

## UNIT III

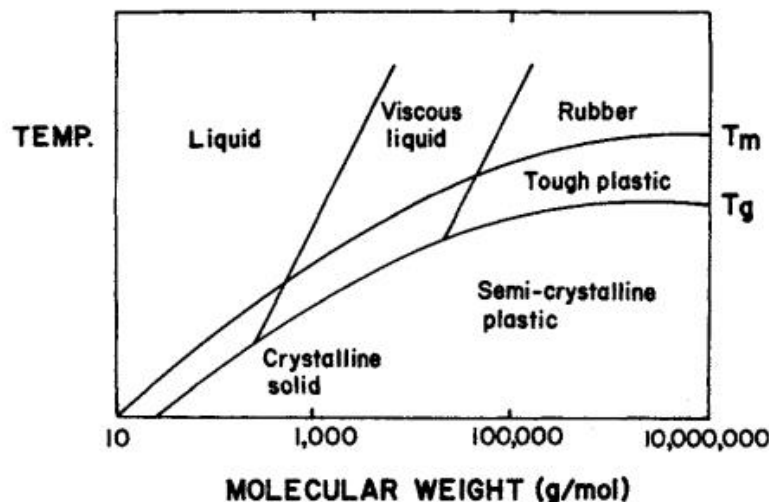
### FACTORS INFLUENCING THE PROPERTIES OF POLYMERS

#### Effect of Structural Modification on Properties:

- The physical properties of polymers can be affected in many ways.
- In particular, the chemical composition and arrangement of chains will have a great effect on the final properties.
- By such means the polymers can be tailored to meet the end use.

#### Effect of Molecular Weight and Composition:

- The molecular weight and its distribution have a great effect on the properties of a polymer since its rigidity is primarily due to the immobilization or entanglement of the chains. This is because the chains are arranged like cooked spaghetti strands in a bowl.
- By increasing the molecular weight the polymer chains become longer and less mobile and a more rigid material results as shown in Fig. 3.4.



**FIGURE 3.4** Approximate relations among molecular weight,  $T_g$ ,  $T_m$ , and polymer properties.

- Equally important is that all chains should be equal in length since if there are short chains they will act as plasticizers.
- Another obvious way of changing properties is to change the chemical composition of the backbone or side chains.
- Substituting the backbone carbon of a polyethylene with divalent oxygen or sulfur will decrease the melting and glass transition temperatures since the chain becomes more flexible due to the increased rotational freedom.
- On the other hand if the backbone chains can be made more rigid then a stiffer polymer will result.

### ***Effect of Side Chain Substitution, Cross-Linking, and Branching:***

- Increasing the size of side groups in linear polymers such as polyethylene will decrease the melting temperature due to the lesser perfection of molecular packing, i.e., decreased crystallinity.
- This effect is seen until the side group itself becomes large enough to hinder the movement of the main chain as shown in Table 3.4.

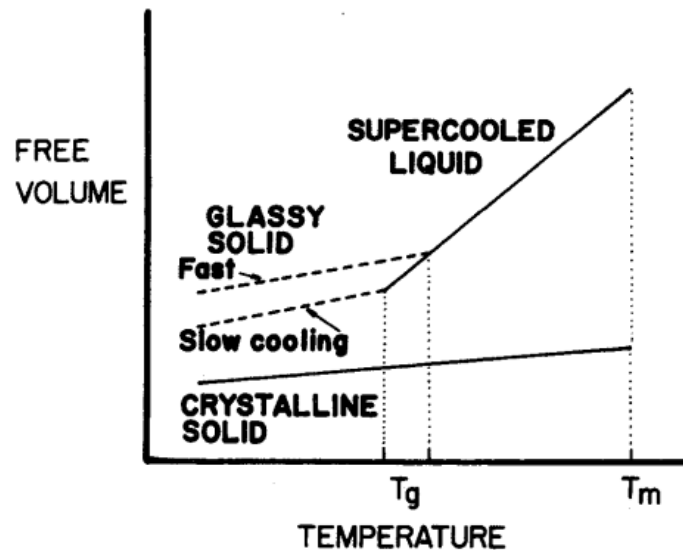
**TABLE 3.4** Effect of Side Chain Substitution on Melting Temperature in Polyethylene

Side Chain	T <sub>m</sub> (°C)
–H	140
–CH <sub>3</sub>	165
–CH <sub>2</sub> CH <sub>3</sub>	124
–CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	75
–CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	–55
–CH <sub>2</sub> CHCH <sub>2</sub> CH <sub>3</sub>	196
$\begin{array}{c} \text{CH}_3 \\   \\ \text{CH}_3 \\   \\ -\text{CH}_2\text{CCH}_2\text{CH}_3 \\   \\ \text{CH}_3 \end{array}$	350

- Very long side groups can be thought of as being branches. Cross-linking of the main chains is in effect similar to the side chain substitution with a small molecule, i.e., it lowers the melting temperature.
- This is due to the interference of the cross-linking which causes decreased mobility of the chains, resulting in further retardation of the crystallization rate.
- In fact, a large degree of cross-linking can prevent crystallization completely.
- However, when the cross-linking density increases for a rubber, the material becomes harder and the glass transition temperature also increases.

### ***Effect of Temperature on Properties:***

- Amorphous polymers undergo a substantial change in their properties as a function of temperature.
- The glass transition temperature, T<sub>g</sub>, is a boundary between the glassy region of behavior in which the polymer is relatively stiff and the rubbery region in which it is very compliant.
- T<sub>g</sub> can also be defined as the temperature at which the slope of volume change vs. temperature has a discontinuity in slope as shown in Fig. 3.5.



**FIGURE 3.5** Change of volume vs. temperature of a solid. The glass transition temperature ( $T_g$ ) depends on the rate of cooling and below ( $T_g$ ) the material behaves as a solid like a window glass.

- Since polymers are noncrystalline or at most semicrystalline, the value obtained in this measurement depends on how fast it is taken.

### BIODEGRADABLE POLYMERS

- Several biodegradable polymers such as polylactide (PLA), polyglycolide (PGA), poly(glycolide-co-lactide) (PLGA), poly(dioxanone), poly(trimethylene carbonate), poly(carbonate), and so on have been used extensively or tested on a wide range of medical applications due to their good biocompatibility, controllable biodegradability, and relatively good processability.
- PLA, PGA, and PLGA are bioresorbable polyesters belonging to the group of poly  $\alpha$ -hydroxy acids. These polymers degrade by nonspecific hydrolytic scission of their ester bonds.
- The hydrolysis of PLA yields lactic acid, which is a normal byproduct of anaerobic metabolism in the human body and is incorporated in the tricarboxylic acid (TCA) cycle to be finally excreted by the body as carbon dioxide and water.
- PGA biodegrades by a combination of hydrolytic scission and enzymatic (esterase) action producing glycolic acid which either can enter the TCA cycle or is excreted in urine and can be eliminated as carbon dioxide and water.
- The degradation time of PLGA can be controlled from weeks to over a year by varying the ratio of monomers and the processing conditions.
- It might be a suitable biomaterial for use in tissue engineered repair systems in which cells are implanted within PLGA films or scaffolds and in drug delivery systems in which drugs are loaded within PLGA microspheres.
- PGA ( $T_m$ : 225–230°C,  $T_g$ : 35–40°C) can be melt spun into fibers which can be converted into bioresorbable sutures, meshes, and surgical products.

- PLA (T<sub>m</sub>: 173–178°C, T<sub>g</sub>: 60–65°C) exhibits high tensile strength and low elongation resulting in a high modulus suitable for load-bearing applications such as in bone fracture fixation.
- Poly-p-dioxanone (T<sub>m</sub>: 107–112°C, T<sub>g</sub>: ~10°C) is a bioabsorbable polymer that can be fabricated into flexible monofilament surgical sutures.