shown in Figure 3.12.
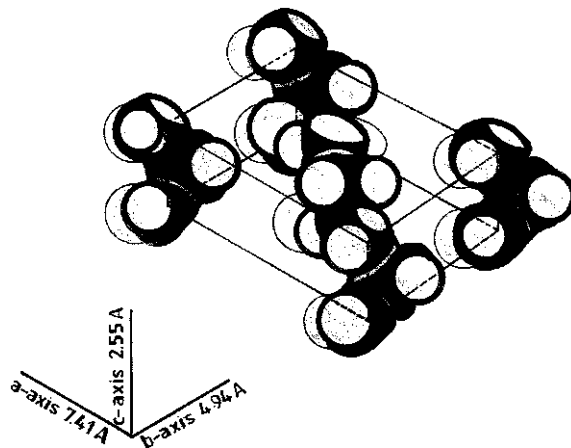

Figure 3.11 *Arrangement of chains in the unit cell of polyethylene. (From Geil, P.H., Polymer Single Crystals, John Wiley & Sons, New York, 1933. With permission.)*

b. Poly(ethylene terephthalate)

The conformation is a slight distortion of the planar zigzag. The benzene ring lies nearly in the plane of zigzag, but the main chains are no longer exactly planar. They make a slight angle with the planar zigzag (Figure 3.13). The unit cell has lattice constants:
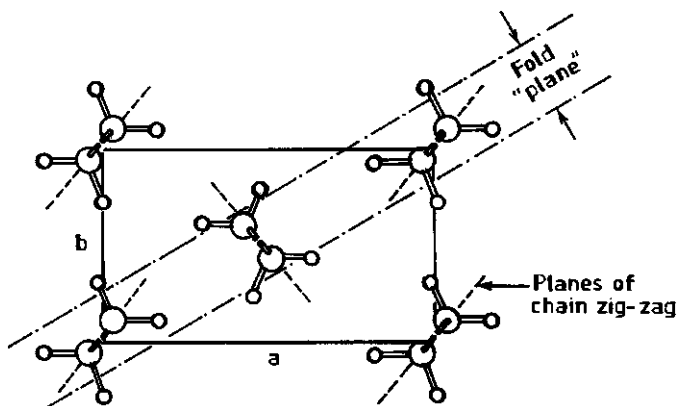
Figure 3.12 *Packing in the crystal structure of polyethylene as viewed along the c-axis. (From Natta, G. and Corradini, P., Rubber Chem. Technol., 33, 703, 1960. With permission.)*

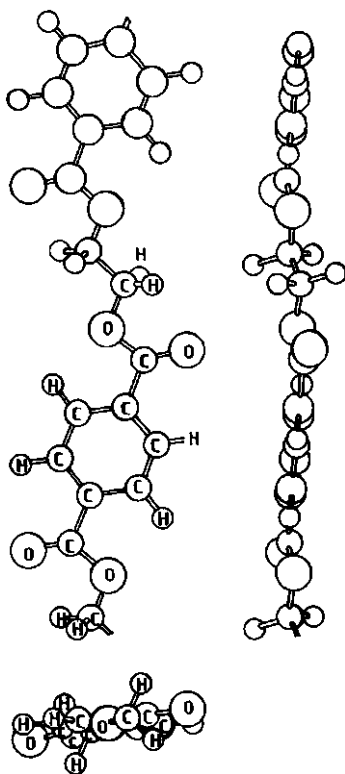**Figure 3.13** *Molecular conformation of polyethylene terephthalate.*

a = 4.56 Å   α = 98.5°
b = 5.94 Å   β = 118°
c = 10.75 Å   δ = 112°

c. *Polypropylene*

We have first seen that polyethylene exists in the planar zigzag conformation. Polypropylene can be considered as having a linear polyethylene backbone, but with the H atom on every other carbon atom

replaced by a methyl [–CH$_3$] group. Polypropylene can exist in either atactic (noncrystallizable) form or in the crystallizable syndiotactic or isotactic forms. For the isotactic form, because of the size of the pendant [–CH$_3$] group (relative to the H atom, in polyethylene), the backbone can no longer exist in the planar zigzag form; it must rotate. The lowest energy state is attained by a regular rotation of 120° by each chemical repeat unit. This means that there are three chemical repeat units per turn. These pack into a monoclinic crystal system (Figure 3.14) whose unit cell has parameters:
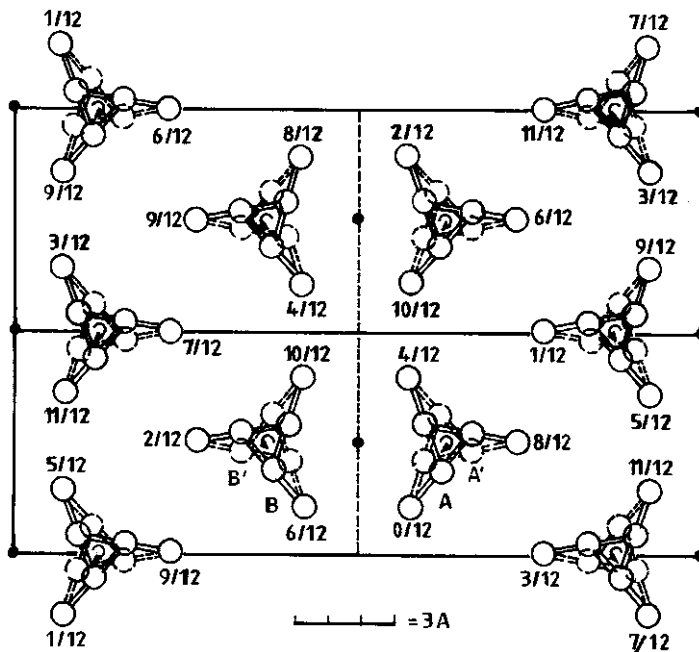

Figure 3.14 *Projection of the monoclinic unit cell of polypropylene along the chain-axis. (From Natta, G. and Corradini, P., Nuovo Cimento Suppl., 15(1), 40, 1960. With permission.)*

a = 6.65 Å + 0.05 Å
b = 20.96 + 0.15 Å   β = 99.° 20′ + 1°
c = 6.50 + 0.04 Å

d. Degree of Crystallinity

We noted earlier that polymers, by virtue of their large size and in contrast to low-molecular-weight materials, are incapable of 100% crystallinity. To visualize this mentally, the term *semicrystalline* is frequently used to describe crystalline polymers. One of the most useful and practical concepts in the characterization of semicrystalline polymers is the degree of crystallinity. Let us now consider how this can be estimated.

We start by treating the semicrystalline polymer as a two-phase system with a distinct demarcation between the crystalline and amorphous material. We know, of course, that this is not strictly true. Now suppose P_m is an actual or measured intensive property of the polymer, while P_c and P_a are the same property due, respectively, to the crystalline and amorphous materials (components) in the same state as exists in the polymer. Then the degree of crystallinity can be deduced from the individual contributions of the crystalline and amorphous components to the measured property:

$$p_m = \phi \, p_c + (1 - \phi) \, p_a \tag{3.12}$$

By rearrangement, Equation 3.12 becomes

$$\phi = \frac{p_a - p_m}{p_a - p_c} \qquad (3.13)$$

The degree of crystallinity may be derived this way by measurement of a material property such as specific volume, specific heat, enthalpy, and electrical resistivity:

Example 3.6: For the polyethylene of Figure 3.15 (lower curve) calculate the fraction of crystalline material at 20°C assuming the coefficient of expansion for amorphous material is the same above and below T_m.
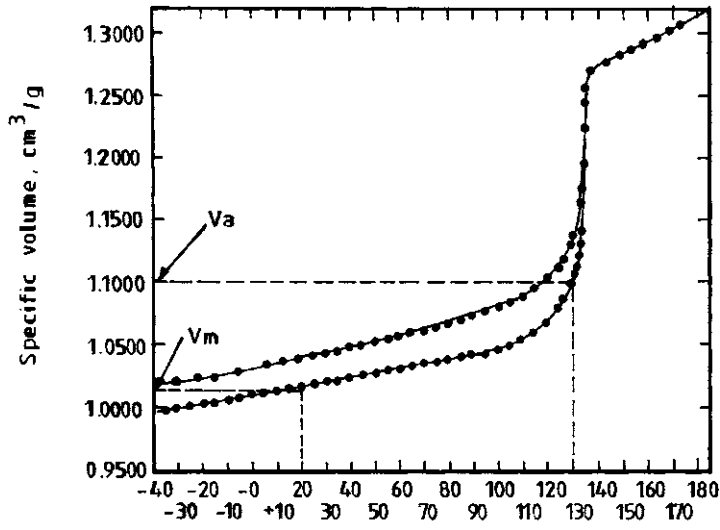

Figure 3.15 *Specific volume–temperature relations for linear polyethylene (Marlex 50). Specimen slowly cooled from melt to room temperature prior to experiments (0) and specimen crystallized at 130°C for 40 days and then cooled to room temperature prior to experiment (0). (From Mardelkern, L., Rubber Chem. Technol., 32, 1392, 1959. With permission.)*

Solution:

$$\phi = \frac{V_a - V_m}{V_a - V_c}$$

where V_a = specific volume due to the amorphous component
      V_m = measured specific volume
      V_c = specific volume due to the crystalline component

At 130°C, the crystallization temperature, the specific volume would be due to the amorphous phase. From Figure 3.15, $V_a = 1.100$ and $V_m = 1.06$ (at 20°C). To calculate the specific volume of the ideal polymer remember that

$$\text{Density of a perfect crystal} = \rho \text{ where}$$

$$\rho = \frac{\text{Mass}}{\text{Volume}} = \frac{nM}{N_A V}$$

where n   = number of polymer repeat units per unit cell

M = molecular weight of repeat unit unit
N_A = Avogadro's number
V = volume of a unit cell

For polyethylene, the unit cell is orthorhombic with lattice parameters:

a = 7.41 Å
b = 4.94 Å
c = 2.55 Å

Besides, each unit cell contains two repeat units, one at the center, four at the corners, but with each shared with four other unit cells. That is a total contribution of one repeat unit by the corners (see Figure 3.12).

$$\rho = \frac{2 \times 28}{\left(6.023 \times 10^{23}\right)\left(7.41 \times 10^{-8}\right)\left(4.94 \times 10^{-8}\right)\left(2.55 \times 10^{-8}\right)}$$

$$= 0.996 \text{ g/cm}^2$$

$$V_C = \text{specific volume} = 1/\rho = 1.004$$

$$\phi = \frac{1.100 - 1.016}{1.100 - 1.004} = \frac{0.084}{0.096} = 0.875$$

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. This was followed by several other reports and for so many polymers this phenomenon is now regarded as universal. 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. This lamellar nature of polymer single crystals has been found to be fundamental. 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 polyethylene 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 (or, in some cases, very nearly 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 polyethylene, for example, it has been demonstrated that only about five chain carbon atoms are required for the chain to fold on itself.

The plane on which the regular folding of chains occurs defines the *fold plane,* while the thickness of the lamella is regarded as the *fold period* (Figure 3.16). Chain ends may either terminate within the crystal, forming a defect, or be excluded from the crystal, forming cilia. In some cases, irregular folding and branch points can also occur.

Let us now consider how this fold conformation fits into the overall morphological features of the polymer single crystal. Figure 3.17 is a schematic representation of the top surface of an idealized model of a diamond-shaped polyethylene single crystal as seen along the (001) (c axis). The curved lines,
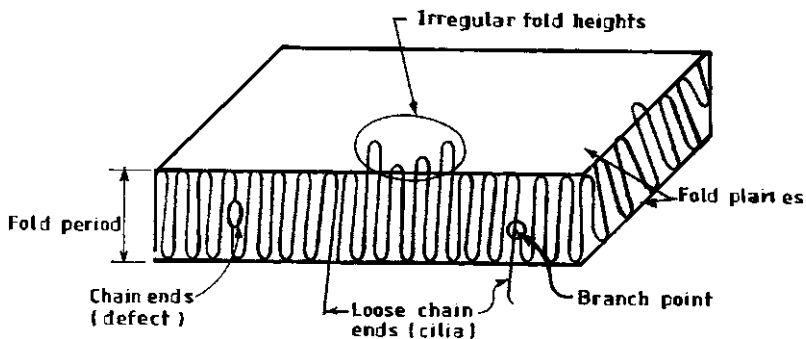
Figure 3.16 *Schematic diagram of chain folding showing conformational imperfections.*
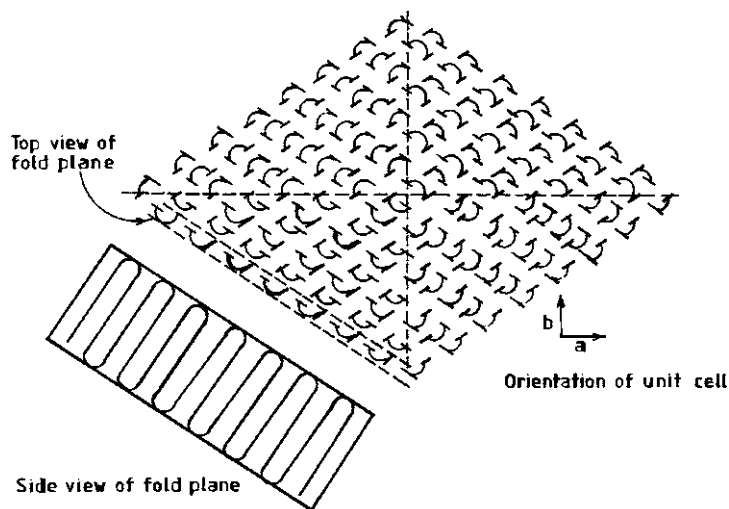

Figure 3.17 *Fold packing in a polyethylene single crystal. (From Reneker, D.H. and Geil, P.H., J. Appl. Phys., 31, 1916, 1960. With permission.)*

which represent the chain folds, terminate on solid lines representing the plane of zigzag. Note the following features:

- The alternating parallel orientation of the planes of zigzag indicates that the chains twist in addition to folding within their fold plane.
- The crystal is divided into four quadrants (broken lines) and, as we shall see shortly, each sector slopes away from the apex of the pyramidal structure. The fold planes in each quadrant are parallel to the outside edge of that quadrant. It follows that the entire crystal is composed of four triangular quadrants that contain rows of fold planes.

c. Hollow Pyramidal Structure

Ridges are formed by pleats of extra material deposited along one of the diagonals of each diamond-shaped crystal. Obviously, therefore, crystals of polyethylene are not simply flat lamellae. Experimental evidence has shown that they may exist in solution as hollow pyramids. These pyramids may or may not be corrugated depending on the crystallization conditions.

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. This results in the formation of a planar pyramid. In other cases, however, the direction of displacement is reversed periodically. In this case, corrugated pyramids are formed.

Besides the structures already discussed, more complex morphologies may be obtained from the growth of polymer crystals from solutions. The structure that emerges from the crystallization of a polymer is a function of a complex interaction of factors that include the type of solvent, solution temperature, concentration, and polymer molecular weight. Some examples of these structures include spiral growth, dendrites, and hedrites.
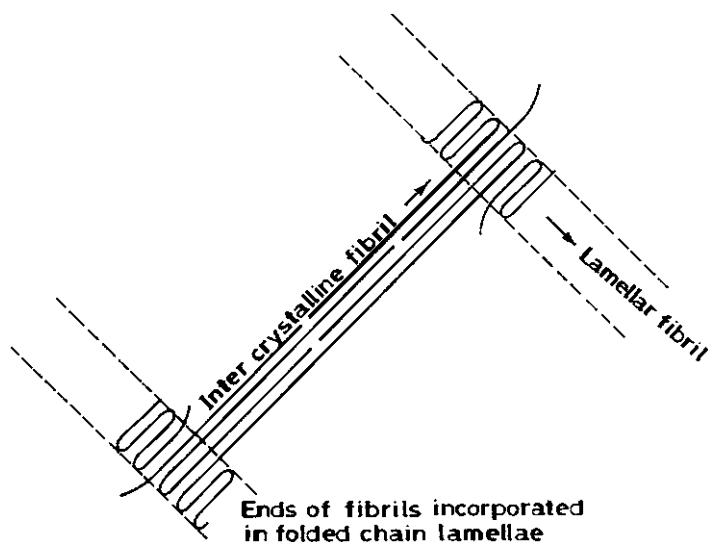

Figure 3.18 *The intercrystalline fibril.*

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 polyethylene, 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. The growth nucleus for crystallization or spherulite development is thought to be a simple crystal that develops by the formation of a multilayer stack. Thereafter, one axis of each lamella extends forming a lamellar fibril. These lamellar fibrils now grow radially from a central nucleus, but have a tendency to twist, diverge, and branch during growth. Since individual lamella do not increase in lateral dimensions, their characteristic branching via screw dislocations is a space-filling process. Lamellae usually have dimensions of 1 μ in length and 100 Å in thickness.

As crystallization proceeds, the growth fronts of two different spherulites meet, and the lamellae extend across spherulite boundaries into uncrystallized material available, thus holding the material together. In addition, interlamellar fibrils tie two or more lamellae together and also bridge spherulite themselves.

One important feature of the interlamellar fibril is that the chain molecules lie parallel to the length of the fibril in contrast to the situation existing in the lamella where chains are oriented at right angles (Figure 3.18). This implies that each interlamellar fibril is an extended chain crystal. The formation of interlamellar links is thought to originate from the inclusion of one chain molecule in two different and possibly widely separated lamellae. This provides the nucleus for subsequent deposition of other molecules, thus producing the intercrystalline ties.

The picture that emerges from the above discussion of the development of spherulitic structure is that 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 fact that the noncrystallizable material in the original melt — which includes catalyst residues, nonstereo-oregular 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. It appears that as spherulite growth proceeds the noncrystallizable material diffuses ahead of the growth front. However, spherulites themselves, while predominantly crystalline, do contain defects such as chain ends, dislocations, and chemical impurities. The defect materials segregate and separate the radiating lamellae and contribute to the overall amorphous content. Consequently, polymers have a wide variety of crystallinity, which varies from 0% in noncrystallizable polymers like atactic PMMA to almost 100% for highly crystallizable polymers like polytetrafluoroethylene and linear polyethylene. For a particular crystallizable polymer, the degree of crystallinity depends on spherulite growth conditions, which determine the size and extent of perfection of the crystals. For example, it is known that higher degrees of lamellar perfection can be obtained generally at high crystallization temperatures (in the neighborhood of the T_m polymers and after prolonged periods at these temperatures.

Given the long-chain nature of polymer molecules, it is obvious that the process of crystallization involves extensive molecular translation from the high degree of disorder characteristic of the melt to the highly ordered state. Also, this must occur in a time that is short relative to the time required for crystallization. Consequently, the degree of crystallinity in most polymers is a function of the rate of crystallization. After rapid crystallization, the amorphous content of the polymer sample is increased. On the other hand, if a molten polymer is crystallized slowly, the crystals develop in a more perfect manner and tend to exclude impurities that could interfere with the ordering process.

VI. CRYSTALLINITY AND POLYMER PROPERTIES

To conclude this discussion, we need to examine how crystallinity is related to polymer properties. As we have seen above, polymers are semicrystalline, which means that they are composed of amorphous and crystalline phases. Since the amorphous phase can exist in the rubbery or glassy state, the overall effect of the semicrystalline nature of crystalline polymers depends, in the first place, on the state of the amorphous phase or the temperature of use. For example, the modulus of crystalline polymers is only about an order of magnitude higher than the modulus of an amorphous polymer in the glassy state, whereas it is about four orders of magnitude higher than the modulus of the amorphous in the rubbery state. This suggests therefore that modification of polymer properties due to crystallization will be more pronounced for a polymer with amorphous component in the rubbery state than for one whose amorphous phase is in the glassy state. For example, the modulus of rubber can be increased dramatically by induced crystallization. However, for polystyrene — whose amorphous component is glassy at room temperature — crystallization, if induced, has a negligible effect on its modulus, which is already high. By similar arguments, it can be seen that any polymer property that is different for both the amorphous and crystalline components of the polymer will be determined by the relative amounts of these two components as well as their form and distribution (i.e., by the polymer morphology). It is therefore obvious that for engineering design of polymers, control of the properties of a semicrystalline polymer resolves into control of its morphology or spherulite development process. The size and degree of perfection of spherulites are controlled by the crystallization conditions that exist during the unit operations involved in the production of a polymer product.

Example 3.7: Poly(ethylene terephthalate) is cooled rapidly from 300°C (state 1) to room temperature (state 2). The resulting material is rigid and perfectly transparent. The sample is then heated to 100°C and maintained at that temperature during which time it gradually becomes translucent (state 3). It is then cooled down to room temperature and is again found to be rigid, but is now translucent rather than transparent (state 4). For this polymer, $T_m = 267$°C and $T_g = 69$°C. Describe the molecular mechanisms responsible for the behavior of the polymer in each state. Sketch a general specific-volume vs. temperature curve for this polymer indicating T_g, T_m, and the locations of states 1–4 described above.

Solution:
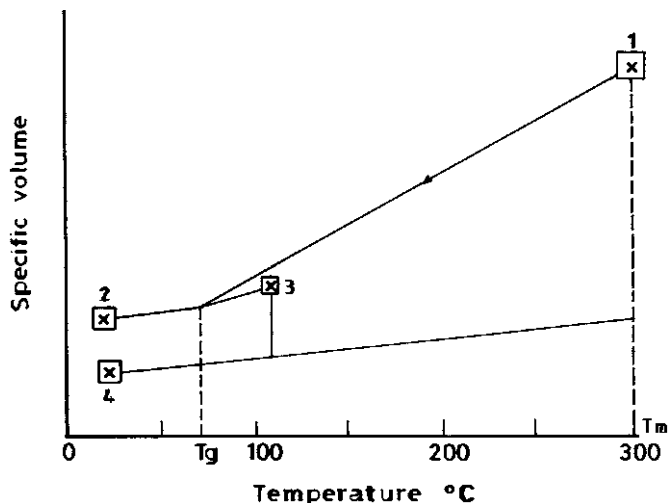
Crystallinity is important in determining optical properties because the refractive index of the crystalline region is always higher than that of the amorphous component irrespective of whether the amorphous component is in the glassy or rubbery state. This difference in refractive indices of the component 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. Therefore the state of polyethylene terephthalate can be explained as follows:

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.

VII. PROBLEMS

3.1   Explain the following observations:

a. Polyisobutylene has a much higher oxidation resistance than natural rubber.

b. Polyethylene is a better material for transformer insulation than poly(p-chlorostyrene).

c. At room temperature, poly(methylmethacrylate) is transparent, while polyethylene is translucent. At temperatures above 135°C, both polymers are transparent.

d. Polyethylene assumes a planar zigzag conformation, while polyisobutylene has a helical conformation.

e. The percentage of moisture absorption of the following polyamides:
   Nylon 6: 1.3–1.9
   Nylon 12: 0.25–0.3

f. Small amounts of chlorination (10 to 50 wt%) of polymethylene (–CH_2–), a saturated paraffin, lower its softening temperature. However, with higher amounts of chlorination (>70 wt%) the softening temperature of the polymer increases again.

g. The addition of glass fibers increases the heat distortion temperature of crystalline polymers like polyethylene and polypropylene, but not that of amorphous polymers like polycarbonate and polysulfone.

h. Both polyethylene and gasoline are hydrocarbons, but high-density polyethylene (HDPE) is used for making automobile gasoline tanks.

i. Teflon is used in nonstick pans.

j. Nylon 6 has a higher melting point than polyethylene.

3.2. A sample of styrene monomer is heated until it is partially polymerized. In order to determine the quantity of polymer formed, the solution of polystyrene in unreacted styrene monomer is poured into a large volume of methanol. The polymer precipitates (methanol has a considerably higher cohesive energy density than polystyrene) and is readily dried and weighed. The CED of water is even higher than that of methanol. Why is water not used in place of methanol for precipitating the polymer? Could the quantity of polymer be determined by distilling off the unreacted monomer and weighing the residue? Explain.

3.3. Two hundred grams of polymer consist of the fractions shown in the following table:

Fraction	Mass (g)	Molecular Weight (g/gmol)
I	100	2×10^3
II	50	2×10^4
III	50	1×10^5

What are the values of $\overline{M}_n$, $\overline{M}_w$, and the polydispersity of the sample.

3.4. Three samples of a polymer were mixed thoroughly without reaction as shown below. Calculate M_n and M_w.

Sample	$\overline{M}_n$	$\overline{M}_w$	Mass in Mixture (g)
A	1.2×10^5	4.5×10^5	200
B	5.6×10^5	8.9×10^5	200
C	10.0×10^5	10.0×10^5	100

3.5. The number-average degrees of polymerization required for good mechanical properties by polymers V and P are 2000 and 1500, respectively. It is known, however, that one of these polymers is poly(vinyl chloride), while the other is poly(vinylidene chloride). On the basis of this information assign polymers V and P. Explain your decision.

3.6. In most cases, free-radical polymerization of a monomer containing a C› C double bond results in a noncrystalline polymer. Explain. Give three examples of monomers that yield crystalline polymers by free-radical polymerization.

3.7. Bristow and Watson[1] reported the following data at 25°C for a 1:39 copolymer of acrylonitrile and butadiene.

Solvent	ΔH_{vap} (cal/mol)	V_1 (cm³/mol)	V_2 (vol fraction) (polymer in gel)
2,2,4-trimethylpentane	8,396	166.0	0.9925
n-Hexane	7,540	131.6	0.9737
CCl_4	7,770	97.1	0.6862
$CHC;_3$	7,510	80.7	0.1510
Dioxane	8,715	85.7	0.2710
CH_2Cl_2	7,004	64.5	0.1563
$CHBr_3$	10,385	87.9	0.1781
Acetonitrile	7,976	52.9	0.4219

From Bristow and Watson, *Trans. Faraday Soc.*, 54, 1731, 1958. With permission.

Calculate the cohesive energy density (CED) and δ_2 for each solvent. Plot $(V_2)^{-1}$ vs. δ_1 to determine δ_2 and CED for the polymer. If the heat of mixing is given by

$$\Delta H_m - V_2 \left(1 - V_2\right) \left(\delta_1 - \delta_2\right)^2,$$

calculate the heat of mixing equal volumes of uncross-linked polymer and acetonitrile.

3.8. Explain the following:

   a. Polyethylene and polypropylene produced with stereo-specific catalysts are each fairly rigid, translucent plastics, while a 65:35 copolymer of the two produced in exactly the same manner is a soft, transparent rubber.
   b. A plastic is commercially available that is similar in appearance and mechanical properties to polyethylene and polypropylene in (a) but consists of 65% ethylene and 35% propylene units. The two components of this plastic cannot be separated by any physical or chemical means without degrading the polymer.

3.9. The polymers of amino acids are termed *nylon n* where n is the number of consecutive carbon atoms in the chain. Their general formula is

$$\left[\begin{array}{c} \text{H} \quad \text{O} \\ | \quad || \\ -\text{N}-\text{C}-(\text{CH}_2)_{n-1} \end{array} \right]_x \qquad \text{(Str. 12)}$$

The polymers are crystalline and will not dissolve in either water or hexane at room temperature. They will, however, reach an equilibrium level of absorption when immersed in each liquid. Describe *how* and *why* water and hexane absorption will vary with n.

3.10. Explain why a styrene–butadiene copolymer with solubility parameter $\delta = 8.1$ is insoluble in both pentane ($\delta = 7.1$) and ethylene acetate ($\delta = 9.1$), but will dissolve in a 1:1 mixture of the two solvents.

3.11. The urea derivatives of the following amines were made by refluxing the amines with stoichiometric amounts of urea. Explain the observed crystallization tendencies and melting points of the resulting urea derivatives of amines.

Amine	Crystallization Tendency
H_2N — $(CH_2)_6$ — NH_2 Hexamethylenediamine	Crystals formed on cooling the reflux product; mp 200°C

H_2N — CH_2 — N — CH_2 — CH_2 — NH_2
                 CH_2
                 CH_2
                 NH_2
Tris(2-aminoethylamine)
	Crystals formed on cooling and leaving the reflux product overnight; mp = 165°C

H_2N — CH_2CH_2O — CH_2CH_2O — CH_2CH_2 — NH_2 Triethyleneoxide-diamine	Crystals formed on cooling and leaving the reflux product for 3 weeks; mp = 135°C
CH_2 — $[OCH_2\ CH(CH_3)$ — $]_x$ — NH_2 CH_3CH_2 — C — $CH_2[O$ — $CH_2CH(CH_3)]_y$ — NH_2 CH_2 — $[OCH_2\ CH(CH_3)$ — $]_z$ — NH_2 Poly(oxypropylene) triamine $x + y + z = 5.3$	Viscous liquid

3.12. For a crystallizable polymer the degree of crystal imperfection is much higher in bulk-crystallized material than in material crystallized from dilute solution. However, the level of crystal perfection can be significantly enhanced if the polymer melt is left for sufficient time at relatively high temperature.

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