# Summary

        The intent of this chapter was to examine and explain polymer properties that depend upon the interrelationship of several molecular chains. This perspective is called the micro view (as compared to the molecular view of the previous chapter and the macro view of ensuing chapters).

        When the polymers are solids, the polymer chains become entangled and portions of the polymer molecules can pack closely together. In some polymers, this packing becomes very regular, often because a polymer will fold back and forth on itself, but other times because it aligns tightly with neighboring molecules. When this close packing occurs, secondary bonds form between the polymers. These areas of close packing are called crystalline regions because of the analogy with metallic and ceramic crystals, which are also regular and held together by bonds between the elements of the crystal. In other molecules, however, the molecules do not pack closely and the overall regions of the molecules are random. These regions are called amorphous. Therefore, regions within molecules can be either crystalline or amorphous, and the molecules themselves are often referred to as being crystalline or amorphous, depending on which type of region dominates. Crystallinity in a polymer increases the density of the polymer.

        Polymer strength and stiffness are increased by crystallinity. Therefore, a direct relationship between density and strength is commonly found.

        When polymers are heated, the heat is absorbed by the polymer through increases in molecular movement. Initially this movement is small and results in only minor increases in volume with very little additional change in polymer properties. With increased heating the motions become very large and the molecules begin to slide and disentangle. When this occurs, the polymer is less able to support loads. A common test in which polymers are subjected to loads at elevated temperatures is called the HDT, which measures the point at which the ability of the polymer to support loads is diminished beyond a set amount.

        Further heating of the polymer will cause increased movement until several atoms within the amorphous regions of the material move in long-range, coordinated movements. The temperature at which this happens is called the glass transition temperature, Tg. Below Tgthe polymer is rigid and hard; above Tg, the polymer is pliable and leathery. There is no Tgpurely crystalline regions.

        An important thermal transition in crystalline and semicrystalline polymers is at the melting point. Here the polymer molecules can move freely from each other. The melting point is quite sharp and corresponds to the breaking of the secondary bonds that hold the crystalline structure together.  
Beyond the melting point, further heating will eventually cause the molecule to degrade because the thermal energy is sufficient to break the primary bonds of the molecules.

        Imagine a polymer of enormous chain length. As this polymer is heated, the energy causes both vibrational and translational motions, as with the normalsized polymer. The enormous polymer, however, is so large that very high energies are required to reach the level of activation needed to melt it. Before the entire polymer can be totally activated, the vibrational energies in the bonds might exceed the bond strengths and the polymer could begin to degrade. The melting point of this polymer has been increased (due to the long chain length) such that the melting temperature has become higher than the decomposition temperature.

        This situation, in which the enormous chain length causes the melting temperature to be higher than the decomposition temperature, can often occur if fully formed polymer chains are bonded together, as occurs in the curing of thermosets. When a primary bond links two chains, the total length of the resultant chain would be approximately double the length of the separate chains. Further bonds between this double-length chain and other chains would give further rapid increases in total chain length until, conceivably, the entire structure could be bonded together with these interchain bonds. These interchain bonds are called crosslinks, and the process of forming these bonds is called crosslinking or curing. Polymers that have these crosslinks are called thermosets; their structures have become rigid (set) with temperature because these bonds between the polymer chains are formed with heating. Because of the very high cumulative length of these crosslinked polymers, these thermoset materials decompose before they melt.

        Plastics can also degrade over long periods of time. This degradation is from the accumulated effects of heat, often from repeated processing or from exposure to high temperatures in use. Hence, elevated temperatures for long periods of time are to be avoided.

        Thermal conductivity is a measure of the ability of a material to conduct thermal energy. Most plastics are poor thermal conductors compared to metals. This lack of thermal conductance allows plastics to be used extensively as insulative handles for cooking pans and for other devices that may get hot.

        When materials get hot, they generally expand. This is called thermal expansion and is generally higher for plastics than for metals and ceramics. Thermal expansion is an important consideration in designing a mold for plastics to ensure that the finished part is the proper size, even after the subsequent normal contraction as the part cools. If the part is constrained so that it cannot change its size with thermal changes, some stresses arise within the part. These are thermal stresses, and they can lead to premature failure in some circumstances if not relieved. They can easily be relieved by annealing.

        The molecular weight of polymers is an important measure of the size of polymer chains. Because polymer chains can be of several different lengths, statistics are used to describe the molecular weight. Hence, molecular weight is described as an average of the polymers contained within the sample. Several types of averages can be determined, the most common being the number average and the weight average molecular weights. The number average molecular weight gives equal weight in the average calculation to every polymer chain, regardless of its size. The weight average molecular weight gives greater emphasis to the large molecular weight chains. If the molecular weight averages can be found experimentally, the degree of polymerization (DP) can be calculated. The degree of polymerization is the number of monomer units that have been linked together in the average polymer chain.

        Molecular weight distribution (MWD) is another statistical measure of polymers. This property describes how similar in size the polymers are. If the MWD is small (narrow), most of the polymers are of the same length, which is usually desirable when injection molding the polymer. A wide MWD indicates that the polymers have a wide variety of sizes, which is often desirable in extrusion processes.

        Melt strength is a property that is related to MWD. Melt strength is a measure of the ability of the polymer to be shaped while in a molten state. Melt strength arises when some of the molecules have become free to move extensively (as they would in a liquid) while other molecules are still strongly interacting with surrounding molecules. Hence, some molecules are melted and others are not. The melted molecules give fluidity to the polymer sample and the nonmelted molecules give strength. Melt strength is enhanced by wide MWD because small molecules can become melted while long molecules are still not melted.

        The melt index is a method of measuring the effects of molecular weight. In this test the tendency of a polymer to melt is measured. High molecular weight materials are more difficult to melt and therefore have a low melt index. Hence, molecular weight and melt index are inversely related.

        Mechanical and physical properties of polymers often increase (nonlinearly) with increasing molecular weight. This relationship is especially true for toughness.

        The density of a polymer is a measure of how tightly the polymer chains can pack together. High density means that the packing is close. Often, close packing is the result of the formation of intermolecular bonding such as crystallinity and dipole bonding.

        The shape of a polymer can strongly affect the polymer's crystallinity. If pendant groups are large, these groups will tend to interfere with the groups on other molecules and prevent close packing. Hence, crystallinity is less likely. The presence of large groups will also effect mechanical and physical properties of the polymer. These effects are complicated and not easily predicted except that the presence of aromatic groups will generally increase strength and toughness.

## 3.12.1. Questions

1.   Contrast the interatomic or intermolecular forces present in solids, liquids, and gases. Explainthe consequences of these forces and how they are normally overcome.  
2.   Can all materials exist as solids, liquids, and gases at various temperatures? Explain.  
3.   Name three methods of reducing the amount of thermal degradation that might occur in a heat-sensitive plastic. How does each reduce thermal degradation?  
4.   What is a heat history, as applied to polymers, and why is it important in polymer technology?  
5.   What are thermal stresses and how are they caused in plastic materials? How can they be relieved?  
6.   What is the difference between a number average and a weight average molecular weight?  
7.   Why must average molecular weights be used for polymers rather than exact molecular weightsbased upon the molecular formula, as is done for small molecules?  
8.   Discuss the relationship between melt index and molecular weight.  
9.   Contrast and discuss the difference between amorphous and crystalline regions in a polymer.  
10. Explain why the properties of a polymer below the glass transition temperature are differentfrom the same properties in the same polymer above the glass transition temperature.  
11. Discuss how you would expect the glass transition to be affected if a large, pendant group wereadded to the monomer unit.  
12. What is the relationship between melt index and viscosity? Explain the relationship using microstructure concepts.  
13. Explain the effects of crosslinking on the glass transition temperature.  
14. Discuss the implications on MWD when the number average molecular weight and the weightaverage molecular weight are widely different.  
15. Explain bimodal distributions of polymers and their usefulness.  
16. Discuss how copolymerization would affect crystallinity.  
17. Given the following data, calculate the number average molecular weight and the weight average molecular weight, and discuss whether the MWD distribution is wide or narrow comparedwith a normal commercial ratio of 20.

Ni(x1024) 5 7 8 9 10 8 6 3 2 1

Mi(x104) 1 2 3 4 5 6 7 8 9 10

18. Why does processing of a crystalline material like nylon require more critical thermal control asopposed to an amorphous material like ABS?

## 3.12.2. References

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