2 Structure and Related Properties of Plastic Polymers

2.1 INTRODUCTION

The adjective *plastic* is derived from the Greek *plastikos*, meaning easily shaped or deformed. It was first introduced into the English language in the nineteenth century to describe the behavior of the recently discovered cellulose nitrate that behaved like clay when mixed with solvents. The noun "plastics" is often defined in dictionaries as a group of synthetic resinous or other substances that can be molded into any form. From a technical viewpoint, *plastics* is a generic term for macromolecular organic compounds obtained from molecules with a lower molecular weight (MW) or by chemical alteration of natural macromolecular compounds. At some stage of their manufacture, they can be formed to shape by flow, aided in many cases by heat and pressure. The term plastics can be used as a noun, singular or plural, and as an adjective.

The standard terms used for plastics are defined in ASTM D833. Commonly, the word "plastic" is used to describe the easily deformable state of the material, and the word "plastics" to describe the vast range of materials based on macromolecular organic compounds. This chapter will describe plastics relevant to food packaging, with particular emphasis on their structure and related properties.

The utility of flexible sheet materials depends on the properties of a special kind of molecular structure: long, flexible molecules interlocked into a strong and nonbrittle lattice. These structures are built up by the repeated joining of small basic building blocks called *monomers*, the resulting compound being called a *polymer*, derived from the Greek roots *meros* meaning parts, and *poly* meaning many. Differences in the chemical constitution of the monomers, in the structure of the polymer chains and in the interrelationship of the chains determine the different properties of the various polymeric materials.

2.2 HISTORY

Although the chemical nature of polymers (and the fact that they consist of enormous molecules) was not understood until well into the mid-twentieth century, the materials themselves, and the industry based on them, existed long before that (Andrady and Neal, 2009).

Since plastics include compounds obtained by chemical alteration of natural macromolecular compounds, then the earliest example of a plastics material would have to be hard rubber. In 1839 Charles Goodyear, an American inventor, found that rubber heated with sulfur retained its elasticity over a wider temperature range than the raw material and that it had greater resistance to solvents. The rubber–sulfur reaction was termed "vulcanization." The significance of the discovery of hard rubber lies in the fact that it was the first thermosetting (defined in Section 2.3.1.1) plastics material to be prepared and also the first plastics material that involved a distinct chemical modification of a natural material.

It is generally considered that the development of the plastics industry began in the 1860s. At the International Exhibition of 1862 in London, Alexander Parkes, an English chemist and metallurgist, displayed a new material (which he later modestly called "Parkesine") that he had made by treating cotton waste with a mixture of nitric and sulfuric acids. This was already a well-known process used for making the explosive called guncotton, but Parkes found that by altering the proportions

and then mixing the resulting material with castor oil and camphor, the compound could be molded into decorative and useful articles. Unfortunately, the Parkesine Company, which he formed in 1866 to commercialize his process, went bankrupt in less than 2 years. In 1869, a collaborator of Parkes, Daniel Spill, formed the Xylonite Company to process materials similar to Parkesine. Once again, economic failure resulted and the company was wound up in 1874. Undaunted, Spill moved to a new site, established the Daniel Spill Company and continued production of Xylonite and Ivoride.

In the 1860s, Phelan and Collander, a U.S. firm manufacturing ivory billiard balls, offered a prize of $10,000 for a satisfactory substitute for ivory because the decimation of elephant herds had resulted in an enormous increase in the price of ivory. In an attempt to win this prize, the U.S. inventor John Wesley Hyatt solved the technical problems that beset Parkes by using camphor in place of castor oil. Although Hyatt did not win the prize, his product, which he patented with his brother in 1870 under the trademark "Celluloid," was used in the manufacture of objects ranging from dental plates to shirt collars. Despite its flammability and liability to deterioration under the action of light, Celluloid achieved notable commercial success.

Other plastics were gradually introduced over the next few decades. Among them were the first totally synthetic plastics, the family of phenol–formaldehyde resins developed by the Belgian–American chemist Leo Hendrik Baekeland and sold under the trademark "Bakelite." The first of his 119 patents on phenol–formaldehyde plastics was taken out in 1907. Other plastics introduced during this period include modified natural polymers such as rayon, made from cellulose products.

The first hypothesis of the existence of macromolecules was advanced by Kekule in 1877 when he proposed that many natural organic substances consist of very long chains of molecules from which they derive their special properties. The step from the idea of macromolecules to the reality of producing them took the genius of the German chemist Hermann Staudinger, who in 1924 proposed linear structures for polystyrene (PS) and natural rubber. In 1920 he had hypothesized that plastics were truly giant molecules or, as he called them, "macromolecules." His subsequent efforts to prove this claim initiated an outburst of scientific investigation that resulted in major breakthroughs in the chemistry of plastics and the introduction of large numbers of new products such as cellulose acetate and poly(vinyl chloride) (PVC) in 1927 and urea–formaldehyde resins in 1929. Staudinger was awarded the Nobel Prize for chemistry in 1953 for his efforts in establishing the new polymer science.

Further developments occurred in the 1920s, but the years 1930–1940 were probably the most important decade in the history of plastics as today's major thermoplastics (PS, PVC and the polyolefins) were developed. Further developments continue, with special purpose rather than general purpose materials having been discovered in recent years.

Although the possibility of discovering dramatically new polymers is remote, the plastics industry continues to grow, despite a serious check to growth following the oil crisis of the 1970s. Current global annual consumption of plastics is about 250 million tonnes, which requires about 8% of world oil production; ~30% of these plastics are used for packaging. With modern society so dependent on plastics, and the food industry a major user of plastics packaging materials, continued research and development will provide new combinations of established plastics materials to perform specific functions in more efficient and cost-effective ways. In order to become more sustainable, some plastics are now being manufactured from biobased materials, for example, biopolyethylene from sugar cane. This is discussed further in Sections 3.3.6.2 and 3.3.6.3.

2.3 FACTORS INFLUENCING POLYMER STRUCTURES AND RELATED PROPERTIES

The properties of plastics are determined by the chemical and physical nature of the polymers used in their manufacture; the properties of polymers are determined by their molecular structure, MW, degree of crystallinity and chemical composition. These factors in turn affect the density of the polymers and the temperatures at which they undergo physical transitions. The discussion that

follows is necessarily brief, and readers are referred to such standard textbooks on polymer chemistry as Sperling (2006), Cowie (2007), van Krevelen and te Nijenhuis (2009) and Carraher (2010) for more detailed treatments.

2.3.1 Molecular Structure

2.3.1.1 Classification of Polymers

Polymers are molecular materials with the unique characteristic that each molecule is either a long chain or a network of repeating units. This can best be understood by considering polyethylene (commonly referred to as polythene), which is one of the simplest polymers and most common food packaging film. A polyethylene (PE) molecule is built up by joining together many molecules of the monomer ethylene (C_2H_4), as indicated in Figure 2.1.

In terms of chemical composition, there are two broad types of polymers—homopolymers and heteropolymers. The former have the same repeating building-block unit throughout their molecules; the latter are polymers with two or more different building-block units regularly or irregularly distributed throughout their length. Heteropolymers are referred to as copolymers when two different monomers are polymerized together and terpolymers when three monomers are used.

Polymers such as the PE used as an example in Figure 2.1 are called linear polymers and consist of a backbone of carbon atoms and a number of side groups that differ from polymer to polymer. An alternative way of describing a linear polymer is shown in Figure 2.2a, in which it is pictured as a covalently bonded chain of monomer units. Linear copolymers may exhibit any of three combinational forms (Figure 2.2b through d). One is the form of a regular copolymer, in which two different repeating units occur alternately along the chain. It is actually equivalent to a homopolymer in terms of regularity. Another form is that of the random copolymer, in which, during polymerization, the units have taken up a statistically random placement along the length of the chain. The third type of structure is, in a sense, a combination of the previous two: it is the block copolymer, which is composed of alternating lengths of homopolymer along the molecular chains. Figure 2.2 shows two types of backbone units in the structure, although in practice there may be more than two.
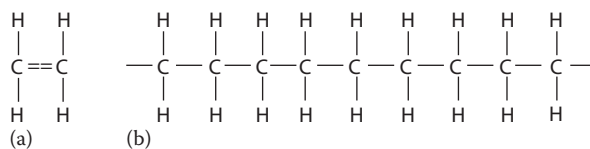

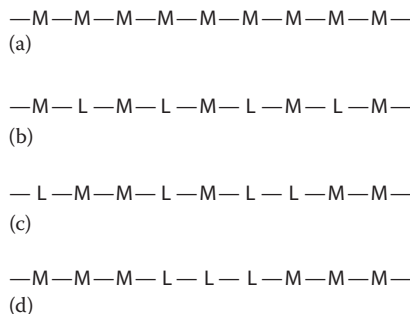**FIGURE 2.1** (a) The monomer ethylene and (b) the polymer PE.

FIGURE 2.2 Copolymers made with different structures. L and M are any monomers. (a) Linear polymer, (b) alternating copolymer, (c) random copolymer and (d) block copolymer.
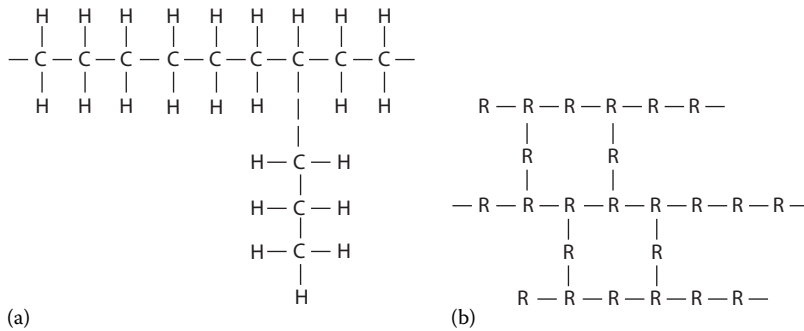
FIGURE 2.3 (a) Branched PE and (b) cross-linked polymer.

Branched PE is shown in Figure 2.3a, while Figure 2.3b shows a cross-linked polymer in which the long chains are connected together, often by relatively short cross-links.

Thus, plastic polymers can be divided into two broad categories: those polymers that extend in one dimension (i.e., they consist of linear chains), and those polymers that have links between the chains, so that the material is really one giant molecule.

The first group is the linear polymers and they are thermoplastic; that is, they gradually soften with increasing temperature and finally melt because the molecular chains can move independently. They are characterized by extremely long molecules with saturated carbon–carbon backbones. Such polymers may be readily molded or extruded because of the absence of cross-links. If their temperature is raised, they become very flexible and can be molded into shape, even at temperatures below their melting point. Not surprisingly, their mechanical properties are rather temperature sensitive. Thermoplastics are the most important class of plastics material available commercially, and account for more than two-thirds of all polymers used in the world today.

The second group is the cross-linked polymers and they are thermosetting. As the name suggests, these polymers become set into a given network when manufactured and cannot be subsequently remolded to a new shape. If the temperature is raised to the point where the cross-links are broken, then irreversible chemical processes also occur that destroy the useful properties of the plastic. This is called degradation. At normal temperatures, the cross-links make the solid quite rigid. Thermosetting polymers do not melt on heating but finally blister (due to the release of gases) and char. Examples of thermosetting plastics are epoxy resins and unsaturated polyesters.

The aforementioned categorization of polymers is convenient since polymers in the two groups differ in their structure, their properties and the chemical processes used in their manufacture. The importance of thermosetting polymers in food packaging is minimal except for epoxy resins that find use as enamels (lacquers) for metal cans.

2.3.1.2 Polymerization Processes

Thermoplastics can be made by joining together a sequence of monomers. Under suitable conditions of temperature and pressure, and in the presence of a catalyst called an initiator, the molecular chains grow by the addition of monomer molecules one by one to the ends of the chains. Branching can occur but cross-links are nearly absent.

The formation of thermoplastics by a process that involves the joining together of monomers to form polymers that have the same atoms as the monomers in their repeating units is called *addition polymerization*. A simple, low MW molecule (which must possess a double bond) is induced to break the double bond and the resulting free valences are able to join up to other similar molecules. This reaction occurs in the form of a chain addition process with initiation, propagation and termination steps.

Under normal conditions with the usual catalysts, the spatial arrangements of the branches of the polymers are random; such polymers are called *atactic*. Some processes give products in which the

branches are arranged in an orderly manner; these are called *isotactic* polymers. In the case of PE, this form of polymerization has the advantage of reducing the number of branches that are formed. Thus, the molecules in linear isotactic PE can line up with one another very easily, yielding a tough, high density compound. Atactic PE is less dense, more flexible than, and not nearly as tough as, the linear polymer, because the molecules are further apart.

Plastic polymers are also prepared by the process of *condensation polymerization* that involves two active sites joining together to form a chemical bond, a small molecule being ejected in the process. In this case, the starting monomers are not identical to those of which the chains are to be composed; the superfluous groups of atoms must be ejected when the monomer is added to the end of the chain. If there are enough groups of such superfluous atoms on each monomer molecule, some of them may be temporarily retained on the side of the chain as it grows. This promotes easy branching and leads rather rapidly to a highly cross-linked structure.

It follows that if monomers with few superfluous groups are used, cross-linking does not occur so that thermoplastic materials may also be made by the process of condensation. Polyesters and polyamides (PAs) (see Sections 2.3.6.4 and 2.3.6.6) are examples of thermoplastic polymers made by the condensation process. However, it should be noted in passing that a thermoset polyester can be made if one (or both) of the reactant molecules has a double bond and a third compound is added; under these circumstances cross-linking occurs. Epoxy resins (basically condensation products of a dihydroxyphenol and a compound containing an epoxy group) are examples of thermosetting plastics formed by condensation.

To summarize, thermoplastic polymers can be formed either by addition or condensation polymerization, whereas thermosetting plastics are formed only by condensation polymerization. The degree of cross-linking in a polymer may vary over a very wide range, thus blurring the boundary between thermosetting and thermoplastic materials.

2.3.2 Molecular Weight

The average number of repeating units in a single molecule of a polymer is known as the *degree of polymerization* or DP. At DP values of about 10–20, the substance formed is a light oil (paraffin if formed from ethylene). As the DP increases, the substance becomes greasy, then waxy and, finally, at a DP of about 1000 it becomes a solid and is then a true polymer. The DP is almost unlimited and may increase to around 100,000 or so. Typical properties and applications of straight chain hydrocarbons are presented in Table 2.1 where it can be seen that as the number of carbon atoms in the chain increases, the materials go from gas to liquid to solid.

TABLE 2.1
Typical Properties and Applications of the Alkane/PE Series

Average Number of Carbon Atoms in Chain	Physical State at Room Temperature	Typical Uses
1–4	Gas	Bottle gas for cooking and heating
5–10	Liquid	Gasoline
11–12	Liquid	Kerosene
13–17	Medium-viscosity liquid	Diesel fuel
18–25	High-viscosity liquid	Oil and grease
26–50	Crystalline solid	Paraffin wax candles
50–1000	Semicrystalline waxy solid	Wax coating of paperboard
1000–5000	Tough plastic solid	Films and bottles
$3–6 \times 10^5$	Fibers	Surgical gloves; bullet-proof vests

Source: Adapted from Carraher, C.E., *Introduction to Polymer Chemistry,* 2nd edn., CRC Press, Boca Raton, FL, p. 24, 2010.

From knowledge of the atomic mass of the repeating unit and the DP, the MW of the polymer molecule can be calculated; it is equal to the DP multiplied by the MW of the monomer. Thus, PE with a DP of 10,000 would have a MW of 280,000 since the MW of the repeating unit [$-CH_2CH_2$] is 28. In the case of copolymers, it is necessary to know not only the MW but also the relative proportions and arrangement of the two structural units in the chain.

In practically all industrial polymerization processes, the molecular chains that are produced vary considerably in dimensions. For this reason, the MW of a polymer is actually a distribution of MWs. Hence, a polymer system has to be characterized in terms of average MW and broadness or molecular weight distribution (MWD).

Two average MWs are commonly employed: the number-average MW (M_n) and the weight-average MW (M_w). If the polymer molecules are averaged in terms of number fractions of various lengths, the M_n is obtained. Most thermodynamic properties are related to the number of particles present and are, thus, dependent on M_n. M_n values are independent of molecular size and are highly sensitive to small molecules present in the mixture. However, many bulk properties such as viscosity and toughness depend as much on the size of the molecules as on their number. In this case, the appropriate function is the M_w, which is more dependent on the number of heavier molecules than M_n.

As the MWD becomes increasingly broad, the weight average assumes numerically larger values than the number average, so that the ratio $M_w:M_n$ (known as the *dispersity index* [DI]) is taken as a measure of the spread of molecular chain lengths. For most commercial polymers, DI falls between 2 and 8.

2.3.3 DENSITY

Density is a function of chemical composition, being dependent on the weight of individual molecules and the way they pack together. The hydrocarbon polymers do not possess heavy atoms, and, therefore, the mass of the molecule per unit volume is rather low. Oxygen, chlorine, fluorine and bromine increase the density of polymers. For example, amorphous hydrocarbon polymers generally have densities of 0.86–1.05 g cm^{-3}, while polymers containing chlorine have densities of 1.4 in the case of PVC and 1.7 for PVdC (poly(vinylidene chloride)).

2.3.4 CRYSTALLINITY

When a low MW material such as a metal crystallizes from the molten state, nucleation occurs at various points, from each of which a crystal or grain grows. Likewise, when a molten crystallizable polymer is cooled, crystallization spreads out from individual nuclei. However, instead of individual grains, a considerably more complex structure develops from each nucleus.

The degree of crystallinity is an important factor affecting polymer properties. The great length of polymer chains means that a certain amount of entanglement normally occurs and this prevents complete crystallization on cooling as in the case of metals. This phenomenon is due to the difficulty of aligning every portion of each chain of the polymer. Thus, crystallinity in plastics consists of thousands of small "islands" of *crystalline* regions surrounded by unordered or *amorphous* (without structure) material, as shown in Figure 2.4.

Figure 2.4 depicts in diagrammatic form the amorphous and crystalline regions of a semi-crystalline polymer. The crystalline region has an orderly arrangement of molecules as the chains are parallel and closely packed, whereas in the amorphous region, the molecular chains are disordered and without structure. The crystalline areas are known as *crystallites*. Unlike crystals of small molecules, crystallites are not composed of whole molecules or molecules of uniform size. High MW, narrow MWD and linearity in the polymer backbone can yield high crystallinity. The crystallization rate is enhanced by the presence of impurities such as catalysts, fillers and pigments.

In crystalline polymers, the degree of crystallinity is normally limited and the crystallites are separated by amorphous supercooled regions. Thus, PE, which crystallizes readily because of its
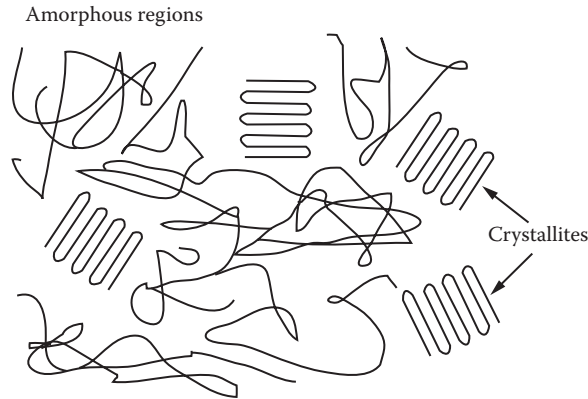
FIGURE 2.4 Schematic diagram of the amorphous (unordered) and crystalline (ordered) regions of a semi-crystalline polymer.

rather simple molecular structure, is tough and flexible rather than brittle because of the presence of the amorphous fraction. Of course, the ultimate strength depends as much on the weaker, amorphous part of the solid as on the strength of the crystallites. PVC, on the other hand, does not crystallize so readily and is more of a supercooled liquid.

The presence of chain branching will tend to reduce the possibility of an ordered arrangement and so reduce the crystallinity. For example, the crystallinity of LDPE (low density polyethylene) usually varies between 55% and 70%, compared with 75%–90% for HDPE (high density polyethylene).

Stretching a film orients the crystallites and realigns other molecules or segments of molecules, causing the total crystallinity of the film to increase. Such oriented films are generally tougher than either amorphous or unoriented crystalline materials. Orientation (see Section 5.7.1) and crystallinity are related in that only polymers that are capable of crystallization can be oriented. During orientation, crystallites become aligned and the total amount of crystalline material increases. The crystallites disappear when the polymer is heated, and the temperature at which crystalline regions vanish is called the crystalline melting point. Noncrystalline, amorphous polymers have no melting point. They simply soften when heated, in much the same way as glass. To summarize, high shear during processing and rapid cooling inhibit crystallinity; annealing and orientation enhance it.

Transparency of unfilled plastics is a function of crystallinity, with noncrystalline polymers such as PS and PC (polycarbonate) having excellent transparency. Other polymers range from cloudy to opaque, depending on the degree of crystallinity, the size of spherulites or other forms of crystal aggregates and the ratio of the density between the crystalline phase and the amorphous phase. Thus, relatively thick films of PE are translucent because of the presence of crystals. Long-chain, highly branched LDPE has low crystallinity and a broad melting point and LDPE blown films have very low haze and high gloss; HDPE chains are largely devoid of branching and so can be crystallized to a greater extent, resulting in translucent films.

2.3.5 Physical Transitions in Polymers

Simple molecules such as water can exist in any one of the three fundamental physical states; that is, solid, liquid and gas, according to the ambient conditions. The change from one state to another (transition) occurs at a specific, sharply defined temperature depending on the atmospheric pressure. In polymers, changes of state are less well defined. There is no transition from the liquid to the gaseous state because the temperature required to completely separate the molecules from one another is far too high; decomposition occurs instead. To date, there is no universally accepted scheme for classifying transitions in polymers, partly due to the diversity of experimental methods used for the study of these phenomena and partly to their complex nature.

Noncrystalline (amorphous) polymers are characterized by a glass transition at a temperature called the *glass transition temperature* (T_g); crystalline polymers are characterized by a melting transition at a temperature called the *crystalline melting temperature* (T_m). T_m and T_g are important parameters that define the upper and lower temperature limits for numerous applications, especially for semicrystalline polymers.

At a sufficiently high temperature, a thermoplastic polymer is a liquid. In this state, it consists of an amorphous mass of wriggling molecular chains. As it is cooled, the thermal agitation decreases, and, at the T_m, the polymer may crystallize. In the crystalline state, the molecules are all aligned and are packed together in a regular fashion. However, this state is not easily achieved because the molecular chains are normally entangled with each other. Therefore, many polymers will crystallize so slowly that supercooling is readily achieved. (Supercooling occurs when a material remains liquid below the temperature at which the crystalline solid melts.) These supercooled polymers remain viscous until a still lower temperature is reached at which the material vitrifies; that is, it becomes a glassy and relatively brittle solid. The temperature at which this occurs is the T_g. In the glassy state, a polymer has physical properties similar to a crystalline solid but has the molecular disorder of a liquid. T_g describes the approximate temperature below which segmental rigidity (i.e., loss of rotational and translational motion) sets in. Although a single value is often cited, in reality, a polymer undergoes the transition over a range of temperatures.

T_g is the main transition temperature found in amorphous polymers. The underlying molecular process is that frozen backbone sequences begin to move at the T_g. Therefore, T_g is determined not only by the main chain architecture but also by its immediate surroundings. Chain ends and low-MW plasticizers lower the T_g of a polymer; a sufficiently large number of cross-links will increase T_g. Above T_g, a few of the carbon atoms in each chain can still move with relative freedom, but below T_g, nearly all the carbon atoms become fixed, and only side groups or very short chain sections can change position.

In linear amorphous polymers such as PS, two transition temperatures are observed: a rigid solid-rubber transition known as the T_g and a very indefinite rubber-liquid transition referred to as the flow temperature, the term melting point being reserved strictly for crystalline polymers. The term *softening point* is associated with T_g for amorphous polymers and with T_m for highly crystalline polymers. In addition, there are many polymers that soften progressively between T_g and T_m, and the value determined for the softening point depends very considerably on the test method used. While melting is something that happens to a crystalline polymer, the glass transition happens only to polymers in the amorphous state. However, a given polymer will often have both amorphous and crystalline domains within it, so the same sample can show a T_m and a T_g, but the chains that melt are not the chains that undergo the glass transition.

The structure of crystalline polymers such as PE and isotactic PP is sufficiently regular so that they are capable of some degree of crystallization. The presence of crystalline regions in a polymer has large effects on such properties as density, stiffness and clarity. In a highly crystalline polymer, there is little difference in properties immediately above and below the glass transition. In fact, finding T_g can prove difficult with some highly crystalline polymers. This is largely because there is little scope for segmented motion as most segments are involved in a lattice formation in which they have low mobility.

For crystalline polymers, an approximate relationship between T_g and T_m is

$$T_g \approx \frac{2}{3} T_m \quad \text{(for unsymmetrical chains)} \tag{2.1}$$

and

$$T_g \approx \frac{1}{2} T_m \quad \text{(for symmetrical chains)} \tag{2.2}$$

when both temperatures are expressed in Kelvin. An important exception to this occurs with copolymers. Copolymerization also tends to broaden the temperature range over which T_g occurs, due to differences in chemical composition among the copolymer chains in the same sample. Generally, the crystalline copolymer is expected to have a lower melting temperature than the corresponding homopolymer. Ordered copolymers exhibit different transition behavior from random copolymers, generally showing a single, characteristic T_g and, if crystallizable, a single, sharp melting temperature.

The physical properties of a thermoplastic polymer depend on the values of T_m and T_g relative to room temperature. If both T_m and T_g lie below room temperature, the polymer is a liquid. If room temperature lies between T_m and T_g, the polymer is either a very viscous supercooled liquid or a crystalline solid. If both T_m and T_g are above room temperature, an amorphous polymer is glassy in nature, tending to be brittle. Other properties such as stiffness (modulus), refractive index, dielectric properties, gas permeability and heat capacity all change at T_g (Carraher, 2010).

The glass transition temperatures of the majority of the commercially important crystallizable polymers lie below 25°C as shown in Table 2.2, which also lists values for T_m and T_m/T_g. The T_g values are low for flexible, linear polymers such as the PEs, and relatively high for stiff chain polymers such as PET (poly(ethylene terephthalate)) and PC, which require higher temperatures for the onset of molecular motions necessary for the glass transitions.

Bulky side groups decrease the mobility of the chain and, thus, raise T_g. For instance, substitution of alternate hydrogens in the PE with methyl groups to give PP, or with phenyl groups to give PS, increases T_g from −110°C to −18°C and +100°C, respectively. Molecular symmetry tends to lower T_g. For instance, PVC has a T_g of 87°C, whereas for PVdC the T_g is −17°C.

Because bulky side groups tend to restrict molecular rotation, they also raise T_m. For example, the CH_3 side groups on PP are larger than the H atoms found on LDPE, and, therefore, the T_ms are 176°C and 115°C, respectively. The presence of polar side groups such as Cl, OH and CN,

TABLE 2.2

Glass Transition and Melting Temperatures of Some Polymers

Polymer	T_g (°C)	T_m (°C)	T_m/T_g[a]
Polyethylene			
Low density	−110	115	2.38
High density	−90	137	2.24
Polypropylene	−18	176	1.76
Poly(ethylene terephthalate)	69	265	1.57
Poly(ethylene naphthalate)	120	265	1.37
Polystyrene (isotactic)	100	240	1.38
Poly(vinyl chloride)	87	212	1.34
Poly(vinylidene chloride)	−17	202	1.86
Polyacrylonitrile	104	317	1.56
Poly(11-aminoundecanoic acid) (nylon-11)	51	185	1.41
Poly(caprolactam) (nylon-6)	47	220	1.54
Poly(hexamethylene adipamide) (nylon-6,6)	57	265	1.49
Poly(hexamethylene sebacamide) (nylon-6,10)	40	277	1.59
Poly(tetrafluoroethylene)	126	327	1.50
Poly(ethylene-co-vinyl alcohol) 29%	62	188	1.38
Poly(ethylene-co-vinyl alcohol) 44%	55	164	1.33
Polycarbonate	150	265	1.16

[a] Ratio calculated from T_m and T_g temperatures in Kelvin.

even though not excessively large, leads to significant intermolecular bonding forces and relatively high T_ms. For instance, the T_m for PVC is 212°C and for PAN (poly(acrylonitrile)) 317°C.

The temperatures T_m and T_g are governed by the strength of the intermolecular forces (just as in inorganic materials) and by the degree of flexibility and length of the chains. Thus, polar side groups such as chloride and hydroxyl groups favor higher melting and glass transition temperatures because they enhance the strength of the intermolecular bonds.

In some cases, the T_g can be lowered by as much as 100° by the efficient use of plasticizers. For example, pure PVC has a T_g of 87°C and is quite brittle at room temperature. The addition of only 15% plasticizer lowers this to 60°C, and with the addition of further plasticizer, PVC becomes tough and flexible at room temperature.

2.3.6 CHEMICAL STRUCTURE

Polymer chains can and do align themselves in ordered structures, and the thermodynamics of this ordered state determines such properties as the melting point, the glass transition temperature, other transition temperatures and the mechanical and electrical properties. However, it is the chemical nature of the polymer that determines its stability to temperature, light, water and solvents.

In the published literature, it is rare to find many details about a particular plastic packaging material apart from its name, sometimes the resin supplier and maybe if it has been oriented. This makes it virtually impossible to replicate the experimental conditions described in the literature since the range of polymers available is vast. For example, the website www.ides.com contains data sheets on over 77,000 commercial polymers from 694 resin manufacturers. Of course, many of these polymers are not approved or suitable for use in food packaging.

2.3.6.1 Polyolefins

Olefin means oil-forming and was originally the name given to ethylene. Today polyolefin is a common term in the plastics industry and refers to the family of plastics based on ethylene and propylene. The term *alkene* is used for hydrocarbons containing a carbon–carbon double bond, for example, ethylene, propylene and octene. The formula, MW, density and boiling point of the alkenes important in food packaging are given in Table 2.3. Polyolefins form an important class of thermoplastics and include low, very low, linear, medium and high density PEs and polypropylene (PP). Industry commonly divides PEs into the following broad categories based on density: HDPE 940–975 kg m^{-3}, MDPE 926–940 kg m^{-3}, LDPE 915–940 kg m^{-3}, LLDPE 915–925 kg m^{-3}, VLDPE 880–915 kg m^{-3}.

2.3.6.1.1 Low Density Polyethylene

This is the largest volume single polymer used in food packaging in both the film and blow molded form. It is a polymer of ethylene, a hydrocarbon gas available in large quantities as a by product of petroleum refining and other processes. Increasing quantities are now also being produced by the catalytic dehydration of ethanol produced by the fermentation of biobased materials, especially sugarcane (Morschbacker, 2009). PE was first produced by Imperial Chemical Industries (ICI) in 1933

TABLE 2.3

Molecular Details and Some Physical Properties of Common Hydrocarbon Monomers

Name	Molecular Formula	Molecular Weight	Density at 15°C (kg m^{-3})	Boiling Point (°C)
Ethylene	C_2H_4	28.05	1.180	−103.7
Propylene	C_3H_6	42.08	1.810	−47.6
Butene-1	C_4H_8	56.11	2.370	−6.3
Hexene-1	C_6H_{12}	84.16	0.678	63
Octene-1	C_8H_{16}	112.24	0.715	121

during a research program devoted to the effects of extremely high pressures on chain reactions, and the basic patent relating to polymerization of ethylene was granted in 1937. It was produced on a pilot plant scale that same year with full commercial-scale production commencing in 1939. For the first few years of its production, it was used in the electrical industry, particularly as an insulating material for underwater cables.

The polymerization of ethylene can occur over a wide range of temperatures and pressures but most commercial high pressure processes utilize pressures between 1000 and 3000 atm and temperatures between 100°C and 350°C (higher temperatures cause degradation of the PE).

The simplest structure for PE is a completely unbranched structure of $-CH_2-$ units as shown in Figure 2.1b. However, the vigorous nature of the high pressure process leads to a great deal of chain branching, with both short and long chains being formed. From Figure 2.3a, it can be seen that the branch contains a terminal methyl ($-CH_3$) group. A convenient way of characterizing branching is by the number of methyl groups per 1000 carbon atoms. Figure 2.5 is a schematic representation of linear and branched polymers of which HDPE short chain branches (SCB) and LDPE with long-chain branches (LCB) are good examples.

The branch chains prevent close packing of the main polymer chains, resulting in the production of PEs of relatively low density (typically 910–940 kg m^{-3}). MWs also tend to be relatively low. The great length of the polymer chains results in a certain amount of entanglement that prevents complete crystallization on cooling. When the polymer melt is cooled slowly, the crystallites may form *spherulites*.

The crystallinity of LDPE usually varies between 55% and 70%. The softening point is also affected by chain branching. The attractive forces between the chains are reduced because they are unable to approach each other closely, and, therefore, less energy (in the form of heat) is necessary to cause them to move relative to each other and thus flow. The softening point of LDPE is just below 100°C, thus precluding the use of steam to sterilize it in certain food packaging applications.

LDPE is a tough, slightly translucent material that can be blow extruded into tubular film, or extruded through a slit die and chill-roll cast, the latter process giving a clearer film. It has good tensile strength, burst strength, impact resistance and tear strength, retaining its strength down to −60°C. While it is an excellent barrier to water and water vapor, it is not a good barrier to gases. One of the great attributes of LDPE is its ability to be fusion welded to itself to give good, tough, liquid-tight seals. It cannot be sealed by high-frequency methods. It has excellent chemical resistance, particularly to acids, alkalis and inorganic solutions, but is sensitive to hydrocarbons, halogenated hydrocarbons, oils and greases. These latter compounds are absorbed by the LDPE, which then swells.

When a polymer is stressed in air to just below its yield point, stress cracking can occur after a certain period of time. However, when simultaneously exposed to both stress and a chemical medium, there is a dramatic reduction in the time to failure. This latter type of failure is termed
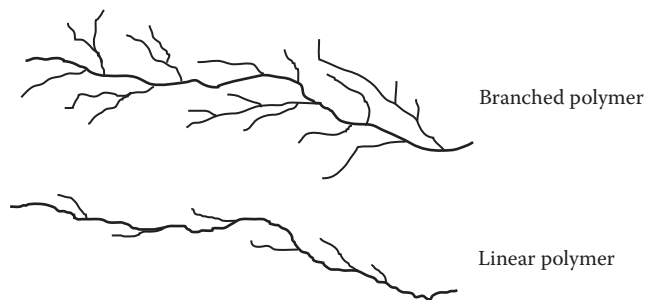

FIGURE 2.5 Schematic representation of branched and linear polymers showing the larger volume swept out by the branched structure, resulting in its lower density. Branches of the main backbone are indicated by narrower lines; they have no direct proportional relationship to cross-sectional dimensions. (From Brown, W.E., *Plastics in Food Packaging: Properties, Design and Fabrication*, Marcel Dekker, New York, p. 106, 1992.)

environmental stress cracking (ESC) and generally manifests itself as surface-initiated cracks or brittle failure (Scheirs, 2000). The stress may be internal (e.g., due to inbuilt molding stress) or external (such as mechanically applied stress). For example, ESC can occur when filled plastic containers are stacked on pallets in a warehouse or during transportation. Although ESC results from the interaction of the polymer with certain chemicals, it is a purely physical mechanism and not a chemical reaction (i.e., not a degradation in the true sense). Interactions between the fluid, the stress and the polymer include local yielding, fluid absorption, plasticization, craze initiation, crack growth and fracture without irreversible chemical change (i.e., without change in MW). The fluid only accelerates the mechanism. ESC is strongly related to the crystallinity of the polymer: the higher the crystallinity, the lower is the ESCR (environmental stress crack resistance). To reduce the crystallinity in polyolefins, comonomers such as butene, hexene, or octene can be used at less than 2%.

Essential oils (a common component of flavorings) and vegetable oils are capable of causing ESC in PEs and PS, and whenever a new flavor is introduced for an existing product, adequate testing must be carried out to ensure that ESC does not result. ASTM D2561 details test methods to measure the ESCR of containers, which is the summation of the influence of container design, resin, blow-molding conditions, posttreatment or other factors that can influence ESC. Three procedures are provided and procedure A can be useful for determining the effect of container design on the ESCR of a blow-molded HDPE package containing a liquid food product. However, any tests have to be correlated with actual field performance to be of practical use. The inability to measure the extent of ESC under controlled laboratory conditions makes it very difficult to understand the role of any one variable, the interaction between variables and the mechanisms of ESC.

PE is one of the most inert polymers and constitutes no hazard in normal handling.

Besides films, LDPE also finds use as a rigid packaging material as it can be easily blow molded into bottles where its flexibility enables the contents to be squeezed out. It is also widely used in the form of snap-on caps, collapsible tubes and a variety of spouts and other dispensers. The surface of PE containers can be treated with fluorine after blow molding to form a very thin, polar, cross-linked surface that decreases the permeability of the PE to nonpolar penetrants. It also eliminates the need for treating the surface by corona-arc discharge or flame techniques (see Section 5.3.1.2) to improve printability properties. The process has been cleared by the U.S. Food and Drug Administration (FDA) for use with food containers.

At the present time, there are many hundreds of grades of LDPE available, most of which differ in their properties in one way or another. Differences arise from the following variables:

1. Variation in the degree of short chain branching in the polymer
2. Variation in the degree of long chain branching
3. Variation in the average MW
4. Variation in the MWD (which may in part depend on the long-chain branching)
5. Presence of small amounts of comonomer residues
6. Presence of impurities or polymerization residues, some of which may be combined with the polymer

2.3.6.1.2 Linear Low Density Polyethylene

The first production of LLDPE was made in a solution process in 1960. Attempts in the 1970s to produce LDPE, either by low pressure gas-phase polymerization or by liquid-phase processes similar to those used for producing HDPE, led to the development of LLDPE and its commercialization in 1977. The term *linear* in LLDPE is used to imply the absence of LCBs. LLDPE has a similar molecular structure to HDPE and although virtually free of LCBs, it does contain numerous short side chains. These arise as a result of copolymerizing ethylene with a small amount of a higher alkene (α-olefin) such as butene. An α-olefin has the chemical formula C_xH_{2x} and a double bond at the primary or alpha (α) position. The general formula for ethylene copolymers with α-olefins is $-CH_2-CHR-$, where R is C_2H_5 in ethylene-1-butene copolymers, n-C_4H_9 in ethylene-1-hexene

copolymers and n-C_6H_{13} in ethylene-1-octene copolymers (Kissin, 2005). An increase in α-olefin content results in a decrease in crystallinity and density and a significant reduction of the polymer mechanical modulus (stiffness). Industry convention is not to indicate the presence of a copolymer such as octene in PE if its concentration is less than 10%.

Due to the linearity of its molecules, LLDPE is more crystalline and, therefore, stiffer but less transparent than LDPE, resulting in an increase of 10°C–15°C in the melting point of LLDPE compared to LDPE. The linearity provides strength, while the branching provides toughness. LLDPEs made with hexene and octene have better puncture resistance, impact strength and tear strength, but are more costly relative to LLDPE made with butene comonomer. The crystallinity and, consequently, the density of PE are controlled by the amount and type of α-olefin incorporated into the backbone. Decreasing α-olefin content leads to higher densities. The concentration of α-olefin in a copolymer varies from 1 mol% in MDPE to 2.5–3.5 mol% in LLDPE and 10–15 mol% in VLDPE (Kissin, 2005).

LLDPE combines the main features of both LDPE and HDPE, a major feature being that its MWD is narrower than that of LDPE. Generally, the advantages of LLDPE over LDPE are improved chemical resistance, improved performance at low and high temperatures, higher surface gloss, higher strength at a given density, better heat sealing properties and a greater resistance to ESC. In film form, LLDPE has higher tensile strength, puncture resistance, tear properties and elongation than LDPE. High-clarity film produced with LLDPE manufactured with metallocene catalysts is widely used for food packaging films and blow molding of bottles. The superior properties of LLDPE have led to its use in new applications for PE as well as the replacement of LDPE and HDPE in some areas; LLDPE is also often blended with LDPE.

2.3.6.1.3 *Very Low Density Polyethylene*

VLDPE (sometimes referred to as ultralow density polyethylene or ULDPE) is a subclass of LLDPE with a density <915 kg m^{-3}. It has an α-olefin content (normally octene) of >4 mol% and a crystallinity of <25% (Kissin, 2005). In stretch film applications, VLDPE exhibits excellent stretchability as well as good physical and cling properties. VLDPE can also be utilized for the production of blown film requiring a combination of excellent optical properties, outstanding tear and impact strength and very good sealability. VLDPE copolymer is also used as a skin layer in cast film and has excellent low temperature hot tack properties combined with outstanding tear and impact strength. VLDPE can be blended with other PE and PP-based resins to enhance clarity, sealability and toughness of the materials and can be used as a sealant in multilayer film structures. VLDPE also offers greater low temperature flexibility and flex crack resistance. VLDPE is mostly used for the packaging of fresh produce, milk, meat and cheese, as well as for the manufacture of multilayer coextruded film.

2.3.6.1.4 *High Density Polyethylene*

Prior to 1950, the only commercial polymer of ethylene was the highly branched polymer LDPE. The technique for making a linear polymer was discovered by Nobel laureate Karl Ziegler of Germany in the early 1950s. Ziegler prepared HDPE by polymerizing ethylene at low pressure and ambient temperatures using mixtures of triethylaluminum and titanium tetrachloride. Another Nobel laureate, Giulio Natta of Italy (he shared the Nobel Prize for chemistry with Ziegler in 1963), used these complex coordination catalysts to produce crystalline PP; these are now known as Ziegler–Natta (Z–N) catalysts. However, the credit for first producing stereospecific olefin polymers and HDPE belongs to J. Paul Hogan and Robert Banks of Phillips Petroleum Company, who did so in 1952 using chromium trioxide supported on a silica-alumina catalyst (Carraher, 2010).

HDPE is a nonpolar, linear thermoplastic that possesses a much more linear structure than LDPE. It has up to 90% crystallinity, whereas LDPE exhibits crystallinities as low as 50%. Although some branch chains are formed, these are short and few in number. HDPE film is stiffer and harder than LDPE and densities range from 940 to 975 kg m^{-3}. Because HDPE contains a crystalline phase and

an amorphous phase, the measured density directly reflects the percentage of each. Typical homo-polymer is normally 70% crystalline and has a density of 960–965 kg m⁻³. Higher densities can be achieved by low MW and slow cooling. The MW of typical commercial HDPE grades can vary from 20,000 to >3,000,000, depending on the application. Its softening point is about 121°C, and its low temperature resistance is about the same as LDPE. Tensile and bursting strengths are higher but impact and tear strengths are both lower than LDPE. Of interest is the fact that due to the linear nature of the HDPE molecules, they tend to align themselves in the direction of flow and, thus, the tear strength of the film is much lower in the machine direction (MD) than the transverse direction (TD). This difference can be accentuated by orientation to give a built-in tear tape effect.

The chemical resistance of HDPE is also superior to that of LDPE and, in particular, it has better resistance to oils and greases. The film offers excellent moisture protection, a much decreased gas permeability compared with LDPE film, but is much more opaque. Heat sealing is considerably more difficult compared to LDPE film. The melting point is a function of both MW and branch content. A decrease in MW from ~1,000,000 to 40,000 is accompanied by a decrease in melting point from 137°C to 128°C.

HDPE film has a white, translucent appearance and, therefore, tends to compete more with paper than transparent films. To be competitive with paper on a price-per-unit-area basis, it must be thin, and, consequently, much of the HDPE film used is only 10–12 μm thick.

HDPE is blow molded into bottles for a variety of food packaging applications, although its uses in this area have tended to be taken up by PET bottles that generally have better barrier properties than HDPE.

The basic properties of various PE films are shown in Table 2.4. The melting point of PEs is primarily a function of their densities, the melting point increasing with density, as does the softening temperature.

2.3.6.1.5 Irradiated Polyethylene

Irradiated PE is produced by passing ordinary LDPE film continuously under an electron beam accelerator that produces high-energy ß rays. This converts it to an infusible film, which causes cross-linking between the chains and gives it exceptional strength from the point of view of stretch resistance and shrink tension. Other effects include the evolution of H_2 and a reduction in crystallinity. The process slightly reduces gas and water vapor transmission rates but increases the heat sealing range to make a practical shrink film from PE. The film has good clarity. It is sealed by welding the overlaps together on a hot plate and shrunk by passing through a hot air tunnel at 220°C.

2.3.6.1.6 Polypropylene

Early attempts to polymerize propylene using the high pressure process used to make LDPE gave only oily liquids or rubbery solids of no commercial value. Work by Natta in Italy using Ziegler-type catalysts led to the development in 1954 of a stereospecific catalyst that controlled the position of each monomer unit as it was added to the growing chain, thus giving a polymer of regular structure. Today, typical processes take place at about 100 atm and 60°C. A significant innovation in PP

TABLE 2.4
Basic Properties of Various PE Films

Type of Polyethylene	Water Vapor Transmission	Gas Transmission		Tensile Strength (MPa)	Softening Point (°C)	CH₃ Groups per 1000 C's
		O_2	CO_2			
Low density (920 kg m⁻³)	1.4	500	1350	9–15	120–180	20–33
Medium density (940 kg m⁻³)	0.6	225	500	21	120–180	5–7
High density (960 kg m⁻³)	0.3	125	350	28	135–180	<1.5

production has been the Spherizone process technology, which is based on a multizone circulating reactor (MZCR). In comparison to traditional multistep technologies, the MZCR provides a step change in the polymer homogeneity of the final product by continuously circulating the growing polymeric granules between two interrelated zones where different gas phase compositions are realized (Mei et al., 2009). The Spherizone process can produce all conventional PP grades as well as new and improved products including highly modified random copolymers. In addition to traditional Z–N catalysts, metallocene catalysts are also being introduced in PP manufacture (see next section).

PP is a linear polymer containing little or no unsaturation. Depending on the type of catalyst and polymerization conditions, the molecular structure of the resulting polymer consists of the three different types of stereo configurations: *isotactic*, *syndiotactic* and *atactic*, as shown in Figure 2.6. Industrial processes are designed to minimize the production of atactic PP (where the methyl groups are randomly distributed on either side of the chain), which results when polymerization occurs in the absence of stereospecific catalysts. This noncrystalline material has a density of about 850 kg m^{-3} and is soft, tacky and soluble in many solvents. It is a lower-value product and finds use mainly in hot-melt adhesives.

The most regular crystalline polymer produced by stereospecific catalysts is known as the isotactic form, the name stemming from the original idea that the methyl groups were always above or below the horizontal plane. Isotactic PP, the most common commercial form of PP homopolymer, is never perfectly stereoregular, the degree of isotacticity varying from 88% to 97%. It is a highly crystalline material with good chemical and heat resistance but poor transparency. Two other forms are syndiotactic, where the methyl groups alternate above and below the horizontal plane, and stereoblock, where blocks of methyl groups are alternately above and below the horizontal plane. The regular helices of the isotactic form can pack closely together, whereas the atactic molecules have a more random arrangement.

While atactic PP is an amorphous, rubbery material of little value, isotactic PP is stiff, highly crystalline and has a high melting point. In commercial polymers, the greater the amount of isotactic material, the greater is the crystallinity and, thus, the greater the softening point, tensile strength and hardness, all other structural features being equal (Carraher, 2010). Impact-resistant PP is a mixture of isotactic PP and amorphous ethylene–propylene copolymer.

PP has a lower density (900 kg m^{-3}) and a higher softening point (140°C–150°C) than the PEs, low water vapor transmission, medium gas permeability, good resistance to greases and chemicals, good abrasion resistance, high temperature stability, good gloss and high clarity, with the latter two factors making it ideal for reverse printing.

PP can be blow molded and injection molded, the latter process being widely used to produce closures for HDPE, PET and glass bottles, as well as thin-walled pots and crates. The T_g of PP is placed between 10°C and −20°C with the result that the polymer can become brittle as subzero
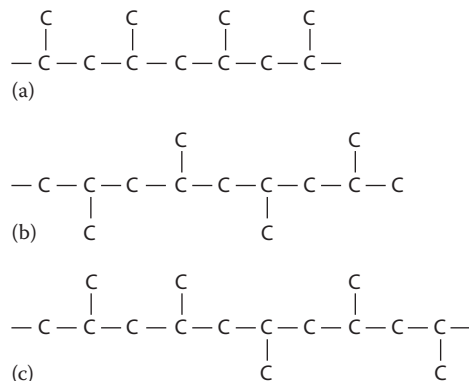

FIGURE 2.6   Types of PP: (a) isotactic, (b) syndiotactic and (c) atactic.

temperatures are approached. The T_m is in the range of 160°C–178°C, enabling foods inside PP containers to be sterilized by heat or reheated in microwave ovens. Copolymerization with 4%–15% ethylene improves the strength and clarity, reduces stiffness, increases impact resistance and lowers the T_m and T_g. For example, homopolymer PP with 3%–4% atactic fraction has a T_m of ~165°C, while a random copolymer with 2% ethylene has a T_m of about 150°C. Such copolymers are often preferred to the homopolymer in injection molding and bottle blowing applications and also find use in shrink wrapping where the lower melting point is an advantage.

Although free from ESC problems, PP is more susceptible to oxidative degradation at elevated temperatures, necessitating the inclusion of antioxidants in all commercial PP compounds. Whereas PE cross-links on oxidation, PP degrades to form lower MW products. A similar effect is observed when PP is irradiated.

Nonoriented PP film is often referred to as cast PP film because it is generally made by the chill-roll cast process, although other methods can be used. PP film is a very versatile material, being used as a thermoformable sheet, in cast form for film and bags, and as thin, strong biaxially oriented films for many applications. Cast and oriented PP are sufficiently different that they do not compete for the same end uses, the cost of cast PP being much lower than that of oriented PP. The cast form has PE-type uses while the oriented form has regenerated cellulose film (RCF)-type uses and has largely replaced RCF in food packaging applications. Cast PP use in food packaging is limited owing to its brittleness at below freezing temperatures, and it is generally not recommended for use with heavy, sharp or dense products unless laminated to stronger, more puncture-resistant materials. The relatively high temperature resistance of PP permits its use as the seal layer in retortable pouches, hot-filled bottles and microwavable packaging.

In recent years there has been a large increase in the use of oriented polypropylene (OPP) for food packaging. Wide variations are possible in the extent of orientation in two directions, leading to a wide range of properties. However, biaxially oriented polypropylene (BOPP) film has a high clarity because layering of the crystalline structures reduces the variations in refractive index across the thickness of the film and this in turn reduces the amount of light scattering. OPP can be produced by the blown tubular or high expansion bubble process, or the tenter frame process.

BOPP film has a tensile strength in each direction roughly equal to four times that of cast PP film. Although tear initiation is difficult, tear resistance after initiation is low. Biaxial orientation also improves the moisture barrier properties of PP film and its low-temperature impact strength. OPP film is not considered to be a gas barrier film but this deficiency can be overcome by coating with PVdC copolymer. OPP films often have a stiff feel and tend to audibly crinkle.

If heating sealing is required, PP is normally coated with a lower melting point polymer because shrinkage tends to occur when highly stretched film is heated. LDPE, PVdC copolymer and acrylic polymers are used as fusible coatings for OPP film. LDPE is cheaper, but PVdC copolymer confers far better resistance to water vapor and O_2 permeability; acrylic polymer adds no barrier properties to OPP film.

Another addition to the family of OPP films is white opaque film, generally made by the tenter frame process and known as cavitated or pearlized film because the diffusion of light gives the film the visual effect of pearlescence. Homopolymer resin is evenly mixed with a small amount of foreign particulate matter such as starch or titanium dioxide. In one product, when the thick filled sheet is oriented, the PP pulls away from each particle creating an air-filled void or closed cell. After heat stabilization, the OPP film is similar to a micropore foamed product. In the second product, the material produced is a filled film without voids, the opacity being a direct result of the amount of particulate material included in the film. The primary opacification is caused by light rays bouncing off the PP cell walls and the air within each cell. White opaque OPP film is widely used for cold seals and finds application in snack food packaging, candy-bar overwraps, ice cream novelties, beverage bottle labels, soup wrappers and other applications that have traditionally used specialty paper-based packaging materials (Mount, 2009).

Another new technology exploits the unique combination of properties, including melt strength, of PP grades for use in foam applications. For example, foamed PP food packaging trays are used for meat, fish, poultry, fruits and cheese where the material overcomes the typical expanded polystyrene (EPS) limitations, that is, aromatics release and susceptibility to cracking (Mei et al., 2009).

2.3.6.1.7 Metallocenes

Metallocenes are a relatively old class of organometallic complexes first discovered in 1951. They are based on a metal atom such as titanium, zirconium or hafnium. As early as 1957 Natta reported the (unsuccessful) polymerization of ethylene with a titanocene catalyst. The current interest in metallocenes originated with a discovery by Kaminsky at the University of Hamburg in the mid-1970s. While studying a homogenous polymerization system, water was accidentally introduced into the reactor, leading to an extremely active ethylene polymerization system. Subsequent studies revealed that the high activity was due to the hydrolysis of the cocatalyst trimethyl aluminum. Because of the discovery of this new cocatalyst, metallocenes are sometimes called "Kaminsky" catalysts (Scheirs and Kaminsky, 2000).

Metallocene-based catalyst technology has revolutionized the polyolefin industry, particularly in the PE and PP markets. Metallocenes have been deemed the single-most important development in catalyst technology since the discovery of Z–N catalysts. Compared to conventional Z–N technology, metallocenes offer some significant process advantages and produce polymers with very favorable properties. The development of metallocene polymers has brought forth the concept of single-site catalysis of which metallocenes are just one example, albeit the first commercial success.

Metallocene catalysts allow the production of consistent, controllable molecular polymer structures that can be designed to improve toughness, provide excellent impact resistance, reduced haze and better clarity (Janiak, 2002). Since 1991, various polyolefins have been produced with the aid of single-site metallocene catalysts. By altering the metallocene structure, the types of polymers produced can be controlled. This characteristic of metallocenes is very important when producing polymers that can have different side branches such as isotactic and syndiotactic PP. These new polymers have features such as lower melting points, better optical characteristics, better heat stability, increased impact strength and toughness, better melt characteristics and improved clarity as films. These advantages are obtained through the control of polymer MW, MWD (elimination of both high- and low-MW fractions), comonomer distribution and content and tacticity.

Metallocenes are important in the production of PE in that they allow the control of side branching due to the single activity site found at the metal center. Traditional Z–N catalysts are hard to control because they have several active sites and polymers are produced by adding monomers to the end of the chain.

Using traditional catalysts, PP is produced as a mixture of the three forms consisting of 95% isotactic, some undesirable atactic and even less of the syndiotactic PP. With metallocene technology, the amount of each type of PP can be controlled through changes in the catalysts' stereochemistry. Isotactic PP made with classical Z–N catalysts still has some atactic fractions. The presence of atactic PP fractions reduces stiffness, heat distortion temperature and cleanliness. The absence of atactic PP in metallocene isotactic PP means higher stiffness, higher use temperature and lower extractable content (Janiak, 2002). New isotactic PP resins can be produced with improved stereoregularity and controlled comonomer content resulting in higher stiffness, clarity and melt strength. Comonomers employed to produce these enhanced PP resins include ethylene, butene and octene. To differentiate polymers produced with metallocenes from polymers manufactured using older, conventional catalysts, a lower case m is placed in front of the polymer abbreviation, for example, mLDPE.

Metallocene-catalyzed resins have expanded beyond PEs and PPs to polystyrenes, ethylene–styrene copolymers and cyclic olefin copolymers, and polymers made using metallocene catalysts have achieved significant market penetration in a wide array of applications including food packaging films and stretch/shrink films.

2.3.6.2 Copolymers of Ethylene

For copolymers of ethylene, the other comonomer can be an alkene such as propene, butene, hexene or octene, or a compound having a polar functional group such as vinyl acetate (VA), acrylic acid (AA), ethyl acetate (EA), methyl acrylate (MA) or vinyl alcohol (VOH). The polymer can be classified as either a copolymer or homopolymer if the molar percent of the comonomer is less than 10%. LLDPE and LDPE-PP copolymers discussed earlier can rightly be considered as copolymers of ethylene. In addition, there are four further copolymers of ethylene of particular importance in food packaging.

2.3.6.2.1 Ethylene–Vinyl Acetate

Ethylene–vinyl acetate (EVA) is a random copolymer of ethylene and VA whose properties depend on the VA content and MW. EVA with a VA content of 3%–12% is similar in flexibility to plasticized PVC and has good low-temperature flexibility and toughness. The impact strength increases with VA content and MW. As the VA content increases, EVA becomes less crystalline and more elastic; as the crystallinity decreases, the permeability to gases, moisture, fats and oils increases and the clarity improves. EVA is totally amorphous (transparent) when the VA content reaches 50%. As the MW increases, the viscosity, toughness, heat seal strength, hot tack and flexibility all increase. The absence of leachable plasticizer provides a clear advantage over plasticized PVC in some food applications. The addition of antiblocking and slip additives reduces sparkle and clarity and increases haze.

EVA copolymers are not competitive with normal film because of their high surface tack and friction that make them difficult to handle on conventional processing machinery. However, they do have three advantages over LDPE: the heat sealing temperature is lower, the barrier properties are better and they have excellent stretch properties, the first 50% of extension at room temperature being elastic. Thus, they find use as a stretch film for food packaging (particularly fresh meat) and cling-wrap purposes and have replaced PVC for many stretch-wrapping applications. Some EVA is used in coextrusion processes for the manufacture of laminated material. As a heat sealing layer, EVA is used in the extrusion coating of PET and BOPP films.

2.3.6.2.2 Ethylene–Vinyl Alcohol

EVOH copolymers were commercialized in Japan by the Kuraray Company in 1972 and in the United States and Europe in the early 1980s. EVOH copolymer is produced by transforming the VA group into VOH in a controlled hydrolysis of EVA copolymer; there is no VOH involved in the copolymerization (Marten, 2002). Ethylene and vinyl acetate are copolymerized in a solvent system to produce EVA and then saponified (hydrolyzed) with NaOH in a methanol mixture to produce EVOH, followed by coagulation and washing to become purified EVOH copolymer (Ozeki and Kim, 1996). The vinyl alcohol base has exceptionally high gas barrier properties but is water soluble and difficult to process.

EVOH copolymers offer not only excellent processability, but also superior barriers to gases, odors, aromas and solvents. It is these characteristics that have allowed plastic containers containing EVOH barrier layers to replace many glass and metal containers for packaging food.

EVOH copolymers are highly crystalline in nature and their properties are very dependent on the relative concentration of the comonomers. Generally, as the ethylene content increases, the gas barrier properties decrease, the moisture barrier properties improve and the resins process more easily. For example, EVOH of 27 mol% ethylene offers a barrier to dry O_2 10 times as great as one of 42 mol% ethylene, while providing a poorer barrier to moisture vapor (Brown, 1992). When the VOH content ranges from 50% to 70%, the EVOH copolymers combine the processability and water resistance of LDPE with the gas and odor barrier properties of polyvinyl alcohol (PVOH).

The most outstanding characteristic of EVOH is its ability to provide a barrier to gases and odors. Its use in a packaging structure enhances flavor and quality retention by preventing O_2

from penetrating the package. In those applications where gas-fill packaging techniques such as MAP are used, EVOH effectively retains the CO_2 or N_2 used to blanket the product. EVOH also provides a very high resistance to oils and organic vapors, but this resistance decreases as the polarity of the penetrant increases. For example, the resistance to linear and aromatic hydrocarbons is outstanding, yet for ethanol and methanol it is low, with EVOH absorbing up to 12% of ethanol (Hernandez, 1997).

Due to the presence of hydroxyl groups in their molecular structures, EVOH resins are hydrophilic and will absorb moisture. As moisture is absorbed, the gas barrier properties are affected. However, through the use of multilayer technology to surround the EVOH layer with high moisture barrier resins such as polyolefins, the moisture content of the barrier layer can be controlled.

EVOH resins have high mechanical strength, elasticity and surface hardness, very high gloss, low haze, excellent abrasion resistance, very high resistance to oils and organic solvents and provide an excellent barrier to odors. When used as the core of a multilayer material, they provide excellent performance. EVOH copolymers are the most thermally stable of all the high barrier resins. This stability allows the regrinding and reuse of scrap generated during processing back into the package being produced. Many of the rigid packaging containers being produced today have regrind layers containing up to 15% EVOH.

Rigid and semirigid containers such as bottles, trays, bowls and tubes, flexible films and paperboard beverage cartons containing EVOH as the functional barrier layer are commercially available. Most multilayer structures have five or six layers, with seven- and nine-layer structures being produced for special applications, the EVOH always being surrounded by polymers such as polyolefins that provide a good barrier to water vapor. When using EVOH in multilayer structures, it is necessary to use an adhesive or tie layer to gain adequate bonding strength to the other polymers (Foster, 2009).

Coextruded films containing EVOH together with LDPE, LLDPE, HDPE and EVA are used for milk powder and wine in bag-in-box packs. Coextruded, blow-molded bottles containing EVOH with PP, PET and HDPE are used for a wide range of foods including ketchup, mayonnaise, fruit juices, carbonated beverages and beer. EVOH is also used in coextruded cups and trays and thermoformed with HDPE and PP for a wide range of foods.

For multilayer packages that will be retorted after filling, the structures outlined previously may not provide a sufficient barrier to water vapor to prevent unacceptable quantities of O_2 permeating into the product. Recently, Mokwena et al. (2011) measured oxygen transmission rates (OTRs) of two multilayer films containing EVOH after water absorption at 121°C to simulate retorting conditions. The films were PET/EVOH/PP and PET/PP/PA-6/EVOH/PA-6/PP, respectively. OTR increased with water absorption for both films, the OTR of the first film going from 0.034 to 3 mL m^{-2} day^{-1} after 60 min, while the second film went from 0.021 to 5.25 mL m^{-2} day^{-1}; water absorbed by the films after 60 min was 7.3% and 5.3%, respectively.

2.3.6.2.3 *Ethylene–Acrylic Acid*

By copolymerizing ethylene with acrylic acid, a copolymer containing carboxyl groups along the main and side chains of the molecule is obtained. EAA copolymers are flexible thermoplastics possessing chemical resistance and barrier properties similar to LDPE. However, EAA is superior to LDPE in strength, toughness, hot tack and adhesion. Crystallinity decreases, clarity increases, adhesion strength increases and heat seal strength decreases with increasing AA content.

A related copolymer is ethylene–methacrylic acid (EMA) produced by free radical copolymerization of ethylene with methacrylic acid. EAA and EMA copolymers have excellent adhesion to metals such as aluminum and are used in adhesive lamination as an extrusion-coating tie layer between aluminum foil and other polymers. EAA and EMA are also used as precursors to ionomers (Malpass, 2010). EAA films are used for the packaging of foods such as meat, cheese and snack foods, and in skin and blister packaging.

2.3.6.2.4 Ionomers

Ionomeric polymers with unique properties result when olefinic polymers are prepared in the presence of metallic salts of organic monomers,. The term ionomers was coined by researchers at DuPont in the 1960s to describe polymers having both ionic and covalent linkages and marketed under the trade name Surlyn® (Morris, 2009). They are prepared by copolymerizing ethylene with a small amount (1%–10% in the basic patent but today it ranges from 7% to 30%) of an unsaturated carboxylic acid such as acrylic acid or methacrylic acid using the high-pressure process. Such copolymers are then neutralized to varying degrees (15%–80%) with the derivative of a metal such as sodium or zinc salts, lithium methoxide or lithium acetate, causing the carboxylic acid to ionize. This leads to the formation of ionic cross-links that confer enhanced stiffness, transparency and toughness on the material at ambient temperatures (the puncture resistance of ionomer film is equal to LDPE film of twice the gauge) as well as higher melt strength. There are more than 50 commercial grades of ionomer resin with a wide range of properties. A recent development has been a potassium-based ionomer that can be blended with polyolefins to reduce static buildup (Morris, 2009).

In comparison with LDPE, ionomers have excellent oil and grease resistance, excellent resistance to ESC, greater clarity, lower haze, greater abrasion resistance and higher water vapor permeability due to lower crystallinity. Ionomers containing unneutralized acid groups have found wide utility as the seal layer in extrusion-coated aluminum foil structures (the acid groups provide adhesion to the foil) and are particularly useful in composite structures with films and paperboard to provide an inner layer with good heat sealability. Ionomers have the ability, shared with certain other polymers, of bonding by heat sealing through particles of food that may be trapped between package layers during the filling process. Ionomers also have excellent hot tack—the ability of a newly formed (still molten) heat seal bond to resist an opening force (Morris, 2009). Laminated or coextruded films with PAs or polyesters are widely used for packaging meat and cheese where formability, toughness and visual appearance are important (Brown, 1992). Their exceptional impact and puncture resistance (even at low temperatures) makes them ideal for skin packaging of sharp objects such as meat cuts containing bone. Another advantage is their high infrared absorption that leads to fast heating during the shrink process. Their disadvantages include their poorer slip and block characteristics and relatively poor barrier to O_2.

2.3.6.2.5 Cyclic Olefin Copolymer

COC is based on the polymerization of ethylene and norbornene (2,2,1 bicyclohept-2-ene) using metallocene catalysts. Norbornene (C_7H_{10}) consists of a cyclohexene ring bridged with a methylene group in the *para* position; it carries a double bond that induces significant ring strain and reactivity. COC copolymers can have a T_g ranging from 33°C to 180°C, depending on the comonomer ratio, and a density from 1020 to 1080 kg m^{-3}. As an amorphous polymer, COC does not have a T_m and instead starts to soften above the T_g, becoming increasingly fluid as temperatures are increased. This colorless, crystal-clear material offers strong compatibility with conventional PEs but is most compatible with highly linear PEs such as LLDPE. Those most commonly used for olefin blends have T_gs ranging from 33°C to 78°C; higher T_g grades are sometimes used to enhance the heat resistance of films. On a molar basis, COC typically contains 40%–70% ethylene. However, because of the relatively high MW of the comonomer, this corresponds to only 15%–35% ethylene on a weight basis. COC are specialty resins produced in very small quantities (Malpass, 2010).

COC is also being increasingly used in polyolefin blends to produce barrier films for packaging because it has one of the highest moisture barriers of any polymer (four to five times better than LDPE). COC is not considered to have a high gas barrier but it is still significantly better than LDPE and is a much better barrier to aromas. When incorporated into the heat seal layer of bags or stand-up pouches, COC can improve hot tack and ultimate seal strength without altering the seal initiation temperature.

COC is most commonly used as a blend component to enhance modulus and allow thickness reduction of monolayer films. As little as 10% of COC added to LLDPE will double or triple its modulus while maintaining low haze. As part of a coextruded structure, a LLDPE/COC blend often

allows a thinner film to provide the same performance at a reduced cost per m² of film. However, addition of COC to LLDPE significantly reduces tear strength, especially in the machine direction, although it does improve the puncture resistance of the film. Typical uses for COC blends include fresh-cut produce bags and pouches for drinks, cereals, candies, soups and pet foods. Monolayer COC films have good twist-wrap behavior and can be easily metallized.

2.3.6.3 Substituted Olefins

The simplest substituted olefins are those in which each ethylene group has a single substituent; these monomers are called *vinyl* compounds. Disubstituted monomers with two substituents on the one carbon are called *vinylidene*. Structures of some common monomers based on the ethylene chain are shown in Figure 2.7.

2.3.6.3.1 Polystyrene

If ethylene and benzene are reacted together with a suitable catalyst, ethylbenzene is formed and, by a process of catalytic dehydrogenation, styrene (commonly known as vinyl benzene) is produced. PS is made by the addition polymerization of styrene and typically consists of ~1000 styrene units. The polymer is normally atactic and is thus completely amorphous because the bulky nature of the benzene rings prevents a close approach of the chains. With the use of special catalysts and polymerization techniques, isotactic PS has been prepared but it reverts to the atactic form on melting.

PS was the first of the moldable clear rigid plastics to reach the commercial market in large volumes in the late 1940s. It could be rapidly molded into finished shapes because of its ease of flow in the melt and its fast-setting nature from the melt. However, an increase in monomer content from 0% to 5% can cause a 30°C reduction in softening point.

2.3.6.3.1.1 General-Purpose Polystyrene In this form, it is commonly referred to as crystal-grade PS and is the unmodified homopolymer of styrene. At temperatures in the range at which food packages are stored it is glassy and noncrystalline since its T_g is in the range 90°C–100°C because of the stiffening effect of the benzene ring. This results in a material that is stiff and brittle at room temperature with no melting temperature but excellent optical properties.

PS makes a distinctly metallic sound when dropped onto a hard surface. It has a high refractive index (1.592), which gives it a particularly high brilliance. Although acids and alkalis have no effect on it, it is soluble in higher alcohols, ketones, esters, aromatic and chlorinated hydrocarbons and some oils. Even if it is not soluble in the material, ESC and even chemical decomposition of PS
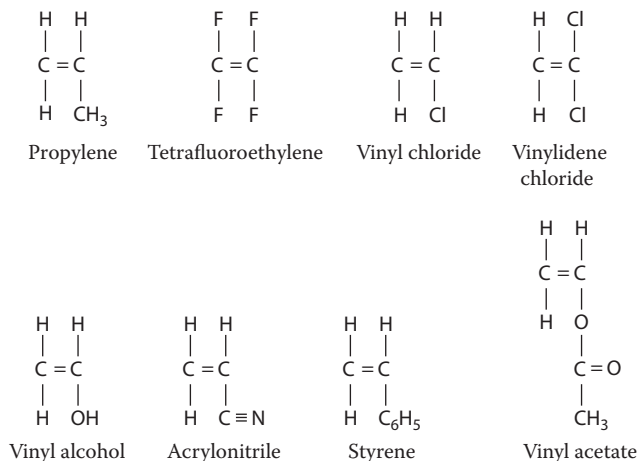

FIGURE 2.7 Structure of some common monomers based on ethylene.

may occur. The extent of the decomposition depends on the grade of PS, the time and temperature of exposure and the concentration of the reagent. In addition, many materials that do not attack PS individually do so in combination, so shelf life studies before marketing a food in PS are essential to test for any synergistic effect. PS is a poor barrier to water vapor and gases.

Crystal-grade PS can be made into film but it is brittle unless the film is biaxially oriented. The oriented film can be thermoformed into a variety of shapes, although special techniques have to be used because orientation gives it a tendency to shrink on heating. Oriented PS film, in addition to being heat shrinkable, offers a high degree of optical clarity, high surface gloss, and excellent dimensional stability, particularly with regard to relative humidity. One of its largest uses is for packaging fresh produce because it is highly permeable to O_2 and water vapor.

New applications of PS involve coextrusion with barrier resins such as EVOH and PVdC copolymer to produce thermoformed, wide-mouthed containers for shelf-stable food products and multilayer blow-molded bottles.

2.3.6.3.1.2 High Impact Polystyrene To overcome the brittleness of PS, synthetic rubbers (typically 1,3-butadiene isomer $CH_2=CH–CH=CH_2$) can be added during polymerization at levels generally not exceeding 25% w/w for rigid plastics. The rubbers act by restricting the propagation of microcracks formed during impact loading. At the start of the process, polybutadiene is dissolved in the styrene monomer. As the polymerization proceeds, two phases are formed: a polybutadiene-rich phase and a PS-rich phase with grafted polybutadiene. The grafting arises when some of the styrene-free radicals react with the polybutadiene. Controlling the sizes of the homopolymer blocks formed by each of the monomers determines the properties of the resulting copolymer. Blocks of PS in SB (styrene–butadiene) copolymers confer typical styrenic properties of stiffness, glossiness and ease of processing, while blocks of polybutadiene contribute great flexibility and extensibility. SB copolymer is sometimes referred to as K resin. Although copolymerization increases impact strength and flexibility, the transparency, tensile strength and thermal resistance is much reduced. The chemical properties of this toughened or high impact polystyrene (HIPS) are much the same as those for unmodified polystyrene.

HIPS is an excellent material for thermoforming. Because it is transparent, the use of radiant heat for thermoforming is inefficient and pigmented sheet is often used. It is injection molded into tubs that find wide use in food packaging, despite their being opaque. Transparent unit packs are made from untoughened PS.

2.3.6.3.1.3 Expandable Polystyrene Sheet The properties of PS that make it useful for many applications as a solid polymer also make it very desirable as a foam. PS foam has a high tensile strength, good water resistance, low moisture transmission, ease of fabrication and low cost. Closed-cell foams have excellent thermal insulating capability, low weight and good cushioning characteristics. The combination of those properties provides a wide spectrum of products.

Extruded PS foam sheet is a closed cell, 0.13–6.4 mm thick sheet with densities ranging from 32 to 160 kg m^{-3}. It can be made by a variety of extrusion processes but is most commonly made using a tandem extrusion process. A large percentage of foam sheet is thermoformed using matched metal molds. CO_2 is commonly used as a blowing agent, which results in improved organoleptic properties that have opened up new applications in food packaging. Most PS foam sheet is used for disposable packages such as meat and produce trays, egg cartons, disposable dinnerware and containers for take-away or carry-out meals.

2.3.6.3.2 Poly(Vinyl Chloride)
Ethylene dichloride is formed by an addition reaction of chlorine with ethylene, and the dichloride is then dehydrochlorinated or "cracked" to give vinyl chloride monomer (VCM). Addition polymerization of VCM produces PVC with a DP ranging from 500 to 3500. From the structure of VCM, it can be seen that addition of molecules to the growing chain can take place either head to head, head

to tail or in a completely random manner. PVC polymerizing in either of the first two forms would be expected to be crystalline, while the random arrangement would be amorphous. Generally, PVC polymerizes in the atactic form and, thus, is largely an amorphous polymer.

In 1974, there was widespread publicity resulting from the announcement that a rare and invariably fatal form of liver cancer had been diagnosed among workers in VC polymerization plants in Britain and the United States. Food and drug administrators around the world became particularly interested in the VCM content of PVC material used for food packaging and the likelihood of it migrating into the food. This topic is discussed further in Chapter 22 but suffice it to say that the levels of VCM in PVC packaging material are currently extremely low.

Vinyl polymers and copolymers make up one of the most important and diversified groups of linear polymers. This is because PVC can be compounded to produce a wide spectrum of physical properties. This is reflected in the variety of uses to which it is put: from exterior guttering and water pipes to very thin, flexible surgical gloves. It is the second-most widely used synthetic polymer after PE and is commonly referred to simply as "vinyl."

A range of PVC films with widely varying properties can be obtained from the basic polymer. The two main variables are changes in formulation (principally plasticizer content) and orientation. The former can give films ranging from rigid, crisp films to limp, tacky and stretchable films. The degree of orientation can also be varied from completely uniaxial to balanced biaxial.

Unplasticized PVC tends to degrade and discolor at temperatures close to those used in its processing, so suitable stabilizers have to be included in the formulation. The stabilizers used are generally the salts of tin, lead, cadmium, barium, calcium or zinc along with epoxides and organic phosphites, and these must be carefully selected for nontoxic applications. The use of lead and cadmium compounds as stabilizers is not generally allowed in food contact materials. Approval by the U.S. FDA of certain octyltin compounds for use in stabilizing PVC during blow molding of containers expanded the use of this polymer for food packaging.

Extremely clear and glossy films can be produced having a high tensile strength and stiffness. The density is high at around 1400 kg m^{-3}. The water vapor permeability is higher than that of the polyolefins but the gas permeability is lower. Unplasticized PVC has excellent resistance to oils, fats and greases and is also resistant to acids and alkalis.

To a large extent, the properties of plasticized PVC depend on the type of plasticizer used, as well as the quantity. For these reasons, it is difficult to be very specific about the physical properties of PVC due to the wide range of plasticization possible. Rigid PVC has a T_g of 82°C, with plasticizers decreasing T_g and the processing temperature.

The plasticizers used (about 80% of all plasticizers are used with PVC) are organic liquids of low volatility that facilitate internal movement of the molecular chains. Combinations of different compounds are used, the esters of phthalic acid being the most common. The amount can vary up to 50% of the total weight of the final material. Because plasticizers are not bound chemically, they tend to migrate to the surface where they are lost by abrasion, solution or slow evaporation, leaving a more brittle, stiffer material behind. Internal plasticization may be brought about by copolymerization of VC with monomers such as vinyl acetate, ethylene or methylacrylate.

Films with excellent gloss and transparency can be obtained provided that the correct stabilizer and plasticizer are used. Both plasticized and unplasticized films can be sealed by high-frequency welding techniques. PVC is inert in its chemical behavior and self-extinguishing when exposed to a flame. Thin, plasticized PVC film is widely used for the stretch wrapping of trays containing fresh red meat and produce. The relatively high water vapor transmission rate (WVTR) of PVC prevents condensation on the inside of the film. Oriented films are used for shrink wrapping of produce and fresh meat but LLDPE films have increasingly replaced them in many applications.

Unplasticized PVC as a rigid sheet material is thermoformed to produce a wide range of inserts from chocolate boxes to biscuit trays. Unplasticized PVC bottles have better clarity, oil resistance and barrier properties than those made from HDPE. However, they are softened by certain solvents,

notably ketones and chlorinated hydrocarbons. Although they made extensive penetration into the market for a wide range of foods including fruit juices and edible oils, in recent years they have been increasingly replaced by PET.

2.3.6.3.3 Poly(Vinylidene Chloride)

PVdC homopolymer has a melting temperature only a few degrees below the temperature at which it decomposes and yields a rather stiff film, which is unsuitable for packaging purposes. Therefore, copolymers were synthesized in an effort to overcome these properties. Acrylates were found to be among the most useful comonomers, along with VC and AN (Brown, 1992).

A soft, tough and relatively impermeable film results when PVdC is copolymerized with 5%–50% (but typically 20%) of VC. These copolymers were first marketed by Dow in 1939 under the trade name Saran™ but are also produced by other companies under various trade names, for example, Ixan® and Diofan®. Although the films are copolymers of VdC and either VC or AN, they are usually referred to simply as PVdC copolymer and such a convention is followed in this book. The specific properties of PVdC copolymer vary according to the degree of polymerization and the properties and relative proportions of the copolymers present.

The properties of PVdC copolymer film include a unique combination of low permeability to water vapor, gases, odors, greases and alcohols, and good ESCR to a wide variety of agents. The good barrier properties of PVdC copolymers are a consequence of crystallinity and low free volume in the amorphous phase. The symmetrical nature of the VdC unit in the polymer leads to nested packing that is adequate for crystallization and leaves very little dead volume in the amorphous phase. Although highly transparent, it has a yellowish tinge. Food packaging applications for PVdC copolymer monolayer films include packaging of processed meats, cheese and other dairy products, and bakery goods. It is an important component of many laminates and is the best coating for RCF. PVdC copolymers can be sealed to themselves and to other materials. By itself, the copolymer is frequently used as a shrink film because orientation improves tensile strength, flexibility, clarity, transparency and impact strength. As well, gas and moisture permeabilities are lowered and tear initiation becomes difficult. The shrink film can be heat sealed using impulse sealing with Teflon®-coated heating bars.

Rigid containers for food packaging can be made from coextruded sheet that contains a layer of PVdC copolymer as a barrier; PVdC has the ability to withstand hot filling and retorting. A simple example is a sheet with five layers that has a total thickness of ~1.3 mm. The outermost layers might be PP, HDPE, PS, HIPS or other nonbarrier polymers having good mechanical properties. The innermost barrier layer is ~125 μm of PVdC copolymer. Adhesive layers connect the outer layers and the barrier layer. This coextruded sheet can be formed into containers by any of several techniques, and the final container has a total wall thickness of ~500 μm and a barrier layer that is ~50 μm thick.

2.3.6.3.4 Poly(Tetrafluoroethylene)

The high thermal stability of the carbon–fluorine bond has led to considerable interest in fluorine-containing polymers as heat resistant plastics and rubbers. Chemically, the fluorine-containing polymers are set apart from other vinyl polymers because their monomers are the only ones that need not bear any hydrogen on the ethylenic carbons in order to be polymerizable. Physically, they are further set apart by their outstanding stability. Poly(tetrafluoroethylene) (PTFE) was a chance discovery by Roy Plunkett while working for DuPont in 1938. He had a cylinder of TFE gas, which, although apparently empty, had not yielded the theoretical amount of gas. When the cylinder was cut open, it was partly filled with a waxy white powder that was identified as a polymer. First marketed in 1945, today it accounts for about 80% of the fluorinated polymers produced and is commonly referred to by the trade name Teflon®.

The monomer TFE is made by reacting hydrofluoric acid with chloroform. Hydrogen chloride is displaced, forming $CHClF_2$, which can be pyrolyzed to TFE. PTFE is a linear polymer free from any significant amount of branching, with an MW that can exceed 30 million atomic mass units,

making it one of the largest molecules known. Because the C–C and C–F bond strengths are very high, PTFE has very high heat stability, even when heated above its T_m of 327°C. Its chemical inertness, nonadhesive properties and excellent heat resistance and low coefficient of friction make PTFE ideal for certain specific applications.

In food packaging, PTFE finds wide use as a nonstick separating surface between thermoplastic films and the jaws of heat sealers. It is common to use a band of PTFE (often reinforced with glass fibers) on continuous heat sealers. The main disadvantages of PTFE are its very high cost and unsuitability for the processing techniques conventionally applied to plastics, poor scratch resistance and mechanical properties.

2.3.6.4 Polyesters

The polymers that have been discussed so far are all based on carbon-to-carbon links and are generally formed commercially by addition polymerization. In contrast, polyesters are based on carbon–oxygen–carbon links where one of the carbons is part of a carbonyl group, and are formed by the process of condensation polymerization. In this process, two molecules are joined together through the elimination of a smaller molecule (typically H_2O) whose atoms derive from both the parent molecules. Simple polyesters are derived from the condensation of a polyhydric alcohol and a polyfunctional acid and are sometimes described as *alkyds* (from *al*cohol and aci*d*). Each component needs a functionality (i.e., number of reactive groups such as –OH, –COOH, –NH$_2$ per molecule) of two to form a linear chain, while if one (or both) monomer has a functionality of at least 3, cross-linkage can occur resulting in a much more rigid three-dimensional lattice structure.

Fiber-forming polyesters have been the subject of extensive investigations ever since the American chemist Wallace Carothers, who worked for DuPont, began his classical research that led to the development of PAs. However, while Carothers largely confined his research to aliphatic polyesters, John Whinfield and James Dickson, working for the Calico Printers Association in England, investigated aromatic materials. This led to the discovery in 1940 and subsequent successful exploitation of poly(ethylene terephthalate) (PET) by ICI with DuPont licensed by ICI to manufacture PET in the United States (McIntyre, 2003).

2.3.6.4.1 Poly(Ethylene Terephthalate)

PET can be produced in an esterification reaction where ethylene glycol (EG) reacts with terephthalic acid (TPA). Alternatively, a *trans*-esterification reaction where the dimethyl ester of TPA (dimethyl terephthalate or DMT) reacts with EG is preferred as it is a more controllable reaction. Water is a by-product of the first reaction and methanol of the second; it can be recovered for further use. The output of both these processes is bis(hydroxyethyl) terephthalate (BHET). A pre-polymerization step follows in which BHET is polymerized to a DP of up to 30 after which a polycondensation process increases the DP further to 100. After polymerization in the melt phase, the MW is further increased by solid-state polymerization (SSP) to a DP of 150 (Awaja and Pavel, 2005). The overall scheme of the reaction is shown in Figure 2.8. The product has a carboxyl group at one end and a hydroxyl group at the other, so it can condense with another molecule of alcohol and acid. The PET repeating unit has an MW of 176, resulting in a final MW of up to 27,000. EG is obtained from ethylene, mostly by the direct hydration of ethylene oxide. DMT is prepared by the catalytic partial oxidation of *p*-xylene, itself a by-product of the petroleum industry; *p*-xylene can also be converted into TPA.

PET is a linear, transparent thermoplastic polymer with a T_m of 267°C and a T_g between 67°C and 80°C. It has the capacity to crystallize under certain controlled conditions. PET is strong, stiff, ductile and tough while in the glassy state (i.e., at temperatures below T_g where side motion is restrained) and can be oriented by stretching during molding and extrusion, which increases its strength and stiffness still further. PET bottles and films are largely amorphous (APET) with small crystallites and excellent transparency. However, crystalline PET (CPET) containers have a higher degree of crystallinity, larger crystallites and are an opaque white (see Section 5.12 for further discussion of APET and CPET).
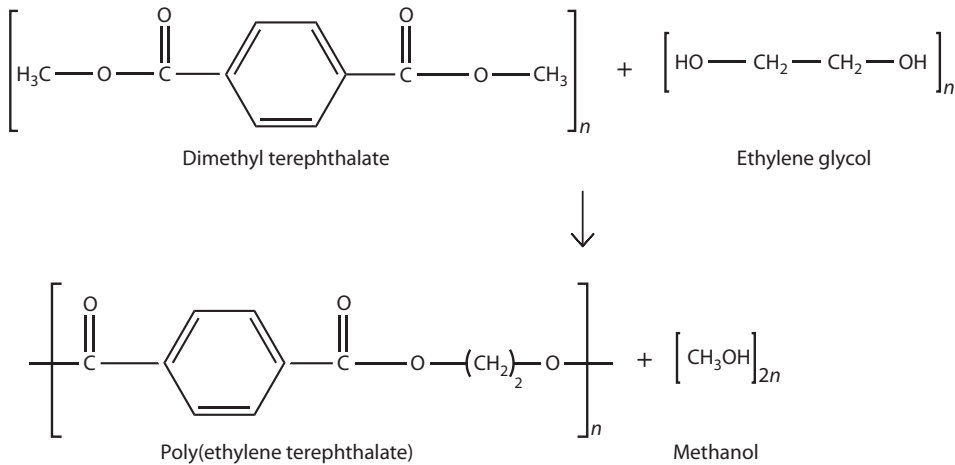
FIGURE 2.8 Reaction scheme for formation of poly(ethylene terephthalate) (PET).

PET films are most widely used in the biaxially oriented, heat stabilized form. There are virtually no applications for the material in its unoriented form because, if crystalline, it is extremely brittle and opaque, and if amorphous, it is clear but not tough. In a two-stage process, machine direction stretching induces 10%–14% crystallinity and this is raised to 20%–25% by transverse orientation. In order to stabilize the biaxially oriented film, it is annealed (or heat set) under restraint at 180°C–210°C, which increases the crystallinity to around 40% without appreciably affecting the orientation and reduces the tendency to shrink on heating. Subsequent coatings are applied to obtain special barrier properties, slip characteristics or heat sealability.

PET film's outstanding properties as a food packaging material are its great tensile strength, excellent chemical resistance, light weight, elasticity and stability over a wide range of temperatures (−60°C to 220°C). This latter property has led to the use of PET for "boil-in-the-bag" products that are frozen before use (the PET is usually laminated to or extrusion coated with LDPE and is typically the outside and primary support film of such laminations), and as oven bags where they are able to withstand high temperatures without decomposing.

APET has nearly the same thermoforming characteristics as PS and has attracted some interest as a replacement for PVC. The properties of unoriented APET are similar to those of semicrystalline oriented PET with the exceptions of strength and stiffness that are enhanced by orientation (Brown, 1992).

To improve the barrier properties of PET, coatings of LDPE, PVdC copolymer or PVdC-co-AN have been used. PET film extrusion coated with LDPE is very easy to seal and very tough. It can be sealed through powders and some liquids, and the integral seal will withstand sterilization by UV. Two-side, PVdC copolymer-coated grades provide a high barrier; a major special application was the single-slice cheese wrap.

Although many films can be metallized, PET is the most common. Metallization (see Section 5.5) results in a considerable improvement in barrier properties. Reductions in WVTRs by a factor of 40 and O_2 permeabilities by over 300 are obtainable. Coextruded, heat sealable films are frequently metallized and used as the inner ply of snack food packages. Rigid grades of metallized PET can be used in thermoformable applications.

PET is also used to make "ovenable" trays for frozen food and prepared meals, where they are preferable to foil trays because of their ability to be microwaved without the necessity for an outer paperboard carton. These trays are thermoformed from cast PET film and crystallized, the crystallization heat setting the tray and preventing deformation during cooking and serving. The properties of the various physical states of PET are summarized in Table 2.5.

TABLE 2.5
Properties of PET

Physical State	Property	Application
Amorphous	0%–5% crystallinity, heat stable to 67°C, clear	Blister packs
Oriented amorphous	5%–20% crystallinity, heat stable to 73°C, clear	Bottles
Crystalline	25%–35% crystallinity, heat stable to 127°C, opaque	Food trays
Oriented crystalline	35%–45% crystallinity, heat stable to 140°C–160°C, clear	Hot-fill containers, films

In the 1970s, the benefits of biaxial orientation of PET were extended from sheet film to bottle manufacture. Nathaniel Wyeth (brother of artist Andrew) and Ronald Roseveare were issued a series of patents (assigned to DuPont) in 1973 (filed in 1970) for a stretch blow molded, biaxially oriented bottle prepared from PET. DuPont chose not to embark on bottle production itself but instead to license the product to others (McIntyre, 2003). The first PET test market was held in New York State during 1975/1976 and the first commercial production appeared on the market in 1977. As a result, important new markets developed, particularly for carbonated beverages.

The bottles are stretch blow molded, the stretching or biaxial orientation being necessary to get maximum tensile strength and gas barrier, which in turn enables bottle weights to be low enough to be economical. The presence of moisture during the extrusion of PET reverses the condensation reaction and produces some depolymerization. Therefore, before extrusion, PET must be dried to a moisture content of less than 0.005% to minimize hydrolytic breakdown and loss of properties.

The major significant volatile compound in PET is acetaldehyde (AA), which is present as a thermal degradation product formed during the melt condensation reaction and melt processing of PET. AA itself is also unstable and readily oxidizes and polymerizes when exposed to air. AA possesses a distinct odor and taste, generally described as sweet, plastic-like and fruity, with a low sensory detection threshold. Present manufacturing techniques have dramatically reduced residual AA levels in PET packaging. The first generation of resins typically had residual AA levels of 2–3 ppm, but today these are <1 ppm. However, AA increases when the pellets are remelted and converted into preforms.

PET bottles used for packaging carbonated beverages are also susceptible to ESC (Morrison et al., 2010). A large crack forms in the base portion of the bottle through which all of the liquid contents can be lost. These cracks initiate on the outside bottle wall and progress inward, consistent with chemical attack as a first step. Thus, in PET stress cracking, the chemical environment on the outside of the bottle must be considered; the contents of the bottle are irrelevant. In the past, attempts have been made to relate ESC of PET bottles with water alkalinity but Morrison et al. (2010) found it was not possible to correlate ESC to water alkalinity without also accounting for water hardness. The metric for water that is relevant to PET stress cracking is excess alkalinity. Most often, naturally occurring water has hardness equal to or greater than alkalinity, that is, it has no excess alkalinity. Ion exchange softening of water removes all hardness and leaves in all alkalinity, in which case all alkalinity originally present becomes excess alkalinity. For this reason, it is important to prevent contact of filled, carbonated PET bottles with water softened by ion exchange as it removes all the hardness but none of the alkalinity.

In 2009, PTI developed the first lightweight foamed PET bottle/jar blow molding process. It is based on microcellular foam injection molding technology to mold preforms, which can then be blow molded on conventional equipment. The package has significant light barrier characteristics

with up to 95% reduction in transmitted light. One early application has been for single serve beer. In addition to PET, the foam bottle technology is applicable to other resins such as poly(lactic acid) (PLA) and poly(ethylene napthalene) (PEN).

2.3.6.4.2 Poly(Ethylene Naphthalate)

In the late 1980s, a high-barrier polyester called PEN was developed. The precursor for PEN is 2,6-dimethylnaphthalene (DMN), which can be oxidized and esterified to give 2,6-dimethylnaphthalene dicarboxylate (NDC). This monomer undergoes polycondensation with EG to form PEN (poly(ethylenenaphthalene-2,6-dicarboxylate)), a semicrystalline polymer similar to PET but with a double ring structure that makes it more rigid and improves its barrier and mechanical properties.

PEN provides approximately five times more barrier to CO_2, O_2 and water vapor than PET, giving it obvious advantages as a flexible film, or as a rigid container for beer and carbonated beverages. It has a T_g of 120°C (51° higher than for PET) and is stronger and stiffer (but more expensive) than PET. The FDA gave final approval for food use of PEN homopolymers in April 1996 (the petition was filed in 1988), and for PET–PEN copolymers in March 2000.

Because the PEN homopolymer is priced at a significant premium to PET (PEN resin is about four times the cost of PET), attractive applications for PEN are those where its physical advantages outweigh its cost disadvantage. PEN extrusion blow molded containers exhibit excellent properties in hot-fill food (baby food, ketchup) and drink applications, reusable packaging, and packaging of O_2 sensitive foods such as beer. PEN, like PET, has good clarity. The advantages of PEN over PET are its 35°C–55°C higher use temperature, 50% greater tensile strength, and fivefold better barrier performance. Additional markets for PEN encompass laminates, copolymers and blends. However, if PEN homopolymer is to penetrate large-volume applications such as beer and single-serve carbonated beverage bottles, then the cost of making 2,6-DMN will need to be reduced. Like PET, PEN film can be vacuum metallized or coated with aluminum or silica oxides.

2.3.6.4.3 Copolyesters

The term copolyester is applied to those polyesters whose synthesis uses more than one glycol and/or more than one dibasic acid. The copolyester chain is less regular than the monopolyester chain and, therefore, has a reduced tendency to crystallize. As a result, some of the copolyesters are amorphous, some are crystalline and some can be made to be either crystalline or amorphous, depending on processing conditions.

An important cycloaliphatic diol used in a variety of commercial copolyesters is 1,4-cyclohexanedimethanol (CHDM), which is produced by the catalytic hydrogenation of DMT; it can exist as the *cis* or *trans* isomer, and the isomer ratio plays an important role in determining the final properties of the copolyester. The polyester of CHDM with TPA is poly(1,4-cyclohexylenedimethylene terephthalate) (PCT), which melts at 300°C. When this structure is modified with an acid such as IPA, the abbreviation PCTA (acid-modified PCT) is used. PCT polyesters with glycol modification of up to 50 mol% EG are abbreviated as PCTGs. Likewise, PET polyesters with up to 50% CHDM content are called PETGs. The abbreviations of PETG, PCTG, and PCTA are generally reserved for compositions that contain enough of the comonomer to render the backbone slow to crystallize or amorphous (Turner et al., 2003).

A well-established application for extruded unreinforced PCTA is in the preparation of crystallized, thermoformed trays for foods. Crystallized PET is widely used for this application, but where higher temperature performance is needed, PCTA may be chosen. Such trays are formed from extruded sheet, using a hot mold to promote crystallization (Turner et al., 2003).

In recent years, PET manufacturers have tended to produce copolymers of PET containing minor amounts (<5 mol%) of such comonomers as IPA or CHDM to reduce the polymer melting point by ~4°C–12°C. This improves the molding characteristics of PET and assists in imparting enhanced clarity to stretch blow molded bottles by modifying the crystallization characteristics of the PET backbone. Other performance benefits of PCT versus PET include improved toughness, hydrolysis resistance and color.

PETG copolyester is a clear, amorphous polymer with a T_g of 81°C. It can be readily molded or extrusion blow molded and normally remains amorphous, clear and virtually colorless even in very heavy thicknesses. It has high stiffness and hardness and good toughness, retaining an acceptable degree of toughness even at low temperatures. However, it is a poorer barrier than PET.

PET–PEN copolymers, which are made up primarily of PET with DMN as a comonomer at 10%–25%, meet market hot-fill requirements up to 95°C at a much more economical cost than PEN homopolymer, which has a maximum hot-fill temperature of 85°C. PET and PEN can also be blended together. PEN homopolymers, copolymers and blends have not yet been used for any major, high-volume, food packaging application.

2.3.6.5 Polycarbonates

PCs are polyesters of unstable carbonic acid and have carbonate (–O–(C=O)–O–) linkages. They were originally produced by the reaction of phosgene (also known as carbonyl chloride [$COCl_2$]) with bisphenol A (BPA) and, hence, have the name poly(bisphenol-A carbonate). While BPA is still the most commonly used phenol, diphenyl carbonate has replaced phosgene. PCs have an outstanding combination of high temperature resistance, high impact strength and clarity, retaining their properties well with increasing temperature. Chemically they are resistant to dilute acids but strongly attacked by alkalis and bases such as amines. Permeability to both water vapor and gases is high, and if appreciable barrier properties are required, they must be coated. While PCs can be oriented, there is no decrease in permeability, although tensile strength increases. PCs are not suitable as shrink films since the rate of shrinkage above their heat distortion point is extremely slow.

Because PCs are amorphous, they soften over a wide temperature range; the T_m of bisphenol A PCs is 220°C–265°C and the T_g 150°C. The melting point of PCs is decreased from 225°C to 195°C when the methyl pendant groups are replaced by propyl groups. Thermoforming of PC film is readily carried out and deep draws with good mold detail are obtainable.

PCs are used to a very limited extent in food packaging as components of multilayer coextrusions and co-injection moldings to provide transparency and high strength to containers that undergo hot filling or hot processing after filling (Brown, 1992). PC can be laminated or coextruded to PP, PE, PET, PVC and PVdC copolymer; coextrusions with EVOH or PAs are carried out with the help of adhesives. Multilayered bottles typically contain a central EVOH layer to reduce O_2 ingress, with the PC layers on either side providing strength. However, the relatively high cost of PC limits its use in these applications.

Another application for PCs is ovenable trays for frozen foods and prepared meals where low-temperature impact strength adds durability and toughness; they are commonly coextruded with PET. The film has been used for boil-in-bag packs and, when coated with LDPE, skin packaging. Uses as a retort pouch and for microwave oven cookware are possible because of good stability at high temperatures. Vacuum metallizing gives good results because of PCs transparency, with the finished product having a high gloss.

Although the film is biaxially oriented for electrical applications, it is not used in this form in food packaging. However, blow and injection molded PC is used for reusable bottles (particularly bottles for babies), which take advantage of PC's toughness and clarity. As well, PC has high resistance to staining by tea, coffee, fruit juices, tomato sauces, lipstick, ink, soaps and detergents.

2.3.6.6 Polyamides

PAs are condensation, generally linear, thermoplastics made from monomers with amine and carboxylic acid functional groups resulting in amide (–(C=O)–NH–) linkages in the main polymer chain that provide mechanical strength and barrier properties. Their development was not fortuitous but the result of a long search for a family of polymers that would resemble silk, the most highly valued of all natural textile fibers.

The early development of the nylons (originally the DuPont brand name for the family of synthetic polyamides) is largely due to the work of Carothers and his colleagues at DuPont between 1928 and 1937. They first synthesized nylon-6,6 in 1935 after extensive research into condensation polymerization. Commercial production of this polymer for subsequent conversion into fibers was commenced by DuPont in 1939. There is no evidence for the popular belief that nylon is a contraction of the names of the cities, *New York* and *Lon*don. In 1940, John W. Eckelberry of DuPont stated that the letters "nyl" were arbitrary and the "on" was copied from the names of other fibers such as cotton and rayon. A later publication by DuPont explained that the name was originally intended to be "No-Run" (run in this context meaning unravel as an early application was for stockings) but was then modified to avoid making such an unjustified claim and to make it sound better. The word nylon was never trademarked.

In an attempt to circumvent the DuPont patents, German chemists investigated a wide range of synthetic fiber-forming polymers in the late 1930s. This work resulted in the successful introduction of nylon-6 (where a six-carbon molecule contained an acid group at one end and an amine group at the other) and between them nylons-6 and -6,6 account for nearly all of the PAs produced for fiber application.

Today, two different types of PA films are available based on their resin manufacture. One type is made by the condensation of mixtures of diamines and dibasic acids. These are identified by the number of carbon atoms in the diamine, followed by the number of carbon atoms in the diacid. The other type is formed by the condensation of single, hetero-functional amino acids, known as omega or ω-amino acids since the amino and carboxyl groups are at opposite ends of the polyamides. Identification is made by a single number signifying the total number of carbon atoms in the amino acid. Water is released as a by-product of the condensation reaction. The average DP is ~200 for a typical nylon-6 and about 100 for nylon-6,6.

Although a large number of likely combinations have been tried on a laboratory scale, commercial production has been limited to those where the starting materials can be produced most cheaply. PAs did not become a commercial reality for packaging film applications until the late 1950s. Although considered a specialty film, many presently available food packages would not be possible without PAs:

- Nylon-6 refers to PA made from the monomer ε-caprolactam that already contains an amide link and contains six carbon atoms (Figure 2.9). During polymerization, the ring opens and the molecules join up in a continuous chain.
- Nylon-11 refers to PA made from the monomer ω-undecanolactam that contains 11 carbon atoms.
- Nylon-6,6 (sometimes written nylon-66) is formed by reacting hexamethylenediamine with adipic acid. Both materials each contain six carbon atoms.
- Nylon-6,10 (nylon 610) is made by reacting hexamethylenediamine with sebacic acid ($HOOC-(CH_2)_8-COOH$). The diamine has six carbon atoms and is numerically first, followed by the acid that contains 10 carbon atoms.

Most PA packaging films in the United States are produced from nylon-6 while European films are usually nylon-11, due to lower raw material costs. Films from nylon-6 have higher temperature, grease and oil resistance than nylon-11 films. The structures of three common PAs are depicted in Figure 2.9.

PAs produced with greater than six-carbon chains result in films with a lower melting point and an increased resistance to water vapor. Again, the key to successful commercialization is to find cheap sources of the monomers.

In addition to the homopolymers discussed earlier, copolymerization is used to introduce many additional varieties. Nylon-6,6 and -6,10 can be copolymerized to yield a film with a lower melting point than either of the homopolymers. Fillers, plasticizers, antioxidants and stabilizers can also be used with any or all of the many types of PA films. Over 100 different formulations are
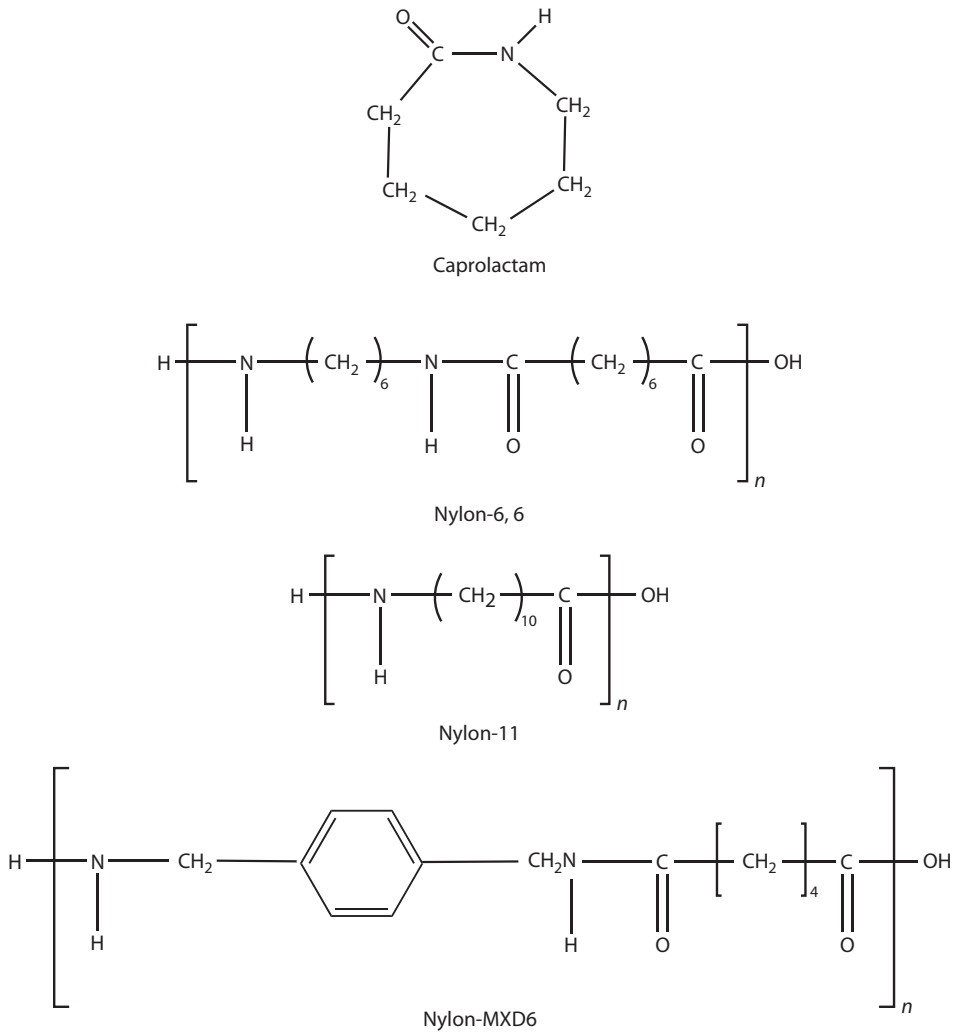
FIGURE 2.9   Structures of the monomer ε-caprolactam (used to make nylon-6) and three other common polyamides.

available in the production of PA film, but most of those used in food packaging applications consist of nylons-6,6, -6 and -11.

The distance between the repeating polar amide (–CONH–) group can considerably affect the properties of PAs. As the length of the aliphatic segment (i.e., the number of methylene groups between amide groups in the chain) increases, there is a reduction in melting point, tensile strength and water absorption, and an increase in elongation and impact strength. Thus, nylon-11 (where the distance is approximately twice that of nylon-6) has a lower interchain attraction, has a lower melting point, has a lower water absorption and is softer. Nylon-11 may be considered to be intermediate in structure and properties between nylon-6 and LDPE. The T_gs of PAs are in the range of 40°C–60°C, while the T_ms are as follows: nylon-6 = 215°C, nylon-6,6 = 255°C, nylon-6,10 = 220°C and nylon-11 = 190°C. The high T_ms of PAs such as nylon-6,6 is a function of both the strong hydrogen bonding between the chains and the crystal structure. This also allows the materials to retain significant stiffness above the T_g and almost up to the melting point.

As might be expected, copolymerization tends to inhibit crystallization by breaking up the regular polymer chain structure and, consequently, results in lower T_ms than the corresponding homopolymer. The properties of PAs are considerably affected by the amount of crystallization. Although each variety of PA film has its own characteristic properties, certain similarities exist. PA films are characterized by excellent thermal stability, that is, they are capable of withstanding steam at temperatures up to 140°C and dry heat to even higher temperatures; low temperature flexibility is excellent and they are resistant to alkalis and dilute acids. Strong acids and oxidizing agents react with PAs.

In general, PAs are highly permeable to water vapor since the amide group is polar. The absorbed water has a plasticizing effect, which causes a reduction in tensile strength and an increase in impact strength. Their permeability to O_2 and other gases is quite low when the films are dry. PVdC copolymer-coated PAs offer improved O_2, water vapor, grease and UV light barrier properties. Odor retention is excellent and the films are odorless and nontoxic. Other important attributes of PAs are their excellent thermoformability, flex-crack resistance, abrasion resistance and mechanical strength up to 200°C.

For most applications, PAs are combined with other materials such as LDPE, ionomer and EVA to add moisture barrier and heat sealability. Multilayer films containing a PA layer are used principally in the vacuum packing of processed meats and cheeses.

Biaxial orientation of PA films provides improved flex-crack resistance, mechanical strength and barrier properties. These films have applications in packaging foods such as processed and natural cheese, fresh and processed meats and frozen foods. They are used in pouches and bag-in-box structures. In some applications the PAs compete with biaxially oriented PET; although oriented PAs offer better gas barrier, softness and puncture resistance, oriented PET offers better rigidity and moisture barrier.

In the 1980s, a new polymer, nylon-MXD6, was introduced by the Mitsubishi Gas Chemical Company in Japan. It is made from meta-xylylenediamine (MXD) and adipic acid and is technically referred to as poly(meta-xylylene adipamide); the 6 indicates the number of carbon atoms in the acid. It has a T_g of 64°C and a T_m of 243°C (between those of nylon-6 and PET). Nylon-MXD6 has better gas barrier properties than nylon-6 and PET at all humidities and is better than EVOH at 100% RH, due to the existence of the benzene ring in the MXD6 polymer chain (see Figure 2.9). For example, nylon-6 is 5 times as permeable as MXD6 at 0% RH and 12 times as permeable at 75% RH (Brown, 1992). Biaxially oriented film produced from nylon-MXD6 is used in several packaging applications as it has significantly higher gas and moisture barrier properties and greater strength and stiffness than other PAs. When nylon-MXD6 is blended at up to 50% with nylon-6 or nylon-6,6, it can dramatically improve thermoformability by lowering the thermoforming temperature and, thus, shortening the preheat time; the gas barrier performance is also enhanced.

Together with its high clarity and good processability, the aforementioned properties make nylon-MXD6 film suitable as a base substrate for laminated film structures for use in lidding and pouches, especially when the film is exposed to retort conditions. As the T_g and T_m of nylon-MXD6 are similar to those of PET, blending or coextruding nylon-MXD6 and PET at any ratio give films with good processability. Nylon-MXD6/PET multilayered bottles, made by co-injection molding and stretch blow molding, improve on the gas barrier properties and are used for beer and wine.

In the early 1990s, amorphous polyamides (APAs) appeared in food packages as gas barriers intermediate to the higher barrier EVOH and PVdC copolymer and the lower barrier PET and PVC. Their manufacture involves introducing a ring into the linear nylon chain that prevents crystallization (Brown, 1992). Consequently, they remain in the amorphous state and are, therefore, transparent. An unusual property is the fact that their gas barrier properties improve with increasing absorption of moisture in contrast to "normal" PAs because of their high T_gs (125°C).

2.3.6.7 Acrylonitriles

The ready availability of acrylic acid derivatives from propylene has led to their use in numerous industrial polymer products. AN (sometimes referred to by its synonym vinyl cyanide, especially by those who seek to raise fears about the safety of the polymer as a food contact material since the monomer is carcinogenic), b.p. 70°C, is produced mainly by the ammoxidation of propylene and contains a carbon–nitrogen triple bond.

2.3.6.7.1 Polyacrylonitrile

Polyacrylonitrile (PAN) is produced in quantity as a fiber being commonly referred to simply as "acrylic" and often containing small quantities of other monomers, typically methyl acrylate, methyl methacrylate and vinyl acetate.

The pure nitrile polymer PAN is 49% nitrile and is an amorphous, transparent polymer. It has a relatively low T_g (87°C) and provides an outstanding barrier to gas permeation and exceptional resistance to a wide range of chemicals. However, it is of no commercial value in packaging, due largely to its inability to be melt processed since it degrades at 220°C. It is, therefore, copolymerized with other monomers that impart melt processability, thus making its desirable properties available in a packaging form.

AN can be copolymerized with styrene in a ratio of about 1:3 by weight to yield styrene–acrylonitrile copolymer (SAN), an amorphous and transparent material with a poor gas barrier because of its relatively low AN content. When grafted onto a polybutadiene backbone, the graft copolymer acrylonitrile–butadiene–styrene (ABS) can be produced. However, SAN and ABS find limited use in food packaging apart from the thermoforming of some ABS sheet into trays and tubs for fat-based spreads since it has better ESCR than PS.

2.3.6.7.2 High-Nitrile Resins

2.3.6.7.2.1 Acrylonitrile–Styrene   Acrylonitrile–Styrene (ANS) copolymers are produced by combining AN and styrene in a 70:30 ratio. The backbone of ANS copolymers is characterized by a high degree of chain-to-chain attraction as a result of polarity, resulting in chain stiffness and immobility, high T_g and chemical inertness; most of these properties are attributed to the high nitrile content of the copolymer.

The realization of the excellent gas and moisture barriers of these high-percentage AN copolymers, coupled with new and improved molding techniques, led to their development for carbonated beverage packaging in the 1970s but toxicological problems with AN monomer surfaced. The FDA withdrew its sanction for the use of high-nitrile resins in beverage packaging in September 1977 because of concern about potential AN migration from the bottle into the beverage, but amended its position in 1984 to limit the residual AN content of the finished container to 0.1 ppm. This limit can be met with modern processing methods. However, by this time PET had been successfully commercialized for carbonated beverages, gaining a commanding lead that proved impossible to overcome (Brown, 1992).

2.3.6.7.2.2 Rubber-Modified Acrylonitrile–Methyl Acrylate   Acrylonitrile–methyl acrylate (ANMA) copolymers have high barrier properties and are made by copolymerizing AN and methyl acrylate (MA) in a 75:25 ratio onto a nitrile rubber backbone (Lund and McCaul, 2009). It was originally developed as a bottle blowing material for carbonated beverages, having good clarity, excellent gas barrier properties and a high resistance to creep. In addition, it has good impact strength and is insoluble in most organic solvents.

ANMA is also produced in film and sheet form and, when laminated with other materials such as LDPE, it is suitable for thermoforming into containers for products such as cheese and meat.

ANS and ANMA copolymers have similar barrier properties, their gas barrier properties being surpassed only by EVOH and PVdC copolymer. However, high-nitrile resins show an affinity for

water because of the polarity that the nitrile group imparts to the molecule. Thus, their moisture barrier is lower than that of the nonpolar polyolefins but their polarity does mean that they are resistant to many solvents. ANMA is tougher than ANS because of the rubber content. Furthermore, ANMA can be blown into bottles using conventional bottle-blowing methods, whereas ANS requires stretching to improve toughness.

2.3.7 ADDITIVES IN PLASTICS

Early in the development of the plastics industry it was realized that to obtain better products, additives needed to be added to the base polymer. Within the context of thermoplastics materials technology, the term additive is used to denote an auxiliary ingredient that enhances the properties of the parent polymer without appreciably altering its chemical structure.

In food packaging, all additives should have received clearance by the appropriate food regulatory authority. The problem of the migration of additives from plastic packaging materials into foods is discussed in Chapter 22. In this section, the major additives that could be encountered in plastic food packaging materials will be briefly discussed, together with the reasons for their inclusion in the packaging materials.

2.3.7.1 Processing Additives

The degradation of polymers frequently involves oxidation reactions by a free radical mechanism, and at high temperatures, interaction of O_2 with C–H bonds leads to the formation of hydroperoxide groups. These decompose into very reactive OH radicals and lead to molecular scissions. Because it is practically impossible to eliminate O_2 from the system, additives are used to inhibit oxidation reactions.

This is accomplished by using primary stabilizers or antioxidants such as hindered phenols or aromatic amines, which interrupt the chain reaction by combining with the free radicals; secondary stabilizers or peroxide decomposers such as organic thioesters, phosphites and metal thiocarbamates, which react with hydroperoxides as they are formed; and chelating agents or metal deactivators such as organic phosphites and hydrazides, which protect the polymer by immobilizing metal ions through coordination reactions.

With PVC, heat stabilizers or acid absorbers that retard the decomposition of PVC into HCl and dark, degraded polymers must also be used, and octyltin mercaptide, calcium-zinc compounds and methyltin have been given FDA clearance.

The tendency for polymers such as PVC and polyolefins to stick to metal parts during processing can be reduced by adding lubricants such as PE waxes, fatty acid esters and amides, metallic stearates such as zinc and calcium stearate, and paraffin.

2.3.7.2 Plasticizers

Brittle polymers such as PVC must be plasticized to obtain flexible films and containers. The plasticizer also gives the material the limp and tacky qualities found in "cling" films. About 80% of all plasticizers are used in PVC. Typically, phthalic esters such as dioctyl phthalate (DOP), also known as di-2-ethylhexylphthalate (DEHP), and dioctyl adipate (DOA), also known as di-2-ethylhexyladipate (DEHA), are used, as well as epoxidized oils and low-MW polyesters. Safety concerns about the use of phthalates in food packaging have been raised and are discussed in Chapter 22. Internal plasticization may be brought about by copolymerization as in the case of PVC, which can be copolymerized with vinyl acetate, ethylene or methylacrylate.

2.3.7.3 Antiaging Additives

Aging is the process of deterioration of materials resulting from the combined effects of atmospheric radiation, temperature, O_2, water, microorganisms and other atmospheric agents (e.g., gases), indicating that a chemical modification in the structure of the material has occurred. Antioxidants have

already been mentioned under processing aids, but they are also necessary in polymeric films such as PP, which degrade in the atmosphere. BHT has been cleared by the FDA and acts as a free radical scavenger. Organophosphites act as hydroperoxide decomposers. It is common for different antioxidants to be used together for synergistic effects.

UV stabilizers are used to prevent the deterioration of polymeric films by photooxidation. They act by absorbing high-energy UV radiation and releasing it as lower-energy radiation.

2.3.7.4 Surface Property Modifiers

Static electricity is generated on a polymer surface by friction or by rubbing it against another surface. It can also be generated on fast-moving film during converting operations or on filling lines. Antistatic agents are used to prevent the accumulation of electrical charges in polymeric films, an undesirable effect caused by the fact that polymers are nonconductors of electricity. Electrification of films results from a segregation of charges (electrons and ions), which occurs when two surfaces are parted after close initial contact. The addition of ethoxylated fatty amines, polyhydric alcohols and derivatives, and nonionic and quaternary ammonium compounds overcomes the problem; they migrate to the surface and form a conducting layer through the absorption of atmospheric moisture, which permits the discharge of electrons.

In some food packaging applications, moisture tends to condense as small droplets on the internal surface and prevent a clear view of the package contents. The droplets are formed when the polymer surface tension is lower than the surface tension of water, which prevents the formation of a continuous layer of water. The addition of nonionic ethoxylates or hydrophilic fatty acid esters such as glycerol and sorbitol stearate promotes the deposition of continuous films of moisture by increasing the critical surface tension of the polymer surface. These so-called antifogging agents can be applied on the surface of the material or compounded internally in the packaging material at levels ranging from 0.5% to 4%.

Many packaging films or sheets tend to stick together because they are nonconductors of electricity, a phenomenon known as blocking. Blocking (which may develop under pressure during storage or use) can be reduced by incorporating chemicals such as stearamide, calcium stearate, alkylamines and alkyl quaternary ammonium compounds in the polymer prior to processing. Other materials such as colloidal silica, clays, starches and silicones may be applied to the surface either during or after processing to reduce blocking. Anti-blocking agents are used at levels ranging from 0.1% to 0.5%.

2.3.7.5 Optical Property Modifiers

The optical properties of a material from a technological aspect are normally described in terms of their ability to transmit light, exhibit color and reflect light from the surface (i.e., gloss). The majority of food packaging films are not pigmented, although some are colored by the addition of colorants that can be dyes (which are soluble in the plastic and tend to migrate, thus limiting their use) and pigments (which are insoluble in the plastic matrix). The principal pigments for use as colorants in packaging are carbon black, white titanium dioxide, red iron oxide, yellow cadmium sulfide, molybdate orange (consisting of a solid solution of sulfate, molybdate and chromate compounds of lead), ultramarine blue (consisting primarily of a double silicate of aluminum and sodium with some sulfides or sulfates), blue ferric ammonium ferrocyanide, chrome green (Cr_2O_3) and blue and green copper phthalocyanines (Rosato, 1997). The FDA has questioned the use of some of these colorants in packaging material in contact with food, its concern being with colorants that can migrate from the packaging into the food.

2.3.7.6 Foaming Agents

Foaming or blowing agents are used for the production of cellular products and are normally classified into physical and chemical types, according to whether the generation of gases to produce the cells takes place through a physical transition (i.e., evaporation or sublimation) or by a chemical

process (i.e., decomposition reactions that result in evolution of gases). In food packaging applications, physical blowing agents are commonly used. After the Montreal Protocol on Substances That Deplete the Ozone Layer entered into force in 1989, chlorofluorocarbons (CFCs) that had been used as blowing agents were replaced by butane and pentane. These have now been largely replaced by CO_2, which results in improved organoleptic properties that have opened up new applications in food packaging. Today, expanded and extruded PS foams are made using mainly CO_2 or sometimes a light aliphatic hydrocarbon such as pentane or butane as the blowing agent. Expanded PET, PP and PVC foams are produced using chemical blowing agents.

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