POLYMER CHEMISTRY

SEM-6, DSE-B3
Transition Phenomena in Polymers

PART-5, PPT-17

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Part-5: Glass Transition Temperature

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- ***Factors Affecting Glass Transition Temperature (T_g)***
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Factors Affecting Glass Transition Temperature (T_g)

- As glass transition (T_g) marks the onset of molecular motion, a number of factors that affect rotation about links (necessary for movement of polymer chains) will also influence the T_g of a polymer. These include (a) chain flexibility, (b) molecular structure (steric effects), (c) molecular weight, and (d) branching and crosslinking, etc.

- In general, factors that increase the energy required for the onset of molecular motion increase T_g; those that decrease the energy requirements lower T_g. Glass transition temperature of a polymer depends on many factors. A few of them is summarized in **Table 1.**

Table 1: Factors affecting T_g

Increase T_g	**Decrease T_g**
Intermolecular forces	**In-chain groups promoting flexibility (double-bonds and ether linkages)**
High Cohesive energy density (CED)	**Flexible side group**
Intrachain steric hindrance	**Symmetrical substitution**
Bulky, stiff side groups	**Length of the side group**

Factors Affecting T_g

1. ***Effect of Molecular weight:*** In case of straight chain polymers, increase in molecular weight leads to decrease in chain end concentration. This results in decreased free volume at end group region and increase in T_g. If end groups of chain are changed, molecular weight dependence of T_g can be changed. Decrease in chain end concentration (low molecular weight) and stronger interactions at end groups increase T_g.

- It can be seen that for relatively short chains the, T_g increases sharply with increasing molecular weight, but then levels off and appears to asymptotically approach a limiting value. The free volume approach accounts for this. The concept of free volume is associated with cooperative motions.
- The ends of a chain have more freedom of motion than the segments in the center of a chain. Low molecular weight chains have more ends per unit volume than long chains hence a higher free volume, hence a lower T_g.
- *Note: **Cooperative segmental mobility** is a phenomenon associated with mobility of tens to a few hundreds of repeat units of a polymer and is important in defining the transition between glassy and rubbery state of the polymer.*

Factors Affecting T_g

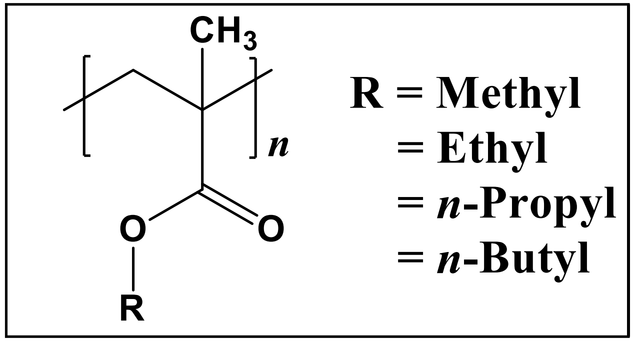
2. *The Effect of Chemical Structure*

a) *Bulky, inflexible side group*

- Insertion of bulky, inflexible side group increases T_g of material due to decrease in mobility. Stiffer chains and those with stronger intermolecular interactions would have a higher T_g. This is because chain stiffness affects chain mobility, in other words the ease of rotation around the bonds of the polymer backbone becomes difficult. Free volume decreases, and a consequent increase in T_g.

b) *Presence of flexible side group:* If a flexible side chain is attached to the main chain, as for example, in the methacrylates, T_g decreases with increasing chain length. The substituents closest to the chain, the -CH_3 (methyl) and COO (ester) group, provide the bulk of the steric hindrance. The rest of the attached side chain can "get out of the way" of motions of the main chain through rotations around side-chain bonds.

Factors Affecting *T_g*



- Because the side chains increase the free volume through their effect on the packing of the chains (and also affect it through their mobility), the T_g is lowered.

c) *Length of the side group:* As length of side group increases the polymer chains move apart from each other and that increases free volume in the molecule resulting in decreased T_g. Example: Poly(vinyl *n*-butyl ether) showed decreased T_g with increase in chain length.

d) *Double bond in back bone*

- Double bonds in backbone of a molecule decrease bond rotation leading to increase in free volume and ultimately decrease in T_g. **Example:** Polybutadienes show low T_g (175 K), which is less than analogous polymer containing side chain double bond. If there are bulky groups, such as benzene rings, in the backbone of the polymer chain, there is a high energy barrier to rotations which then only occur at higher temperatures.

Factors Affecting T_g

e) Chemical cross-linking:

- Increase in cross-linking increases T_g. The effect of cross-linking can be explained on the basis of simple free volume arguments. Cross-linking decreases mobility of the chain because parts of the chain are tied more closely together. This leads to decrease in free volume, hence the T_g increases.

f) Polar groups/Presence of secondary forces/Bond interactions:

- Presence of polar groups increases intermolecular forces. Inter chain attraction and cohesion lead to decrease in free volume resulting in increase in T_g. Strong intermolecular attractions also act to raise the T_g.
- For example, comparing the T_g's of polypropylene and poly(vinyl chloride), it can be said that the chlorine atom and methyl group have approximately the same effect on bond rotations.

Factors Affecting T_g

- The polar character of the Cl atom leads to stronger forces of attraction between chains, however, which in turn means that on average those groups engaging in such interactions are closer together. The free volume is less and the T_g is higher **(Figure 1)**.

- High secondary forces due to the high polarity or hydrogen bonding lead to strong crystalline forces that require high temperatures for melting. So, these high secondary forces give rise to high T_g due to the decreased mobility of amorphous polymer chains.

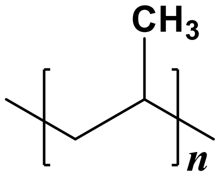
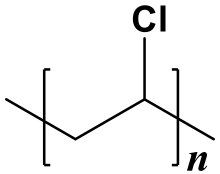
Polymer	**Chemical Structure**	T_g
Atactic Polypropylene		**- 10 ^{o}C**
Atactic Poly(vinyl chloride)		**87 ^{o}C**

Figure 1: Glass Transition Temperatures

***g) Branching*:** Increased branching gives rise to decreased mobility of polymer chains and increased chain rigidity results in high T_g. Example: T_g s of polystyrene (95 °C) and poly (methyl methacrylate), (105 °C).

Factors Affecting T_g

3. *Flexibility of polymer chain*

- Some polymers show high T_g and some show low because of the ease with which the polymer chains move. A very low T_g will be shown by the polymer chains which can move around easily, while one that doesn't move will have a high T_g. Factors affecting mobility of polymer chains responsible for easy movement of one polymer chain than the other are:

a) Backbone flexibility

- More flexible backbone chain results in better movement of the polymer chain and lowers its T_g. Examples: The major class is of silicones like polydimethylsiloxane. Its backbone is so flexible that it has a T_g -127°C and is in liquid state at room temperature. In case of poly (phenylene sulfone) backbone is so stiff and rigid that it doesn't have a T_g. It will stay in the glassy state up to the higher temperature. It will decompose before it undergoes a glass transition. By substituting flexible group like ether in the backbone chain, the polymer's T_g can be decreased.

Factors Affecting T_g

b) Pendant groups

- It has been observed that pendant groups affect chain mobility by acting as a fish hook that will catch on nearby molecules when the polymer chain tries to move. Pendant groups can also catch on each other when chains try to slither past each other. The pendant groups like big bulky adamantyl group derived from adamantine, gives a high T_g.
- This adamantyl group acts not only like a hook that catches on nearby molecules and avoids the polymer movement, but also its mass is such a load for its polymer chain that, it allows the movement of a polymer chain much more slowly.

- It is observed that the substitution of big bulky pendant groups can also lower T_g because of the limitation of the close packing of the polymer chains together. Thus they are away from each other giving more free volume. This facilitates easy movement, resulting in decrease in the T_g, similar to plasticizer.

Factors Affecting T_g

- In the series of methacrylate polymers, a decrease in T_g is observed with the substitution of one carbon each time, as seen in poly(methyl methacrylate), T_g 100-120 °C; For poly(ethyl methacrylate), T_g : 65 °C; poly(propyl methacrylate), T_g : 35 °C; poly(butyl methacrylate), Tg: 20 °C.

- Similarly, the presence of bulky pendant groups attached to the polymer backbone also raises the T_g, through steric hindrance to bond rotations. This effect is clearly illustrated with the examples shown in **Figure 2**.
- As the pendant group gets larger, the T_g increases. There is a limit to this, however, as at some point the attached groups no longer get in the way of bond rotations as they get further and further away from the chain.

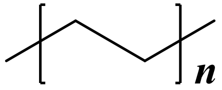
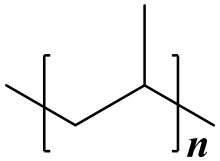
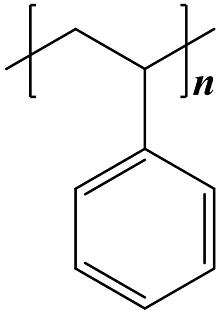
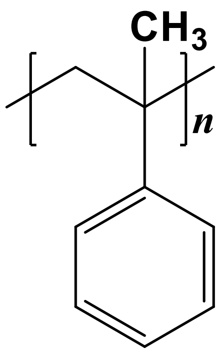
Polymer	**Chemical Structure**	T_g
Polyethylene		**- 80 ^{o}C**
Atactic Polypropylene		**- 10 ^{o}C**
Atactic Polystyrene		**100 ^{o}C**
Atactic Poly(α-methyl styrene)		**175 ^{o}C**

Figure 2: Glass Transition Temperatures

Factors Affecting T_g

- The flexibility of the chain may be considered to be the most important factor that influences the T_g of a polymer. If the chain is highly flexible, T_g will generally be low and if the chain is rigid, the T_g value will be high. The chain flexibility depends on the rotation or torsion of skeletal bonds. Chains made up of bond sequences which are able to rotate easily are flexible, and hence polymers containing $-(-CH_2-CH_2-)-$, $-(-CH_2-O-CH_2-)-$, or $–(-Si-O-Si-)-$ links will have correspondingly low values of T_g. For example, poly(dimethyl siloxane), which has Si-O bonds in the backbone chain, has one of the lowest T_g values known (-123 °C).

- The value of T_g increases markedly with the insertion of groups that stiffen the chain by impeding rotation, since more thermal energy is then required to set the chain in motion. Particularly effective in this respect is the ***p***-phenylene ring, $-C_6H_4-$.

- Some examples of such polymers are poly(xylylene), $-(-CH_2-C_6H_4-CH_2-)_n-$, $T_g \approx 280$ °C and poly(phenylene oxide), $-(-C_6H_4-O-)_n-$, $T_g = 83$ °C, as compared to polyethylene $-(-CH_2-CH_2-)_n-$, $T_g = -93$ °C and poly(ethylene oxide) $-(-CH_2-CH_2-O-)_n-$, $T_g = -67$ °C, respectively.

Factors Affecting T_g

- **Problem:** Presence of flexible pendant groups reduces the glass transition of the polymer, whereas bulky or stiff side groups increase it. Why?
- ***Answer:*** In general, factors that increase the energy required for the onset of molecular motion increase T_g and those that decrease the energy requirement lower T_g. Flexible pendant groups act as "inherent diluents" and lower the frictional interaction between chains, reducing the T_g thereby. Bulky or stiff side groups, on the other hand, increase interchain friction and energy requirement for molecular motion, thereby increasing T_g.

4. Plasticizer

- On addition of plasticizer to polymer, plasticizer gets in between the polymer chains and spaces them apart from each other increasing the free volume. This results in polymer chains sliding past each other more easily. As a result, the polymer chains can move around at lower temperatures resulting in decrease in T_g of a polymer.
- Example of plasticizer includes, nitrobenzene, β-naphthyl salicylate, carbon disulphide; glycerine, propylene glycol, triethyl citrate, polyethylene glycol, etc.

Factors Affecting T_g

5. *Water or moisture content*

- Increase in moisture content leads to increase in free volume due to formation of hydrogen bonds with polymeric chains increasing the distance between polymeric chains. The increased free volume between polymeric chains result in decreased T_g. Simultaneously, low hydrogen bonding between drug and polymer provides more hydrogen bonding sites for water molecules resulting in decreased physical stability.

6. *Effect of pressure*

- Increase in pressure of surrounding leads to decrease in free volume and consequently T_g increases. Free volume is the unoccupied space arising from inefficient packing of disordered chains and is the space available for polymer to undergo rotation. Increasing pressure decrease this free volume in the polymer.

7. *Cooling rate*

- If rate of cooling of molten solid is higher, T_g is higher and if rate of cooling is slower, then T_g obtained is low.

Factors Affecting T_g

8. *Polymer film thickness*

- Mobility of molecules increase when polymer film thickness decreases, resulting in decrease in T_g. Increase in film thickness increases compaction and results in an increased T_g. When a polymer is added to substrate, the T_g increases due to decreased mobility. In case of thin free standing films, T_g decreases more due to high mobility than bulk polymer.
- In case of sandwiched films, compaction leads to increase in T_g. Example: Polystyrene has shown decrease in T_g with decrease in its film thickness. Similar effect has been observed in poly (methyl methacrylate) films on Au.

9. *Effect of entropy and enthalpy*

- The value of entropy for amorphous material is higher and low for crystalline material. If value of entropy is high, then value of T_g is also high.

Factors Affecting T_g

10. Polymer solutions, co-polymers and blends

- It has been shown that T_g strongly depends on solvent used and the composition of polymer solutions. T_g is found to be decreased with addition of solvent to polymer due to plasticization. Hence, T_g becomes inversely proportional to concentration of solvent. Immiscible blends show separate T_g for each of the individual components. So, two T_gs are observed for binary blends. In case of miscible blends, a single T_g appears in between T_gs of mixed components.
- Example: Decrease in T_g of poly(vinyl chloride) due to plasticization by di(ethylhexyl)-phthalate; immiscible blend of polystyrene and styrene-butadiene co-polymer has shown separate T_gs.

11. The Effect of Diluents and Copolymerization

- It is expected that if a polymer with a T_g of about 100 °C is mixed with a second component, either another polymer or a low molecular weight material with a T_g of say -50 °C, then the T_g of the mixture would be somewhere in-between and would depend upon the relative proportions of the components present.

Factors Affecting T_g

- This is generally what is observed, although there are one or two exceptions (e.g., blends that have very strong intermolecular interactions, where the T_g of the mixture can be higher than either of the pure components). The addition of low molecular weight materials to a polymer to make it more flexible is known as plasticization and the diluent is called a plasticizer. For example, the addition of a low molecular weight species increases the free volume of the system and hence lowers the T_g .

12. Effect of Tacticity on T_g

- The effect of tacticity on T_g is significant. In disubstituted vinyl polymers, the energy difference between the two predominant rotational isomers is greater for the *syndiotactic* configuration than for the *isotactic* configuration. In monosubstituted vinyl polymers, where the other substituent is hydrogen, the energy difference between the rotational states of the two pairs of isomers is the same. Thus the polyacrylates (*isotactic* or *syndiotactic*) have the same T_g for the two isomers, whereas the poly(methyl methacrylates) show distinctly different T_g's, with the *isotactic* form always having a lower T_g than the *syndiotactic* form.

Factors Affecting T_g

13. Interfacial energy and thickness

- The T_g of polymer films was less than their bulk values for low values of the interfacial energy, while on other hand, the T_g of polymer films was greater than their bulk values for high values of the interfacial energy. The deviations of the T_g s of the films from bulk values have shown increase with decrease in film thickness. Example: T_gs of polystyrene and poly(methyl methacrylate).

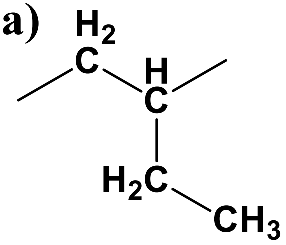
14. Functionality

- Mono functional aliphatic monomers due to high flexibility exhibit low T_g.
- Example: Isooctyl acrylate, tridecyl acrylate, lauryl acrylate. Higher functionality materials have similar molecular weights due to higher cross-link density results in higher T_g.

Problems on T_g

- **Problem:** Account for the differences in glass transition temperatures for the following pairs of isomeric polymers:
  (a) Poly(but-1-ene) (-24 °C) and poly(but-2-ene) (-73 °C).
  (b) Poly(ethylene oxide) (-67 °C) and poly(vinyl alcohol) (85 °C).
  (c) Poly(methyl acrylate) (6 °C) and poly(vinyl acetate) (28 °C)
  (d) Poly(ethyl acrylate) (-24 °C) and poly(methyl methacrylate) (105 °C)

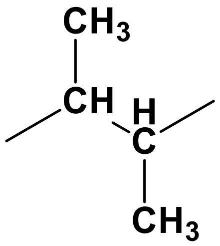
Answer: (a)



Poly(but-1-ene)

T_g = -24 °C

The long and bulky side groups makes rotation difficult

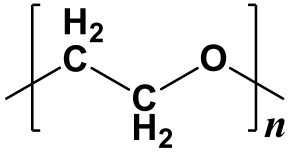


Poly(but-2-ene)

T_g = -73 °C

The side groups are shorter, this makes rotation easier

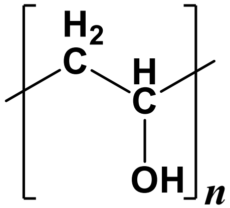
Answer: (b)



Poly(ethylene oxide)

$T_g = -67\ ^{o}\mathrm{C}$

The backbone chain is flexible, so rotation is easy

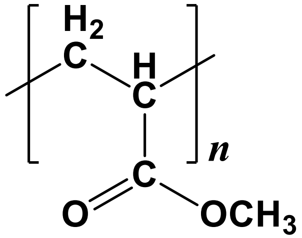


Poly(but-2-ene)

$T_g = 85\ ^{o}\mathrm{C}$

The steric effect of the -OH group restricts rotation. Superimposed on this is the effect of polarity which increases the lateral forces in the bulk state and leads to higher T_g.

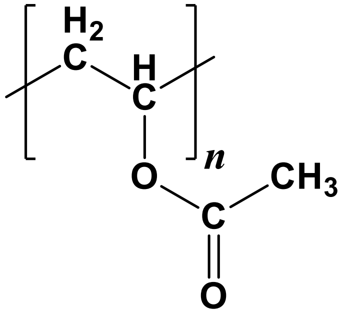
Answer: (c)



Poly(methyl acrylate)

$T_g = 6\ ^{o}\mathrm{C}$

The bulky group hinders rotation causing T_g to increase.

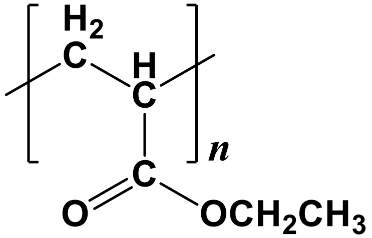


Poly(vinyl acetate)

$T_g = 28\ ^{o}\mathrm{C}$

The bulky part of the side group is farther from the chain, making rotation more difficult.

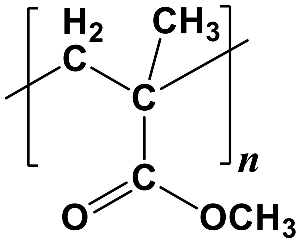
Answer: (d)



Poly(Ethyl acrylate)

$T_g = -24\ ^{o}\mathrm{C}$

The side group is long but flexible, so rotation is easier.



Poly(methyl methacrylate)

$T_g = 105\ ^{o}\mathrm{C}$

The presence of two side groups makes rotation more difficult, leading to a higher T_g.