

18 Polymer Overview and Definitions

To troubleshoot and solve extrusion process problems, it is important to understand both the equipment operation and the polymer being processed. Understanding either the equipment or the polymers alone may not provide enough information to solve a particular extrusion problem. Polymer behavior in the molten state is different from that in normal liquids such as water, because polymer melts have both elastic and viscous components, whereas liquids, such as water, have only a viscous component. For this reason, polymers are called viscoelastic non-Newtonian fluids, and water is known as an inelastic Newtonian fluid. The non-Newtonian shear rate versus viscosity behavior, discussed briefly in Part 1, Chapter 3, is that polymer viscosity decreases with increasing shear rate. A Newtonian fluid shows no viscosity change as the shear rate changes. This drop in polymer viscosity is referred to as shear thinning. The elastic component makes molten polymer behave differently from nonelastic liquids.

This chapter covers the definition of polymers, how they are formed, different types of polymers, and their structures.

18.1 Overview

Polymers comprise many atoms connected together to form long chains, referred to as the polymer backbone. The atoms in the backbone are usually carbon (C), oxygen (O), nitrogen (N), or sulfur (S), combined

in a configuration that is unique for each polymer. Other atoms attached to the long polymer backbone are normally some combination of hydrogen (H), carbon, oxygen, chlorine (Cl), fluorine (F), and/or bromine (Br), and these differentiate one polymer from another. Each polymer has a unique spatial arrangement of atoms combined in a regular, repeating pattern with specific physical properties and rheological (flow) properties, resulting in different property performance in end-use applications and processing characteristics. No two polymer types have the exact same processing characteristics in extrusion or the same property performance profile relative to impact, tensile and flexural strength, tensile and flexural modulus, color, heat resistance, transparency, electrical properties, and so forth.

Carbon is the major atom in a polymer backbone. Each carbon atom has four chemical bonds spatially arranged around it in a tetrahedron. The simplest carbon molecule is methane. Table 18.1 lists the name, chemical formula, approximate melting points, and boiling points of the first five alkanes, from methane to pentane. Note that methane has the lowest boiling point at -259°F (-162°C). Adding more carbon atoms to the molecule increases the boiling point. Methane through butane are gases at room temperature, and pentane is a liquid at room temperature.

Below five carbon atoms in the molecular backbone, the materials are flammable gases at room temperature. Between five and 20 carbon atoms, the molecules

Table 18.1 Formulas, Melting Points, and Boiling Points of Five Alkanes

Hydrocarbon	Formula	Melting Point		Boiling Point	
		$^{\circ}\text{F}$	$^{\circ}\text{C}$	$^{\circ}\text{F}$	$^{\circ}\text{C}$
Methane	CH_4	-297	-183	-259	-162
Ethane	C_2H_6	-298	-183	-127	-89
Propane	C_3H_8	-306	-188	-44	-42
Butane	C_4H_{10}	-217	-134	31	-0.5
Pentane	C_5H_{12}	-202	-130	97	36

become flammable liquids at room temperature. Above 20 carbon atoms, molecules become solids at room temperature. Above 36 carbon atoms in the molecular backbone, the material becomes grease. Above 140 carbon atoms, the product is a polyethylene wax. Increasing the carbon atoms to >500 results in a polyethylene polymer. Commercially available polyethylene polymers have on average approximately 7000–15,000 carbon atoms bound together to form the polymer backbone.

The carbon bond angle when four other atoms are bound to it is 109° . This results in a tetrahedral structure about the central carbon atom. **Figure 18.1**

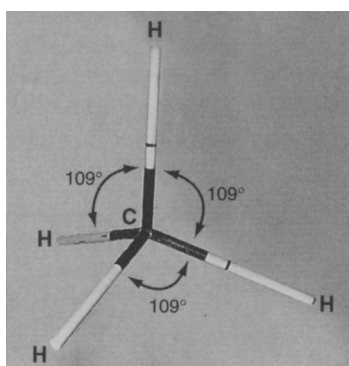


Figure 18.1 Simulated methane molecule with bond angles.

models methane (CH_4). The four hydrogen atoms are uniformly distributed around the central carbon atom in a tetrahedral arrangement. Due to the 109° bond angle, adjacent carbon atoms are not linearly aligned, as suggested by two-dimensional chemical formulas drawn on paper. **Figure 18.2** models

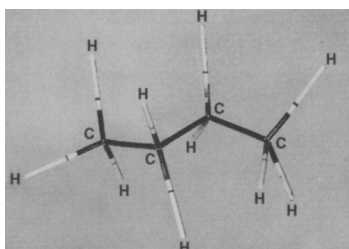


Figure 18.2 Model butane molecule.

a butane molecule with four carbon atoms. Note how the carbon atoms are not aligned in a straight line or in a flat plane. Instead, the carbon backbone in **Figure 18.2** forms a zigzag-type repeating pattern. Combining the zigzag structure with the ability of atoms to rotate 360° about their bond axes, entire

sections can move from one location to another by a simple rotation about a C–C bond in the chemical backbone. Rotations do not occur in the solid state. However, as heat energy is added to the system, the distance between individual molecules increases. With sufficient heating, a state change to a liquid or gas occurs, and rotation about the C–C bonds constantly occurs. It is easy to envision long polymer chains with thousands of carbon atoms becoming entangled with each other and with themselves as these rotations occur. In the polymer melt, rotations cause entanglements that remain after the polymer solidifies. Polymer chain entanglement in the solid state is responsible for the high strengths and toughness of polymeric materials. It is important to understand the difference between solid, liquid, and gaseous states and the molecular chains in different polymeric materials, as this directly impacts the polymer property performance and processing characteristics.

Long chain polymer molecules are similar to a pot of boiling spaghetti where the individual molecules, like spaghetti strands, become entangled with other polymer molecules. In the molten state, the polymer chains resemble the boiling spaghetti. For amorphous polymers in the solid form, the polymer chains resemble the spaghetti after the water has been removed, and the spaghetti remains in relatively discrete locations. **Figure 18.3** models

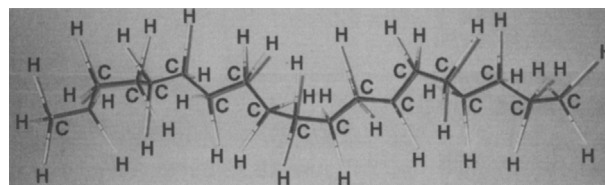


Figure 18.3 Model of a short linear section of polyethylene molecules.

a short linear polyethylene chain section that is oriented in one direction. Imagine a 10,000 carbon atom chain pulled out in one direction. Assume that there is a second chain next to this that is also pulled out or stretched in the same manner to produce limited entanglement between the adjacent chains. Now assume that there are many molecular chains lying parallel to each other. **Figure 18.4** represents this, with oriented strings lying side by side. If you pick up the ends of the various strings or polymer molecules and pull on them, they are very strong, and it takes a large force to break the strings or, in

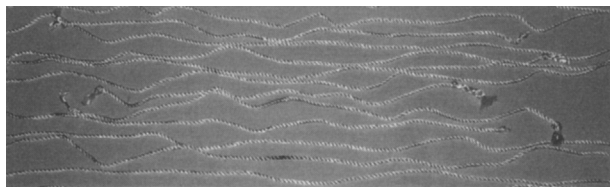


Figure 18.4 Oriented strings simulating oriented polymer molecules.

the case of polymers, the molecular chains. However, if the strings or polymer molecules are pulled perpendicular to the lengthwise direction of the strings or polymer molecules, it is very easy to pull the strings apart.

This string analogy can be applied to extruded polymer molecules. As the molten polymer exits the die, the puller draws it in the machine direction, tending to stretch and align the molecules. Consequently, the extruded product has higher tensile and flexural properties in the machine direction than in the crossmachine or transverse direction. In oriented films or monofilaments, the polymer is drawn with supplemental heat outside of the extruder to orient the molecules in the machine direction, resulting in improved properties in one direction. Biaxial-oriented film is pulled in the solid state, in both the machine and transverse directions, under controlled temperatures outside the extruder to yield improved properties in both directions. Figure 18.3 shows a short molecular section that is oriented in one direction. Figure 18.5 shows the same short segment

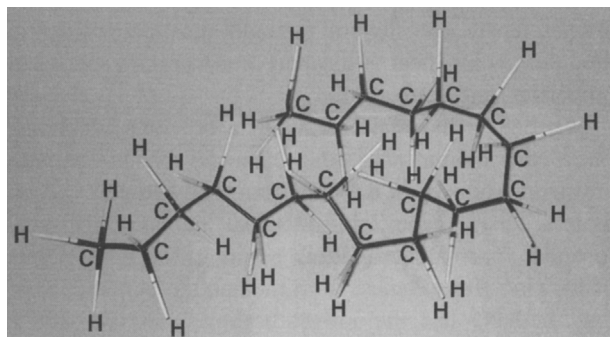


Figure 18.5 Model of a short section of a folded chain of polyethylene.

with some rotation about the C—C bonds. This allows the molecule to fold back on itself or change direction. Figure 18.5 is a better representation of the polymer as it exits the die. Drawing by the puller aligns some of the molecules in the machine direction; however, unless the draw ratio is very large,

a large percentage of the molecules tend to relax and entangle with each other as they leave the die land area. In the die land area, the molecules tend to be oriented in the machine direction due to the polymer flow in the die land area. Upon exiting the die, the polymer relaxes and folds back on itself, entangling with itself and neighboring molecules. This generates the extrudate swell, sometimes referred to as “die swell”, associated with extrusion.

Going back to the string analogy, consider the strings going through the die. It is difficult to push a string through a die hole and the associated die land area. As it is pushed, one end tends to buckle and be crunched up into a small volume. Instead, the string is pulled through the die hole, elongating in the machine direction. Immediately upon leaving the die, the string relaxes and reentangles as it folds back on itself and the neighboring polymers.

Envision long polymer chains made up of a huge number of carbon atoms connected together in some particular spatial arrangement. Figure 18.6

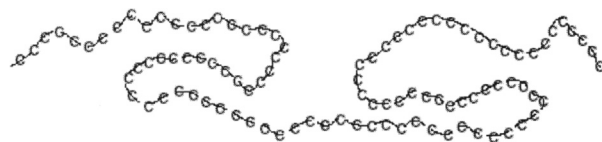


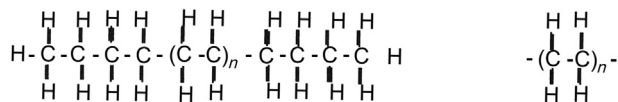
Figure 18.6 Simulated polymer chain of polyethylene.

shows a polyethylene polymer backbone with a large number of carbon atoms connected. (The number of carbon atoms depicted is significantly less than is normally seen in a polyethylene molecule.) Removing the carbon atoms from the drawing in Figure 18.6, the polymer chains are represented by the curved line shown in Figure 18.7. As the polymer has many chemical



Figure 18.7 Typical representation of a polymer chain.

entities that repeat numerous times to form the long polymer chain, the chemical formula is written as



where n is the number of repeating units. The number of repeating units, n , will vary, depending on the polymer and how many repeating units are required to produce the optimum property performance profile with acceptable processing characteristics. For polyethylene, n is approximately 4000. Figure 18.8 shows polymer chains entangled



Figure 18.8 Schematic of a group of individual polymer chains.

together to form a section of a plastic part. (Different shades are used to identify the individual chains in the drawing.) In the solid state, polymer chains are entangled with limited space between the chains. As the polymer is heated, the space between the chains becomes larger, and in the molten state, the space is very large, allowing the chains to actually flow past one another. As the space between the chains becomes larger, rotations about the C–C bonds in the polymer backbone become more numerous. Polymer degradation occurs when the C–C bonds or other bonds along the polymer backbone rupture and the chains become shorter. Going back to Figure 18.8, one can start to understand why shorter chains with less entanglement will have lower properties. As the entanglement and chain length decrease, the polymer matrix can support less stress. Going back to the spaghetti analogy, longer spaghetti lengths in the solid state, compared to shorter lengths, are more difficult to pull out and remove from the bulk spaghetti mass.

18.2 Thermoplastic versus Thermoset

Polymers fall into two distinct categories: thermoplastic or thermoset. Thermoplastics can be repeatedly softened and resolidified by adding or removing heat, allowing materials to be processed in extrusion, injection molding, and other melt

processing equipment numerous times. Thermosets are heated to accelerate a chemical crosslinking reaction called curing, where a new chemical species is formed into a solid. After cooling, reheating a thermoset does not result in softening and polymer flow. Thermoplastics are easily recycled into other shapes or forms by heating to the softening or melting point and reprocessing. At one time, thermosets were not considered recyclable; however, different processes are in use today, providing mechanisms to recycle the material as filler or to reclaim the raw materials. However, unlike thermoplastics, thermosets cannot simply be heated above their melting or softening point and reprocessed into another article.

Thermoplastics include polymers such as the following:

- polyethylene (PE)
- polypropylene (PP)
- polystyrene (PS)
- polyvinyl chloride (PVC)
- polymethylmethacrylate (PMMA or acrylic)
- acrylonitrile butadiene styrene (ABS)
- polycarbonate (PC)
- polyethylene terephthalate (PET)
- polybutylene terephthalate (PBT)
- polyamide (PA or nylon)
- polyphenylene sulfide (PPS)
- polyphenylene oxide/polystyrene blend (Noryl[®])
- polyetherimide (PEI)
- polysulfone (PSO)

The polymers listed above are the more common thermoplastic polymers used in extrusion applications.

Thermoset materials are made by a chemical reaction between different components to produce a new crosslinked matrix that cannot be remelted. A typical thermoset reaction is epoxy, which is composed of a resin and hardener that are mixed together and cured, forming a strong new material that is impervious to heat and most chemicals. Polyurethanes are formed by reacting an isocyanate with a polyol. Some thermoset materials are produced by crosslinking a resin matrix to produce a solid part that cannot be remelted during processing. EPDM rubber (ethylene propylene diene monomer (M-class) rubber) is a thermoset material that can contain a crosslinking agent. The material containing a crosslinking agent is extruded at low temperature into a desired shape, e.g. a gasket

around a car door. After extrusion, the product is heated to promote the crosslinking reaction in the solid state, producing a final product that is impervious to heat and will not melt because of the crosslinking step.

Elastomeric polymers are materials that can be repeatedly deformed when a force is applied and return to their original shape after the force is removed. Elastomers can be either thermoplastic or thermoset polymers, depending on their chemistry and the processing mechanism. The EPDM cross-linked rubber mentioned in the previous paragraph is a thermoset elastomer. Thermoplastic elastomers include styrene butadiene copolymers, ethylene propylene polymers, and polyurethanes.

Crosslinking to produce thermoset products is accomplished when sites on two adjacent polymer chains react to form a bond joining the two individual chains together. Once the two chains are bonded together, heat does not allow the chains to separate and flow individually. High crosslinking levels join the individual polymer backbones, producing one large structure. This prevents crosslinked materials from flowing by either melting or softening. Crosslinking is a chemical reaction that changes the polymer matrix. The two general methods used to form crosslinked material are as follows:

- Adding a chemical additive that reacts with each chain to form a common site, bonding two polymer chains together.
- Breaking bonds between carbon atoms by heating them or by keeping them at an elevated temperature for too long a time. Broken bonds form free radicals, which react to form crosslinked sites between two polymer molecules.

Figure 18.9 shows polymer chains that are crosslinked and their crosslink sites. Polyethylene is known to crosslink during extrusion if the polymer gets held up in a stagnant dead spot within the extruder or die and sits for a long time at a high temperature. Small particles that do not melt and appear in the final product as small hard particles, described as “fisheyes” or gels,

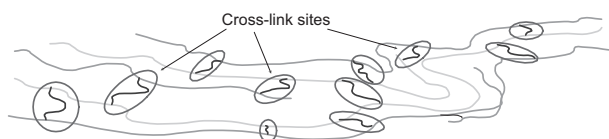


Figure 18.9 Example of crosslinked polymer chains.

may be crosslinked and thermoset in nature. It is important that all flow paths between the extruder and the die and within the dies be streamlined to prevent stagnation, as stagnation allows crosslinking or degradation to occur over time.

18.3 Polymer Formation

Small molecules are combined in polymerization reactions using specific processing conditions, procedures, raw materials, end groups, and catalysts to generate long chain polymers of approximately the same length. The starting molecules are called monomers. Polyethylene is produced from ethylene gas, which is shown in the model in Figure 18.10. Each carbon atom has four bonds to other atoms, with two

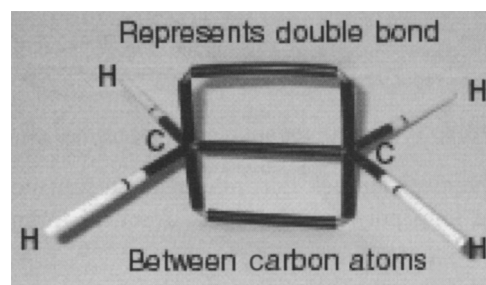
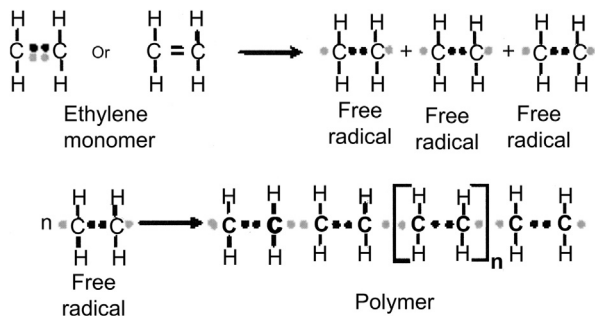


Figure 18.10 Model of ethylene molecule with double bond between carbon atoms.

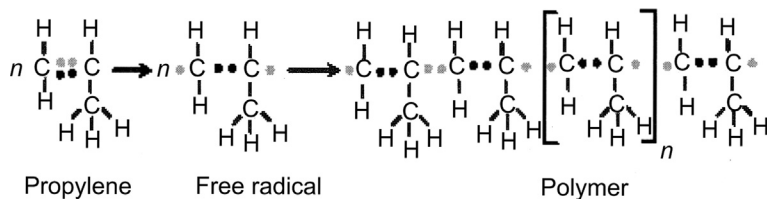
electrons (small negative particles) shared between carbon and the adjoining atom to which it is bonded. In ethylene, the four bonds around each carbon atom come from bonds to two hydrogen atoms and bonds to the two adjacent carbon atoms. If a carbon atom bond is broken and a single electron stays with each carbon atom, a free radical is formed. The free radical now has three bonds around each atom (two to hydrogen and one to carbon) plus a free electron. Free radicals are not a stable chemical species, as the carbon atoms want to attract another electron to form a fourth bond. If a free radical comes together with another molecule, a bond is formed with the free radical moving to the end of the added molecule. This can be the addition of a second ethylene group to the initial ethylene group. By repeating this process numerous times, polymers are formed by a process called an addition reaction, as monomers are added to the polymer chain. When the chain becomes the right length to provide the optimum property profile and processing characteristics, the chain length is terminated with an end group that has a free radical or free electron on the molecule.

The reaction sequence for the formation of polyethylene is as follows:

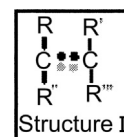


The single electrons on the free radicals combine to form a bond. Free radicals continue to combine until a high-molecular-weight polymer is formed.

A similar reaction sequence is used to produce polypropylene. A free radical addition reaction that polymerizes propylene molecules is similar to polyethylene polymerization. Propylene free radical formation and the subsequent polymerization steps are shown below.



Numerous polymers are made by this free radical or other additional polymerization reactions, as an ethylene double bond is broken to form different polymers with unique properties. When the hydrogen atoms in polyethylene are replaced with other atoms or groups of atoms, a different polymer is produced. Table 18.2 shows a listing of the different groups that replace one or more hydrogen atoms in Structure I to form various polymers. The structures of some common polymers referred to in Table 18.2 are given in Figure 18.11.



Polypropylene, polystyrene, and other similar polymers exist in three distinct structural configurations, depending on the polymerization conditions. For polypropylene, when the pendant methyl (CH₃) groups are all on one side of the polymer chain, this

Table 18.2 Polymer Structures Based on C—C

Polymer	R	R''	R'	R'''
Polyethylene	H	H	H	H
Polypropylene	CH ₃	H	H	H
Polystyrene	C ₆ H ₅	H	H	H
Polyvinylchloride	Cl	H	H	H
Polymethylmethacrylate	CH ₃	COOCH ₃	H	H
Polyvinylidenechloride	Cl	Cl	H	H
Polytetrafluoroethylene (Teflon)	F	F	F	F
Polyvinylidene fluoride	F	F	H	H
Polychlorotrifluoroethylene	F	F	F	Cl
Polyhexafluoropropylene	F	F	F	CF ₃
Polyacrylonitrile	CN	H	H	H
Polybutylene	CH ₂ CH ₃	H	H	H
Polybutylene	CH ₃	CH ₃	H	H
Ethylene vinyl alcohol	OH	H	H	H
Polyvinylacetate	OOCCH ₃	H	H	H

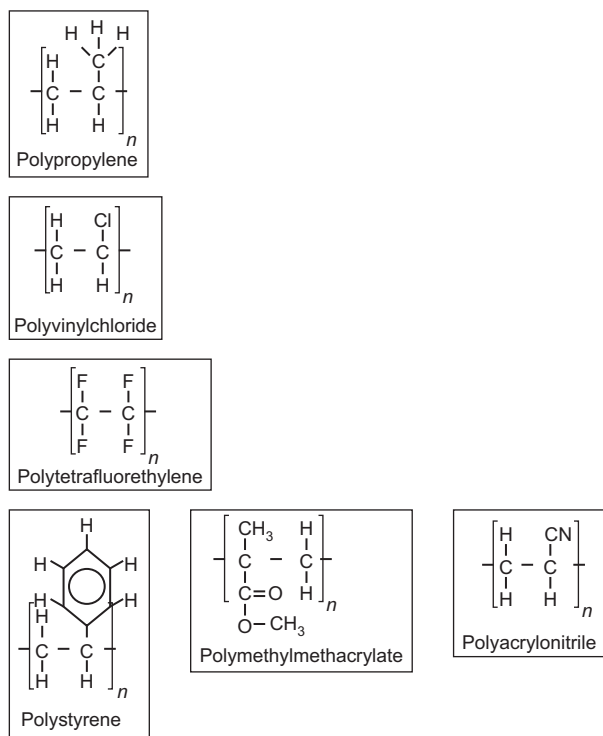


Figure 18.11 Structures of some common polymers.

is the isotactic form. When the methyl groups are on alternating sides of the polymer chain, it is the syndiotactic form. When the methyl groups are randomly oriented along the polymer chain, it is the atactic form. These forms are shown for polypropylene in Figure 18.12 with all the hydrogen

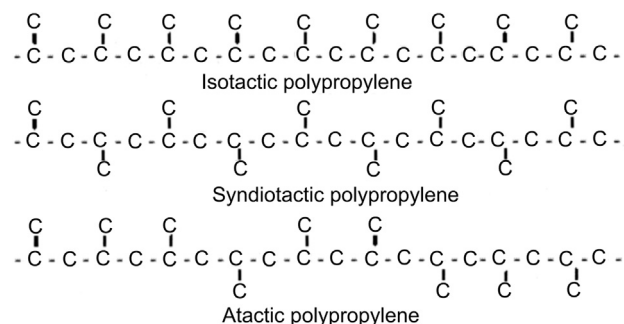


Figure 18.12 Various structural configurations of polypropylene and other polymers.

atoms eliminated from the structure for simplicity. Polypropylene sold for commercial applications is of almost 100% isotactic grade. Isotactic polypropylene crystallizes (discussed later) easily to provide its property profile. The pendant methyl group orientation in syndiotactic and atactic polypropylene hinders crystallization, resulting in lower

property profiles. Commercial polystyrene has the atactic configuration. The pendant benzyl groups of the ethylene backbone create steric hindrance that prevents crystallization. Polystyrene is amorphous with an atactic structure and has outstanding transparency.

18.4 Molecular Weight

Each chemical element has a specific weight called the atomic mass unit. The atomic mass unit, or a.m.u., is an arbitrarily defined unit of mass using carbon as a reference and was created by scientists for measuring the masses of atoms and molecules. Adding the atomic weights of the atoms in an individual polymer chain gives a value called the molecular weight. Generally, the greater the polymer molecular weight, the higher the tensile, flexural, and impact properties become, while the resistance to flow or viscosity increases, making the polymers more difficult to process.

Each element has a specific atomic weight that is given in the chemical Periodic Table of Elements. Typical atomic weights found in polymers are as follows:

- Hydrogen—1
- Carbon—12
- Nitrogen—14
- Oxygen—16
- Fluorine—19
- Sulfur—32
- Chlorine—35.5
- Bromine—80

Molecular weight calculations for the small molecules discussed earlier are as follows:

- Methane, $\text{CH}_4 = 16$. Carbon a.m.u. is 12 and that of hydrogen is 1. So the total $= 12 + 4(1) = 16$.
- Ethane, $\text{C}_2\text{H}_6 = 30$. Two carbon atoms plus six hydrogen atoms is $2(12) + 6(1) = 30$.
- Butane, $\text{C}_4\text{H}_{10} = 58$. $4(12) + 10(1) = 58$.

As the molecular weight increases, the molecules at room temperature go from gas to liquid and finally to solid. Each small molecule discussed above has a distinctive molecular weight that is unique to that molecule. Pentane, C_5H_{12} , will always have a molecular weight of 72. This is true as long as special isotopes are not present. Isotopes are atoms of the same element that vary in the number of neutrons in their nuclei.

Polymer molecular weights, unlike small molecules, do not have a unique value; instead, polymers have a molecular weight distribution that relates to the different polymer chain lengths. Polymerization is a random process, so each polymer chain does not end up with the same number of atoms. The molecular weight is a range that is presented as a molecular weight distribu-

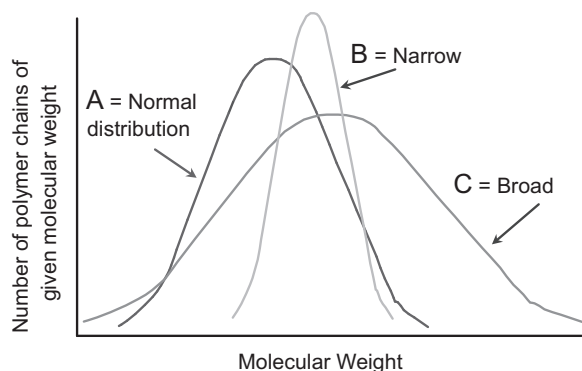


Figure 18.13 Normal molecular weight distribution curves.

tion. Figure 18.13 shows a typical molecular weight distribution curve. There are both short and long polymer lengths, with an average molecular weight near the center of the distribution curve. Plotted on the y-axis is the number of polymer chains with a given molecular weight, whereas the x-axis is the individual molecular weight. Molecular weight distributions can have different shapes, depending on the chain lengths within the polymer. A normal distribution is the bell-shaped curve shown as curve A in Figure 18.13. In a normal distribution, there are as many long high-molecular-weight chains as there are short low-molecular-weight chains. The majority has a common molecular weight range in the center of the graph. Within a normal molecular weight distribution, it is possible to have a narrow molecular weight distribution, curve B, or a broad molecular weight distribution, curve C in Figure 18.13. Other molecular weight distribution curves, shown in Figure 18.14, can be skewed toward low or high molecular weight, curves D and E, or bimodal, with two molecular ranges, curve F. Polymers associated with the curves in Figures 18.13 and 18.14 process differently because the molecular weight distribution and the average molecular weights differ. If all the materials had the same average molecular weight, then they would process

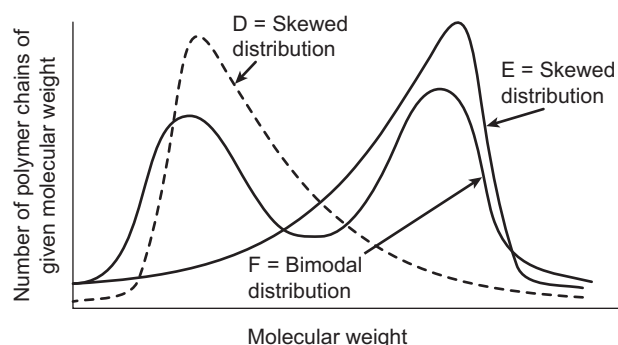


Figure 18.14 Skewed and bimodal molecular weight distribution curves.

differently because the molecular weight distribution curves are not the same.

The polymer molecular weight and the molecular weight distribution directly affect the extrusion process. Comparing two polymers with different molecular weights, the polymer with the higher molecular weight will require more energy to process, i.e. higher drive torque or amps due to a higher melt viscosity have better melt strength, be stiffer, and possess better ductility. Conversely, a lower-molecular-weight polymer has a lower viscosity at a given temperature (flows more easily), poorer melt strength, potential handling difficulties as low-viscosity polymer sticks more to gloves and other handling tools in the string up procedure, and requires less energy for the extrusion process. Extrusion processes normally use higher-molecular-weight polymers for better melt strength and melt handling characteristics, while injection molding tends to use lower-molecular-weight resins that flow more easily into thin sections of parts.

One molecular weight measure is the melt flow index (MFI), which measures how much polymer flows through a specified die orifice in 10 min. Figure 18.15 shows the test equipment for measuring

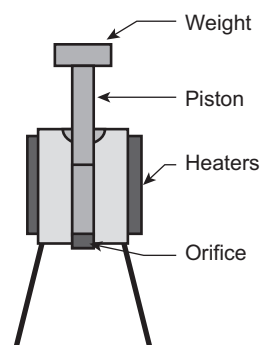


Figure 18.15 Measuring melt flow index.

the MFI. The piston is removed and resin is added to the heated barrel, where it is compacted and allowed to come to equilibrium temperature. After a few minutes, the weight is added to the piston, and resin flows out of the orifice at the barrel bottom. The grams extruded out the barrel in 10 min with an orifice, barrel temperature, and weight specified by American Society for Testing and Materials test method D-1238 for a particular polymer resin are the resin MFI. The higher the MFI, the lower the resin viscosity and molecular weight. A low MFI correlates with a high viscosity (less resin extruded through the orifice during the 10-min test) and high-molecular-weight resins. The actual molecular weight and molecular weight curves are generated by gel permeation chromatography, also known as GPC.

Referring back to the molecular weight distribution curves shown in Figures 18.13 and 18.14, answer the following processing questions (assume that the molecular weight values are equivalent at the origin of each graph and that the x -axis scale is similar):

- Identify the polymer(s) with the highest MFI value.
- Identify the polymer(s) with the lowest MFI value.
- Identify the polymer that is the easiest to extrude and explain why.
- Identify the polymer with the broadest processing window.
- Identify the polymer with the smallest processing window.
- Identify the polymer that is most likely to contain gels. (Gels are defined as high-molecular-weight particles that pass through the extruder without melting.)
- Identify the polymer(s) that you want to be purchased for processing in your plant and explain why.

The polymer with the highest MFI value is the material with the lowest average molecular weight, which is probably curve A in Figure 18.13. A case could be made for curve D in Figure 18.14 due to the high level of low-molecular-weight polymer; however, curve D has a long high-molecular-weight tail that will retard the flow through the MFI barrel in 10 min. The polymer with the lowest MFI is sample E in Figure 18.14, which appears to have the highest average molecular weight plus the highest concentration of high-molecular-weight polymer.

The easiest resins to extrude are polymers A and B, as both have a relatively small and uniform molecular weight distribution. Both polymers will melt in a relatively small temperature range because the molecular weights of all the polymer chains in each sample are similar. Although both resins A and B are easy to process, polymer B, with the narrowest molecular weight distribution, is probably the material of choice. All polymer molecules will melt at approximately the same melt temperature. There is no significant amount of low-molecular-weight resin that is apt to melt early in the feed zone of the extruder and coat the barrel walls, causing succeeding feed material to slip on the barrel walls, leading to poor feed characteristics. Likewise, there is no large amount of high-molecular-weight particles that are hard to melt and may be unmelted at the end of the transition zone in a single screw extruder. High-molecular-weight particles require more energy to be put into the melting section in a twin screw extruder to ensure that all melting is complete.

The polymers with the largest processing windows are polymers A and B, assuming that the largest processing window is defined as the widest temperature range over which all the polymer molecules can be uniformly melted. Although polymers A and B have the narrowest molecular weight distributions, both materials can be processed in a small range of melt temperature due to the narrow weight distribution. However, if both materials have good thermal stability, they can also be processed at a higher melt temperature range with assurance that all the material will melt and process uniformly because of the small-molecular-weight distribution. Therefore, these two polymers have a large temperature processing window where all the polymer is anticipated to either melt or soften uniformly.

The smallest processing window is difficult to determine from polymer curves D, E, and F. All three materials will have a narrow processing window for different reasons. Consider the skewed molecular weight distribution curve for D first. A lower molecular weight requires less energy and heat in the extruder to melt and process the material. Selecting an appropriate temperature to process the low-molecular-weight material may not supply enough energy to melt the polymer in the high-molecular-weight tail. If a low temperature is set to prevent the low-molecular-weight material from melting prematurely in the feed section, it may be impossible

to supply enough energy at an acceptable throughput rate to melt the high-molecular-weight polymer. In a single screw extruder, there may still be solid particles at the end of the transition zone, causing solid bed breakup and solid floating in the melt in the metering zone. Assuming that the solid in the melt in the metering zone is a high-molecular-weight material, it may be impossible to melt by the end of the extruder, clogging the screen pack. If a barrier screw is used for mixing, excessive heat generated in this section to melt any solid high-molecular-weight particles may cause lower-molecular-weight particles to degrade.

Consider the polymer E molecular weight distribution curve next. Extruder temperatures are set higher than in the case of sample D to ensure that all the high-molecular-weight material is melted in the transition section of a single screw extruder or the melting section of a twin screw extruder. However, premature melting due to the higher barrel temperatures in the feed area may lead to feed problems caused by surging, or in the worse scenario, a melt bridge. A low-viscosity melt film acts as a lubricant in the feed section, allowing the feed material to slip on the barrel walls. A second potential problem is that the low-molecular-weight material acts as a lubricant at the barrel wall interface in the transition section, reducing the shear heating in the melting film region. This can interfere with the melting mechanism of the high-molecular-weight material, preventing all the resin from being melted in the transition section, leading to solid bed breakup and high-molecular-weight particles in the melt in the metering section. Finally, and maybe the most important consideration, does the heat required to melt the high-molecular-weight fraction cause the low-molecular-weight material fraction to degrade into even shorter polymer segments that can affect physical properties, i.e. tensile, flexural, and impact?

Curve F, with the bimodal molecular weight distribution, is probably the worst scenario. At low temperatures, the high-molecular-weight fraction does not melt in the transition section and is carried along as a filler particle floating in a molten resin matrix. At higher processing temperatures, premature low-molecular-weight melting in the feed section can cause feed problems due to slippage on the barrel wall. In addition, a low-viscosity material in the melt region may not allow as much shear heat to be generated, reducing the melting rate of the high-molecular-weight material. The barrel temperatures and screw speeds have to be set correctly in a small processing range to

balance all effects and ensure that there is sufficient heat to melt all materials, while not supplying so much heat that feeding and other issues are created.

The polymers most likely to have gels are those represented by molecular weight distribution curves D and F. Gels are high-molecular-weight particles that do not melt during processing, due to their high-molecular-weight or crosslinked particles. Molecular weight distribution curve D, with the majority of the polymer being of low molecular weight and requiring lower processing temperatures, is likely to have some high-molecular-weight particles in the long high-molecular-weight tail that do not melt. Curve F, a bimodal distribution, is a likely candidate for gels from the small high-molecular-weight hump and tail in the higher molecular weights.

Of the six materials represented in curves A–F in Figures 18.13 and 18.14, the most desirable resins for extrusion processing are molecular weight distribution curves A and B. They have the smallest molecular weight distribution, so all of the polymer chains will melt or soften over a small temperature range. If the polymers are thermally stable, it is relatively easy to have a very broad temperature range over which these materials can be extruded.

Not enough attention is paid to the molecular weight and molecular weight distribution of polymers being processed during extrusion. If a material with a molecular weight distribution curve similar to E in Figure 18.14 is being processed, it is easy to envision supplying too much heat to the low-molecular-weight chains, causing them to degrade and become even shorter, thus affecting the physical properties.

A common practice in extrusion operations is to regrind out of specification material and add it back to the extrusion process with the virgin resin to reduce the raw material cost and reduce issues associated with scrap disposal. Does the previous heat history change the molecular weight distribution curve? Assuming that some thermal degradation occurs during the first or second heat history experienced by the resin, the molecular weight distribution curve is now shifted toward lower molecular weight. Adding regrind that is partially degraded may create a bimodal molecular weight distribution for processing. The blend has the potential problems discussed with processing material represented by curve F in Figure 18.14. In addition to a smaller processing window, the regrind or lower-molecular-weight material melts first, coating the barrel wall and preventing the

high-molecular-weight material from processing correctly. Add to this the effect of feeding and melting different size regrind particles, and serious processing issues can result.

Blending two very different melt flow resins results in a bimodal molecular weight distribution. Processing conditions must be properly balanced to melt both the low- and high-molecular-weight portions efficiently, while preventing any feed problems associated with premature melting of the low-molecular-weight fraction or not melting the higher-molecular-weight resin in the transition section of a single screw extruder. The same problems are not as serious in twin screw extruders, where a melt seal can be formed to maximize melting in one section followed by efficient dispersive mixing to uniformly mix the high- and low-molecular-weight entities.

A problem is what data to use to compare the molecular weights of two different resins. The MFI does not describe the molecular weight distribution; it supplies average resin flow at very low shear rate. (Shear rate is at least 10-fold below the shear rates experienced in extrusion.) End-group analysis, boiling point elevation, freezing point depression, vapor pressure, and osmotic pressure are techniques used to measure the number-average molecular weight. The number-average molecular weight is a direct average of the molecular weights, where the molecular weight of each chain is added together to obtain a total molecular weight, which is divided by the number of polymer chains. Using a normal molecular weight distribution curve, the number average is the center of the bell-shaped curve, as shown in Figure 18.16.

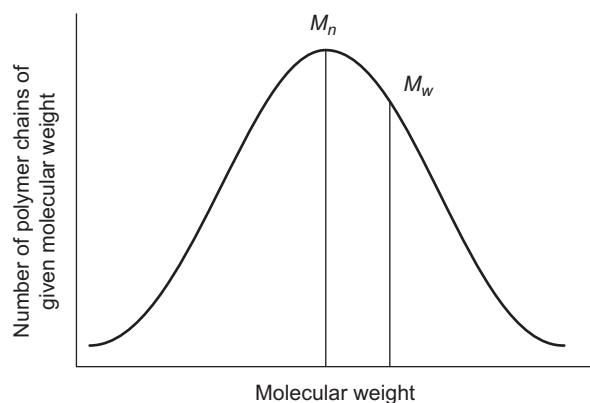


Figure 18.16 Normal molecular weight distribution curves.

The number-average molecular weight is calculated from Eqn (18.1):

$$M_n = \frac{\sum n_i (MW_i)}{\sum n_i} \quad (18.1)$$

where

M_n = Number-average molecular weight

MW_i = Molecular weight of chain i

n_i = Number of polymer chains of molecular weight MW_i

The weight-average molecular weight is weighted toward higher-molecular-weight polymer chains. The weight-average molecular weight is always higher than the number-average molecular weight and is measured by GPC or light scattering techniques. The weight-average molecular weight is given by Eqn (18.2):

$$M_w = \frac{\sum w_i (MW_i)}{\sum w_i} \quad (18.2)$$

where $w_i = n_i(MW)_i$.

The degree of polymerization, given by Eqn (18.3), is the average number of monomer units per polymer molecule:

$$DP = \frac{M_n}{MW_{mer}} \quad (18.3)$$

where

DP = Degree of polymerization

MW_{mer} = Molecular weight of the monomer

Generally, polymers with acceptable physical properties have a DP >500, with most commercial resins having a DP in the range of 1000 to 10,000.

Polydispersity index (PI) is the weight-average to number-average molecular weight ratio and is given by Eqn (18.4):

$$PI = \frac{M_w}{M_n} \quad (18.4)$$

Usually, polydispersity is between 1.5 and 2. However, higher polydispersity, between 3 and 8, is quite common. If the polydispersity is not between 1.5 and 8, the molecular weight distribution is unusual.

Another viscosity measure is intrinsic viscosity (IV), which is commonly used with PET, PBT, and nylon. IV is directly proportional to the polymer viscosity and correlates with a higher molecular weight and typically higher physical properties. Intrinsic viscosities are solution-based viscosities and are normally supplied by resin manufacturers.

To ultimately understand resin viscosity and how a particular resin performs in either extrusion or injection molding, it is necessary to compare shear rate versus viscosity curves. These will be discussed in more detail in Chapter 20.

The physical properties to molecular weight and processability relationship is shown in Figure 18.17. As the molecular weight increases, the processability

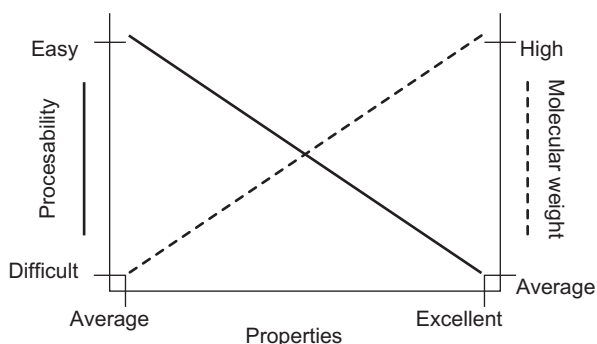


Figure 18.17 Comparison of processing, properties, and molecular weight.

decreases and the property performance increases. Polymers of low molecular weight have low viscosity and are easy to shape, but they may have inferior properties and end-use performance.

18.5 Copolymers

Copolymers are formed when two monomers are polymerized together to form a polymer. Terpolymers are formed when three monomers are used. Copolymers are classified as random or block copolymers, depending on whether the repeating groups in the backbone are randomly arranged or are in segments. Assume that copolymer is produced from monomers A and B. Figure 18.18 shows random and block copolymer backbones. Alternating copolymers have every other monomer changing identity, as $-A-B-A-B-$, etc. Block

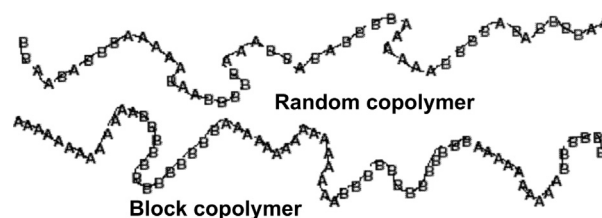


Figure 18.18 Schematic of random and block polymers.

copolymers are categorized as diblocks, shown in Figure 18.18, where alternating monomer A and B blocks occur, or triblocks, where there is a block of A followed by a block of B and then another block of A.

Block copolymers are formed by polymerizing oligomers, which are short chains. Oligomer polymer chains by themselves are too short and have insufficient molecular weight to have acceptable properties. These short chains are later polymerized to form high-molecular-weight block copolymers from small blocks of A and B oligomers.

Copolymers are produced to combine the optimum resin properties of at least two different monomers, generating a new resin with superior properties (in some specific area) relative to the individual components. Styrene and butadiene are combined as a hard and soft segment, respectively, imparting elastomeric-type properties to a copolymer that contains hard segments to yield higher modulus and stiffness. Ethylene vinyl acetate (EVA) combines ethylene monomers with EVA monomers. The copolymer has good adhesion to both polar (resin systems containing atoms other than carbon or hydrogen) and nonpolar resin systems (resins containing only carbon or hydrogen). EVA is used in extrusion as a tie layer or adhesive between different substrates in coextrusion, film coatings, or lamination. Copolymers are used as compatibilizers when blending two dissimilar resin matrices. The copolymer provides an interface to enhance adhesion and mechanical compatibility of the two different phases.

Some commercial copolymers are shown in Figure 18.19.

18.6 Polymer Structures

Long chain polymer molecules distributed in a polymer matrix were discussed previously and

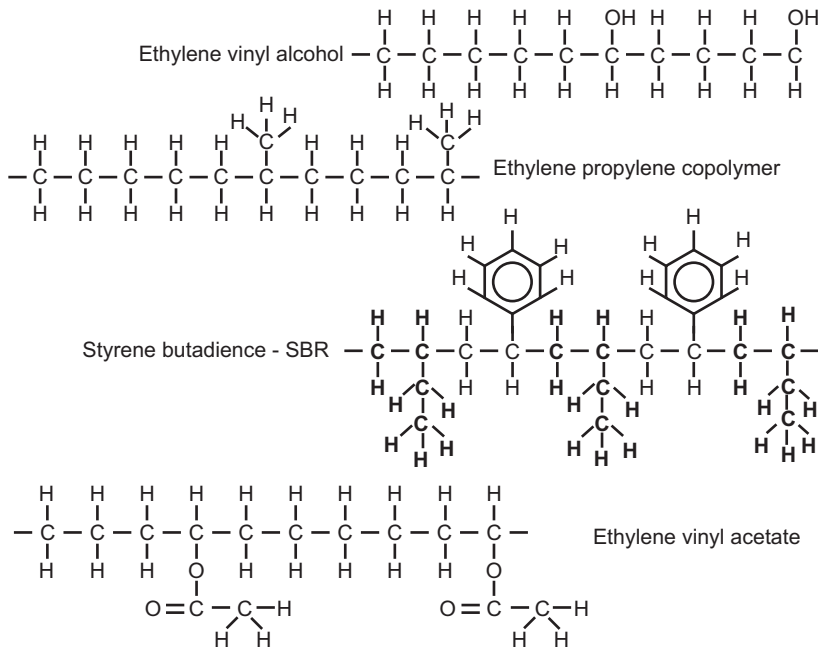


Figure 18.19 Schematic of random and block polymers.

shown in Figure 18.8. The long chains are like wet spaghetti strands entangled with each other to impart significant properties to the polymer matrix. As the polymer backbone is modified with atoms that provide steric hindrance, the backbone becomes stiffer, with less molecular motion (rotation) about the carbon bonds. Stiffer polymer

the C—C double bond being broken to form free radicals followed by polymerization through free radical addition. Other chemical reactions (i.e. condensation and grafting) are used to generate polymers with different chemical backbones. Some polymers with stiffer backbones and higher properties are shown in Figure 18.20.

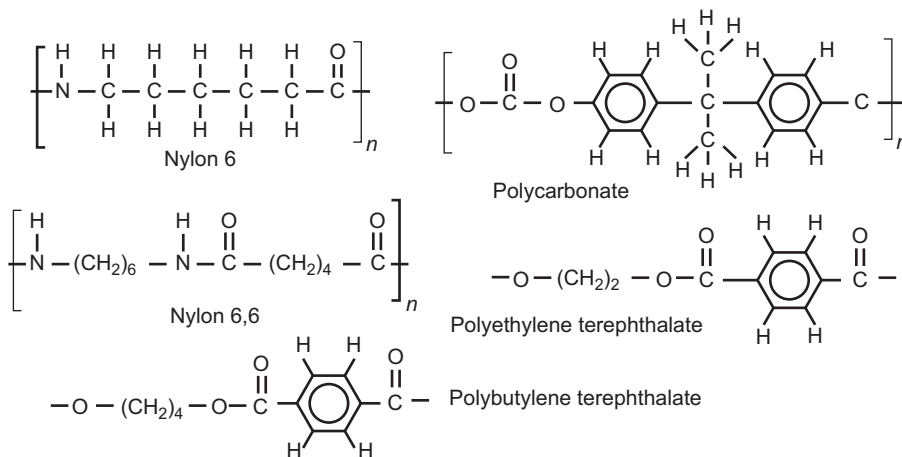
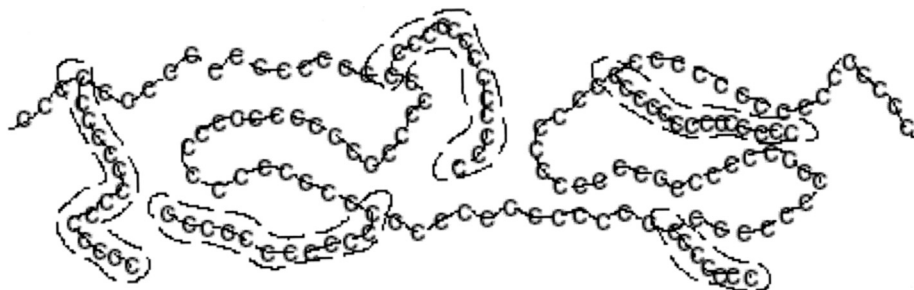


Figure 18.20 Chemical composition of some engineering thermoplastics.

backbones generally have higher property performance, as measured by tensile, flexural, impact, and heat properties. Polymers discussed to this point have been based on ethylene chemistry, with

Crosslinked structures occurring in thermoset materials were discussed previously and shown in Figure 18.9. A chemical bond occurs between different polymer chains, locking in the polymer

Figure 18.21 Side chain branching in polyethylene molecule.



structure. These chemical bonds prevent a cross-linked polymer from melting or softening. Typically, two or more components are mixed together at room temperature and placed in a mold at high temperature where the reaction is accelerated to produce a final part, which is removed from the tool or mold at the elevated temperature. Cycle times are determined by the time required for the chemical reaction to be completed.

Some thermoplastic polymers have side chain branches. These branches alter the resin processing and physical properties. Figure 18.21 shows side chain branching in a polyethylene molecule. The major difference between low-density polyethylene (LDPE), high-density polyethylene (HDPE), and linear low-density polyethylene (LLDPE) is the type and degree of side chain branching. Generally, polyethylene has 1–10 branches for each 100 carbon atoms along the polymer backbone. Low density has very frequent, irregular-length chain branching. HDPE has longer chain branches that occur less frequently compared to that of LDPE. The branching in LLDPE is controlled by the type and concentration of comonomers added during the polymerization reaction. Using 1-octene as a comonomer generates hexyl branches along the polymer backbone, 1-hexene results in butyl branches, and 1-butene generates ethyl branches. The various comonomers are shown in Figure 18.22.

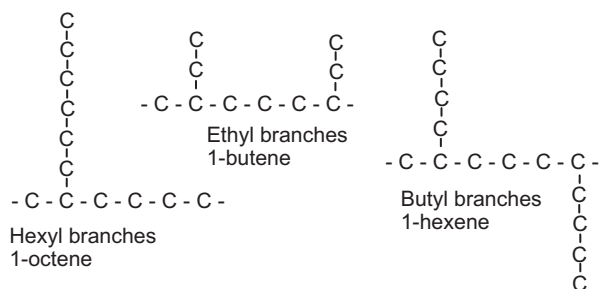


Figure 18.22 Different types of branching in LLDPE depending on the monomers used in polymerization.

Comparing branched and linear polymers in extrusion processing, the branched polymers require higher energy to process, are stiffer, have a higher viscosity and lower MFI, better melt strength, and better handling characteristics. Branched resins are particularly useful in extrusion blow molding, where high polymer melt strength is critical to support a large parison. The melt strength is directly proportional to the degree of branching.

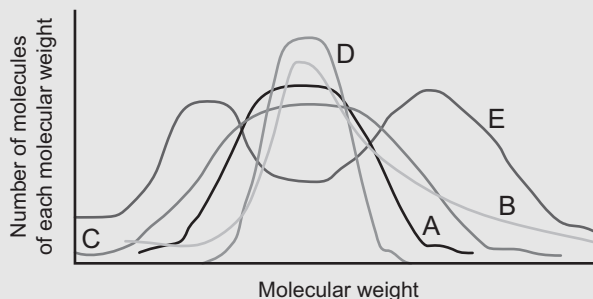
The last type of polymer structure is a network, where one polymer is interspersed with another, and the crosslinks between the polymer chains actually cross one another. Figure 18.23 shows a network polymer matrix.



Figure 18.23 Network polymer structure.

Review Questions

1. What is a polymer?
2. What is the importance of polymer molecular weight?
3. What causes molecular orientation and how does this affect physical properties?
4. Why is rotation about carbon atoms important for physical properties?
5. How are typical molecular chains in a polymer matrix represented?
6. What is the difference between thermoplastic and thermoset polymers?
7. Are elastomers thermoplastic or thermoset polymers? Explain.
8. Can thermoset plastics be extruded, and if so, what cautions must be exercised during extrusion?
9. What is crosslinking?
10. What gives polymers their strength and properties?
11. What is a copolymer?
12. How are polyethylene and polystyrene formed by free radical reactions?
13. What is the importance of polymer molecular weight and how does it affect processing?
14. What is MFI, how is it measured, what does it measure, and what is the difference between a 12 MFI resin and a 35 MFI resin?
15. How does viscosity relate to molecular weight? In extrusion, is a high or low viscosity better and why?
16. Using the molecular weight distribution curves given below, answer the following questions with explanations:
 - a. Lowest molecular weight?
 - b. Highest viscosity?
 - c. Smallest processing window?
 - d. Largest processing window?
 - e. Most likely to contain gels?
 - f. Most difficult to process?
 - g. Lowest melt flow index?
 - h. Highest melt flow index?



17. Why might the addition of regrind interfere with the extrusion of virgin resin?

Review Questions (continued)

18. What is the difference between weight-average and number-average molecular weight?
19. What is the degree of polymerization?
20. What is polydispersity index?
21. What is the difference between a block and a random copolymer?
22. What is the difference in branching on HDPE, LDPE, and LLDPE?
23. Why is it important to understand polymer behavior and polymers in general to troubleshoot extrusion problems?