

Structure and Property Relationship

For a very large proportion of polymeric materials in commercial use, mechanical properties are of paramount importance, because they are used as structural materials, fibers, or coatings and these properties determine their usefulness. Properties that also determine their utilization are compressive, tensile, and flexural strength, and impact resistance. Hardness, tear, and abrasion resistance are also of concern. In addition, polymers may be shaped by extrusion in molten state into molds or by deposition from solutions on various surfaces. This makes the flow behaviors in the molten state or in solution, the melting temperatures, the amount of crystallization, as well as solubility parameters important.

The physical properties of polymer molecules are influenced not only by their composition, but also by their size and by the nature of their primary and secondary bond forces. They are also affected by the amount of symmetry, by the uniformity in their molecular structures, and by the arrangements of the macromolecules into amorphous or crystalline domains. This, in turn affects melting or softening temperatures, solubilities, melt and solution viscosities, and other physical properties. Due to the large sizes of polymeric molecules, the secondary bond forces assume much greater roles in influencing physical properties than they do in small organic molecules. These secondary bond forces are van der Waal forces and hydrogen bonding. The vander Waal forces can be subdivided into three types: dipole-dipole interactions, induced dipoles, and time varying dipoles.

Effects of Dipole Interactions

Dipole interactions result from molecules carrying equal and opposite electrical charges. The amounts of these interactions depend upon the abilities of the dipoles to align with one another. Molecular orientations are subject to thermal agitation that tends to interfere with electrical fields. As a result, dipole forces are strongly temperature dependent. An example of dipole interaction is an illustration of two segments of the molecular chains of linear polyester. Each carbonyl group in the ester linkages sets up a weak field through polarization. The field, though weak, interacts with another field of the same type on another chain. This results in the formation of forces of cohesion. Because polymeric molecules are large, there are many such fields in polyesters. While each field is weak, the net effect is strong cohesion between chains. The interactions are illustrated in **Fig. 1**.

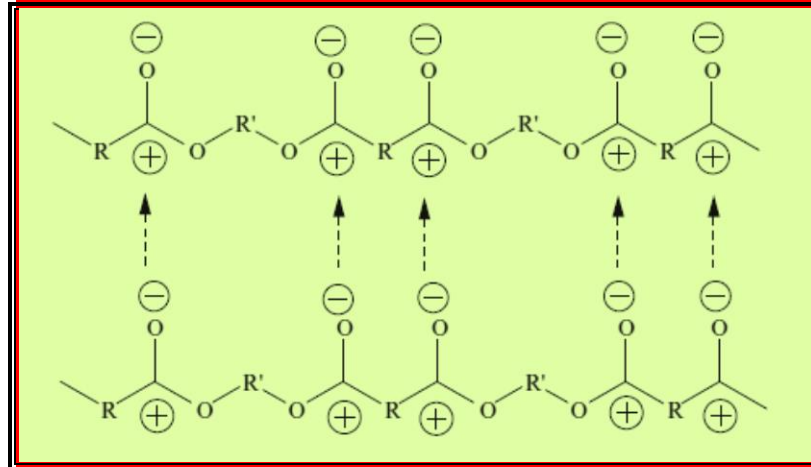


Fig. 1: Intramolecular forces

Induction Forces in Polymers

Electrostatic forces also result from slight displacement of electrons and nuclei in covalent molecules from proximity to electrostatic fields associated with the dipoles from other molecules. These are induced dipoles. The displacements cause interactions between the induced dipoles and the permanent dipoles creating forces of attraction. The energy of the induction forces, however, is small and not temperature-dependent.

There are additional attraction forces that result from different instantaneous configurations of the electrons and nuclei about the bonds of the polymeric chains. These are time varying dipoles that average out to zero. They are polarizations arising from molecular motions. The total bond energy of all the secondary bond forces combined, including hydrogen bonding, ranges between 2 and 10 kcal/mole. Of these, however, hydrogen bonding takes up the greatest share of the bond strength. In **Table 1** are listed the intramolecular forces of some linear polymers.


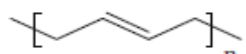
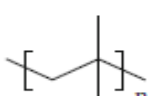
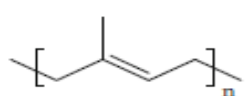
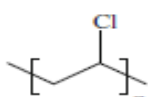
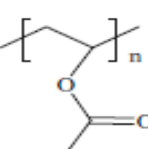
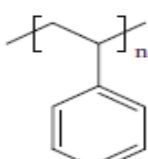
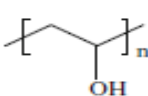
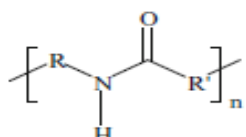
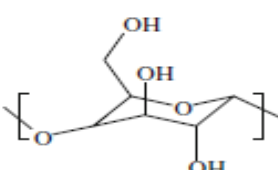
As can be seen in **Table 1**, polyethylene possesses much less cohesive energy than does a polyamide. This difference is primarily due to hydrogen bonding. A good illustration is a comparison of molecules of a polyamide, like nylon 11, with linear polyethylene. Both have similar chemical structures, but the difference is that nylon 11 has in its structure periodic amide linkages after every tenth carbon, while such linkages are absent in polyethylene. The amide linkages participate in hydrogen bonding with neighboring chains. This is illustrated in **Fig. 2**.

Due to this hydrogen bonding, nylon 11 melts at 184–187°C and is soluble only in very strong solvents. Linear polyethylene, on the other hand, melts at 130–134°C and is soluble in hot aromatic solvents. The energy of dipole interactions, (ϵ_k) can be calculated from the equation [1]:

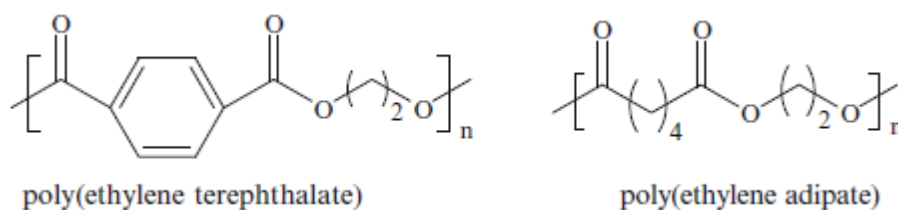
$$\epsilon_k = -(2\mu^4/3RT)r^{-6} \quad [1]$$

where, m represents the dipole moment of the polarized section of the molecule, r is the distance between the dipoles, T is the temperature in Kelvin, and R is the ideal gas constant.

Table 1. Molecular cohesion of some linear polymers

Polymer	Cohesion/5 Å chain length	Polymer structure
Polyethylene	1.0	
Polybutadiene	1.1	
Polyisobutylene	1.2	
Polyisoprene (<i>cis</i>)	1.3	
Poly(vinyl chloride)	2.6	
Poly(vinyl acetate)	3.2	
Polystyrene	4.0	
Poly(vinyl alcohol)	4.2	
Polyamides	5.8	
Cellulose	6.2	

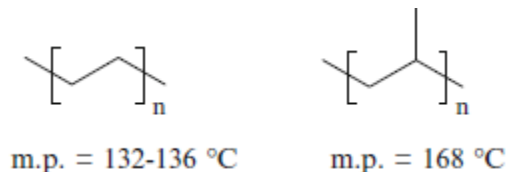
Intermolecular forces affect the rigidity of all polymers. Should these forces be weak, because the cohesive energy is low (1-2 kcal/mole), the polymeric chains tend to be flexible. Such chains respond readily to applied stresses and can exhibit typical properties of elastomers. High cohesive energy, on the other hand, (5 kcal/mole or higher) causes the materials to be strong and tough. These polymers exhibit resistance to applied stresses and usually possess good mechanical properties. The temperatures and the flexibility of polymeric molecules govern both the sizes of molecular segments, the motion, and the frequency at which that occurs. This in turn determines the rate at which the polymer molecules respond to molecular stresses. In flexible polymers, if the thermal energy is sufficiently high, large segments can disengage and slip past each other quite readily in response to applied stress. All elastomers possess such properties. Properties of polymers depend also upon morphology or upon the arrangement of their polymeric chains. This arrangement can be amorphous or crystalline. The term amorphous designates a lack of orderly arrangement. Crystalline morphology, on the other hand, means that the chains are aligned in some orderly fashion. Generally, the freedom of molecular motion along the backbones of polymeric chains contributes to lowering the melting temperature. Substituents that interfere with this motion tend to raise the melting point. For instance, isotactic polypropylene melts at a higher temperature than does linear polyethylene. If the substituent is bulky or rigid it raises the melting point because it interferes with molecular motion. Dipole interactions, as discussed above, have a similar effect. A good illustration is a comparison of poly(ethylene terephthalate) that melts at 265°C with poly(ethylene adipate) that melts at only 50°C. In the first polyester, there is a rigid benzene ring between the ester groups while in the second one there is only a flexible chain of four carbons.



This flexibility of the four carbon segment in poly(ethylene adipate) contributes significantly to the lowering of the melting point.

Linear polymers that possess only single bonds between atoms in their backbones, C-C, or C-O, or C-N, can undergo rapid conformational changes. Also ether, imine, or cis-double bonds reduce energy barriers and, as a result, “soften” the chains, causing the polymer to become more rubbery and more soluble in various solvents. The opposite is true of cyclic structures in the backbones, as was shown in poly(ethylene terephthalate). Actually, cyclic structures not only inhibit conformational changes but

can also make crystallization more difficult. Among the polymers of α -olefins the structures of the pendant groups can influence the melting point. All linear polyethylene melts between 132 and 136°C. Isotactic polypropylene, on the other hand melts at 168°C.



As the length of the side chain increase, however, melting points decrease and are accompanied by increases in flexibility until the length of the side chains reached six carbons. At that point, the minimum takes an upturn and there is an increase in the melting points and decrease in flexibility. This phenomenon is believed to be due to crystallization of the side-chains.

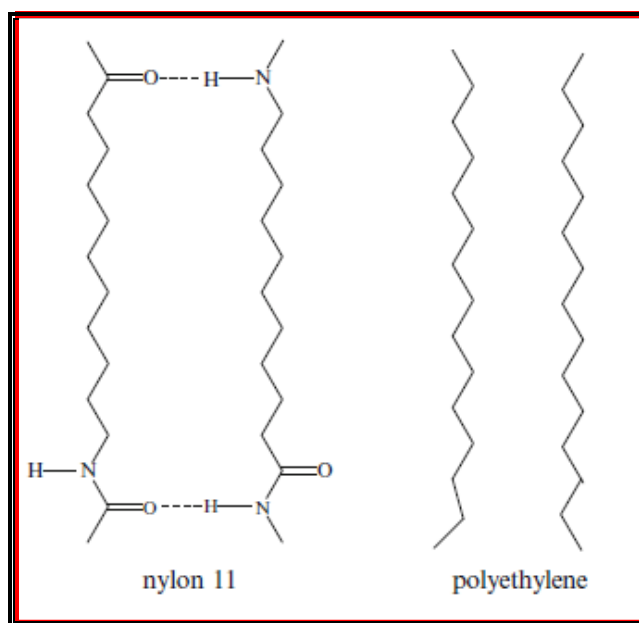


Fig. 2: Hydrogen bonding in (a) nylon 11, and absent in (b) polyethylene

Alkyl substituents on the polymers of α -olefins that are on the α -carbon yield polymers with the highest melting points. Isomers substituted on the β -carbon, however, if symmetrical, yield polymers with lower melting points. Unsymmetrical substitutions on the β -carbon, on the other hand, tend to lower the melting points further. Additional drop in the melting points result from substitutions on the γ -carbon or further out on the side-chains. Terminal branching yields rubbery polymers.

Copolymers melt at lower temperatures than do homo-polymers of the individual monomers. By increasing the amount of a co-monomer the melting point decreases down to a minimum (this could perhaps be compared to a eutectic) and then rises again.

The tightest internal arrangement of macromolecules is achieved by crystallinity. As a result, the density of a polymer is directly proportional to the degree of crystallinity, which leads to high tensile strength, and to stiff and hard materials that are poorly soluble in common solvents. The solubility of any polymer, however, is not a function of crystallinity alone, but also of the internal structure and of the molecular weight. The solubility generally decreases with increases in the molecular weight. The fact that crystalline polymers are less soluble than amorphous ones can be attributed to the binding forces of the crystals. These binding forces must be overcome to achieve dissolution. Once in solution, however, crystalline polymers do not exhibit different properties from the amorphous ones. One should also keep in mind the fact that cross-linked polymers will not melt and will not dissolve in any solvent. This is due to the fact that the cross-links prevent the chains from separating and slipping past each other.