Chapter 4

Thermal Transitions in Polymers

I. INTRODUCTION

When a block of ice is heated, its temperature increases until at a certain temperature (depending on the pressure) it starts to melt. No further increase in temperature will be observed until all the ice has melted (solid becomes liquid). If heating is continued, the same phenomenon is observed as before and as the liquid starts to boil (liquid turns to vapor). It is pertinent to make two observations here:

- Water exists in three distinct physical states — solid, liquid, and gas (vapor).
- Transitions between these states occur sharply at constant, well-defined temperatures.

The thermal behavior of all simple compounds, such as ethanol or toluene, is analogous to that of water. However, the transitions in polymers are somewhat different and certainly more complex. In the first place, those molecules large enough to be appropriately termed polymers do not exist in the gaseous state. At high temperatures, they decompose rather than boil since what we would consider conventionally as their "boiling points" are generally higher than their decomposition temperatures. Second, a given polymeric sample is composed of a mixture of molecules having different chain lengths (molecular weights). In contrast to simple molecules, therefore, the transition between the solid and liquid forms of a polymer is rather diffuse and occurs over a temperature range whose magnitude (of the order of 2 to 10°C) depends on the polydispersity of the polymer (Figure 4.1). On melting, polymers become very viscous (viscoelastic) fluids, not freely flowing as in the case of low-molecular-weight materials.

In addition, there is a still more fundamental difference between the thermal behavior of polymers and simple molecules. To understand, first recall that molecular motion in a polymer sample is promoted by its thermal energy. It is opposed by the cohesive forces between structural segments (groups of atoms) along the chain and between neighboring chains. These cohesive forces and, consequently, thermal transitions in polymers depend on the structure of the polymer. In this regard, two important temperatures at which certain physical properties of polymers undergo drastic changes have been identified:

- The glass transition temperature, T_g
- The crystalline melting point, T_m

If a polymer is amorphous, the solid-to-liquid transition occurs very gradually, going through an intermediate "rubbery" state without a phase transformation. The transition from the hard and brittle glass into a softer, rubbery state occurs over a narrow temperature range referred to as the glass transition temperature. In the case of a partially crystalline polymer, the above transformation occurs only in the amorphous regions. The crystalline zones remain unchanged and act as reinforcing elements thus making the sample hard and tough. If heating is continued, a temperature is reached at which the crystalline zones begin to melt. The equilibrium crystalline melting point, T_m, for polymers corresponds to the temperature at which the last crystallite starts melting. Again, in contrast to simple materials, the value of T_m depends on the degree of crystallinity and size distribution of crystallites. The general changes in physical state due to changes in temperature and molecular weight are shown in Figure 4.2 for amorphous and crystalline polymers.

The thermal behavior of polymers is of considerable technological importance. Knowledge of thermal transitions is important in the selection of proper processing and fabrication conditions, the characterization of the physical and mechanical properties of a material, and hence the determination of appropriate end uses. For example, the glass transition temperature of rubber determines the lower limit of the use of rubber and the upper limit of the use of an amorphous thermoplastic. We take up discussion of these transition temperatures in succeeding sections.

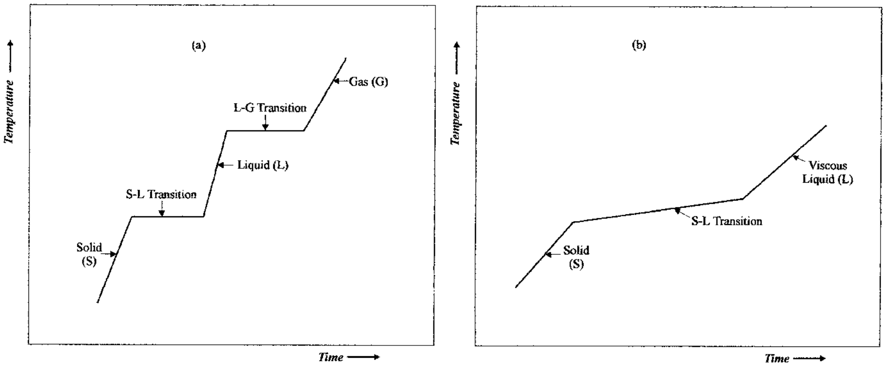


Figure 4.1 *Relative thermal responses of simple molecules (a) and polymers (b).*

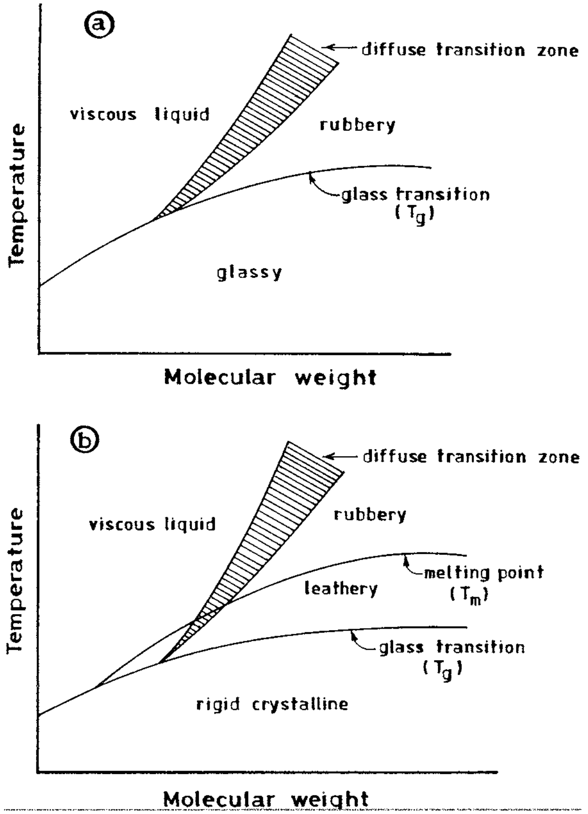


Figure 4.2 *Temperature–molecular weight diagram. (a) For amorphous polymer; (b) for crystalline polymer.*

II. THE GLASS TRANSITION

To illustrate the concept of glass transition, let us consider the specific volume–temperature behavior for both amorphous (ABCD) and crystalline (ABEF) polymers, as shown in Figure 4.3. As the amorphous polymer (line ABCD) is heated from the low-temperature region (region D), the volume expands at a

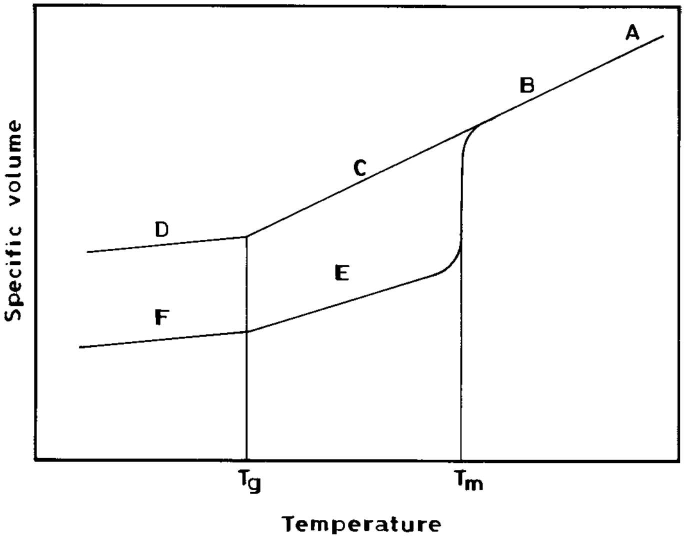


Figure 4.3 *Specific volume–temperature curves for a semicrystalline polymer. (A) Liquid region; (B) viscous liquid with some elastic response; (C) rubbery region; (D) glassy region; (E) crystallites in a rubbery matrix; (F) crystallites in a glassy matrix.*

constant rate. At a characteristic temperature, T_g, the rate of volume expansion increases suddenly to a higher constant level, i.e., there is a change in the slope of the volume–temperature curve from a lower to a higher volume coefficient of expansion. At the same time, there is an abrupt change in physical behavior from a hard, brittle, glassy solid below T_g (region D) to a soft, rubbery material above T_g (region C). On further heating, the polymer changes gradually from the rubbery state to a viscous liquid (region B) whose viscosity decreases with increasing temperature until decomposition sets in.

For a crystalline polymer, the changes at T_g are less drastic. This is because these changes are restricted mainly to the amorphous domains while the crystalline zones remain relatively unaffected. Between the glass transition (T_g) and the melting temperature (T_m) (region E) the semicrystalline polymer is composed of rigid crystallites immersed (dispersed) in a rubbery amorphous matrix. In terms of mechanical behavior, the polymer remains rigid, pliable, and tough. At the melting temperature, the crystallites melt, leading to a viscous state (region B). Above T_m the crystalline polymer, like the amorphous polymer, exists as a viscous liquid.

A. MOLECULAR MOTION AND GLASS TRANSITION

In polymers, *intra*molecular bonds are due to primary valence bonds (covalent) while the *inter*molecular attractions usually are due to secondary bonding forces. The intermolecular forces are opposed by thermal agitation, which induces vibration, rotation, and translation of a molecular system. Atomic vibrations exist at all temperature levels. The stability of the molecular system depends on the vibration energy of the chemical bonds. In polymers, thermal degradation occurs when the energy of vibration exceeds the primary bonding between atoms, while the transitional phenomena associated with crystalline melting point, the glass transition temperature, and the polymer deformations are related to rotation and vibration of molecular chains.

Bearing this in mind, let us consider what happens on a molecular scale when an amorphous polymer is heated from below its glass transition temperature. At very low temperatures — i.e., in the glassy state — chain segments are frozen in fixed positions; atoms undergo only low-amplitude vibratory motion about these positions. As the temperature is increased, the amplitude of these vibrations becomes greater, thereby reducing the effectiveness of the secondary intermolecular bonding forces. Consequently, the cooperative nature of the vibrations between neighboring atoms is enhanced. At the glass transition temperature, chain ends and a substantial number of chain segments have acquired sufficient energy to overcome intermolecular restraints and undergo rotational and translational motion. Therefore, the glass transition temperature is referred to as the onset of large-scale cooperative motion of chain segments (of the order of 20 to 50 consecutive carbon atoms). Rotational and translational modes of motion provide important mechanisms for energy absorption. This accounts for glassy-to-rubbery transition and the tough nature of an amorphous polymer above its glass transition temperature.

Below the T_g, or in the glassy state, only atoms or small groups of atoms such as short sections of the main chain or pendant/side groups move against the local restraints of intermolecular interactions. This movement may result in other transitions, which are designated α, β, γ, etc., in order of decreasing temperature. The fully extended chain, which is the conformation of minimum energy, is the preferred conformation at low temperatures. Therefore, as the molecules straighten out, the free volume, as we shall see in the next section, decreases. Consequently, flow becomes difficult and the polymer assumes the characteristic hard and brittle behavior of glasses.

As we said above, the molecular motion of the T_g is restricted only to segmental motion; entire molecular motion is as yet precluded by chain entanglements. However, above the T_g, or in the rubbery state, there is a sharp increase in the number of possible conformations. The molecular motion in the rubbery state requires more free volume, and this rise in the relative free volume leads to the observed higher volume expansion coefficient above the T_g. As heating is continued into the liquid region, molecules acquire increased thermal energy, and the amplitudes of associated molecular motions also increase. Translation, or slip of entire molecules, becomes possible; large changes in conformation occur and elasticity virtually disappears.

B. THEORIES OF GLASS TRANSITION AND MEASUREMENT OF THE GLASS TRANSITION TEMPERATURE

The fundamental nature of the glass transition is still unclear. It is a complex process that involves equilibrium, thermodynamic and kinetic factors. The various theories of the glass transition, however, have used either the thermodynamic or the kinetic approach. The thermodynamic approach is based on entropy considerations of the glassy state, while the kinetic theory of the glass transition considers the relaxation phenomena associated with the glass transition. Each approach gives only a partial explanation to the observed behavior of polymers. We now briefly discuss these theories along with the free volume theory.

1. Kinetic Theory

The kinetic concept of glass transition considers the glass transition as a dynamic phenomenon since the position of the T_g depends on the rate of heating or cooling. It predicts that the value of T_g measured depends on the time scale of the experiment in relation to that of the molecular motions arising from the perturbation of the polymer system by temperature changes. A number of models have been proposed to correlate these molecular motions with changes in macroscopic properties observed in the experiment. One approach considers the process of vitrification (glassification) as a reaction involving the movement of chain segments (kinetic units) between energy states. For the movement of a chain segment from one energy state to another to occur, a critical “hole” or empty space must be available. To create this hole sufficient energy must be available to overcome both the cohesive forces of the surrounding molecules and the potential energy barrier associated with the rearrangement. The temperature at which the number of holes of sufficient size is great enough to permit flow is regarded as the T_g. This theory permits a description of the approach to thermodynamic equilibrium. When a polymeric material above T_g is cooled, there is sufficient molecular motion for equilibrium to be achieved. However, the rate of approach to equilibrium, and hence the T_g, depends on the cooling rate employed in the experiment.

2. Equilibrium Theory

The equilibrium concept treats the ideal glass transition as a true second-order thermodynamic transition, which has equilibrium properties. The ideal state, of course, cannot be obtained experimentally since its realization would require an infinite time. According to the theory of Gibbs and DiMarzio,[1] the glass transition process is a consequence of the changes in conformational entropy with changes in temperature. The reduced level in molecular reorganization observed near the transition temperature is attributed to the reduction in the number of available conformations as the temperature is lowered. The equilibrium conformational entropy becomes zero when a thermodynamic second-order transition is reached ultimately. Thereupon, the conformations are essentially “frozen in” since the time required for conformational changes becomes virtually infinite. The glass transition temperature, T_g, therefore approaches the true transition temperature as the time scale of experiment becomes longer. Based on this reasoning and using a statistical thermodynamics treatment that utilizes a quasi-lattice theory, Gibbs and DiMarzio[1] developed quantitative predictions of the second-order phase transition that are in agreement with experiment.

3. Free Volume Theory

A most useful and popular theory of glass transition is the "free volume" model of Fox and Ferry and, later, of Williams, Landell, and Ferry.[2] This theory considers the free volume, V_f, of a substance as the difference between its specific volume, $\bar{V}$, and the space actually occupied by the molecules, V_0, where V_0 is expressed as:

$$V_o = V' + \alpha_g T \tag{4.1}$$

where V' = the extrapolated volume of glass at absolute zero
α_g = thermal expansion coefficient of the glass

This model further defines the free volume fraction, f, at temperature T as

$$\begin{aligned} f &= V_f / \bar{V} \\ &= f_g + \alpha_f (T - T_g) \end{aligned} \tag{4.2}$$

and

$$\alpha_f = \alpha_1 - \alpha_g = \frac{df}{dT} = \frac{1}{V_f}\frac{dV_f}{dT} \tag{4.3}$$

where f_g = free volume fraction at T_g
α_1 = thermal expansion coefficient above T_g
α_g = thermal expansion coefficient below T_g

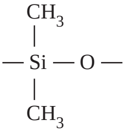
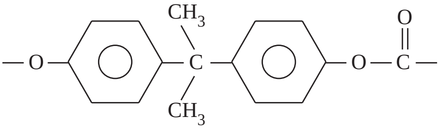
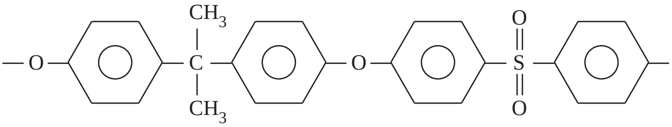
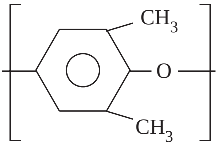
For most amorphous polymers, the free volume fraction at the glass transition temperature is found to be a constant, with a value of 0.025. Amorphous polymers, when cooled, are therefore supposed to become glassy when the free volume fraction attains this value. Thereupon no significant further change in the free volume will be observed.

Many important physical properties of polymers (particularly amorphous polymers) change drastically at the glass transition temperature. The variations of these properties with temperature form a convenient method for determining T_g. Some of the test methods include the temperature variation of specific volume (dilatometry) as discussed in Section II, refractive index (refractometry), and specific heat (calorimetry, DSC or DTA). Others include temperature-induced changes in vibrational energy level (infrared spectroscopy), proton environment (nuclear magnetic resonance or NMR), dipole moment (dielectric constant and loss), elastic modulus (creep or stress relaxation), and mechanical energy absorption (dynamic mechanical analysis or DMA). Discussion of details of these test methods is beyond the scope of this volume.

C. FACTORS AFFECTING GLASS TRANSITION TEMPERATURE

We have seen from the previous discussion that at the glass transition temperature there is a large-scale cooperative movement of chain segments. It is therefore to be expected that any structural features or externally imposed conditions that influence chain mobility will also affect the value of T_g. Some of these structural factors include chain flexibility; stiffness, including steric hindrance, polarity, or inter-chain attractive forces; geometric factors; copolymerization; molecular weight, branching; cross-linking; and crystallinity. External variables are plasticization, pressure, and rate of testing.

Table 4.1 *Effect of Chain Flexibility on T_g*

Polymer	Repeat Unit	T_h (°C)
Polyethylene	$—CH_2—CH_2—$	–120
Polydimethylsiloxane	 $—Si(CH_3)_2—O—$	–123
Polycarbonate		150
Polysulfone		190
Poly(2,6-dimethyl-1,4-phenylene oxide)		220

1. Chain Flexibility

Chain flexibility is determined by the ease with which rotation occurs about primary valence bonds. Polymers with low hindrance to internal rotation have low T_g values. Long-chain aliphatic groups — ether and ester linkages — enhance chain flexibility, while rigid groups like cyclic structures stiffen the backbone. These effects are illustrated in Table 4.1. Bulky side groups that are stiff and close to the backbone cause steric hindrance, decrease chain mobility, and hence raise T_g (Table 4.2).

The influence of the side group in enhancing chain stiffness depends on the flexibility of the group and not its size. In fact, side groups that are fairly flexible have little effect within each series; instead polymer chains are forced further apart. This increases the free volume, and consequently T_g drops. This is illustrated by the polymethacrylate series (Table 4.3).

2. Geometric Factors

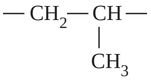
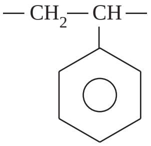
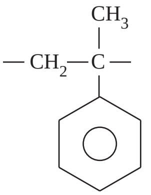
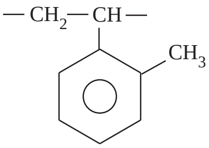
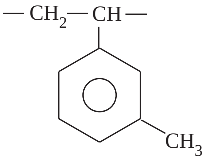
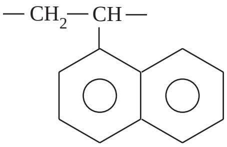
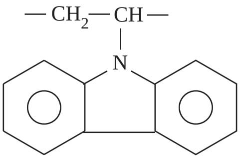
Geometric factors, such as the symmetry of the backbone and the presence of double bonds on the main chain, affect T_g. Polymers that have symmetrical structure have lower T_g than those with asymmetric structures. This is illustrated by two pairs of polymers: polypropylene vs. polyisobutylene and poly(vinyl chloride) vs. poly(vinylidene chloride) in Table 4.4. Given our discussion above on chain stiffness, one would have expected that additional groups near the backbone for the symmetrical polymer would enhance steric hindrance and consequently raise T_g. This, however, is not the case. This “discrepancy” is due to conformational requirements. The additional groups can only be accommodated in a conformation with a “loose” structure. The increased free volume results in a lower T_g.

Another geometric factor affecting T_g is *cis–trans* configuration. Double bonds in the *cis* form reduce the energy barrier for rotation of adjacent bonds, “soften” the chain, and hence reduce T_g (Table 4.5).

3. Interchain Attractive Forces

Recall from our earlier discussion that intermolecular bonding in polymers is due to secondary attractive forces. Consequently, it is to be expected that the presence of strong intermolecular bonds in a polymer chain, i.e., a high value of cohesive energy density, will significantly increase T_g. The effect of polarity, for example, can be seen from Table 4.6. The steric effects of the pendant groups in series (CH_3, –Cl,

Table 4.2 *Enhancement of T_g by Steric Hindrance*

Polymer	**Repeat Unit**	**T_g(°C)**
Polyethylene	$-CH_2-CH_2-$	–120
Polypropylene	 $-CH_2-CH(CH_3)-$	–10
Polystyrene		100
Poly(α-methylstyrene)		192
Poly(*o*-methylstyrene)		119
Poly(*m*-methylstyrene)		72
Poly(α-vinyl naphthalene)		135
Poly(vinyl carbazole)		208

and –CN) are similar, but the polarity increases. Consequently, T_g is increased in the order shown in the table. The same effect of increased T_g with increasing CED can be observed when one considers going from the intermolecular forces in poly(methyl acrylate), an ester, through the strong hydrogen bonds in poly(acrylic acid) to primary ionic bonds in poly(zinc acrylate) (Table 4.7).

Recall again that secondary bonding forces are effective only over short molecular distances. Therefore, any structural feature that tends to increase the distance between polymer chains decreases the cohesive energy density and hence reduces T_g. This effect has already been clearly demonstrated in the polyacrylate series where the increased distance between chains due to the size of the alkyl group, R, reduced T_g.

Table 4.3 *Decrease of T_g with Increasing Flexibility of Side Chains for Polymethacrylate Series*

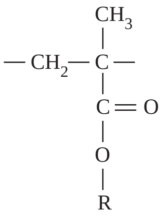
Generalized Formula	R	T_g (°C)
 $-CH_2-\overset{\substack{CH_3\\ \vert}}{\underset{\substack{\vert\\ C=O\\ \vert\\ O\\ \vert\\ R}}{C}}-$	methyl	105
	ethyl	65
	n-propyl	35
	n-butyl	21
	n-hexyl	–5
	n-octyl	–20
	n-dodecyl	–65

Table 4.4 *Effect of Symmetry of T_g*

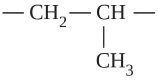
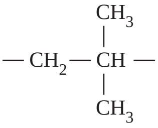
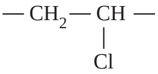
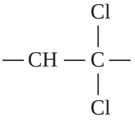
Polymer	Repeat Unit	T_g(°C)
Polypropylene	 $-CH_2-\underset{\substack{\vert\\ CH_3}}{CH}-$	–10
Polyisobutylene	 $-CH_2-\overset{\substack{CH_3\\ \vert}}{\underset{\substack{\vert\\ CH_3}}{CH}}-$	–70
Poly(vinyl chloride)	 $-CH_2-\underset{\substack{\vert\\ Cl}}{CH}-$	87
Poly(vinylidene chloride)	 $-CH-\overset{\substack{Cl\\ \vert}}{\underset{\substack{\vert\\ Cl}}{C}}-$	–17

Table 4.5 *Relative Effects of cis–trans Configuration on T_g*

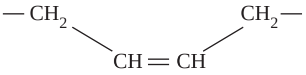
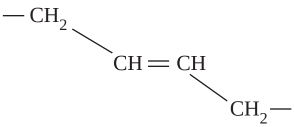
Polymer	Repeat Unit	T_g(°C)
Poly(1,4-*cis*-butadiene)		–108
Poly(1,4-*trans*-butadiene)		–83

Table 4.6 *Effect of Polarity on T_g*

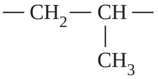
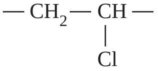
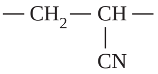
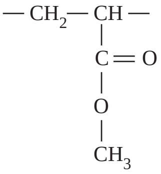
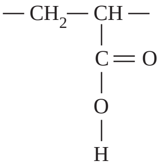
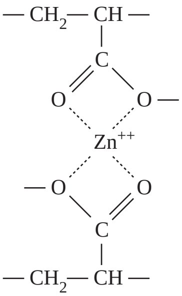
Polymer	Repeat Unit	Dielectric Constant at 1kHz	T_g(°C)
Polypropylene	 $-CH_2-CH(CH_3)-$	2.2–2.3	–10
Poly(vinyl chloride)	 $-CH_2-CH(Cl)-$	3.39	87
Polyacrylonitrile	 $-CH_2-CH(CN)-$	5.5	103

Table 4.7 *Effect of Polarity on the T_g of Some Acrylic Polymers*

Polymer	Repeat Value	T_g(°C)
Polymethylacrylate	 $-CH_2-CH(C(=O)-O-CH_3)-$	3
Poly(acrylic acid)	 $-CH_2-CH(C(=O)-O-H)-$	106
Poly(zinc acrylate)		>400

4. Copolymerization

The transition temperatures T_g and T_m are important technological characteristics of polymers. It is desirable — in fact, valuable — to be able to control either T_g or T_m independent of each other. This, however, is often impossible. Polymer chemists have circumvented this problem to some extent by polymer modification via copolymerization and polyblending. These procedures have become powerful tools for tailoring polymer systems for specific end uses.

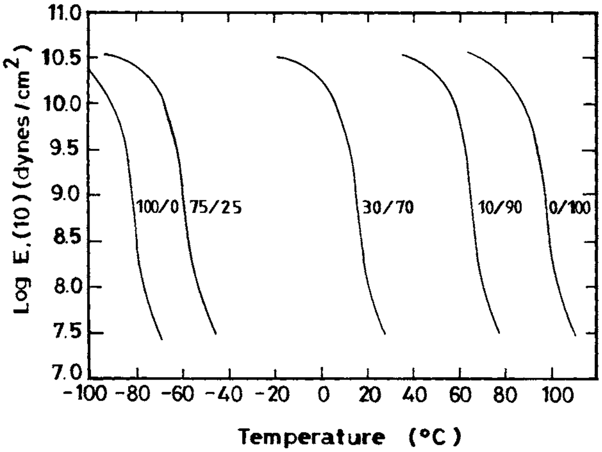


Figure 4.4 *E_r vs. fraction ratios of butadiene–styrene copolymers. (From Tobolsky, A.V., Properties and Structure of Polymers, John Wiley & Sons, New York, 1960. With permission of Dorothy Tobolsky.)*

A copolymer system may be characterized either by the geometry of the resulting polymer — that is, the arrangement of the different monomers (random, alternating, graft, or block) — or by the compatibility (miscibility) of the two monomers.

a. Isomorphous Systems (Homogeneous Copolymers or Compatible Polyblends)

In isomorphous systems, the component monomers occupy similar volumes and are capable of replacing each other in the crystal system. The resulting copolymer, irrespective of its geometry, is necessarily homogeneous, and polyblends of the individual homopolymers or copolymers have similar transition properties. Copolymerization merely shifts the T_g to the position intermediate between those of the two homopolymers; it does not alter the temperature range or the modulus within the transition region (Figure 4.4). This shift is illustrated in Figure 4.4, which shows the modulus temperature curves for polybutadiene (100/0) and polystyrene (0/100) and for various compositions of butadiene–styrene copolymer.

For this system, if the glass transitions (T_{g1} and T_{g2}) of the individual homopolymers (1 and 2) are known, it is possible to estimate the T_g of the copolymer (or polyblend) using the relation

$$T_g = V_1 T_{g2} + V_2 T_{g2} \tag{4.4}$$

where V_1 and V_2 are the volume fractions of components 1 and 2, respectively. This is shown schematically in Figure 4.5 (line 1).

b. Nonisomorphous Systems

In nonisomorphous systems, the specific volumes of the monomers are different. In this case, the geometry of the resulting polymer becomes important.

Random or alternating — For these copolymers, the composition is necessarily homogeneous (no phase separation) and, as discussed above, the glass transitions are intermediate between those of the two homopolymers. The increased disorder resulting from the random or alternating distribution of monomers enhances the free volume and consequently reduces T_g below that predicted by Equation 4.4 (line 2, Figure 4.5). The T_g of the copolymer whose components have weight fractions W_1 and W_2 and glass transitions T_{g1} and T_{g2}, respectively, can be calculated from the relation

$$\frac{1}{T_g} = \frac{W_1}{T_{g_1}} + \frac{W_2}{T_{g_2}} \tag{4.5}$$

Examples of this type are methyl methacrylate–acrylonitrile, styrene–methyl methacrylate, and acrylonitrile–acrylamide copolymers. It is also possible that monomers involved in the copolymerization process

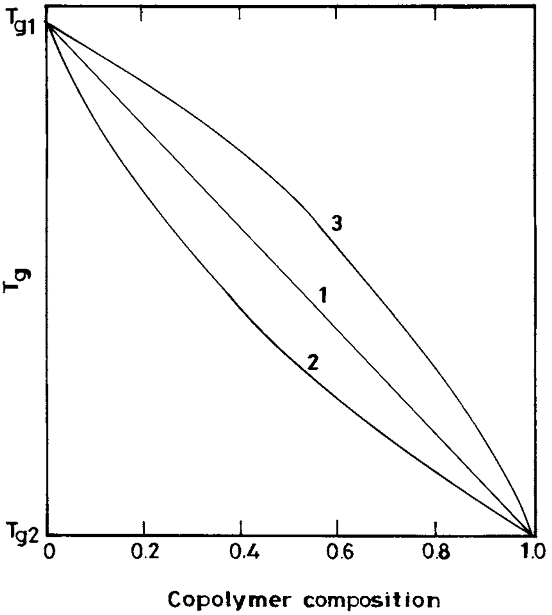


Figure 4.5 *Variation in glass transition temperature with copolymer composition (schematic).*

(as in the copolymers methylacylate–methylmethacrylate and vinylidene chloride–methylacrylate) introduce significant interaction between chains. In this case the T_g will be enhanced relative to the predicted value (Figure 4.5, line 3).

Block and graft copolymers (incompatible copolymers) — For block or graft copolymers in which the component monomers are incompatible, phase separation will occur. Depending on a number of factors — for example, the method of preparation — one phase will be dispersed in a continuous matrix of the other. In this case, two separate glass transition values will be observed, each corresponding to the T_g of the homopolymer. Figure 4.6 shows this behavior for polyblends of polystyrene (100) and 30/70 butadiene–styrene copolymer (0).

Example 4.1: What is the T_g of butadiene–styrene copolymer containing 10 vol% styrene?

Solution: Butadiene and styrene form a completely compatible random copolymer. Therefore the following relation is applicable: $T_g = V_1T_{g1} + V_2T_{g2}$.

$$\text{Assume } 1 = \text{polybutadiene}$$

$$2 = \text{polystyrene}$$

$$T_{g1} = -80°C,\ T_{g2} = 100°C$$

$$T_g = 0.90\,(-80) + 0.10\,(100)$$

$$= -62°C$$

---

5. Molecular Weight

Since chain end segments are restricted only at one end, they have relatively higher mobility than the internal segments, which are constrained at both ends. At a given temperature, therefore, chain ends provide a higher free volume for molecular motion. As the number of chain ends increases (which means a decrease in M_n), the available free volume increases, and consequently there is a depression of T_g. The effect is more pronounced at low molecular weight, but as M_n increases, T_g approaches an asymptotic value. An empirical expression relating the inverse relations between T_g and $\overline{M}_n$ is given by Equation 4.6.

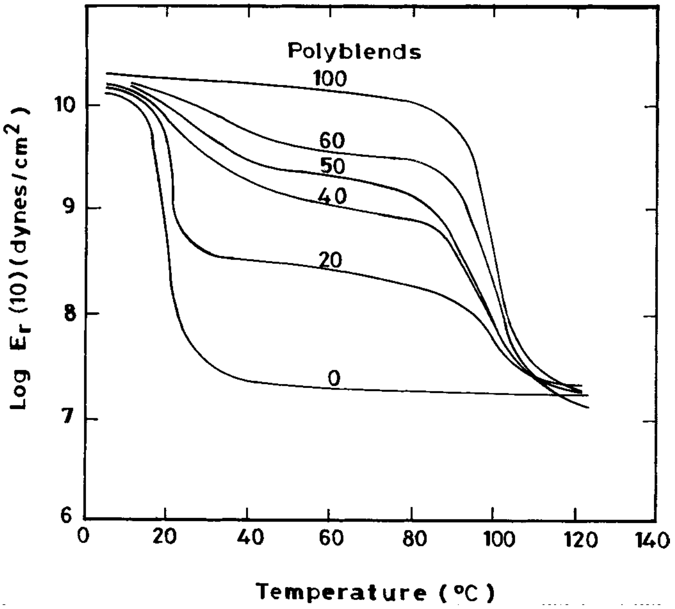


Figure 4.6 *E_r(10) vs. temperature for polyblends of polystyrene and a 30/70 butadiene–styrene copolymer. Numbers on the curves are the weight percent of polystyrene in the blend. (From Tobolsky, A.V., Properties and Structure of Polymers, John Wiley & Sons, New York, 1960. With permission of Dorothy Tobolsky.)*

$$T_g = T_g^{\infty} = K/\overline{M}_n \tag{4.6}$$

where T_g^{∞} = T_g of an infinite molecular weight
K = a constant

For polystyrene it has been found that T_g^{∞} = 100°C while K is about 2×10^5.

Example 4.2: What is the T_g of polystyrene of $\overline{M}_n = 3000$?

Solution: From above, $T_g^{\infty} = 100$, $K = 2 \times 10^5$.

$$T_g = 100 - \frac{2 \times 10^5}{3000}$$

$$= 33°C$$

---

6. Cross-Linking and Branching

By definition, cross-linking involves the formation intermolecular connections through chemical bonds. This process necessarily results in reduction in chain mobility. Consequently, T_g increases. For lightly cross-linked systems like vulcanized rubber, T_g shows a moderate increase over the uncross-linked polymer. In this case, T_g and the degree of cross-linking have a linear dependence, as shown by the following approximate empirical equation.

$$T_g - T^0 = \frac{3.9 \times 10^4}{M_c} \tag{4.7}$$

where T_g = the glass transition temperature of the uncross-linked polymer having the same chemical composition as the cross-linked polymer
M_c = the number-average molecular weight between cross-linked points

For highly cross-linked systems like phenolics and epoxy resins, the glass transition is virtually infinite. This is because the molecular chain length between cross-links becomes smaller than that required for cooperative segmental motion.

Like long and flexible side chains, branching increases the separation between chains, enhances the free volume, and therefore decreases T_g.

7. Crystallinity

In semicrystalline polymers, the crystallites may be regarded as physical cross-links that tend to reinforce or stiffen the structure. Viewed this way, it is easy to visualize that T_g will increase with increasing degree of crystallinity. This is certainly not surprising since the cohesive energy factors operative in the amorphous and crystalline regions are the same and exercise similar influence on transitions. It has been found that the following empirical relationship exists between T_g and T_m.

$$\frac{T_g}{T_m} = \begin{Bmatrix} 1/2 & \text{for symmetrical polymers} \\ 2/3 & \text{for unsymmetrical polymers} \end{Bmatrix} \tag{4.8}$$

where T_g and T_m are in degrees Kelvin.

8. Plasticization

Plasticity is the ability of a material to undergo plastic or permanent deformation. Consequently, plasticization is the process of inducing plastic flow in a material. In polymers, this can be achieved in part by the addition of low-molecular-weight organic compounds referred to as plasticizers (see Chapter 9). Plasticizers are usually nonpolymeric, organic liquids of high boiling points. Plasticizers are miscible with polymers and, in principle, should remain within the polymer. Addition of plasticizers to a polymer, even in very small quantities, drastically reduces the T_g of the polymer. This is exemplified by the versatility of poly(vinyl chloride) which, if unmodified, is rigid, but can be altered into a flexible material by the addition of plasticizers such as dioctylphthalate (DOP).

The effect of plasticizer in reducing T_g can be interpreted in several ways. Plasticizers function through a solvating action by increasing intermolecular distance, thereby decreasing intermolecular bonding forces. Alternatively, the addition of plasticizers results in a rapid increase in chain ends and hence an increase in free volume. A plasticized system may also be considered as a polyblend, with the plasticizer acting as the second component. In this case, our earlier relations for polyblends would apply (Equations 4.1 and 4.2). Since plasticizers generally have very low T_g, between –50°C and –160°C, addition of small amounts of the plasticizer would be expected to result in a substantial decrease in the T_g of a polymer. This is illustrated in Figure 4.7 for a poly(vinyl chloride)–diethylhexyl succinate system.

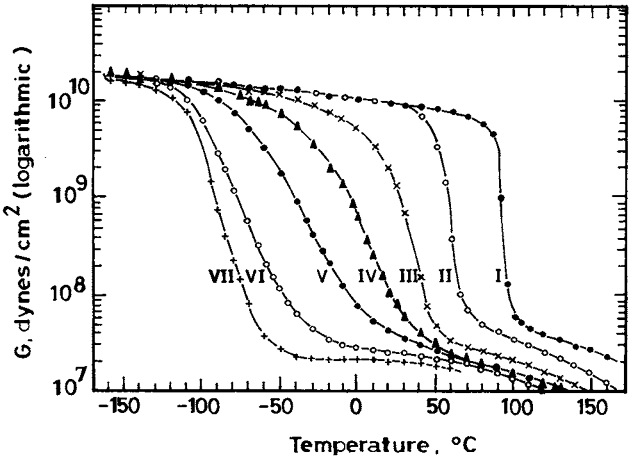


Figure 4.7 *Shear modules, G vs. temperature, measured for a time scale of approximately 1 s, poly(vinyl chloride) plasticized with diethylhexyl succinate. I, 100% monomer; II, 91%; III, 79%; IV, 70.5%; V, 60.7%; VI, 51.8%; VII, 40.8%. (From Schneider, K. and Wolf, K., Kolloid Z., 127, 65, 1952.)*

Observe that in addition to the reduction in T_g, there is a considerable broadening of the transition region in plasticized PVC.

Example 4.3: Toluene behaves as a plasticizer for polystyrene. Estimate T_g of a polystyrene sample containing 20 vol% toluene.

Solution: Since toluene is completely compatible with polystyrene, we may use the relation

$$T_g = V_A T_{gA} + V_B T_{gB}$$

where T_{gA}, T_{gB} = glass transition temperature of polystyrene and toluene, respectively
V_A, V_B = volume fraction of polystyrene and toluene, respectively

Assuming T_{ga} = melting point of toluene = –50°C.

$$\begin{aligned} T_g &= (1 - V_B)\, T_{gA} + V_B\, (T_{gB}) \\ &= 0.8 \times 100 \times 0.2\, (-50) \\ &= 70°\text{C} \end{aligned}$$

III. THE CRYSTALLINE MELTING POINT

Melting involves a change from the crystalline solid state into the liquid form. For low-molecular-weight (simple) materials, melting represents a true first-order thermodynamic transition characterized by discontinuities in the primary thermodynamic variables of the system such as heat capacity, specific volume (density), refractive index, and transparency. Melting occurs when the change in free energy of the process is zero; that is,

$$\Delta G_m = \Delta H_m - T_m \Delta g_m = 0 \tag{4.9}$$

or

$$T_m = \frac{\Delta H_m}{\Delta S_m} \tag{4.10}$$

where ΔH_m = enthalpy change during melting and represents the difference between cohesive energies of molecules in the crystalline and liquid states
ΔS_m = entropy change during melting representing the change in order between the two states

This concept has been extended to melting in crystalline polymeric systems. We must remember, however, that in the case of crystalline polymers:

- The macromolecular nature of polymers and the existence of molecular weight distribution (polydispersity) lead to a broadening of T_m.
- The process of crystallization in polymers involves chain folding. This creates inherent defects in the resulting crystal. Consequently, the actual melting point is lower than the ideal thermodynamic melting point.
- Because of the macromolecular nature of polymers and the conformational changes associated with melting, the process of melting in polymer is more rate sensitive than that in simple molecules.
- No polymer is 100% crystalline.

The factors that determine crystallization tendency have been dealt with earlier (Chapter 3). We simply recap them here.

- Structural regularity — For the effective utilization of the secondary intermolecular bonding forces during the formation of a crystalline polymer, close alignment of polymer molecules is a prerequisite. Any structural feature of a polymer chain that impedes this condition must necessarily detract from crystallinity.
- Chain flexibility — In the process of aggregation to form a crystalline solid, polymer molecules are opposed by thermal agitation, which induces segmental rotational and vibrational motion. Polymers with flexible chains are more susceptible to this agitation than those with stiff backbones. Consequently, chain flexibility reduces the tendency for crystallization.
- Intermolecular bonding — Since secondary bonding forces are responsible for intermolecular bonding, polymer molecules with specific groups that promote enhanced intermolecular interaction and whose structural features lead to identity periods are more crystallizable.

As we said earlier, melting is a true first-order thermodynamic transition involving a phase change and is associated with discontinuities in primary extensive thermodynamic properties. In principle, therefore, any property whose values are different for the crystalline and amorphous states provides a convenient method for measuring the crystalline melting point. Methods for measuring the crystalline melting point include dilatometry, calorimetry, and thermal analysis; dynamic techniques (mechanical dielectric, nuclear magnetic resonance); stress relaxation; and creep.

A. FACTORS AFFECTING THE CRYSTALLINE MELTING POINT, T_M

Bearing in mind the peculiar nature of polymers, melting in crystalline polymers can be considered a pseudoequilibrium process that may be described by the free energy equation:

$$T_m = \frac{\Delta H_m}{\Delta S_m} \tag{4.10}$$

In this case, ΔH_m represents the difference in cohesive energies between chains in the crystalline and liquid states, while ΔS_m represents the difference in the degree of order between polymer molecules in the two states. ΔH_m is generally independent of the molecular weight. But, as would be expected, polar groups on the chain — particularly if disposed regularly on the chain so as to encourage regions of extensive cooperative bonding — would enhance the magnitude of ΔH_m. ΔS_m depends not only on molecular weight, but also on structural factors like chain stiffness. Chains that are flexible in the molten state would be capable of assuming a relatively larger number of conformations than stiff chains and hence result in a large ΔS_m. We now discuss these factors that affect T_m in greater detail.

1. Intermolecular Bonding

The cohesive forces in polymers involve the secondary bonding forces ranging from the weak van der Waals forces through the much stronger hydrogen bonds. In some cases, these forces even include primary ionic bonds. Figure 4.8 shows the variation of T_m for a homologous series of various types of polymers. With polyethylene as a reference and neglecting for the moment possible fine details in trends, we observe that:

- The melting points approach that of polyethylene as the spacing between polar groups increases.
- For the same number of chain atoms in the repeat unit, polyureas, polyamides, and polyurethanes have higher melting points than polyethylene, while polyesters have lower.

As would be expected, the decrease in the cohesive energy density associated with the decrease in the density of sites for intermolecular bonding (increased space between polar groups) leads to a reduction in the melting points.

Van Krevelen and Hoftyzer[6] have calculated the contributions of the characteristic groups in various polymers to Y_m, a quantity they termed *molar melt transition function* (identified with ΔH_m in Equation 4.7). These are shown in Table 4.8. For the same number of chain backbone atoms, chain flexibility (ΔS_m) will not be significantly different for the various polymers. From Table 4.8, while the absolute values calculated for the characteristic interunit groups may not be significant, the trend in their magnitudes definitely corresponds to that of the melting points of the various types of polymers. In Figure 4.8, we note specifically that the melting points for polyesters are lower than the T_m of polyethylene.

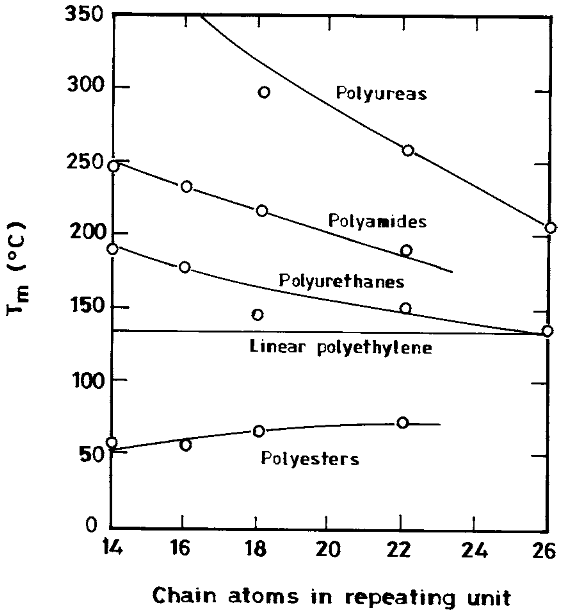
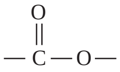
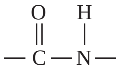
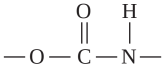
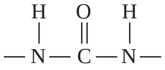


Figure 4.8 *Trend of crystalline melting points in homologous series of aliphatic polymers. (From Hill, R.H. and Walker, E.E., J. Polym. Sci., 3, 609, 1948. With permission.)*

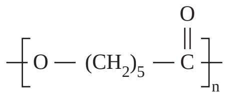
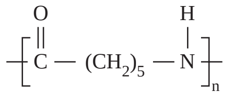
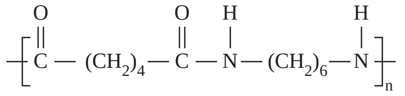
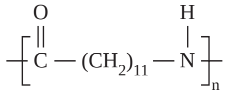
Table 4.8 *Group Contributions to the Melting Point*

Polymer	Characteristic Group	Contribution to Y_m
Polyester	 $-\overset{\overset{O}{\|}}{C}-O-$	1160
Polyamide	 $-\overset{\overset{O}{\|}}{C}-\overset{\overset{H}{\vert}}{N}-$	2560
Polyurethane	 $-O-\overset{\overset{O}{\|}}{C}-\overset{\overset{H}{\vert}}{N}-$	2430
Polyurea	 $-\overset{\overset{H}{\vert}}{N}-\overset{\overset{O}{\|}}{C}-\overset{\overset{H}{\vert}}{N}-$	3250

From Van Krevelen, D.W. and Hoftyzer, P.J., *Properties of Polymers: Correlations with Chemical Structure,* Elsevier, Amsterdam, 1976. With permission.

This is because the enhanced flexibility resulting from the presence of oxygen atoms in the polyester chains considerably offsets the weak polar bonding from ester linkages. This is demonstrated in Table 4.9. The melting points of the nylons reflect the density of the hydrogen-bond-forming amide linkages. The densities of the interunit linkages in polycaprolactone (ester units) and polycaprolactam (amide units) are the same. However, the amide units are more polar than the ester units. Consequently, polycaprolactam has a much higher T_m than polycaprolactone.

Table 4.9 *Effect of Intermolecular Bonding on T_m*

Polymer	Characteristic Group	Melting Temperature (T_m)(°C)
Polycaprolactone	 $\left[O-(CH_2)_5-\overset{\overset{O}{\|}}{C}\right]_n$	61
Polycaprolactam (nylon 6)	 $\left[\overset{\overset{O}{\|}}{C}-(CH_2)_5-\overset{\overset{H}{\|}}{N}\right]_n$	226
Poly(hexamethylene adipamide) (nylon 6,6)	 $\left[\overset{\overset{O}{\|}}{C}-(CH_2)_4-\overset{\overset{O}{\|}}{C}-\overset{\overset{H}{\|}}{N}-(CH_2)_6-\overset{\overset{H}{\|}}{N}\right]_n$	265
Nylon 12	 $\left[\overset{\overset{O}{\|}}{C}-(CH_2)_{11}-\overset{\overset{H}{\|}}{N}\right]_n$	179

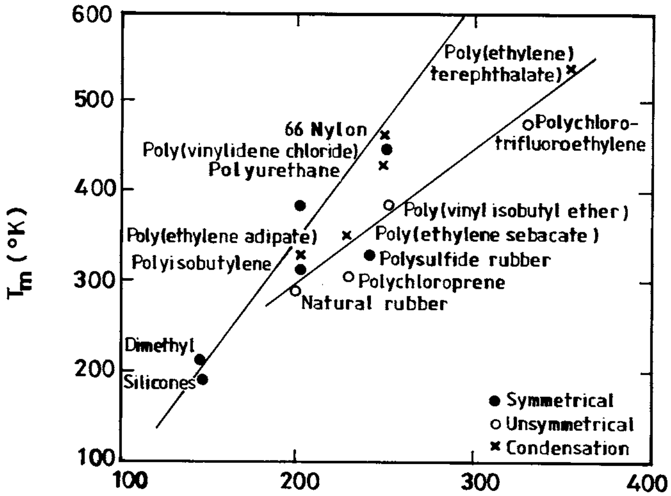


Figure 4.9 *Relation between T_m and T_g for various polymers. (From Bayer, R.F., J. Appl. Phys., 25, 585, 1954. With permission.)*

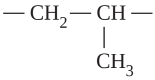
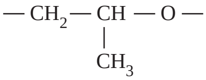
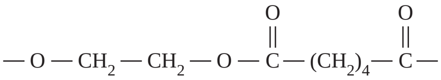
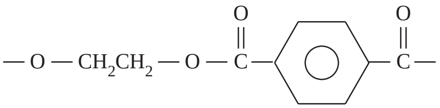
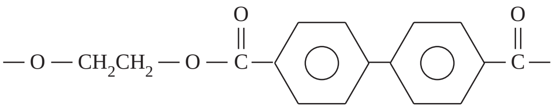
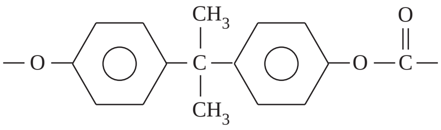
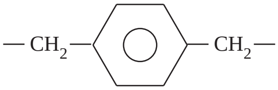
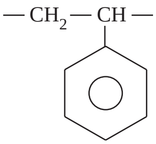
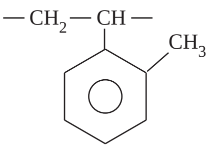
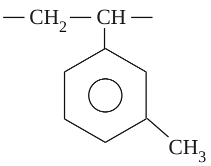
2. Effect of Structure

The structural dependence of the crystalline melting temperature is essentially the same as that for the glass transition temperature. The only difference is the effect of structural regularity, which has a profound influence on crystallizability of a polymer. T_g is virtually unaffected by structural regularity. From a close examination of data for semicrystalline polymers it has been established that the ratio T_g/T_m (K) ranged from 0.5 to 0.75. The ratio is found to be closer to 0.5 in symmetrical polymers (e.g., polyethylene and polybutadiene) and closer to 0.75 in unsymmetrical polymers (e.g., polystyrene and polychloroprene). This behavior is shown in Figure 4.9.

3. Chain Flexibility

Polymers with rigid chains would be expected to have higher melting points than those with flexible molecules. This is because, on melting, polymers with stiff backbones have lower conformational entropy changes than those with flexible backbones. As we saw earlier, chain flexibility is enhanced by the presence of such groups as –O– and –(CO·O)– and by increasing the length of (–CH_2–) units in the main chain. Insertion of polar groups and rings restricts the rotation of the backbone and consequently reduces conformational changes of the backbone, as illustrated by the following polymers (Table 4.10).

Table 4.10 *Effect of Chain Flexibility to T_m*

Polymer	Repeat Unit	T_m(°C)
Polyethylene	$-CH_2-CH_2-$	135
Polypropylene	 $-CH_2-\underset{CH_3}{\underset{\vert}{CH}}-$	165
Polyethylene oxide	$-CH_2-CH_2-O-$	66
Poly(propylene oxide)	 $-CH_2-\underset{CH_3}{\underset{\vert}{CH}}-O-$	75
Poly(ethylene adipate)	 $-O-CH_2-CH_2-O-\overset{O}{\overset{\Vert}{C}}-(CH_2)_4-\overset{O}{\overset{\Vert}{C}}-$	50
Poly(ethylene terephthalate)		265
Poly (diphenyl-4,-4 diethylene carboxylate)		355
Polycarbonate		270
Poly(*p*-xylene)		380
Polystyrene (isotactic)		240
Poly(*o*-methylstyrene)		>360
Poly(*m*-methylstyrene)		215

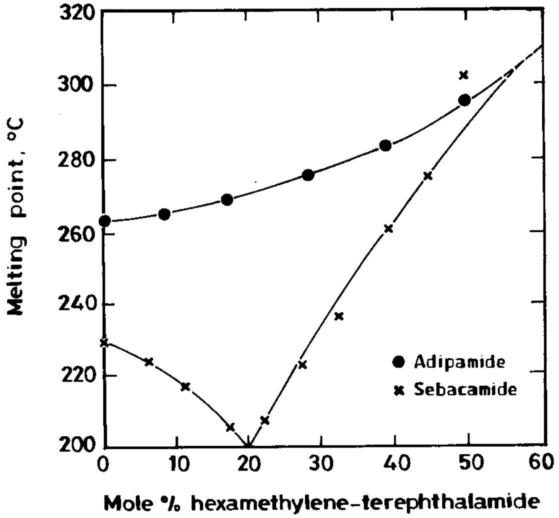


Figure 4.10 *Melting points of copolymers of hexamethylene adipamide and terephthalamide, and of hexamethylene sebacamide and terephthalamide. (From Edgar, D.B. and Hill, R.J., J. Polym. Sci., 8(1), 1, 1952. With permission.)*

4. Copolymerization

The effect of copolymerization on T_m depends on the degree of compatibility of the comonomers. If the comonomers have similar specific volumes, they can replace each other in the crystal lattice (i.e., isomorphous systems), and the melting point will vary smoothly over the entire composition range. On the other hand, if the copolymer is made from monomers each of which forms a crystalline homopolymer, the degree of crystallinity and the crystalline melting point decrease as the second constituent is added to either of the homopolymers. In this case, the T_m of the copolymer (i.e., the reduction in the melting point, T_m° of the homopolymer due to the addition of the second constituent) is given by Equation 4.11.[8]

$$\frac{1}{T_m} = \frac{1}{T_m^\circ} - \frac{R}{\Delta H_m} \ln x \qquad (4.11)$$

where ΔH_m and X are, respectively, the heat of fusion and mole fraction of the homopolymer or crystallizing (i.e., major) component (Figure 4.10). It is obvious from the foregoing that it is impossible to attempt to raise the crystalline melting point of a polymer by copolymerizing with small amounts of a monomer with a high melting point except for isomorphous systems, which are rare in vinyl polymers.

Block and graft copolymers with sufficiently long homopolymer chain sequences crystallize and exhibit properties of both homopolymers and consequently have two melting points, one for each type of chain segment.

Example 4.4: What is the melting point of a copolymer of ethylene and propylene with 90 mol% ethylene?

Solution: From the foregoing discussion:

$$\frac{1}{T_m} = \frac{1}{T_m^\circ} - \frac{R}{\Delta H_m} \ln x$$

$$T_m^\circ = \text{melting point of PE}$$

$$= 135°\text{C} = 408 \text{ K}$$

$$\Delta H_m \text{ for PE} = 66.5 \text{ cal/g} = 7.80 \times 10^3 \text{ J/mol}$$

$$\left(\text{Note molecular weight of PE } [\text{repeat unit}] = 28\right)$$

$$\frac{1}{T_m} = \frac{1}{408} - \frac{8.314}{7.80 \times 10^3} \ln 0.9$$

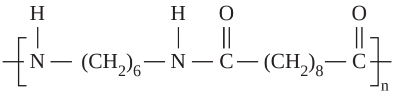
$$= 25.63 \times 10^{-4}$$

$$T_m = 390 \text{ K} = 117°\text{C}$$

IV. PROBLEMS

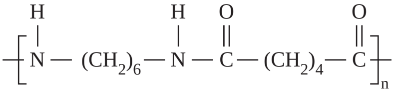
4.1. Arrange the following materials in the probable order of their increasing crystalline melting points and justify your answer. Assume the degree of polymerization, n, for the polymers is the same.

a.



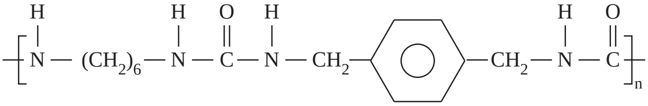
$$\left[\overset{H}{\overset{|}{N}} - (CH_2)_6 - \overset{H}{\overset{|}{N}} - \overset{O}{\overset{\|}{C}} - (CH_2)_8 - \overset{O}{\overset{\|}{C}} \right]_n$$

b.

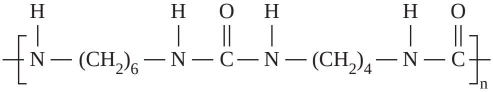


$$\left[\overset{H}{\overset{|}{N}} - (CH_2)_6 - \overset{H}{\overset{|}{N}} - \overset{O}{\overset{\|}{C}} - (CH_2)_4 - \overset{O}{\overset{\|}{C}} \right]_n$$

c.

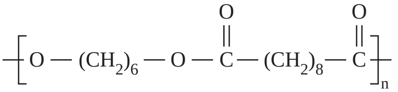


d.



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

e.



$$\left[O - (CH_2)_6 - O - \overset{O}{\overset{\|}{C}} - (CH_2)_8 - \overset{O}{\overset{\|}{C}} \right]_n$$

4.2. The solubility parameters of poly(vinyl chloride) (PVC) and dibutyl sebacate are 9.7 and 9.2, respectively. What amount (in volume percent) of dibutyl sebacate will be required to make PVC a flexible polymer at room temperature? Assume that the T_g of dibutyl sebacate is –100°C and that room temperature is 25°C.

4.3. Arrange the following linear polymers in orders of decreasing crystalline melting points. Explain the basis of your decision.

a. Poly(ethylene adipate)
b. Poly(ethylene terephthalate)
c. Poly(hexamethylene adipate)
d. Poly(ethylene adipamide)

4.4. Cross-linking polystyrene with divinyl benzene increased its T_g by 7.5°C. What is the number of styrene residues between cross-links?

4.5. The T_g of polystyrene is 100°C. What is its melting temperature, T_m?

4.6. The heat of fusion of the repeating unit for a homopolymer that melts at 250°C is 2500 cal/mol. Predict the melting point of a random copolymer of this polymer with 25 mol% of a comonomer.

4.7. Which of the following pairs of polymers will have a higher glass transition temperature, T_g? Explain your choice.

   a. Poly(2-chloroethyl methacrylate) or poly(*n*-propyl methacrylate)
   b. Poly(*n*-butyl methacrylate) or poly(2-methoxyethyl methacrylate)

4.8. What is the free volume fraction of polystyrene at 150°C if its volume coefficient of expansion is 60.0×10^{-6} cm/cm^3 °C?

4.9. Which of each of the following pairs has a higher T_μ? Why?

   a. Polyethylene or a random copolymer of polyethylene and polypropylene
   b. Poly(vinyl chloride) or polytetrafluoroethylene
   c. Nylon 6 or nylon 11

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