Polymer Chemistry

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Polymer Science and Technology

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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).

- 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 is analogous to that of water.

The transitions in polymers are somewhat different and certainly more complex.

Polymers do not exist in the gaseous state. At high temperatures, they decompose rather than boil (their boiling points are generally higher than their decomposition temperatures).

Polymers compose of a mixture of molecules with different chain lengths (i.e. MW).

In contrast to simple molecules, 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**.

On melting, polymers become very viscous (**viscoelastic**) fluids, not freely flowing as in the case of low-molecular-weight materials.

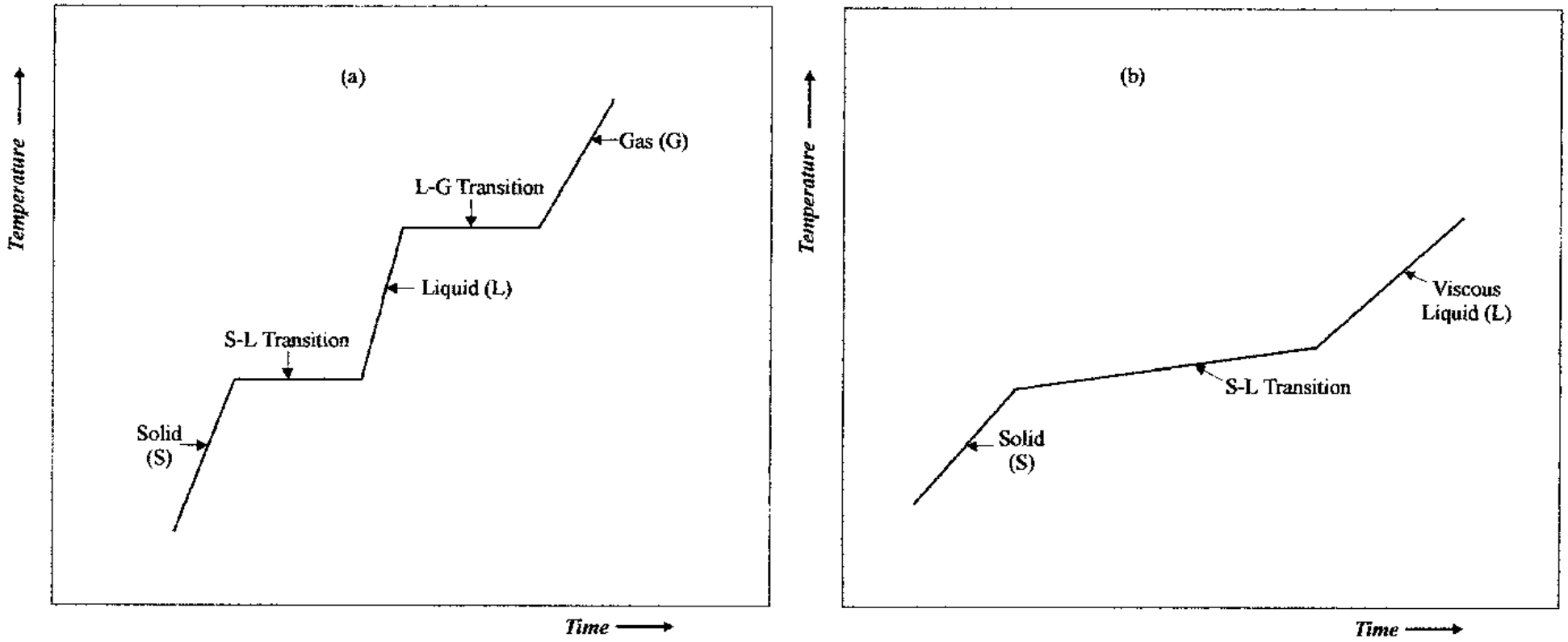


Figure 4.1 *Relative thermal responses of simple molecules (a) and polymers (b).*

There is a still more fundamental difference between the thermal behavior of polymers and simple molecules.

The 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 thermal transitions in polymers **depend** on the **structure of the polymer**.

Two important temperatures have been identified as certain physical properties of polymers undergo drastic changes:

- 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 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.

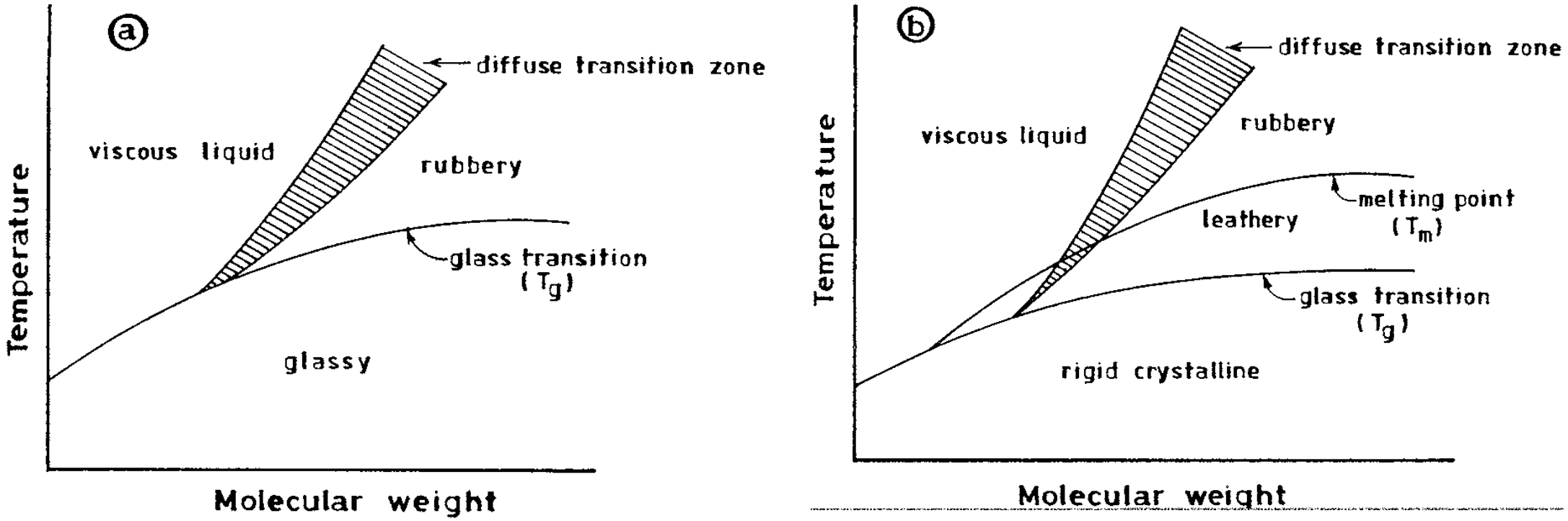


Figure 4.2 *Temperature–molecular weight diagram. (a) For amorphous polymer; (b) for crystalline polymer.*

The equilibrium **crystalline melting point**, T_m, for polymers corresponds to the temperature at which the **last crystallite starts melting**.

In contrast to simple materials, the value of T_m **depends** on the **degree of crystallinity** and **size distribution** of crystallites.

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.

II. THE GLASS TRANSITION

The concept of glass transition will be considered by the **specific volume**–temperature behavior for both amorphous (ABCD) and crystalline (ABEF) polymers.

As the **amorphous polymer** (line ABCD) is heated from the low-temperature region (region D), the volume expands at a 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 Tg (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.

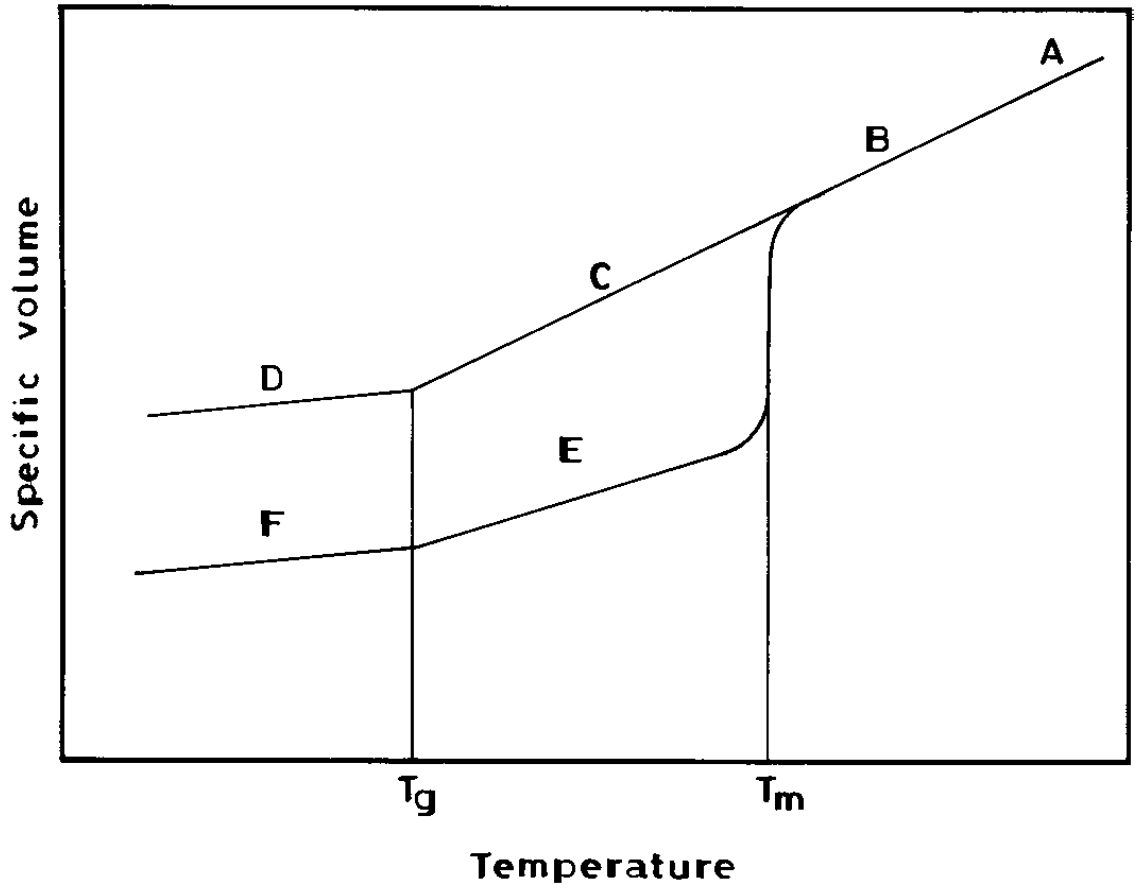


Figure 4.3 *Specific volume–temperature curves for a semicrystalline polymer. (A) Liquid region; (B) viscous liquid with some elastic response; (C) rubbery region; (D) glassy region; (E) crystallites in a rubbery matrix; (F) crystallites in a glassy matrix.*

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, the *inter*molecular 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 the T_m, the T_g, and the polymer deformations are related to rotation and vibration of molecular chains.

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. 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).

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 decreases. Consequently, flow becomes difficult and the polymer assumes the characteristic hard and brittle behavior of glasses.

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.

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),
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).

C. FACTORS AFFECTING GLASS TRANSITION TEMPERATURE

At the glass transition temperature, there is a large-scale cooperative movement of chain segments. It is 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 (steric hindrance, polarity or interchain attractive forces);
- geometric factors;
- copolymerization;
- molecular weight,
- Branching and cross-linking; and
- crystallinity.

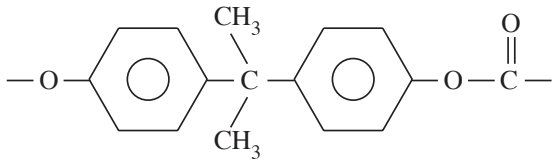
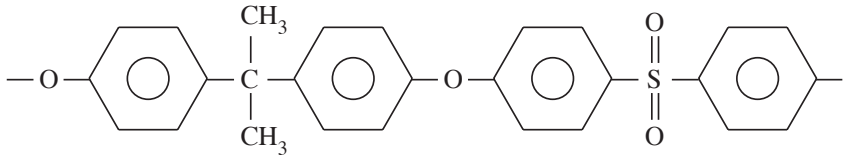
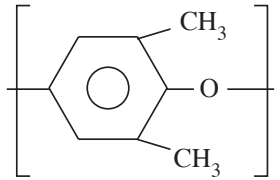
External variables are plasticization, pressure, and rate of testing.

1. Chain Flexibility

Chain flexibility is determined by the ease of rotation about primary valence bonds. Polymers with low hindrance to internal rotation have low T_g values.

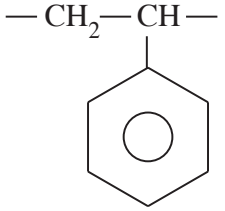
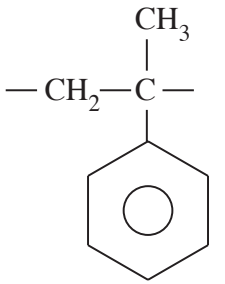
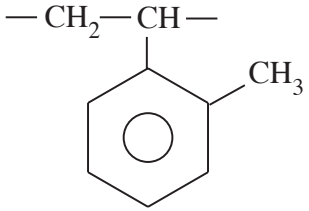
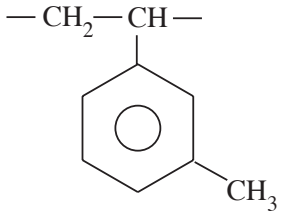
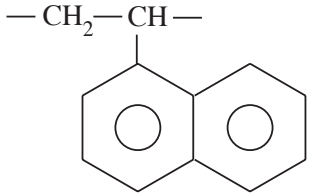
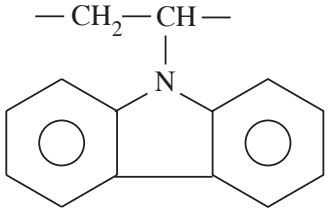
Long-chain aliphatic groups (ether and ester linkages) enhance chain flexibility, while rigid groups like cyclic structures stiffen the backbone.

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

Bulky side groups that are stiff and close to the backbone cause steric hindrance, decrease chain mobility, and hence raise T_g.

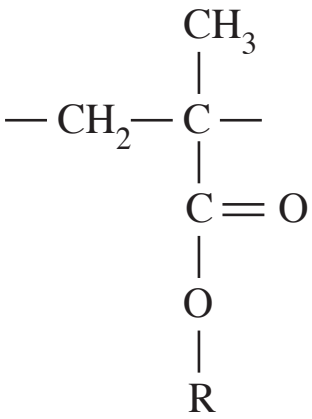
Table 4.2 *Enhancement of T_g by Steric Hindrance*

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

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.

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

Generalized Formula	R	T_g (°C)
	methyl	105
	ethyl	65
	n-propyl	35
	n-butyl	21
	n-hexyl	–5
	n-octyl	–20
	n-dodecyl	–65

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).

Table 4.4 *Effect of Symmetry of T_g*

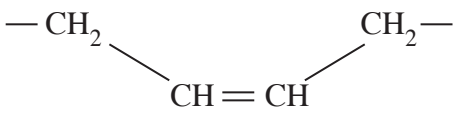
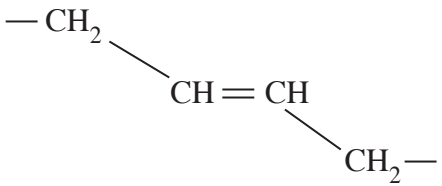
Polymer	Repeat Unit	T_g(°C)
Polypropylene	$-CH_2-CH(CH_3)-$	–10
Polyisobutylene	$-CH_2-C(CH_3)_2-$	–70
Poly(vinyl chloride)	$-CH_2-CH(Cl)-$	87
Poly(vinylidene chloride)	$-CH-CCl_2-$	–17

Based on chain stiffness, it is expected that additional groups near the backbone for the symmetrical polymer would enhance steric hindrance and consequently raise T_g.

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 *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

3. Interchain Attractive Forces

Intermolecular bonding in polymers is due to secondary attractive forces. Consequently, it is expected that the presence of strong intermolecular bonds in a polymer chain (a high value of cohesive energy density) will significantly increase T_g.

The steric effects of the pendant groups in series (CH_3, –Cl, and –CN) are similar, but the polarity increases.

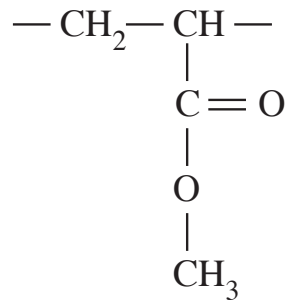
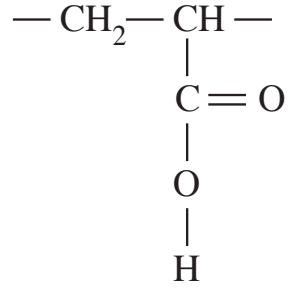
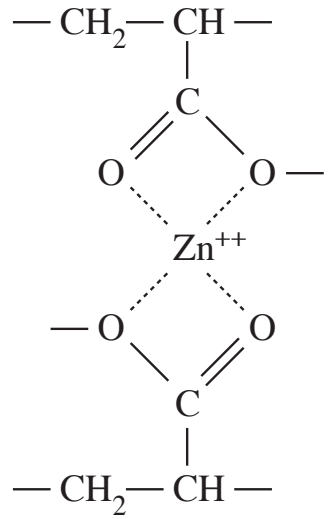
Table 4.6 *Effect of Polarity on T_g*

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

The same effect of increased T_g with increasing CED can be observed: dipole forces in poly(methyl acrylate), strong hydrogen bonds in poly(acrylic acid), and primary ionic bonds in poly(zinc acrylate).

The 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 Tg.

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

Polymer	Repeat Value	T_g(°C)
Polymethylacrylate		3
Poly(acrylic acid)		106
Poly(zinc acrylate)		>400

4. Copolymerization

A copolymer system may be characterized either by the geometry of the resulting polymer (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.

This shift, in Figure 4.4, 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:

$$T_g = V_1 \, T_{g2} + V_2 \, T_{g2}$$

where V_1 and V_2 are the volume fractions of components 1 and 2, respectively.

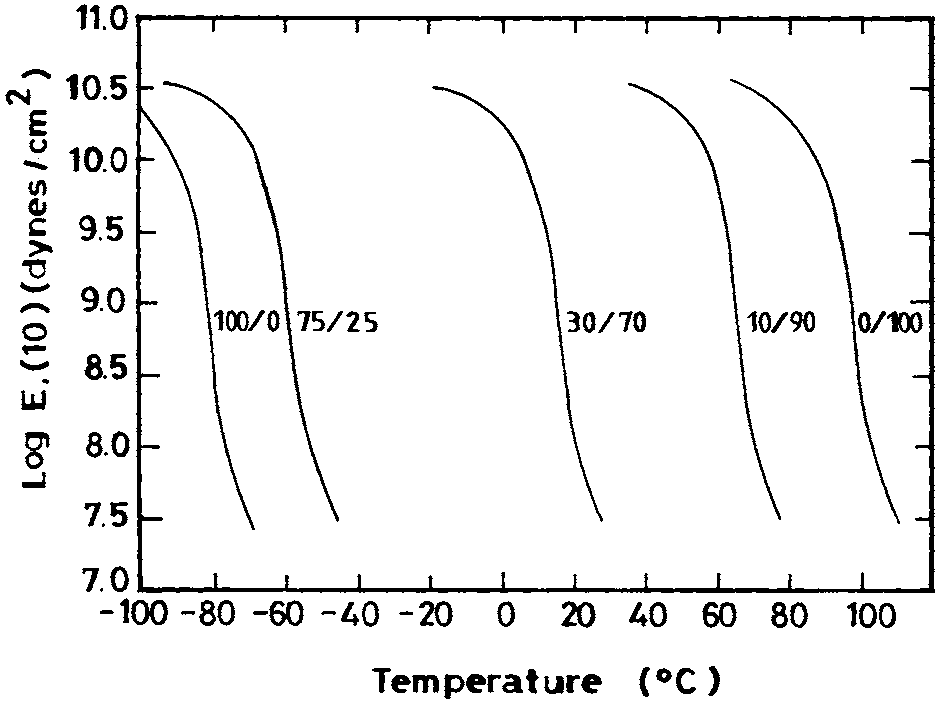


Figure 4.4 *E_r vs. fraction ratios of butadiene–styrene copolymers.*

b. Non-isomorphous Systems

In non-isomorphous systems, the **specific volumes** of the monomers are **different**. In this case, the geometry of the resulting polymer becomes important.

Random or alternating the composition is necessarily homogeneous (no phase separation) and 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 the Equation (above).

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:

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

Examples of this type are methyl methacrylate–acrylonitrile, styrene–methyl methacrylate, and acrylonitrile–acrylamide copolymers.

Block and graft copolymers (incompatible copolymers) if the component monomers are incompatible, **phase separation** will occur.

Depending on a number of factors (e.g. 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.

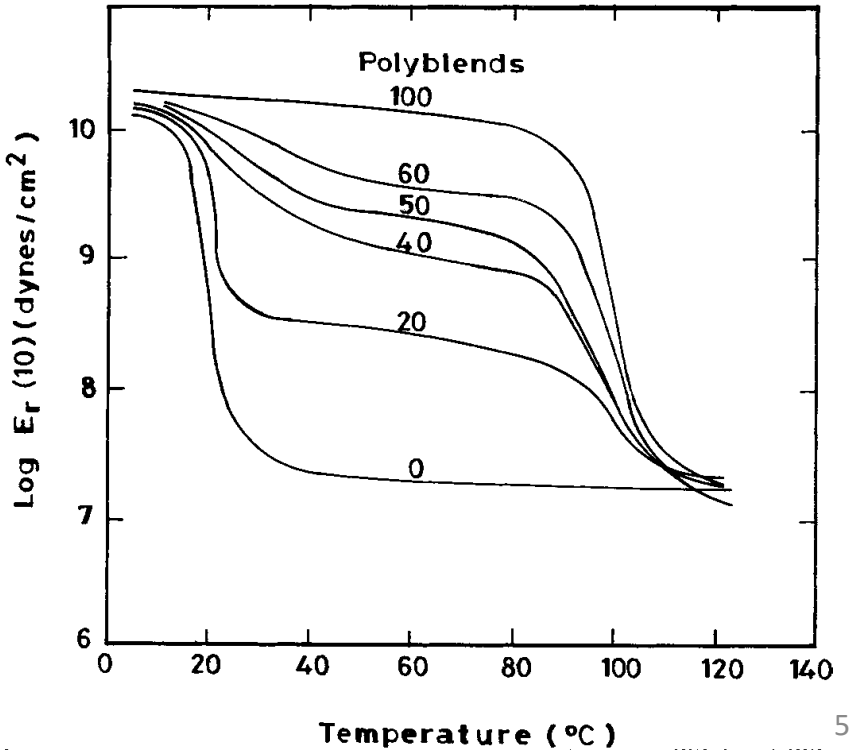


Figure 4.6 *$E_r(10)$ vs. temperature for polyblends of polystyrene and a 30/70 butadiene–styrene copolymer. Numbers on the curves are the weight percent of polystyrene in the blend.*

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, 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 M_n is given by Equation:

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

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.

6. Cross-Linking and Branching

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.

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

where T_g = for 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 T_g is virtually infinite, 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:

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

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.

Plasticizers are usually **nonpolymeric**, **organic liquids** of **high boiling points**.

Plasticizers are **miscible with polymers** and 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.

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.

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

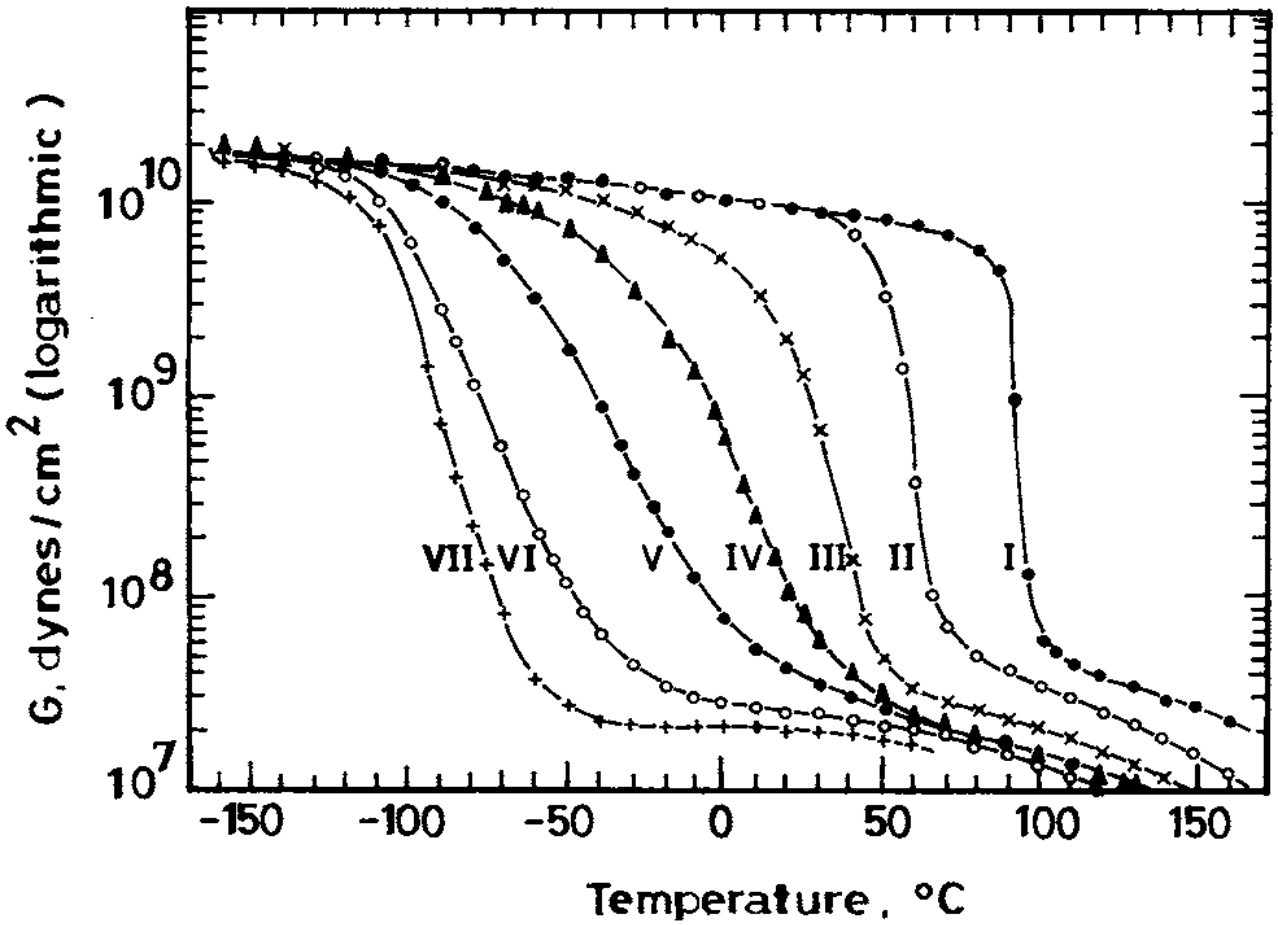


Figure 4.7 *Shear modules, G vs. temperature, measured for a time scale of approximately 1 s, poly(vinyl chloride) plasticized with diethylhexyl succinate. I, 100% monomer; II, 91%; III, 79%; IV, 70.5%; V, 60.7%; VI, 51.8%; VII, 40.8%.*

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,

$$\Delta G_m = \Delta H_m - T_m \Delta g_m = 0 \qquad T_m = \frac{\Delta H_m}{\Delta S_m}$$

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.

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**.

Melting is a true first-order thermodynamic transition involving a phase change and is associated with discontinuities in primary extensive thermodynamic properties.

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, TM

Melting in crystalline polymers can be considered a pseudo-equilibrium process that may be described by the free energy equation:

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

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.

$\Delta \mathbf{H_m}$ is generally **independent** of the **molecular weight**. Polar groups on the chain would enhance the magnitude of ΔH_m.

$\Delta \mathbf{S_m}$ **depends** on **molecular weight** and **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.

1. Intermolecular Bonding

The cohesive forces in polymers involve the secondary bonding forces.

Van Krevelen and Hoftyzer have calculated the contributions of the characteristic groups in various polymers to Y_m, a quantity they termed ***molar melt transition function*** (Table 4.8).

Table 4.8 *Group Contributions to the Melting Point*

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

The enhanced flexibility resulting from the presence of oxygen atoms in the polyester chains considerably offsets the weak polar bonding from ester linkages.

The melting points of the nylons reflect the density of the hydrogen-bond-forming amide linkages. The same for polycaprolactone (ester units) and polycaprolactam (amide units).

The amide units are more polar than the ester units.

Table 4.9 *Effect of Intermolecular Bonding on T_m*

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

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**.

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).

3. Chain Flexibility

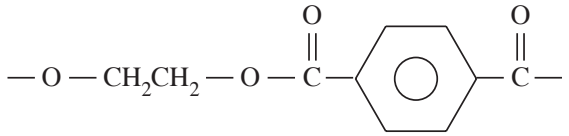
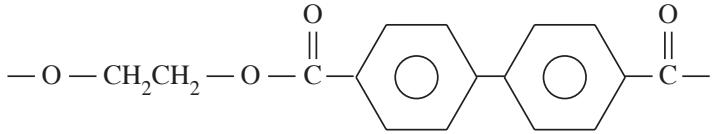
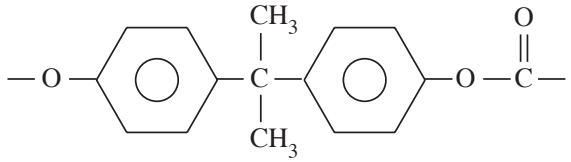
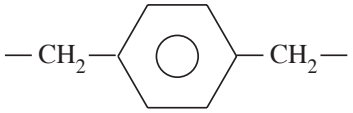
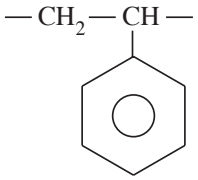
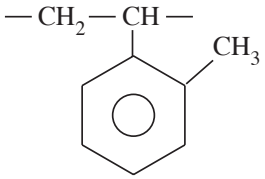
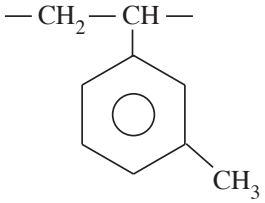
Polymers with rigid chains would be expected to have higher melting points than those with flexible molecules.

Polymers with stiff backbones have lower conformational entropy changes than those with flexible backbones.

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.

Table 4.10 *Effect of Chain Flexibility to T_m*

Polymer	Repeat Unit	T_m(°C)
Polyethylene	$-CH_2-CH_2-$	135
Polypropylene	$-CH_2-CH(CH_3)-$	165
Polyethylene oxide	$-CH_2-CH_2-O-$	66
Poly(propylene oxide)	$-CH_2-CH(CH_3)-O-$	75
Poly(ethylene adipate)	$-O-CH_2-CH_2-O-C(=O)-(CH_2)_4-C(=O)-$	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

4. Copolymerization

The effect of copolymerization on $\mathbf{T_m}$ 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.

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.

T_m of the copolymer ($T_m°$ of the homopolymer) is given by Equation:

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

where ΔH_m and X are, respectively, the heat of fusion and mole fraction of the homopolymer or crystallizing (i.e., major) component.

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.