Physical Properties of Polymers

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Polymers

Made up of chain molecules → long-range connections throughout material

In practice, mostly carbon atoms along length of the chain + various side-groups (e.g. -H, -Cl,-OH, $-CH_3$) attached to it at regular intervals

Polymer materials

High Density Polyethylene for storm water drainage system.

Replaces fired clay ceramics (brittle, difficult to make long sections, difficult to join) and cast iron (heavy, low corrosion resistance)

Also used in domestic plumbing, displacing copper (expensive)

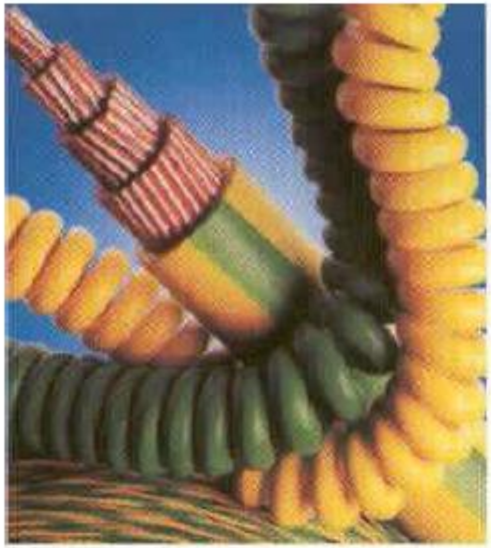
Polymer materials

Kevlar for body armour.

Replaces iron (heavy, stiff)

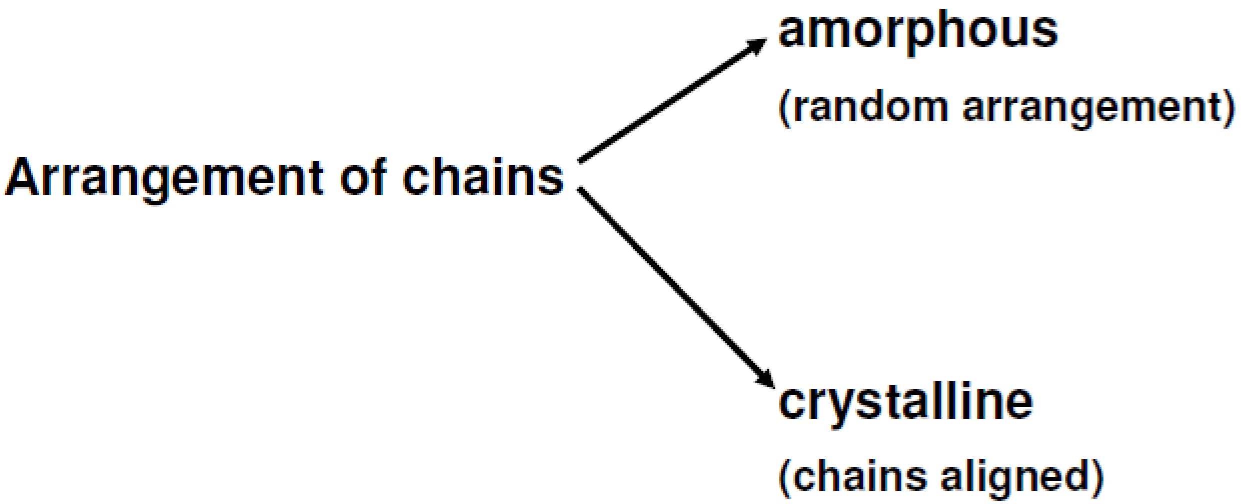
Polymer materials

Polyvinyl chloride for cable insulation: flexible, easily formed, thermally and electrically insulating.



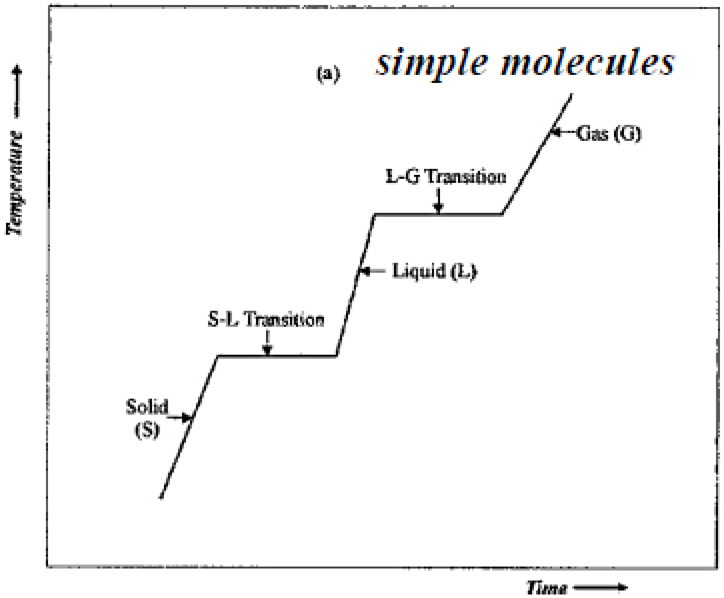
Nylon for fabrics, replacing silk (expensive)

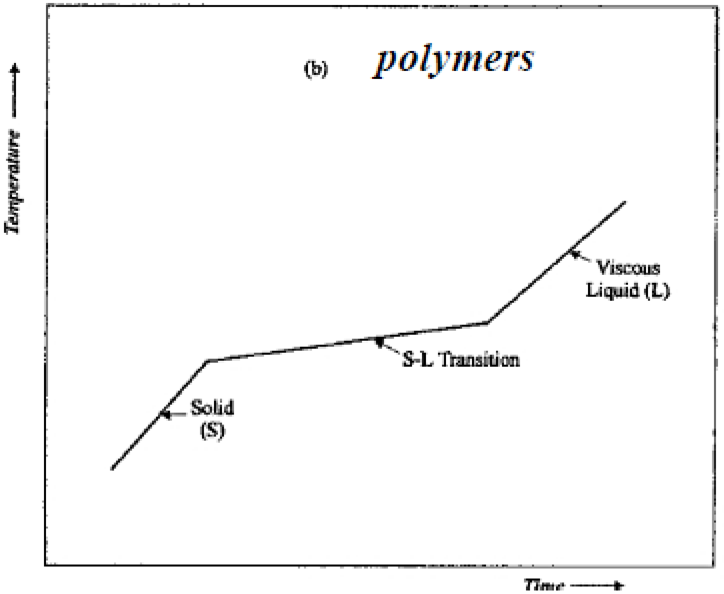
Describing polymers (cont.)



Arrangement of chains

- amorphous
  (random arrangement)
- crystalline
  (chains aligned)

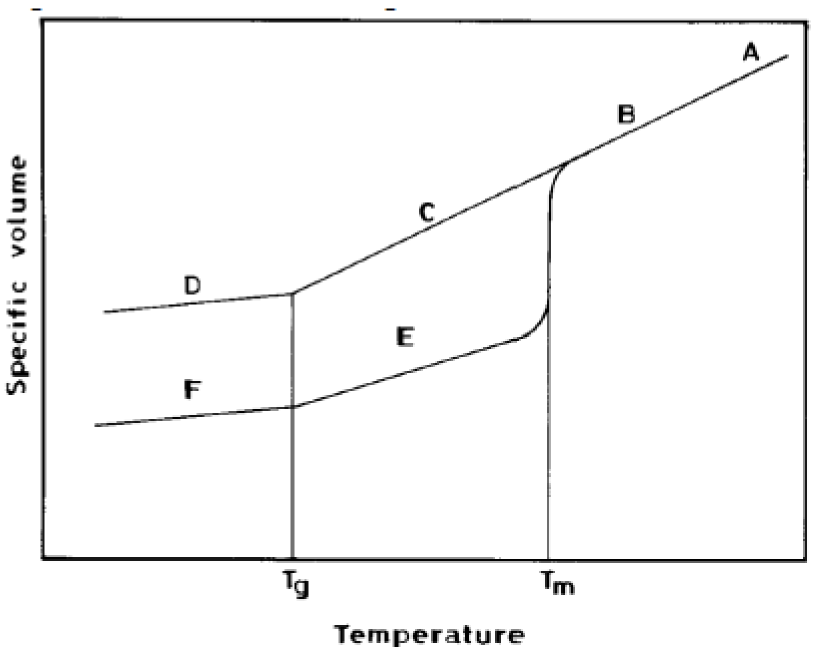

(a)
simple molecules
Temperature
Time
Gas (G)
L-G Transition
Liquid (L)
S-L Transition
Solid
(S)


(b)
polymers
Temperature
Time
Viscous
Liquid (L)
S-L Transition
Solid
(S)

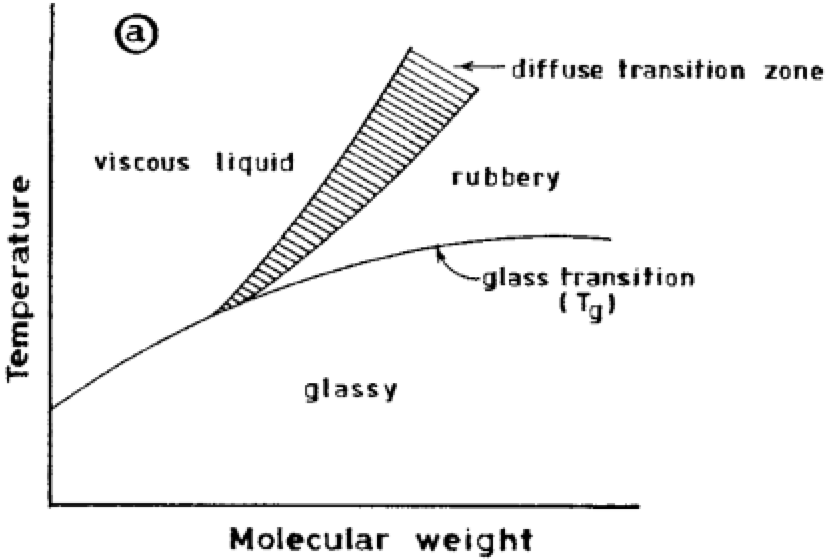
Morphology

Think of crystalline materials like ramen noodles. When in their solid state, they have a compact ordered arrangement

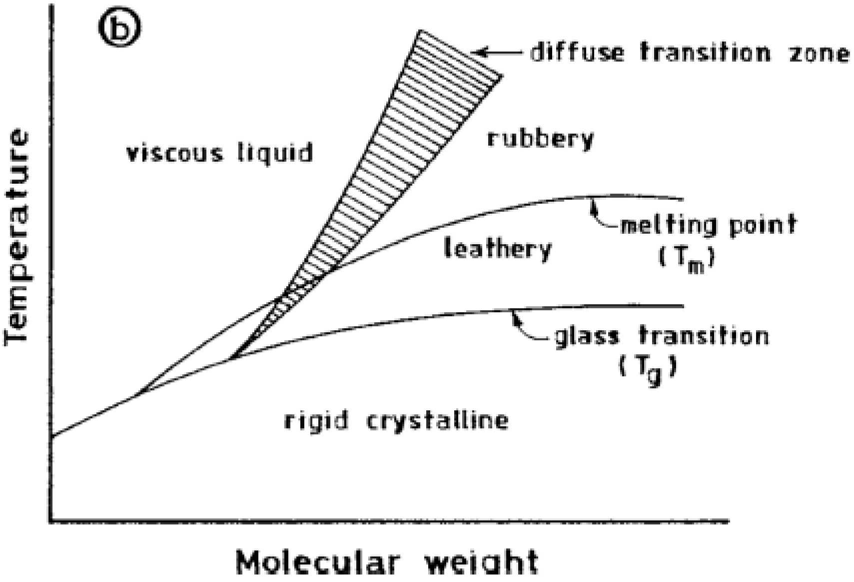
Amorphous materials are like cooked ramen noodles in that there is a random arrangement of the molecules and there are no crystals present to prevent the chains from flowing



(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.



amorphous polymer



crystalline polymer

The Glass Transition

THEORIES OF GLASS TRANSITION AND MEASUREMENT OF THE GLASS TRANSITION TEMPERATURE

Free Volume Theory

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 Tg.

Kinetic Theory

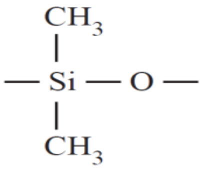
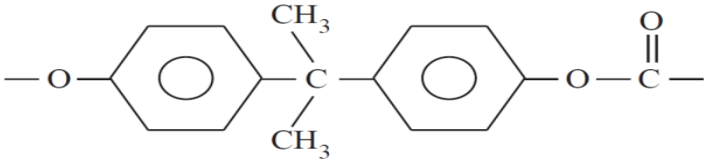
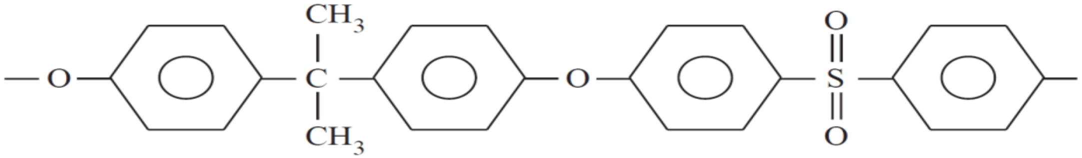
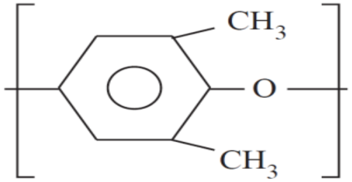
The kinetic concept of glass transition considers the glass transition as a dynamic phenomenon since the position of the Tg depends on the rate of heating or cooling. It predicts that the value of Tg measured depends on the time scale of the experiment in relation to that of the molecular motions arising from the perturbation of the polymer system by temperature changes

Equilibrium Theory

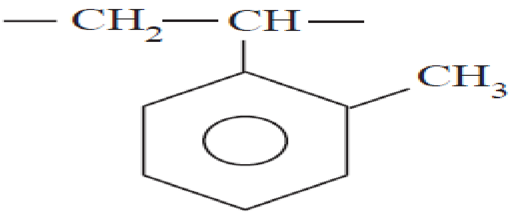
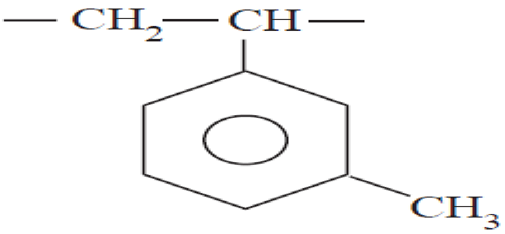
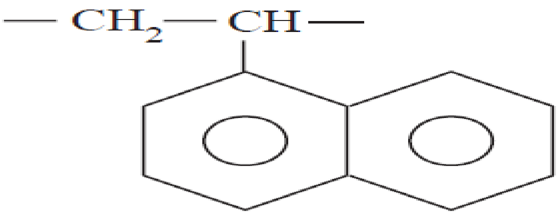
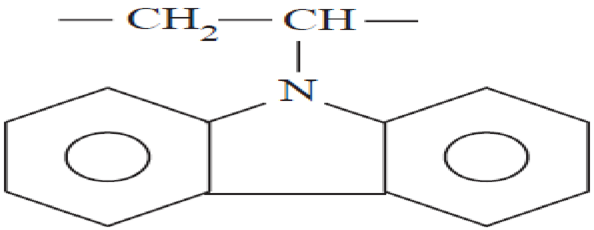
The equilibrium concept treats the ideal glass transition as a true second-order thermodynamic transition, which has equilibrium properties. The ideal state, of course, cannot be obtained experimentally since its realization would require an infinite time.

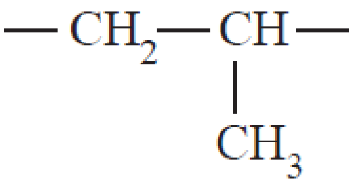
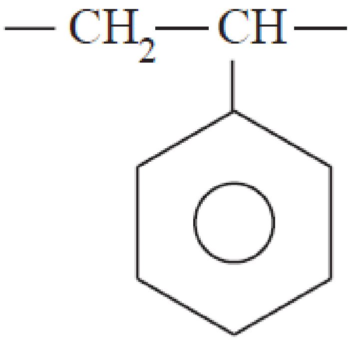
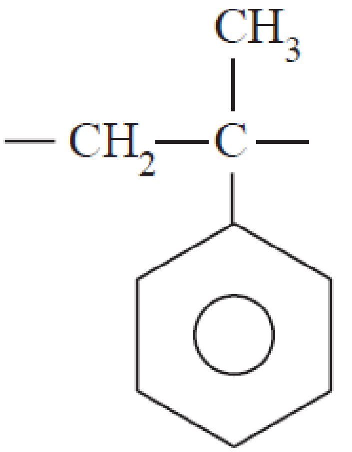
FACTORS AFFECTING GLASS TRANSITION TEMPERATURE

1. Chain Flexibility

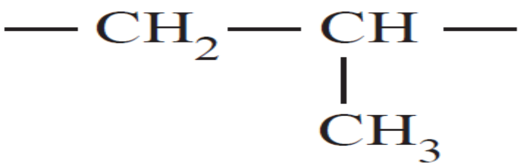
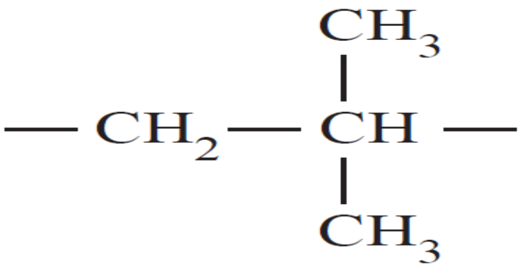
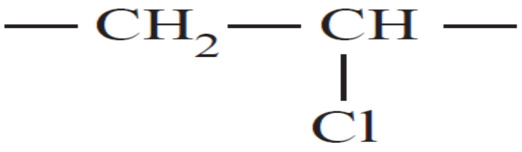
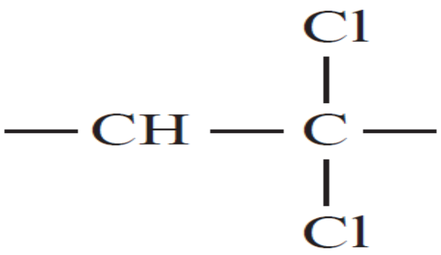
Polymer	**Repeat Unit**	**T_h (°C)**
Polyethylene	$—CH_2—CH_2—$	−120
Polydimethylsiloxane	 $—\overset{\displaystyle CH_3 \atop \displaystyle |}{\underset{\displaystyle | \atop \displaystyle CH_3}{Si}}—O—$	−123
Polycarbonate		150
Polysulfone		190
Poly(2,6-dimethyl- 1,4-phenylene oxide)		220

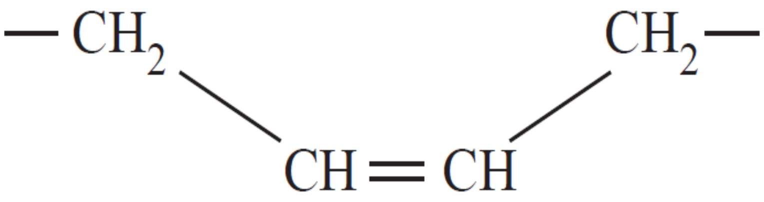
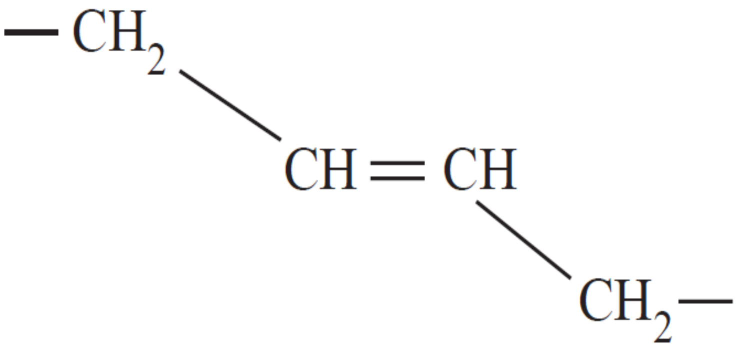
2-steric hindrance

Polymer	Repeat Unit	T_g(°C)
Poly(*o*-methylstyrene)		119
Poly(*m*-methylstyrene)		72
Poly(α-vinyl naphthalene)		135
Poly(vinyl carbazole)		208

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

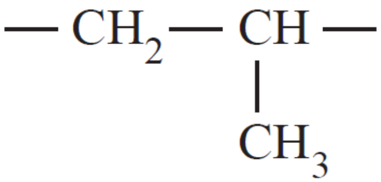
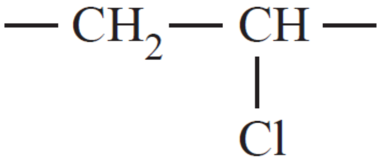
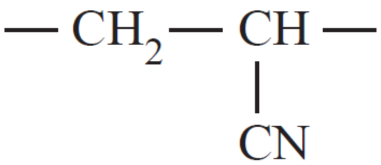
3. Geometric Factors

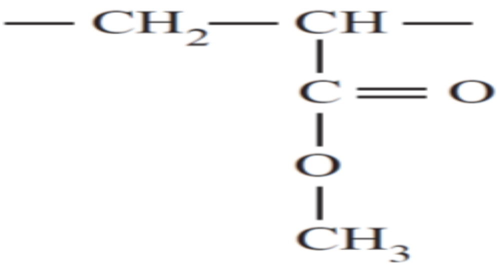
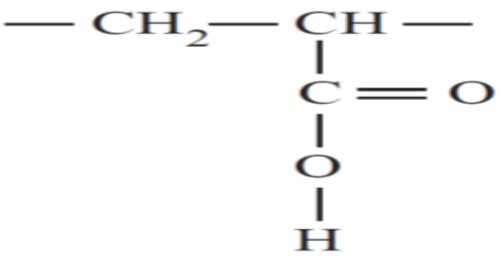
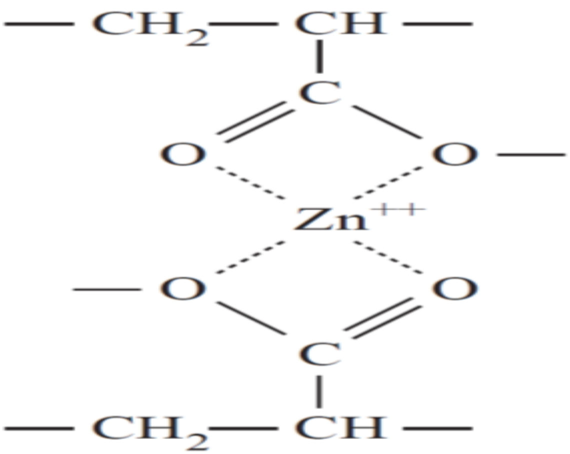
Polymer	**Repeat Unit**	**T_g(°C)**
Polypropylene	 $-CH_2-\underset{CH_3}{\underset{\mid}{CH}}-$	−10
Polyisobutylene	 $-CH_2-\overset{CH_3}{\overset{\mid}{\underset{CH_3}{\underset{\mid}{CH}}}}-$	−70
Poly(vinyl chloride)	 $-CH_2-\underset{Cl}{\underset{\mid}{CH}}-$	87
Poly(vinylidene chloride)	 $-CH-\overset{Cl}{\overset{\mid}{\underset{Cl}{\underset{\mid}{C}}}}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

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

4. Interchain Attractive Forces

Effect of Polarity on T_g

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

Polymer	**Repeat Value**	**T$_g$(°C)**
Polymethylacrylate	 $-CH_2-CH(COOCH_3)-$	3
Poly(acrylic acid)	 $-CH_2-CH(COOH)-$	106
Poly(zinc acrylate)		>400

5. Copolymerization

$$T_g = V_1 T_{g1} + V_2 T_{g2}$$

where V1 and V2 are the volume fractions of components 1 and 2, respectively

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

weight fractions W1 and W2 and glass transitions Tg1 and Tg2,

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

$T_{g1} = -80°C,\ T_{g2} = 100°C$

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

Assume 1 = polybutadiene

2 = polystyrene

$$T_{g1} = -80°C,\ T_{g2} = 100°C$$

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

$$= -62°C$$

6. Molecular Weight

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

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

For polystyrene it has been found that $T_g^{\infty} = 100°C$ 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, $T_g^{\infty} = 100$, $K = 2 \times 10^5$.

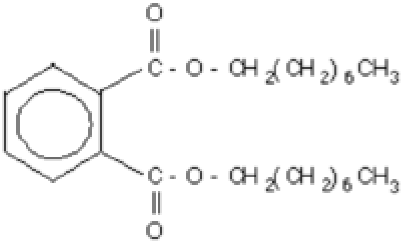
$$T_g = 100 - \frac{2 \times 10^5}{3000}$$

$$= 33°C$$

7. 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, 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).



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.

$$T_g = \left(1 - V_B\right) T_{gA} + V_B \left(T_{gB}\right)$$

$$= 0.8 \times 100 \times 0.2 \left(-50\right)$$

$$= 70°C$$

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,

$$\Delta G_m = \Delta H_m - T_m \Delta S_m = 0$$

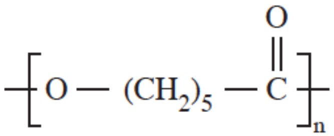
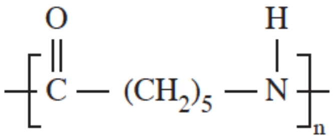
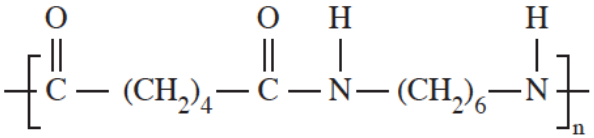
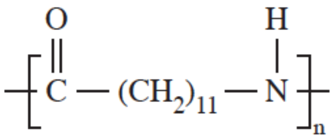
$$T_m = \frac{\Delta H_m}{\Delta S_m}$$

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

FACTORS AFFECTING THE CRYSTALLINE MELTING POINT, TM

1. Intermolecular Bonding

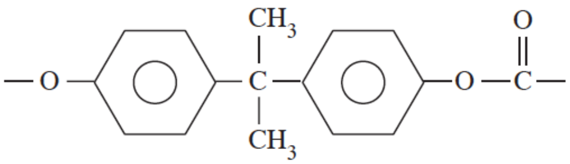
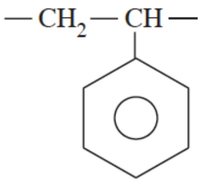
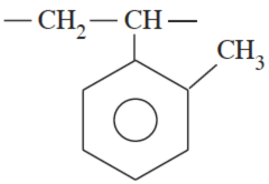
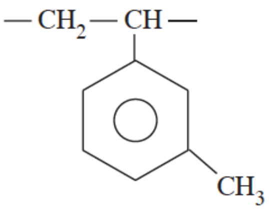
Polymer	**Characteristic Group**	**Melting Temperature (T_m)(°C)**
Polycaprolactone	 $\left[O - (CH_2)_5 - \overset{\overset{O}{\|}}{C} \right]_n$	61
Polycaprolactam (nylon 6)	 $\left[\overset{\overset{O}{\|}}{C} - (CH_2)_5 - \overset{\overset{H}{\vert}}{N} \right]_n$	226
Poly(hexamethylene adipamide)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

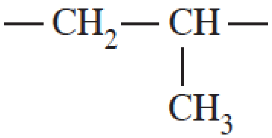
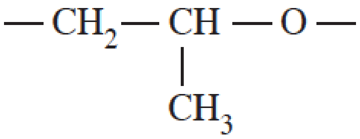
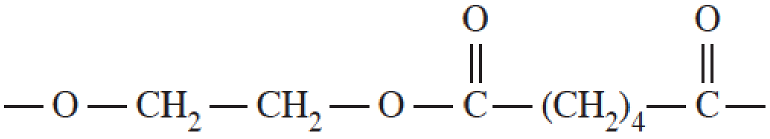
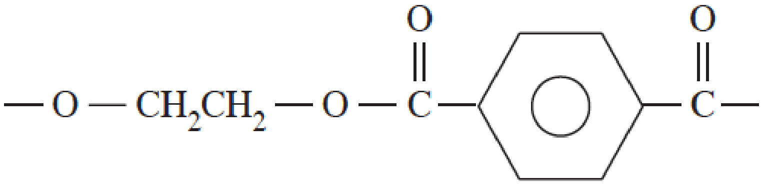
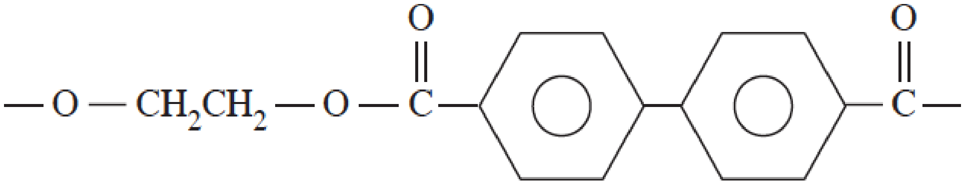
2. Effect of Structure

The structural dependence of the crystalline melting temperature is essentially the same as that for the glass transition temperature

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 (–CH2–) 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.

Polymer	Repeat Unit	T_m(°C)
Polycarbonate		270
Poly(*p*-xylene)		380
Polystyrene (isotactic)		240
Poly(*o*-methylstyrene)		>360
Poly(*m*-methylstyrene)		215

Polymer	**Repeat Unit**	**T_m(°C)**
Polyethylene	$-CH_2-CH_2-$	135
Polypropylene	 $-CH_2-\underset{\displaystyle CH_3}{\underset{\mid}{CH}}-$	165
Polyethylene oxide	$-CH_2-CH_2-O-$	66
Poly(propylene oxide)	 $-CH_2-\underset{\displaystyle CH_3}{\underset{\mid}{CH}}-O-$	75
Poly(ethylene adipate)	 $-O-CH_2-CH_2-O-\overset{\displaystyle O}{\overset{\Vert}{C}}-(CH_2)_4-\overset{\displaystyle O}{\overset{\Vert}{C}}-$	50
Poly(ethylene terephthalate)		265
Poly (diphenyl-4,-4 diethylene carboxylate)		355

4. Copolymerization

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

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

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

Solution: From the foregoing discussion:

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

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

$$= 135°\text{C} = 408\ \text{K}$$

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

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

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

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

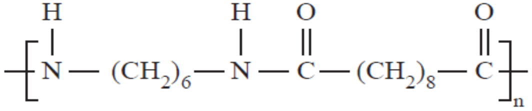
$$T_m = 390 \text{ K} = 117°\text{C}$$

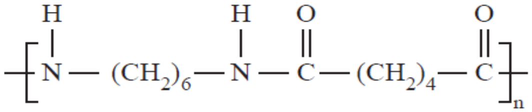
In semicrystalline polymers, the crystallites may be regarded as physical cross-links that tend to reinforce or stiffen the structure. Viewed this way, it is easy to visualize that T_g will increase with increasing degree of crystallinity. This is certainly not surprising since the cohesive energy factors 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.

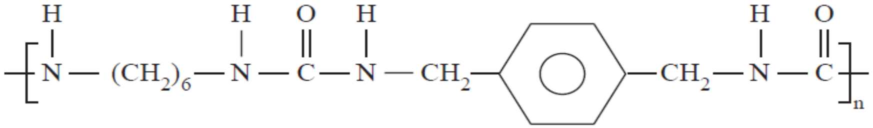
$$\frac{T_g}{T_m} = \begin{Bmatrix} 1/2 \text{ for symmetrical polymers} \\ 2/3 \text{ for unsymmetrical polymers} \end{Bmatrix}$$

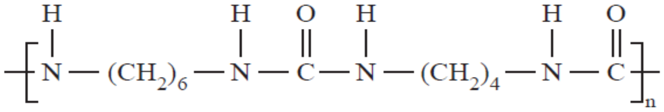
Problems

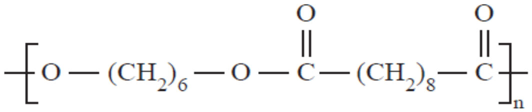
1.Arrange the following materials in the probable order of their increasing crystalline melting points and justify your answer. Assume the degree of polymerization, n, for the polymers is the same

a.

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

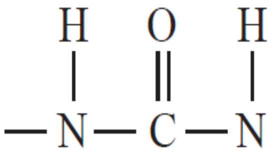
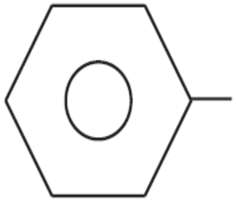
b.

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

c.


d.

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

e.

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

Increasing order of T_m: e < a < b < d < c.

Material	**Comments**
c	With linkages  $-\overset{H}{\overset{\mid}{N}}-\overset{O}{\overset{\|}{C}}-\overset{H}{\overset{\mid}{N}}-$, forms strong H-bonds; phenyl rings  are stiff and rigid. Both increase T_m
d	Urea linkages; high density of hydrogen bonding
b	Amide linkages; same density of hydrogen bonding as d but urea linkages generally stronger than amide linkages
a	Amide linkages but relatively smaller density of hydrogen bonding than b due to longer distances between amides; $(CH_2)_8$ vs. $(CH_2)_4$
e	Ester linkages enhance molecular rotation and hence reduce T_m

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 Tg of dibutyl sebacate is –100°C and that room temperature is 25°C.

Since PVC and dibutyl sebacate have about the same value of solubility parameters, they are compatible and hence the following expression is applicable:

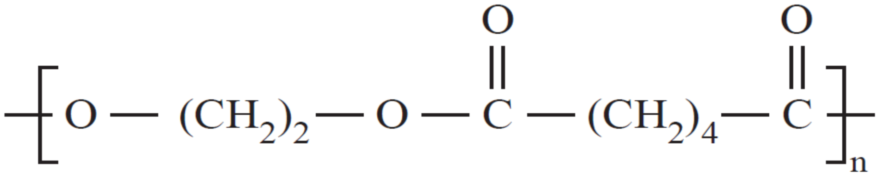
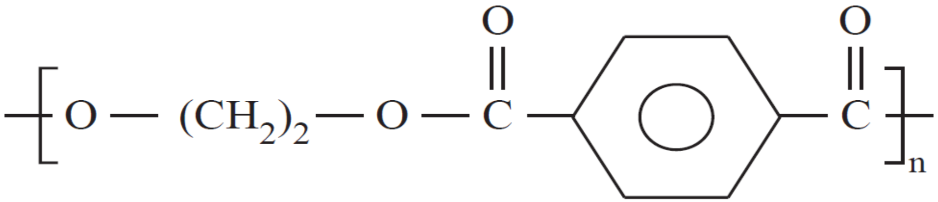
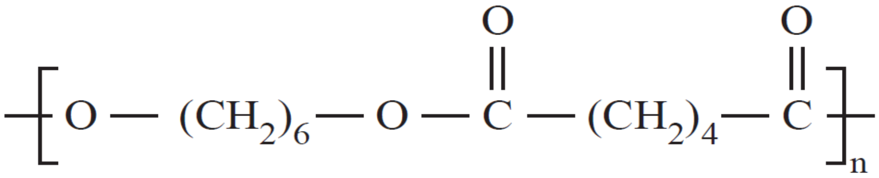
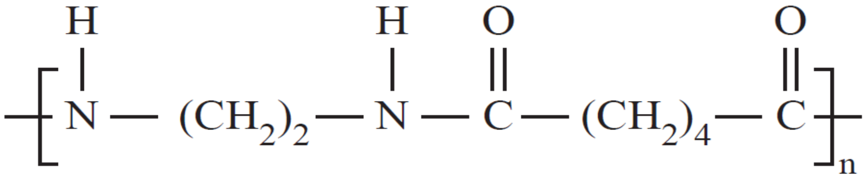
$$T_g = V_A T_{gA} + V_B T_{gB}$$

V_A and V_B are volume fractions of polymer and plasticizer, respectively.

$$25 = \left(1 - V_B\right) 85 + V_B \left(-100\right)$$

$$V_B = \frac{60}{185} = 32.4\%$$

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

Polymer	**Structure**
a. Poly(ethylene adipate)	 $\left[O - (CH_2)_2 - O - \overset{\overset{O}{\Vert}}{C} - (CH_2)_4 - \overset{\overset{O}{\Vert}}{C} \right]_n$
b. Poly(ethylene terephthalate)	
c. Poly(hexamethylene adipate)	 $\left[O - (CH_2)_6 - O - \overset{\overset{O}{\Vert}}{C} - (CH_2)_4 - \overset{\overset{O}{\Vert}}{C} \right]_n$
d. Poly(ethylene adipamide)	 $\left[\overset{\overset{H}{\vert}}{N} - (CH_2)_2 - \overset{\overset{H}{\vert}}{N} - \overset{\overset{O}{\Vert}}{C} - (CH_2)_4 - \overset{\overset{O}{\Vert}}{C} \right]_n$

Order of decreasing melting point: b > d > a > c.

Polymer	Comments
b	Presence of phenyl rings stiffens backbone and increases T_m
d	Amide linkages form hydrogen bonds
a	Ester linkages more flexible than amide linkages in (d)
c	Ester linkages; and more flexible than (a); $(CH_2)_6$ vs. $(CH_2)_2$

4.The Tg of polystyrene is 100°C. What is its melting temperature, Tm?

$$\frac{T_g}{T_m} = \frac{2}{3} \text{ for unsymmetrical polymers}$$

$$T_g = 100°\text{C} = 273 + 100 = 373 \text{ K}$$

$$T_m = \frac{3}{2} \times 373 = 559.5 \text{ K} = 286.5°\text{C}$$