

Part One

Introduction

*If you once enter in the world of polymers,
You will never leave it.
T. Tsuruta*

1

Introduction

1.1 Milestones in the Development of Polymer Science

Regarding its subject of study, *polymer science* belongs to the oldest fields of science (existing since the times when living cells appeared), while as a separate, well-defined science it was formulated less than 100 years ago – between 1920 and 1930 – thanks to the pioneering works of the German chemist *Hermann Staudinger* (Figure 1.1). Polymer materials have always been used by human beings without having any idea what differs these materials from the others. The situation did not change even when the first synthetic polymer material was prepared around 1910 by *Leo Baekeland* –*Bakelite*.¹ First, Baekeland produced soluble phenol-formaldehyde shellac called “Novolak”, but later he succeeded in preparing a hard plastic material.

Bakelite continues to be used for wire insulation, brake pads and related automotive components, and industrial electric-related applications. Bakelite stock is still manufactured and produced in sheet, rod and tube form for industrial applications in the electronics, power generation, and aerospace industries, and under a variety of commercial brand names.

Baekeland was a very talented chemist with an extremely strong feeling for commercially important products. But as a matter of fact, he did not contribute to the creation of polymer science in any theoretical aspect such as, for example,

¹ *Baekeland* was already a wealthy person due to successful sales of his first serious discovery – the photographic paper *Velox*. *E. Kodak*, the designer of the first photographic camera, was so impressed by the new material that he immediately signed a check of one million dollars! In this way Baekeland, who expected to get at least US\$ 10 000, was able to organize at home a chemical laboratory with all necessary equipment. The most important apparatus was the autoclave needed just for studying the condensation reaction between phenol and formaldehyde. Baekeland's initial intent was to find a replacement for shellac, a material that was in limited supply because it was made naturally from the excretion of lac bugs. The germ of his idea came in the chemistry library where he found that the German chemist *Bayer* studied the same reaction and obtained a solid, non-soluble product which he could not remove from the reaction flask, so he threw it away together with the glass flask. *Baekeland* decided that this was what he needed, and he started a systematic study leading to the creation of Bakelite. Phenolic resins have been commonly used in ablative heat shields. Soviet heat shields for warheads and spacecraft re-entry consisted of asbestos textolite, impregnated with Bakelite.

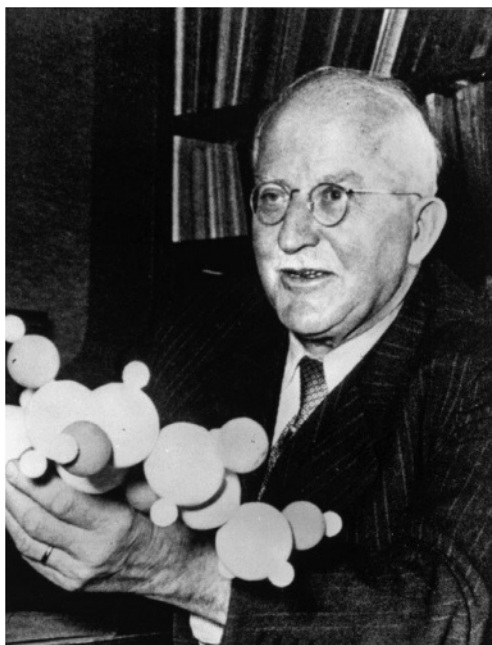


Figure 1.1 H. Staudinger (1881–1965), the “father of polymer science” who received the Nobel Prize in 1953 for his studies.

trying to answer such questions as how does the molecular structure of polymeric substances differ from that of other substances.

It must be stressed that his target was completely different – to create a new material with a well-defined combination of properties needed for a particular application. And he completed his task in an excellent way! Today we know that even if he tried to perform theoretical research, he could hardly have the same success he achieved in material synthesis. This is because his polymer, Bakelite, belongs to a special group of polymers characterized by a rather dense molecular cross-linking, that is, the single molecular chains are connected *via* covalent bonds, forming in this way a giant three-dimensional (3-D) molecular network, where separate linear molecules with a strictly defined start and end no longer exist. What is more, the cross-linked polymers do not display the typical and unique properties of polymers as the non-cross-linked ones do. So, the answer to the question regarding why the molecular structure of polymeric substances differs from that of other substances was given by Hermann Staudinger, who was working around the same time.

Staudinger had been studying natural products as cellulosic derivatives, natural rubber, and others, and particularly their solutions. Thus he got the impression that in these solutions one deals with larger “particles” than in solutions of low molecular weight substances. By the way, the same observation had been made much earlier, around the mid-nineteenth century when the colloid chemistry was formulated and such solutions were called “lyophilic colloids.” Staudinger went further, suggesting that these “particles” are giant molecules comprised of a large number of atoms bonded *via* covalent bonds; and this met a negative reaction



Figure 1.2 W. Carothers (1896–1937), the inventor of nylons and neopren.

from the scientific world. The leading chemists and physicists of that time were against him, stating that it was not possible that such a large number of atoms could be bonded in one molecule.²

Staudinger did not abandon his idea, and step by step, he gathered arguments in favor of his hypothesis which, around 1930, was accepted world-wide. As a matter of fact, he formulated a new science, *polymer science* suggesting and proving that polymers are comprised of large molecules consisting of a huge number of atoms connected to each other by *covalent bonds*. In this way he demonstrated the basic difference in the molecular structure of polymers and low molecular weight substances.

The most serious support for Staudinger's concept was made in 1930 by the American chemist *Wallace Carothers* (Figure 1.2). Carothers was a group leader at the DuPont Experimental Station laboratory, near Wilmington, Delaware, where most polymer research was done. Carothers was an organic chemist who, in addition to first developing Nylon, also helped lay the groundwork for Neoprene. After receiving his PhD, he taught at several universities before he was hired by DuPont to work on fundamental research. In his research, Carothers showed even at this time the high degree of originality which marked his later work. He was never content to follow the beaten path or to accept the usual interpretations of organic reactions. His first thinking about polymerization and

² "Dear Colleague, Leave the concept of large molecules well alone . . . there can be no such thing as a macromolecule." It is said that this advice was given to H. Staudinger just 90 years ago, after a major lecture devoted to his evidence in favor of the macromolecular concept (Olby, 1970).

the structure of substances of high molecular weight began while he was at Harvard.

As a matter of fact, the systematic studies at Du Pont on the condensation process with the aim to prepare a synthetic macromolecules allowed Carothers to start on polyesters using diacids and diols. The obtained products were not of commercial interest because of their low melting temperatures and problems with their low hydrolytic stability. The commercial success came with polyamides – Nylon 6 and Nylon 66 in the mid- to late 1930s.

The commercially important polyester, the poly(ethylene terephthalate), was developed in the United Kingdom around 1940 in a programme initiated by *J. R. Whinfield*. Its commercialization was handled by Du Pont and ICI (UK) since they had a current agreement for joint work on this topic.

Polyesters and polyamides, being the subject of Carothers' studies, are examples of condensation polymers formed by step-growth polymerization. Carothers worked out the theory of step-growth polymerization and derived the *Carothers equation* which relates the average degree of polymerization to the fractional conversion (or yield) of monomer into polymer. This equation shows that, for a high molecular weight, a very high fractional conversion is needed (for step-growth polymer only).

Carothers had been troubled by periods of depression since his youth. Despite his success with Nylon, he felt that he had not accomplished much and had run out of ideas. His unhappiness was compounded by the death of his sister and on the evening of 28 April, 1937 he checked into a Philadelphia hotel room and committed suicide by drinking a cocktail of lemon juice laced with potassium cyanide.

In this way, after the successful synthesis of linear polyesters and polyamides, the further establishment and development of polymer science involved many talented chemists from Europe and the United States. One of the first achievements was the demonstration that the macromolecules are not rigid, non-flexible, rod-like formation, as wrongly suggested by H. Staudinger³ but are extremely flexible formations.

The application of physics and physical chemistry to macromolecular systems dates back to the early attempts made in the late nineteenth century to understand the unusual properties of natural polymers, such as rubber, polysaccharides, and proteins. However, it was not until the 1920–1930 period that *Meyer* and *Mark* in Germany began to establish the structure of cellulose and rubber with the use of X-ray diffraction techniques. Explanations of rubbery elasticity in terms of polymer conformations were put forward by *Kuhn*, *Guth*, and *Mark* between 1930 and 1934. Kuhn, in particular, was the first to apply statistical methods to the study of macromolecules.

³ As mentioned above, the main subject of Staudinger's studies were the derivatives of cellulose. Only many years later it was found that these polymers belong to the class of *liquid-crystalline polymers* which are characterized by "solid" non-flexible, rod-like molecules. In addition, Staudinger studied their behavior in solutions, mostly during flow, and found that they behave as crystallizable substances demonstrating light birefringence in flow. He could not accept that a flexible chain would be able to demonstrate this phenomenon, while a rod-like molecule would do.

The application of light scattering to macromolecular systems was made by *Debye* during World War II. It was also during this period that *Flory* began a series of investigations into the applications of statistical methods, conformational analysis, and other fundamental physicochemical techniques to polymer science. During the early 1950s, *Watson*, *Crick*, *Wilkins*, and particularly *Franklin* successfully applied X-ray diffraction analysis to the structure determination of biological polymers, such as deoxyribonucleic acid (DNA), hemoglobin, and insulin.

Single crystals of polyethylene were first reported by *Keller*, *Fischer*, and *Till*⁴ independently from each other in the same year, 1957. This discovery was possible thanks to the development of electron microscopy. The more recent introduction of solid-state nuclear magnetic resonance (NMR) methods in the 1980s has had a major impact on polymer structural analysis.

Regarding the synthesis of polymers it has to be noted again that a number of important new polymers were prepared and commercialized in the period between 1890 and 1930, many of which were based on the use of chemical reactions (acetylation, nitration) carried out on cellulose. It is perhaps astonishing to realize that most of these technological developments occurred during a time when the polymeric nature of these products was not recognized or believed.

The 15 years between 1930 and 1945 represent the springboard for the development of modern synthetic polymer chemistry, as can be concluded from Table 1.1, which summarizes the development of polymer synthesis.

The development of polymer synthesis in the period 1945 to 1960 was accelerated by the large-scale availability of new monomers from the petrochemical industry, coupled with a series of key scientific discoveries. These include the pivotal development by *K. Ziegler* and *G. Natta* of organometallic compounds as initiators for the polymerization of ethylene and catalysts for the stereoregular polymerization of other olefins.

By the late 1980s it was already evident that polymer science was entering a new phase. This phase of synthetic polymer chemistry involved a subtle shift in emphasis. Many of the most accessible (and inexpensive) “commodity” polymers have now been studied in detail and their applications have been developed extensively. Interest is now focusing on the synthesis and study of entirely new polymers that have specialized, high performance properties, such as very high strength, temperature stability, oil and fuel resistance, biomedical compatibility. In parallel, newer methods of synthesis are developing.

The 1990s and early 2000s saw numerous additional advances. New polymer architectures were developed such as star and dendrite structures, as well as new types of block and graft copolymers. Hybrid polymer-ceramic materials were prepared further, as were polymers for use as semiconductor resists, electroluminescent materials, electrolytes in batteries, and proton-conducting membranes in fuel cells. The interface between biology and medicine continues to be strengthened by intensive research on micelles, vesicles, microspheres, hydro gels, and biocompatible surfaces. Thus, it is clear that polymer science continues to be a vibrant and expanding field with an increasing influence on all other scientific

4 Keller (1957), Fischer (1957), and Till (1957).

Table 1.1 Approximate sequence of polymer synthesis development.

Time	Development
1838, 1839	Polymerization of vinyl chloride and styrene; vulcanization of rubber
1868	“Celluloid” (cellulose nitrate plus camphor)
1893	Rayon (regenerated cellulose)
1910	Styrene-diene copolymers; phenolic resins
1914	Cellulose acetate as aircraft “dope”
1920	Cellulose nitrate lacquers (automobiles)
1924	Cellulose acetate fibers
1927	Cellulose acetate plastics; poly(vinyl chloride) manufacture
1929	Urea-formaldehyde resins
1930	General acceptance of the macromolecular hypothesis
1931	Poly(methyl methacrylate)
1936	Poly(vinyl acetate) and poly(vinyl butyrate) in laminated safety glass; Nylon 66
1937	Polystyrene manufacture
1939	Melamine-formaldehyde resins; neoprene rubber; polysulfide rubber (Thiokol)
1939–1945	Manufacture of polyethylene (UK); polybutadiene rubber (Germany); acrylonitrile-butadiene rubber (Germany); polyurethanes (Germany); styrene-butadiene rubber (USA); polyisobutylene (butyl rubber; USA)
1945–1960	Epoxy resins, acrylonitrile-butadiene-styrene polymers, polyesters, polyacrylonitrile, polysiloxanes (silicones), linear polyethylene, polypropylene, “living” anionic polymerizations, cationic polymerizations, polyoxymethylene, polycarbonates, polyurethane foams, fluorocarbon polymers
1960–1980s	<i>cis</i> -Polyisoprene rubber, <i>cis</i> -polybutadiene rubber, ethylene-propylene rubber, polyimides, poly(phenylene oxides), polysulfones; styrene-butadiene block copolymers, aromatic polyamides, aromatic ladder polymers, group-transfer polymerization, cyclopolymerizations, olefin metathesis polymerization, polyphosphazenes, polysilanes
1980s–2000s	ADMET polymerizations, atom radical polymerizations, polymerizations in super-critical CO ₂ , poly(phenylenevinyls), polyaniline, poly-(ferrocenophanes), non-linear optical polymers, telechelic polymers, dendrimers, ceramers, living polymerizations to polyphosphazenes, polyester synthesis in bacterial cells, and metallocene catalysts

and engineering fields that make use of polymeric materials. In fact, it has become the central science on which nearly every other scientific and technological field depends. This trend is expected to continue for the foreseeable future.

Another unique characteristic feature of polymer science and technology is the fact that the number of synthetic commercially manufactured polymers has remained almost constant during the past decades. At the same time, the need for polymeric materials with new or improved properties is steadily increasing. Their satisfaction, as the experience during the past decades has demonstrated, takes place not *via* the synthesis of new unknown polymers but through the modification of commercially available ones.

The modification approaches used are mostly of a physical type, such as blending, reinforcement, drawing, controlling the crystallization process, and so on. Combining such approaches of physical modification it is possible to compete in some cases with the mechanical performance of traditional non-polymeric materials, or to create a material with a combination of properties unknown for traditional materials. But it has to be stressed that, as a rule, the plastic materials comprising polymers only are characterized by inferior mechanical properties. Therefore, to meet the demands of industry for strength and stiffness they have to be reinforced. Excellent mechanical properties have been achieved with the more traditional fiber reinforcements such as glass or carbon, but increased focus on the complete lifecycle of a product leads to concerns about recycling and environmental impact. This interface between polymer chemistry, engineering, rheology, and solid-state science is often described under the general umbrella term of *material science*. The period since the mid-1960s has seen a striking growth of interest in material science aspects of polymer science as investigators seek to improve the properties of well-known synthetic polymers. This type of work is likely to become even more important as technology continues to demand new materials with improved properties at a time when most of the readily available organic polymers have already been commercialized.

Materials science includes the fields of metals, ceramics, and a wide range of inorganic semiconductors, optics, and electro-optical materials, as well as polymers. Many modern devices and constructs combine and utilize materials from all four of these large areas. It seems clear that the technological future of polymer science will require a close interaction between the synthetic chemist on the one hand and the physical chemist and material scientist on the other.

Concluding this short historical overview on the rise of polymer science it should be stressed that, regardless of the fact that polymer science is extremely young (less than 100 years development), it has achieved remarkable results. Very soon after its formulation, Staudinger organized the first world-wide scientific journal on polymers, named “*Die Makromolekulare Chemie*,” followed by the second journal “*Die Angewandte Makromolekulare Chemie*.” In the United States similar activities were developed by *H. Mark* who used to work in Europe contributing to the establishment of polymer science and later immigrated to the United States. There he organized the “*Journal of Polymer Science*” (in three editions) and the “*Journal of Applied Polymer Science*” as well as the first “*Encyclopedia of Polymer Science and Technology*.” He also founded the first Polymer Institute at Brooklyn Polytechnic. Nowadays the scientific journals dealing with polymer science and technology are more than 100.

In this relatively short period of development the remarkable achievements of polymer scientists were awarded with *Nobel Prizes*. Their names are:

- 1) *Hermann Staudinger*, 1953, for his work in macromolecular chemistry,
- 2) *James Watson*, *Francis Crick*, and *Maurice Wilkins*, 1962, jointly, for their 1953 determination of the structure of DNA,
- 3) *Karl Ziegler* and *Giulio Natta*, 1963, jointly, for polymer synthesis techniques,

- 4) *Paul John Flory*, 1974, for theoretical and experimental work in polymer chemistry,
- 5) *Bruce Merrifield*, 1991, for synthesis on a solid matrix,
- 6) *Pierre-Gilles de Gennes*, 1991, for discovering that methods developed for studying order phenomena in simple systems can be generalized to more complex forms of matter, in particular to liquid crystals and polymers,
- 7) *Alan G. MacDiarmid*, *Alan J. Heeger*, and *Hideki Shirakawa*, 2000, jointly, for electrically conductive polymer,
- 8) *Y. Chauvin*, *R. H. Grubbs*, and *R. Schrock*, 2005, jointly for metathesis reactions.

In addition, many of the prizes in medicine are related to polymers/macromolecules.

In these concluding remarks it seems worth mentioning also the following facts. As noted earlier, polymers are all around us. Over 100×10^9 lb (50×10^6 t) of synthetic polymers are produced annually in the United States (Table 1.2), and growth of the industry is continuing at a fast rate. There is every reason to believe that this polymer age will continue as long as petroleum and other feed stocks are available and as long as consumers continue to enjoy the comfort, protection, and health benefits provided by elastomers, fibers, plastics, adhesives, and coatings. The 100×10^9 lb of synthetic polymers consumed each year in the United States translates to over 300 lb for every man, woman, and child in the United States. This does not include paper- and wood-related products, natural polymers such as cotton and wool, or inorganic polymers.

The number of professional chemists directly employed with polymers as part of their interest and assignment is estimated to be 40–60% of all chemists. As the

Table 1.2 United States production of plastics (2010).

Plastics		Production (millions of pounds)
Thermosetting resins	Epoxies	610
	Ureas and melamines and phenolics, miscellaneous.	12 600
	Total	13 210
Thermoplastics	Low density polyethylene	6700
	High density polyethylene	16 900
	Linear low density polyethylene	13 800
	Polypropylene	17 300
	Polystyrene	5000
	ABS and styrene-acrylonitrile	2600
	Polyamides, nylons	1000
	PVC and copolymers	14 000
	Other thermoplastics	14 800
	Total thermoplastics	90 000
Grand total		103 000

diversity of chemistry increases, the dispersion of those dealing with polymers increases. Polymer chemistry is a major tool applied in biomedical research, synthesis, manufacturing, chemical engineering, pharmaceutical efforts, the environment, communications, and so on (Carraher, 2014).

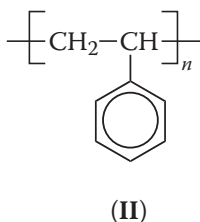
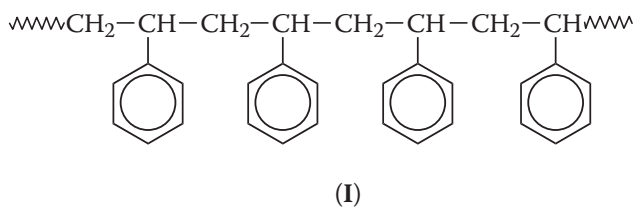
1.2 Basic Terms and Definitions in Polymer Science

Many of the terms, definitions, and concepts used in polymer science are not encountered in other branches of science and must be understood in order to fully discuss the synthesis, characterization, structure, and properties of polymers. While most of these are discussed in detail in subsequent chapters, some are of such fundamental importance that they must be introduced at the beginning.

1.2.1 Polymer

The term *polymer* stems from the Greek roots *poly* (many) and *meros* (part). The word thus means “many parts” and designates a molecule made up by the repetition of some simpler unit called a *mer*. Polymers contain thousands to millions of atoms in a molecule that is large, also called *macromolecule*. Polymers are prepared by joining a large number of small molecules called *monomers*.

The structure of polystyrene, for example, can be written as **I** in Scheme 1.1, or, more conveniently, as **II** in Scheme 1.1, which depicts the *mer* or *repeating unit* of the molecule within parentheses with a subscript, such as *n*, to represent the number of repeating units in the polymer molecule.



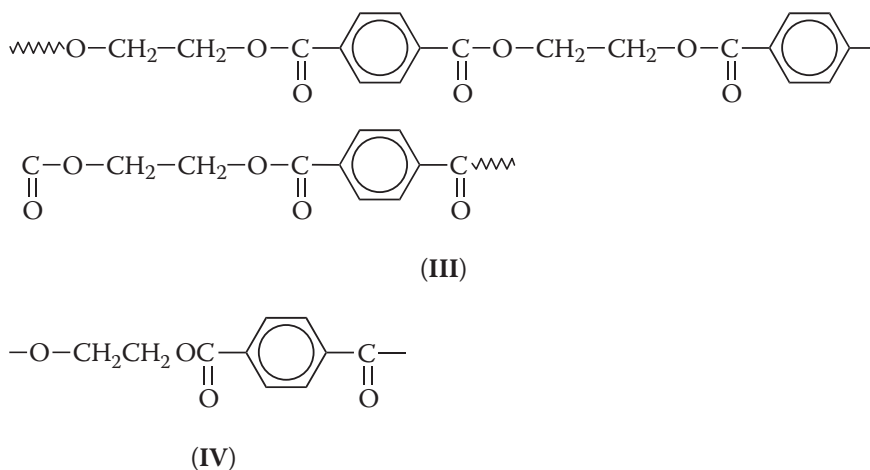
Scheme 1.1

The value of *n* usually ranges from a few hundred to several thousand, depending on the molecular weight of the polymer. The polymer molecular weight may extend, on the higher side to several millions. Often the term *high polymer* is also used to emphasize that the polymer under consideration is of very high molecular weight.

1.2.2 Monomer

Monomers are generally simple organic molecules from which the polymer molecule is made. The structure of the repeating unit of a polymer is essentially that or closely related to that of the monomer molecule(s). The formula of the polystyrene repeating unit **II** is thus seen to be essentially the same as that of the monomer styrene $\text{CH}_2=\text{CH}-\text{C}_6\text{H}_5$.

The repeating unit of a linear polymer is a small portion of the macromolecule such that linking together these units one after another gives rise to the formula of the whole molecule. A repeating unit may be a single component such as **II** for the polymer **I** in Scheme 1.1, or it may consist of the residues of several components, as in poly(ethylene terephthalate), which has the structure **III** in Scheme 1.2. The repeating unit in **III** may be written as **IV** in Scheme 1.2. Thus, the whole molecule of **III** can be built by linking the left-hand atom shown in **IV** to the right-hand atom, and so on.

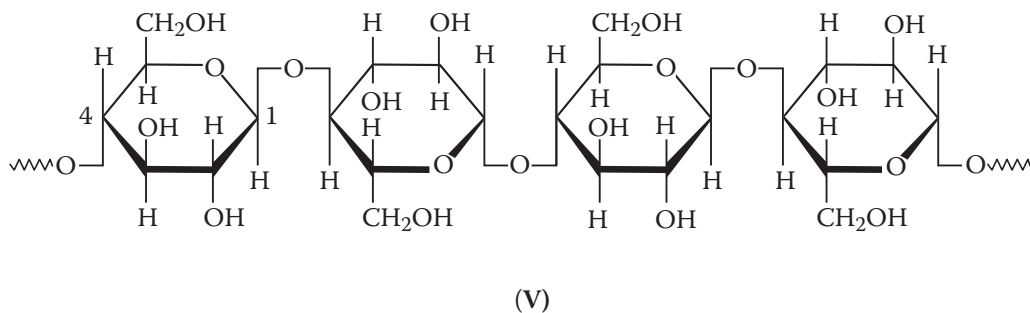


Scheme 1.2

Though it has been stated above that structures of repeating units are essentially those of the monomers from which the polymers are made, this is not always the case. A good example is poly(vinyl alcohol). The obvious precursor monomer for this polymer is vinyl alcohol, $\text{CH}_2=\text{CH}-\text{OH}$, which does not exist. Poly(vinyl alcohol) is instead made by alcoholises of poly(vinyl acetate), which, in turn, is synthesized by polymerization of the monomer vinyl acetate, $\text{CH}_2=\text{CHOOCCH}_3$.

Another example is cellulose, which is a carbohydrate with molecular formula $(\text{C}_6\text{H}_{10}\text{O}_5)_n$, where n is a few thousand. The structure is **V** in Scheme 1.3.

Complete hydrolysis of cellulose by boiling with concentrated hydrochloric acid yields D-glucose, $\text{C}_6\text{H}_{12}\text{O}_6$, in 95% yield but cellulose cannot be synthesized from glucose.



Scheme 1.3

1.2.3 End Groups

None of the above examples of polymer structural representations show the end groups. This is partly because the exact nature of the end groups of polymer molecules is often not known and partly because end groups constitute an insignificant fraction of the mass of high molecular polymers.

1.2.4 Degree of Polymerization

This term refers to the number of repeating units that constitute a polymer molecule. We shall use the abbreviation *DP* for the degree of polymerization defined in this way. The subscript *n* used on the parentheses in the foregoing structural formulas for polymers represents this *DP*. The relation between degree of polymerization and molecular weight *M* of the same macromolecule is given by:

$$M = (DP)M_o \quad (1.1)$$

where *M_o* is the formula weight of the repeating unit.

1.2.5 Copolymers

If a macromolecule is made from only one species of monomer, the product is a *homopolymer*, referred to simply as a polymer. The word homopolymer often is used more broadly to describe polymers whose structure can be represented by repetition of a single type of repeating unit containing one or more species. Thus, a hypothetical polymer $-[AB]_n-$ made from A and B species is also a homopolymer, for example, poly(ethylene terephthalate) (III).

The formal definition of a *copolymer* is a polymer derived from more than one species of monomer. The copolymer with a relatively random distribution of the different mers or repeating units in its structure is commonly referred to as a *random copolymer*. Representing two different mers by A and B, a random copolymer can be depicted as:



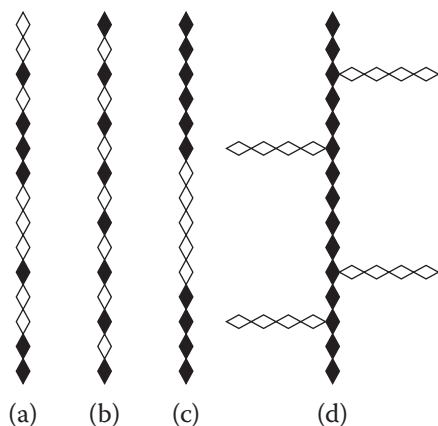


Figure 1.3 Copolymer arrangements: (a) two different types of mers (denoted by open and filled diamonds) are randomly placed, (b) the mers are alternately arranged, (c) a block copolymer, and (d) a graft copolymer.

There are three other copolymer structures: *alternating*, *block*, and *graft* copolymer structure (Figure 1.3). In the *alternating copolymer* the two mers alternate in a regular fashion along the polymer chain:

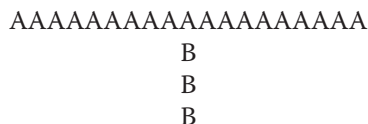


A *block copolymer* is a linear polymer with one or more long uninterrupted sequences of each mer in the chain:



Block copolymers may have a different number of blocks in the molecule. Thus, A_xB_y , $A_xB_yA_x$, $A_xB_yA_xB_y$, $(A_xB_y)_n$ are referred to as AB *diblock*, ABA *triblock*, ABAB *tetrablock*, and AB *multiblock* copolymers, respectively. Since there is a distribution of block lengths and number of blocks along the copolymer chain, x and y as well as n represent average values.

A *graft copolymer*, on the other hand, is a branched copolymer with a backbone of one type of mer and one or more side chains of another mer:



The copolymer arrangements are shown in Figure 1.3.

Copolymerization which, in its objective, may be compared to alloying in metallurgy, is very useful for synthesizing polymer with the required combination of properties.

1.2.6 Average Molecular Weights and Distributions

A major distinguishing feature of high polymers is their enormous molecular weight. Molecular weights of 20 000 daltons (Da) are routine, and values as high as 2 000 000 Da are not uncommon. However, unlike small molecules such as

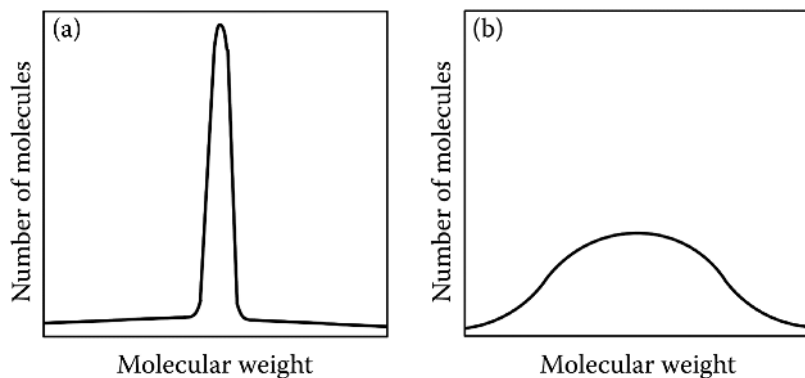


Figure 1.4 Molecular weight distributions: (a) narrow (M_w/M_n close to 1), and (b) broad ($M_w/M_n > 2$).

benzene or chloroform, or biological polymers like enzymes, a sample of a synthetic polymer has no single, fixed molecular weight. Instead, there is a *distribution* of different molecular weights in the same sample of material (Figure 1.4). For this reason, it is necessary to speak of *average* molecular weights rather than a single defining value.

Several different types of average molecular weights are used in polymer chemistry, the most important of which are known as *number average*, \overline{M}_n , and *weight average*, \overline{M}_w , values. They are defined as shown in Equations (1.2) and (1.3):

$$\overline{M}_n = \sum_i X_i M_i = \frac{\sum_i N_i M_i}{\sum_i N_i} \quad (1.2)$$

$$\overline{M}_w = \sum_i W_i M_i = \frac{\sum_i w_i M_i}{\sum_i w_i} = \frac{\sum_i N_i M_i^2}{\sum_i N_i M_i} \quad (1.3)$$

where N_i is the number of molecules of molecular weight M_i , X_i is the *number fraction* or *mole fraction* of molecules having molecular weight M_i , w_i is the weight of molecules of molecular weight M_i , and W_i is the weight fraction of molecules with molecular weight M_i .

As will be seen in Chapter 7, \overline{M}_n can be obtained from the study of the osmotic pressure of polymer solutions, whereas \overline{M}_w values are obtained from light-scattering or ultracentrifugation experiments. The technique known as gel permeation chromatography or size exclusion chromatography (Chapter 7) gives both \overline{M}_n and \overline{M}_w values. In general, \overline{M}_w values are higher than \overline{M}_n because the calculations for \overline{M}_w give more emphasis to the larger molecules, while \overline{M}_n calculations give equal emphasis to all molecules. Their position on the curve of distribution of molecular weights is shown in Figure 1.5.

The fraction M_w/M_n (called the *polydispersity*) is a measure of the molecular weight distribution. If the value of $\overline{M}_w/\overline{M}_n$ is close to 1 (1.01 or 1.02 for instance), the distribution is very narrow. If it is, say, 2 or higher, the distribution is considered to be very broad. These two situations are graphically presented in Figure 1.4.

The molecular weight distribution affects several important polymer properties. For example, polymers with very broad distributions are less prone to

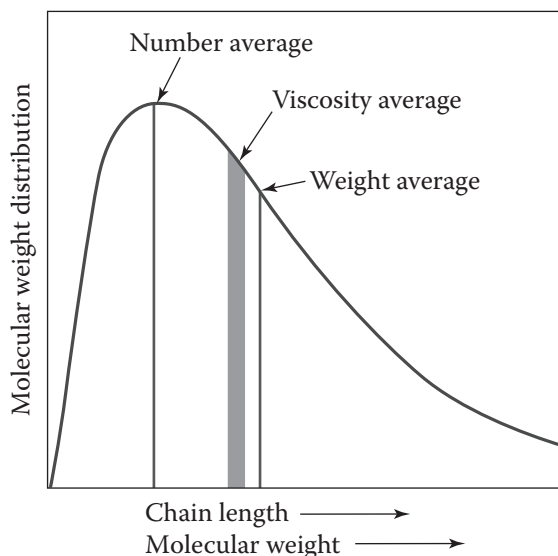


Figure 1.5 Distribution of molecular weights in a typical polymer. Reprinted with permission from Osswald, T. and Menges, G. *Materials Science of Polymers for Engineers*, 3rd edition, 2012, Hanser Publishers, Munich.

crystallize than their narrow distribution counterparts, and they often have lower solidification temperatures. The shorter chains plasticize the bulk material and make it softer. Thus, together with the glass transition temperature, T_g , and the crystalline melting temperature, T_m (see below), M_w/M_n is a crucial characteristic of any synthetic polymer.

1.2.7 Molecular Weight and Molar Mass

The term “molecular weight” is frequently used in practice instead of the term “molar mass,” though the former can be somewhat misleading. Molecular weight is really a dimensionless quantity given by the sum of the atomic weights in the molecular formula. The molar mass of a substance, on the other hand, is the mass of 1 mol of the substance and usually is quoted in units of g/mol or kg/mol. The numerical value of weight is multiplied by the specific units, such as g/mol, to convert it into an equivalent of molar mass in dimensions of g/mol. Thus, a molecular weight of 100 000 is equivalent to mass of 100 000 g/mol or 100 kg/mol.

This book will retain the term “molecular weight” because of its widespread use in the literature. However, when using in numerical calculations we shall substitute the molecular weight by its numerically equivalent molar mass (g/mol) to facilitate dimensional balancing.

Small molecules such as water have a definite structure (H_2O) and a precise molar mass (often called molecular weight, MW; 18 g/mol, do not forget the units!). Proteins, enzymes, DNA, and similar natural polymers have a well-defined structure and a precise molecular weight. Synthetic macromolecules are invariably polymolecular (*polydisperse*): they consist of a mixture of molecules

with many different molecular weights (chain lengths). Some natural polymers such as natural rubber (NR) are also polydisperse. Therefore we needed to define molecular weight averages.

1.2.8 Polymer Morphology

Polymer morphology is the study of the solid-state structure and behavior of polymers. It includes investigations of what happens when polymers are mixed in the solid state, and of phase separations. It also involves crystallinity and other phase transitions, and the influence of materials history on strength, elasticity, and polymer-chain orientation. The field also deals with the response of polymers to temperature changes and exposure to solvents. It also includes the membrane behavior of polymers and the transport of liquids, gases, and ions through the solid polymer structure. Ideally, there should be a seamless interaction between research on the synthesis and structure of polymers at the molecular level and morphological investigations, because both aspects are equally important.

1.2.9 Thermoplastics

Basically, a *thermoplastic* is any material that softens when it is heated. However, the term is commonly used to describe a substance that passes through a definite sequence of property changes as its temperature is raised. An *amorphous* polymeric material contains randomly entangled chains. A microcrystalline (usually abbreviated to “*crystalline*”) material contains domains in which the polymer chains are packed in an ordered array. These “crystalline” domains are embedded in an amorphous polymer matrix.

Both amorphous and semi-crystalline thermoplastics are glasses at low temperatures, and both change from a glass to a rubbery elastomer or flexible plastic as the temperature is raised. This change from glass to elastomer usually takes place over a fairly narrow temperature range (2–5 °C), and this transition point is known as the *glass transition temperature* (T_g). For many polymers, the glass transition temperature is the most important characterization feature. It can be compared to the characteristic melting point of a low molecular weight compound, although care should be taken to remember that T_g is definitely *not* a melting temperature in the accepted sense of the word. It is more a measure of the ease of torsion of the backbone bonds rather than of the ease of separation of the molecules.

At temperatures above T_g , amorphous polymers behave in a different manner from crystalline polymers. As the temperature of an amorphous polymer is raised, the hard rubbery state *gradually* gives way to a soft, extensible elastomeric state, then to a gum, and finally to a liquid. No sharp transition occurs from one state to the other, and only a gradual change in properties is perceptible.

Crystalline polymers, on the other hand, retain their rubbery elastomeric or flexible properties above the glass transition, until the temperature reaches the melting temperature (T_m). At this point, the material liquefies. At the same time, melting is accompanied by a loss of the optical birefringence and crystalline X-ray diffraction effects that are characteristic of the crystalline state.

Some polymers show an additional phase transition between the glass transition temperature and the formation of a true isotropic liquid. These are the so-called *liquid-crystalline polymers*. A liquid-crystalline polymer, when heated, passes through the normal glass and microcrystalline phases but undergoes a quasi-melting transition (T_{lc}) at a temperature below the final liquefaction point (T_m). Between T_{lc} and T_m the polymer has some characteristics of a molten material (e.g., it flows), but physical techniques reveal the retention of some structural order. Side groups may be loosely stacked in this phase, or skeletal segments may retain some alignment. Only at the highest temperature transition (T_m) is all structure lost, and the material then becomes an isotropic liquid.

The amorphous, crystalline, and liquid crystalline behavior described above is characteristic of linear and branched polymers, copolymers, or cyclo-linear polymers. In general, these characteristics are not shown by heavily cross-linked polymers or cyclo-matrix materials. These latter substances retain their rigidity when heated. Melting phenomena occur only when the cross-link units or backbone bonds become thermally broken. Lightly cross-linked polymers show many of the conventional thermoplastic properties, with the exception that the true liquid phase may not be formed.

1.2.10 Elastomers

In view of the information just given, it will be clear that an *elastomer* is a flexible polymer that is in the temperature range between its glass transition temperature and its liquefaction temperature. In practice, elastomeric properties become more obvious if the polymer chains are slightly cross-linked. In particular, the liquefaction temperature may be raised by cross-linking, and the polymer may exhibit elastomeric properties over a wider temperature range.

Elastomeric properties appear when the backbone bonds can readily undergo torsional motions to permit uncoiling of the chains when the material is stretched (Figure 1.6). Cross-links between the chains prevent the macromolecules from slipping past each other and thus prevent the material from becoming permanently elongated when held under tension. An important question connected with elasticity is this: Why do the chains revert to the highly coiled state when the

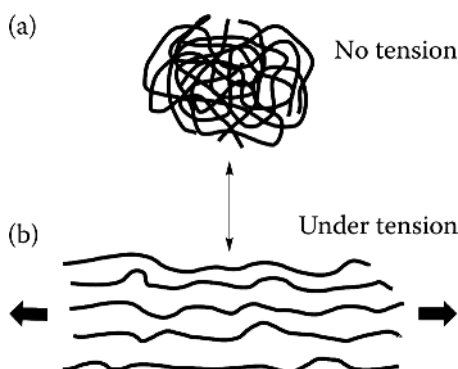


Figure 1.6 Rubbery elastomeric properties result from the stress-induced uncoiling and recoiling of polymer chains: (a) relaxed: high entropy; and (b) stretched ordered: low entropy. Note that this is independent of the contribution to the elasticity played by cross-links.

tension on the elastomer is released? The answer lies in the fact that a highly coiled polymer system has a higher degree of disorder and, therefore, higher entropy than a stretched, oriented sample. Thus, the elastic behavior is a direct consequence of the tendency of the system to assume spontaneously a state of maximum entropy. Since free energy, enthalpy, and entropy are related by the well-known expression, $\Delta G = \Delta H - T\Delta S$, a stretched rubber band immediately held to the lips is warm, and the same material appears cold immediately after contraction.

1.2.11 Plastics

Many neat polymers are too rigid for use as flexible films. Poly(vinyl chloride) in the pure state is a rather rigid material. Only when this polymer is softened by the addition of low-volatility liquids, such as phthalate esters, can it be used as a flexible-film or Tygon tubing. Such liquid additives are known as *plasticizers*. There are also some unusual cases where a low molecular weight material in small amounts can act as an *antiplasticizer*. Apparently these molecules interact so strongly with the polymer chains that they suppress some low-temperature motions, causing a stiffening effect. Increasing the amount of the material beyond the amount required to saturate this interaction then causes the expected plasticization and softening of the material.

1.2.12 Thermosetting Resin

The term *thermosetting polymer* refers to a range of systems which exist initially as liquids but which, on heating, undergo a reaction to form a solid, highly cross-linked matrix. A typical example is provided by the condensation of methylol melamine to give the hard, tough, cross-linked melamine resin. Partly polymerized systems which are still capable of liquid flow are called *prepolymers*. Prepolymers are often preferred as starting materials in technology. In practical terms, an uncross-linked thermoplastic material can be re-formed into a different shape by heating; a *thermosetting* polymer cannot.

1.2.13 Polymer Blends

When two or more polymers are mixed together mechanically, the product is known as a *polymer blend*. Many polymer blends display properties that are different from those of the individual polymers. Polymer blends can be of two main types, *miscible* or *immiscible*. Superimposed on these alternatives are three additional classifications: (i) simple cellular domain mixtures of the polymers, (ii) interpenetrating coils of macromolecules that are randomly mixed at the molecular level, and (iii) secondary block or graft copolymers formed by the physical breaking of bonds, followed by bonding between the different polymeric fragments. The latter type of process can occur when two or more polymers are milled or masticated together. The mechanical shearing can result in the homolytic cleavage of bonds, followed by cross-recombination.

1.2.14 Tacticity

Olefin molecules that contain one unique side group, such as propylene, $\text{CH}_2=\text{CH}(\text{CH}_3)$, or styrene, $\text{CH}_2=\text{CH}(\text{C}_6\text{H}_5)$, yield polymers that possess an *asymmetric center* at each monomer residue. The *tacticity* of a polymer describes the sequencing of these asymmetric centers along the chain. Three primary possibilities exist, called *isotactic*, *syndiotactic*, or *atactic* (heterotactic) sequencing. This subject, like many others, is discussed in more detail later. Here it is sufficient to note that the tacticity of a polymer markedly affects the bulk physical properties. For example, an isotactic polymer may form a microcrystalline solid that has greater strength and rigidity than its atactic counterpart.

1.2.15 Polymerization and Functionality

Polymerization may occur only if the monomers involved in the reaction have the proper functionalities. Functionality is a very useful concept in polymer science. The *functionality* of a molecule is the number of sites it has for bonding to other molecules under the given conditions of the polymerization reaction. Thus, a bifunctional monomer, that is, a monomer with functionality 2, can link to two other molecules under suitable conditions. Styrene, $\text{C}_6\text{H}_5\text{CH}=\text{CH}_2$, for example, has functionality 2 because of the presence of a carbon–carbon double bond. The minimum functionality required for polymerization is 2. A polyfunctional monomer is one that can react with more than two molecules under the conditions of the polymerization reaction.

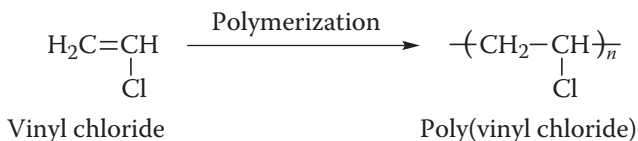
1.2.16 Polymerization Processes

There are two fundamental polymerization mechanisms. Classically, they have been differentiated as *addition polymerization* and *condensation polymerization*. In the addition process, no byproduct is evolved, as in the polymerization of vinyl chloride (see below); whereas in the condensation process, just as in various condensation reactions (e.g., esterification, etherification, amidation, *etc.*) of organic chemistry, a low molecular weight byproduct (e.g., H_2O , HCl , *etc.*) is evolved. Polymers formed by addition polymerization do so by the successive addition of unsaturated monomer units in a *chain reaction* promoted by the *active center*. Therefore, addition polymerization is called *chain polymerization*. Similarly, condensation polymerization is referred to as *step polymerization* since the polymers in this case are formed by *stepwise*, intermolecular condensation of reactive groups. Another quite important difference between the addition polymerization and condensation polymerization is the fact that condensation polymerization is reversible similarly to all condensation reaction in organic chemistry. This means that the condensation polymer in the presence of the evolved low molecular weight byproduct and the respective conditions (temperature, catalyst, *etc.*) can be converted back to the starting monomers. In case that the low molecular weight byproduct is water, this process is called *hydrolysis* and has extremely important role during processing of polymers.

The polymers prepared *via* addition polymerization do not undergo such reactions.

1.2.17 Addition or Chain Polymerization

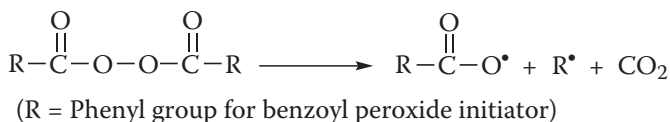
In chain polymerization, a simple, low molecular weight molecule possessing a double bond, referred to in this context as a monomer, is treated so that the double bond opens up and the resulting free valences join with those of other molecules to form a polymer chain. For example, in Scheme 1.4, vinyl chloride polymerizes to poly(vinyl chloride).



Scheme 1.4

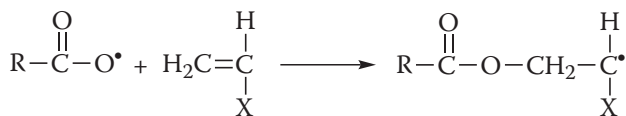
It is evident that no side products are formed; consequently the composition of the mer or repeating unit of the polymer ($\text{--CH}_2\text{--CHCl--}$) is identical to that of the monomer (CH_2CHCl). The identical composition of the repeating unit of a polymer and its monomer(s) is, in most cases, an indication that the polymer is an addition polymer formed by chain polymerization process.

Chain polymerization involves three processes: *chain initiation*, *chain propagation*, and *chain termination*. (A fourth process, *chain transfer*, may also be involved, but it may be regarded as a combination of chain termination and chain initiation.) Chain initiation occurs by an attack on the monomer molecule by a free radical, a cation, or an anion; accordingly, the chain polymerization processes are called *free-radical polymerization*, *cationic polymerization*, or *anionic polymerization*. A free radical is a reactive substance having an unpaired electron and is usually formed by the decomposition of a relatively unstable material called an *initiator*. Benzoyl peroxide is a common free-radical initiator and can produce free radicals by thermal decomposition (Scheme 1.5).



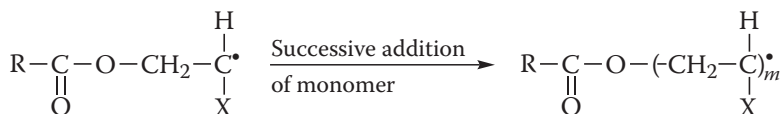
Scheme 1.5

Free radicals are, in general, very active because of the presence of unpaired electrons (denoted in Scheme 1.5 by a dot). A free-radical species can thus react to open the double bond of a vinyl monomer and add to one side of the broken bond, with the reactive center (unpaired electron) being transferred to the other side of the broken bond (Scheme 1.6a).



(X = CH₃, C₆H₅, Cl, etc.)

(a)

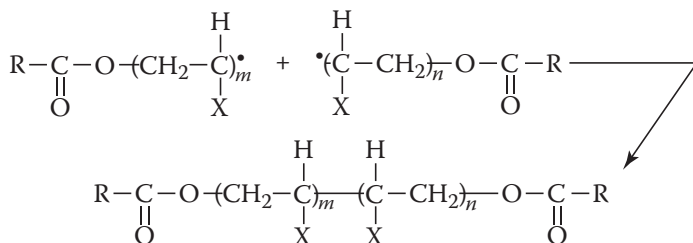


(b)

Scheme 1.6

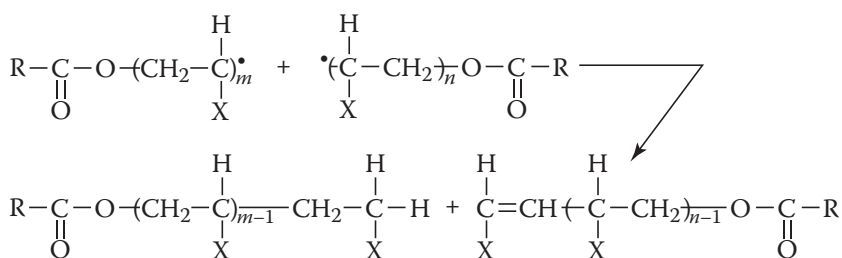
The new species, which is also a free radical, is able to attack a second monomer molecule in a similar way, transferring its reactive center to the attacked molecule. The process is repeated, and the chain continues to grow as a large number of monomer molecules are successively added to propagate the reactive center (Scheme 1.6b).

This process of *propagation* continues until another process intervenes and destroys the reactive center, resulting in the *termination* of the polymer growth. There may be several termination reactions depending on the type of the reactive center and the reaction conditions. For example, two growing radicals may combine to annihilate each other's growth activity and form an inactive polymer molecule; this is called termination by *combination* or *coupling* (Scheme 1.7a).



Inactive polymer molecule

(a)



(b)

Scheme 1.7

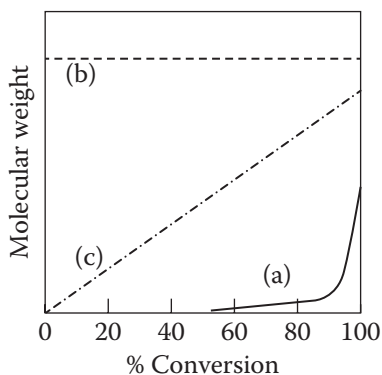


Figure 1.7 Variation of molecular weight with conversion in: (a) step polymerization, (b) radical chain polymerization, and (c) ionic chain polymerization.

A second termination mechanism is *disproportionation*, shown in Scheme 1.7b).

In chain polymerization initiated by free radicals, as in the previous example, the reactive center, located at the growing end of the molecule, is a free radical. As mentioned previously, chain polymerizations may also be initiated by ionic systems. In such cases, the reactive center is ionic, that is, a *carbonium ion* (in cationic initiation) or a *carbanion* (in anionic initiation). Regardless of the chain initiation mechanism – free radical, cationic, or anionic – once a reactive center is produced it adds many more molecules in a chain reaction and grows quite large extremely rapidly, usually within a few seconds or less. (However, the relative slowness of the initiation stage causes the overall rate of reaction to be slow and the conversion of all monomers to polymers in most polymerizations requires at least 30 min, sometimes hours.) Evidently, at any time during a chain polymerization process the reaction mixture will consist only of unreacted monomers, high polymers and unreacted initiator species, but no intermediate sized molecules. The chain polymerization will thus show the presence of high molecular weight polymer molecules at all extents of conversion (see Figure 1.7).

Table 1.3 lists some of the most common addition homopolymers. Comments regarding their basic properties and/or application opportunities are also added.

1.2.18 Step Polymerization

Step polymerization occurs by a stepwise reaction between functional groups of reactants. The reaction leads successively from monomer to dimer, trimer, tetramer, pentamer, and so on, until finally a polymer molecule with large *DP* is formed. Note, however, that reactions occur at random between the intermediates (e.g., dimers, trimers, *etc.*) and the monomer as well as among the intermediates themselves. In other words, reactions of both types occur equally, namely:

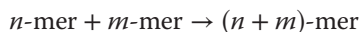
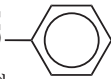



Table 1.3 Typical addition polymers (homopolymers) (Chanda, 2013).

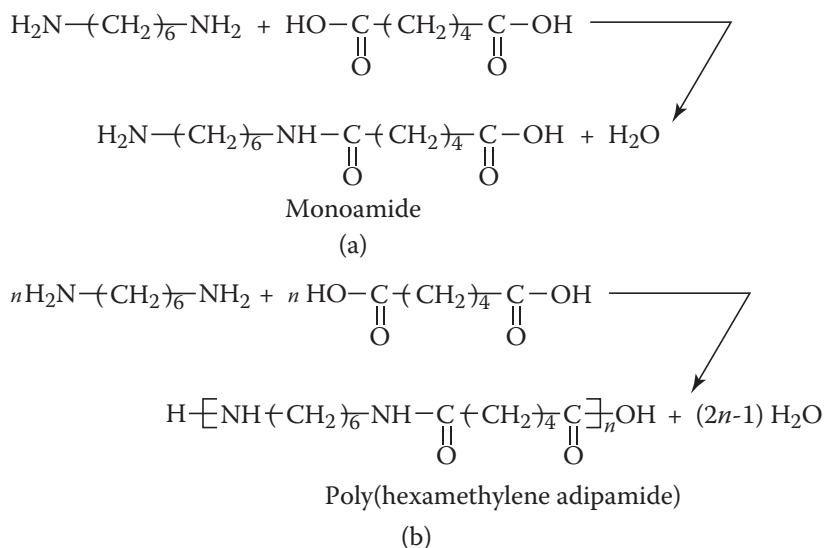
Monomer	Polymer	Comments
1. Ethylene $\text{CH}_2=\text{CH}_2$	Polyethylene (PE) $\text{-(CH}_2\text{-CH}_2\text{)}_n$	High density polyethylene (HDPE) and low density polyethylene (LDPE); molded objects, tubing, film, electrical insulation, household products, insulators, pipes, toys, bottles, for example, Alkathene, Lupolan, Hostalen, Marlex
2. Propylene $\text{CH}_2=\text{CH-CH}_3$	Polypropylene (PP) $\text{-(CH}_2\text{-CH(CH}_3\text{))}_n$	Lower density, stiffer, and higher temperature resistance than PE; used for water pipes, integral hinges, sterilizable hospital equipment, for example, Propathene, Novolen, Moplen, Hostalen, Marlex
3. Styrene $\text{CH}_2=\text{CH-}$ 	Polystyrene (PS) $\text{-(CH}_2\text{-CH(CH}_2\text{-C}_6\text{H}_5\text{))}_n$ 	Transparent and brittle; used for cheap molded objects, for example, Styron, Carinex, Hostyren, Lustrex; modified with rubber to improve toughness, for example, high impact polystyrene (HIPS) and acrylonitrile-butadiene-styrene copolymer (ABS). Expanded by volatilization of a blended blowing agent (e.g., pentane) to make polystyrene foam, for example, Styrocell, Styrofoam
4. Acrylonitrile $\text{H}_2\text{C=CH-CN}$	Polyacrylonitrile $\text{-(CH}_2\text{-CH(CN))}_n$	Widely used as fibers; best alternative to wool for sweaters, for example, Orion, Acrilan
5. Vinylacetate $\text{CH}_2=\text{CH-O-C(=O)CH}_3$	Poly (vinyl acetate) $\text{-(CH}_2\text{-CH(O-C(=O)CH}_3\text{))}_n$	Emulsion paints, adhesives, sizing, chewing gum, for example, Flovic, Mowilith, Mowicoll

6.	Vinyl chloride $\text{CH}_2=\text{CH}-\text{Cl}$	Poly (vinyl chloride) (PVC) $\text{---}\left(\text{CH}_2-\underset{\text{Cl}}{\text{CH}}\right)_n\text{---}$	Water pipes, bottles, gramophone records, plasticized to make PVC film, leather cloth, raincoats, flexible pipe, tube, hose, toys, electrical cable sheathing, for example, Benvic, Darvic, Geon, Hostalit, Solvic, Vinoflex, Welvic
7.	Tetrafluoroethylene $\text{CF}_2=\text{CF}_2$	Polytetrafluoroethylene (PTFE) $\text{---}\left(\text{CF}_2-\text{CF}_2\right)_n\text{---}$	High temperature resistance, chemically inert, excellent electrical insulator, very low coefficient of friction, expensive; moldings, films, coatings; used for non-stick surfaces, insulation, gaskets; for example, Teflon, Fluon
8.	Methyl methacrylate $\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_2=\text{C} \\ \\ \text{C}=\text{O} \\ \\ \text{OCH}_3 \end{array}$	Poly(methyl methacrylate) (PMMA) $\text{---}\left(\text{CH}_2-\underset{\text{C}=\text{O}}{\overset{\text{CH}_3}{\text{C}}}\right)_n\text{---}$ OCH_3	Transparent sheets and moldings; more expensive than PS; known as <i>organic glass</i> , used for airplane windows; for example, Perspex, Plexiglass, Lucite, Diakon, Vedril
9.	Isobutylene $\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_2=\text{C} \\ \\ \text{CH}_3 \end{array}$	Polyisobutylene (PIB) $\text{---}\left(\text{CH}_2-\underset{\text{CH}_3}{\overset{\text{CH}_3}{\text{C}}}\right)_n\text{---}$	Lubricating oils, sealants, copolymerized with 0.5–2.5 mol% isoprene to produce Butyl rubber for tire inner tubes and inner liners of tubeless tires
10.	Isoprene $\begin{array}{c} \text{CH}_2=\text{C}-\text{CH}=\text{CH}_2 \\ \\ \text{CH}_3 \end{array}$	<i>cis</i> -1,4-Polyisoprene $\text{---}\left(\text{CH}_2-\underset{\text{CH}_3}{\text{C}=\text{CH}-\text{CH}_2}\right)_n\text{---}$	Tires, mechanical goods, footwear, sealants, calking compounds, for example, Coral, Natsyn, Clariflex I
11.	Butadiene $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$	<i>cis</i> -1,4-Polybutadiene $\text{---}\left(\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2\right)_n\text{---}$	Tires and tire products, for example, <i>Cis</i> -4, Ameripol-CB, Diene

Thus, at any stage the product consists of molecules of varying sizes, giving a range of molecular weights. The average molecular weight builds up slowly in the step polymerization process, and a high molecular weight product is formed only after a sufficiently long reaction time when the conversion is more than 98% (see Figure 1.7a). In contrast, polymerization by chain mechanism proceeds very fast, a full-sized polymer molecule being formed almost instantaneously after a chain is initiated; the polymer size is thus independent of reaction time (Figure 1.7b). In certain ionic chain polymerizations, which feature a fast initiation process coupled with the absence of reactions that terminate the propagating reactive centers, molecular weight increases linearly with conversion (Figure 1.7c).

Since most (though not all) of the step polymerization processes involve polycondensation (repeated condensation) reactions, the terms “step polymerization” and “condensation polymerization” are often used synonymously. Consider, for example, the synthesis of a polyamide, that is, a polymer with amide ($-\text{CONH}-$) as the characteristic linkage. If we start with, say, hexamethylenediamine and adipic acid as reactants, the first step in the formation of the polymer (Nylon) is the reaction in Scheme 1.8a, producing a monoamide.

The reaction continues step by step to give the polyamide Nylon 66. The overall reaction may thus be represented as in Scheme 1.8b.

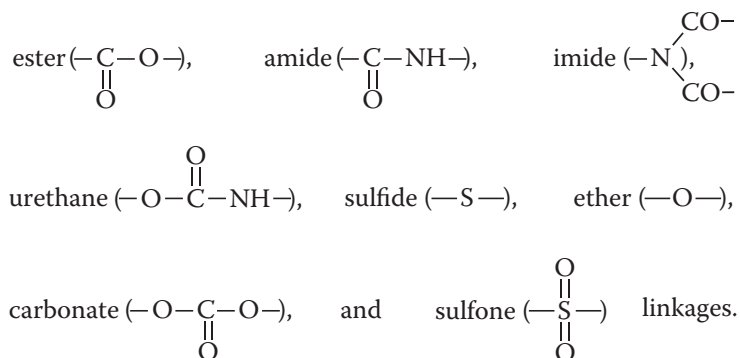


Scheme 1.8

We see that the composition of the repeating unit (enclosed in square brackets) equals that of two monomer molecules minus two molecules of water. Thus a condensation polymer may be defined as one whose synthesis involves elimination of small molecules or whose repeating unit lacks certain atoms present in the monomer(s).

With the development of polymer science and the synthesis of new polymers, the previous definition of condensation polymer is inadequate. For example, in

polyurethanes (Table 1.4), which are classified as condensation polymers, the repeating unit has the same net composition as the two monomers (i.e., a diol and a diisocyanate), which react without eliminating any small molecule. To overcome such problems, chemists have introduced a definition which describes condensation polymers as consisting of structural units joined by internal functional groups, as shown in Scheme 1.9.



Scheme 1.9

A polymer satisfying either or both of the above definitions is classified as a *condensation polymer*. Phenol formaldehyde, for example, satisfies the first definition but not the second. Some condensation polymers along with their repeating units and condensation reactions by which they can be synthesized are shown in Table 1.4.

1.2.19 Molecular Architecture

Polymers can be classified, based on structural shape of polymer molecules, as *linear*, *branched*, or *network (cross-linked)*. Schematic representations are given in Figure 1.8.

Linear polymers have repeating units linked together in a continuous length (Figure 1.8a). In a *linear polymer*, each repeating unit is therefore linked only to two others. When branches protrude from the main polymer chain at irregular intervals (Figure 1.8b), the polymer is termed a branched polymer. Branches may be short, forming a comb-like structure (Figure 1.8b), or may be long and divergent (Figure 1.8c). *Branched polymers* are thus those in which the repeating units are not linked solely in a linear way. A *network polymer* (Figure 1.8d), on the other hand, can be described as an interconnected branched polymer. And finally, a *ladder polymer* consists of two parallel strands with regular cross-links (Figure 1.8e) in between.

1.2.20 Phase

The word “phase” has various meanings in the everyday life, while in science it is very well defined. In the physical sciences, a *phase* is a region of space (a thermodynamic system), throughout which all physical properties of a material

Table 1.4 Typical condensation polymers (Chanda, 2013).

Polymer type	Polymerization reaction ^{a)}	Comments
Polyamide (PA)	$n \text{ H}_2\text{N}-\text{R}-\text{NH}_2 + n \text{ HOC}-\text{R}'-\text{COOH} \longrightarrow \text{H}-\left(\text{NH}-\text{R}-\text{NHC}-\text{R}'-\text{C}\right)_n\text{OH} + (2n-1) \text{ H}_2\text{O}$ $n \text{ H}_2\text{N}-\text{R}-\text{NH}_2 + n \text{ Cl}-\text{C}-\text{R}'-\text{C}-\text{Cl} \longrightarrow \text{H}-\left(\text{NH}-\text{R}-\text{NHC}-\text{R}'-\text{C}\right)_n\text{Cl} + (2n-1) \text{ HCl}$ $n \text{ H}_2\text{N}-\text{R}-\text{COOH} \longrightarrow \text{H}-\left(\text{NH}-\text{R}-\text{C}\right)_n\text{OH} + (n-1) \text{ H}_2\text{O}$	<p>Moldings fibers, tirecord; poly-(hexamethylene adipamide) (Nylon 6,6), for example, Ultramid A; polycaprolactam (nylon-6), for example, Ultramid B, Akulon, Perlenka, poly-(hexamethylene sebacamide) (Nylon-6,10), for example, Ultramid S, Zytel</p> <p>Textile fibers, film bottles, poly-(ethylene terephthalate) (PET), for example, Terylene, Dacron, Melinex, Mylar</p>
Polyester	$n \text{ HO}-\text{R}-\text{OH} + n \text{ HO}-\text{C}-\text{R}'-\text{C}-\text{OH} \longrightarrow \text{HO}-\left(\text{R}-\text{OC}-\text{R}'-\text{CO}\right)_n\text{H} + (2n-1) \text{ H}_2\text{O}$ $n \text{ HO}-\text{R}-\text{OH} + n \text{ R}'\text{O}-\text{C}-\text{R}'-\text{C}-\text{OR}'' \longrightarrow \text{HO}-\left(\text{R}-\text{OC}-\text{R}'-\text{CO}\right)_n\text{R}'' + (2n-1) \text{ R}'\text{OH}$ $n \text{ HO}-\text{R}-\text{COOH} \longrightarrow \text{HO}-\left(\text{R}-\text{CO}\right)_n\text{H} + (n-1) \text{ H}_2\text{O}$	
Polyurethane (PU)	$n \text{ HO}-\text{R}-\text{OH} + n \text{ OCN}-\text{R}'-\text{NCO} \longrightarrow \text{H}-\left(\text{O}-\text{R}-\text{OC}-\text{NH}-\text{R}'-\text{NHC}\right)_n\text{O}-\text{R}-\text{OCNH}-\text{R}'-\text{NCO}$	<p>Rubbers, foams, coatings; for example, Vulkollan, Adiprene C, Chemigum SL, Desmophen A, Moltopren</p>
Polysulfide	$n \text{ Cl}-\text{R}-\text{Cl} + n \text{ Na}_2\text{S}_x \longrightarrow \left(\text{R}-\text{S}_x\right)_n + 2n \text{ NaCl}$	<p>Adhesives, sealants, binders, hose, for example, Thiokol</p>

Polysiloxane	$n \text{ HO}-\underset{\text{R}}{\overset{\text{R}}{\text{Si}}}-\text{OH} \longrightarrow \text{HO}-\left(\underset{\text{R}}{\overset{\text{R}}{\text{Si}}}-\text{O}\right)_n-\text{H} + (n-1) \text{ H}_2\text{O}$	Elastomers, sealants, fluids, for example, Silastic, Silastomer, Silopren
Phenol-formaldehyde (PF)	$n \text{ HO}-\text{C}_6\text{H}_4-\text{OH} + n \text{ CH}_2=\text{O} \longrightarrow \left[\text{HO}-\text{C}_6\text{H}_4-\text{CH}_2-\text{O}-\text{C}_6\text{H}_4-\text{CH}_2-\text{O} \right]_n + (n-1) \text{ H}_2\text{O}$	Plywood adhesives, glass-fiber insulation, molding compound, for example, Hitanol, Sirfen, Trolitan
Urea formaldehyde (UF)	$n \text{ H}_2\text{N}-\text{C}(=\text{O})-\text{NH}_2 + n \text{ CH}_2=\text{O} \longrightarrow \left(\text{NH}-\text{C}(=\text{O})-\text{NH}-\text{CH}_2 \right)_n + n \text{ H}_2\text{O}$	Particle-board binder resin, paper and textile treatment, molding compounds, coatings, for example, Beetle, Resolite, Cibacoid
Melamine formaldehyde (MF)	$n \text{ H}_2\text{N}-\text{C}(=\text{N})-\text{NH}_2 + n \text{ CH}_2=\text{O} \longrightarrow \left[\text{NHC}(=\text{N})\text{NHCH}_2 \right]_n + n \text{ H}_2\text{O}$	Dinnerware, table tops, coatings, for example, Formica, Melalam, Cymel

a) R, R', R'' represent an aliphatic or aromatic ring. The repeating unit of the polymer chain is enclosed in parentheses.

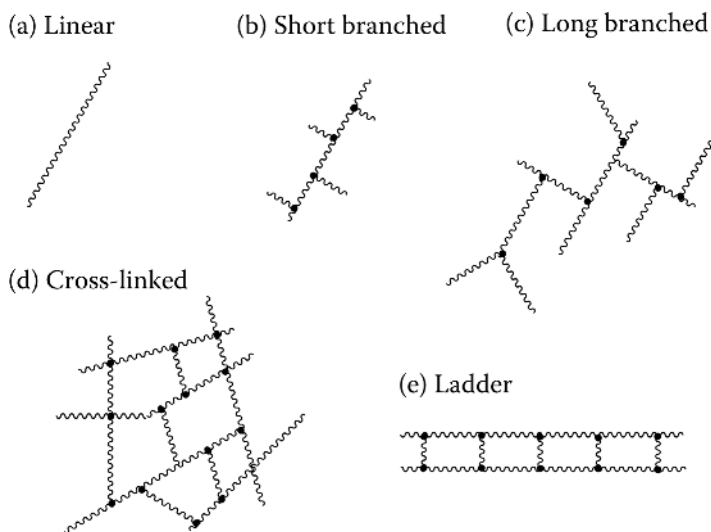


Figure 1.8 Schematic representation of various types of polymer molecules. The branch points and junction points are indicated by heavy dots.

are essentially uniform. Examples of physical properties include density, index of refraction, magnetization, and chemical composition. A simple description is that a phase is a region of material that is chemically uniform, physically distinct, and (often) mechanically separable. In a system consisting of ice and water in a glass jar, the ice cubes are one phase, the water is a second phase, and the humid air over the water is a third phase.

The term *phase* is sometimes used as a synonym for *state of matter*, but there can be several immiscible phases of the same state of matter. Distinct phases may be described as different states of matter such as gas, liquid, solid, plasma or Bose–Einstein condensate. Useful mesophases between solid and liquid form other states of matter. A single material may have several distinct solid states capable of forming separate phases. Water is a well-known example of such a material. For example, water ice is ordinarily found in the hexagonal form ice *Ih*, but can also exist as the cubic ice *Ic*, the rhombohedral ice *II*, and many other forms. *Polymorphism* is the ability of a solid to exist in more than one crystal form. For pure chemical elements, polymorphism is known as *allotropy*. For example, diamond, graphite, and fullerenes are different allotropes of carbon.

However, in polymer science, and particularly in the composite community, a rather wrong practice exists: using the term “*phase*” instead of “*component*” when dealing with composite materials. As mentioned above, the term “*phase*” is strictly defined in thermodynamics and is frequently used in polymer physics for describing the various phases in one-component systems (by the way, the term “*component*” is also well-defined in thermodynamics as *a chemically independent constituent of a system*). A good illustration in this respect is the polymer poly(vinylidene fluoride) (PVDF), which exhibits five crystalline polymorphic modifications (phases!) and one amorphous phase, but is still a one-component system. The use of the term “*phase*” instead of “*component*” would

require the definition of another term to describe the phases in a thermodynamics sense. Obviously, misuse of the term “phase” is a remnant from the time when colloid chemistry was formulated (second half of the nineteenth century, i.e., long before polymer science was defined). Since polymer solutions, even true ones, behave as the colloid systems of low molecular weight substances, they were called “lyophilic colloids” and to them was applied the terminology typical for colloid chemistry – “a dispersed phase!” (Chanda, 2013)

1.3 Bonding Opportunities in Chemistry

The nature of the bonds that hold atoms together in molecules is explained by quantum mechanics in terms of an atom consisting of a small nucleus, concentrating the mass and positive charge, surrounded by clouds or shells of electrons relatively far away. It is among the outermost, more loosely bound electrons, called *valence electrons*, that chemical reactions and primary bond formation take place.

1.3.1 Primary Bonds

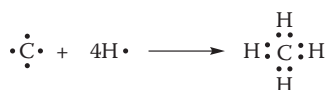
Ionic bond. The most stable electronic configuration for most atoms (except hydrogen) important in polymers is a complete outer shell of eight electrons, called an *octet*. In inorganic systems this structure may be obtained by the donation of an electron by one atom to another to form an ionic bond (Scheme 1.10).



Scheme 1.10

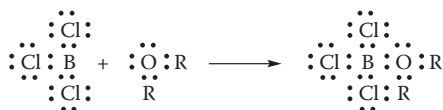
These bonds are not usually found in macromolecular substances except in the use of divalent ions to provide “cross-links” between carboxyl groups in natural resins, and in *ionomers*.

Covalent bond. These bonds are formed when one or more pairs of valence electrons are shared between two atoms, again resulting in stable electronic shells (Scheme 1.11). The covalent bond is the predominant bond in polymers.



Scheme 1.11

Coordinate bond. This bond is similar to the covalent bond in that electrons are shared to produce stable octets; but in the coordinate bond both of the shared electrons come from one atom. The addition compounds of boron trichloride are common examples (Scheme 1.12), where R is an organic group. The *coordinate* or *semipolar* bond has properties between those of the ionic and covalent bonds. No polymers containing true coordinate bonds have reached commercialization.



Scheme 1.12

Metallic bond. In the metallic bond the number of valence electrons is far too small to provide complete outer shells for all the atoms. The resulting bonds involve the concept of positively charged atoms embedded in a permeating “gas” of electrons free to move about at will. The metallic bond is not utilized in polymeric systems.

1.3.2 Typical Primary Bond Distances and Energies

From studies of the positions of atoms and molecules and the energetics of molecular formation and dissociation it is possible to assign typical energies and lengths to primary bonds. Table 1.5 lists some of these properties of interest in polymeric systems. The angles between successive single bonds involving the atomic arrangements usual in polymers range between 105° and 113° , not far from the tetrahedral angle of $109^\circ 28'$.

1.3.3 Secondary Bond Forces

Even when all the primary valences within covalent molecules are saturated there are still forces acting between the molecules. These are generally known as *secondary valence* or *intermolecular forces*, or *van der Waals forces*. In physical

Table 1.5 Typical primary-bond lengths and dissociation energies.

Bond	Bond length (Å)	Dissociation energy (kJ/mol)
C—C	1.54	347
C=C	1.34	611
C—H	1.10	414
C—N	1.47	305
C=N	1.15	891
C—O	1.46	360
C=O	1.21	749
C—F	1.35	473
C—Cl	1.77	339
N—H	1.01	389
O—H	0.96	464
O—O	1.32	146

chemistry the van der Waals force (or van der Waals interaction) is the sum of the attractive or repulsive forces between molecules (or between parts of the same molecule) other than those due to covalent bonds or to the electrostatic interaction of ions with one another or with neutral molecules. The term includes: the force between two permanent dipoles (*Keesom force*), the force between a permanent dipole and a corresponding induced dipole (*Debye force*), and the force between two instantaneously induced dipoles (*London dispersion force*). It is also sometimes used loosely as a synonym for the totality of intermolecular forces. Van der Waals forces are relatively weak compared to normal chemical bonds, but play a fundamental role in fields as diverse as supramolecular chemistry, structural biology, polymer science, nanotechnology, surface science, and condensed matter physics. Van der Waals forces define the chemical character of many organic compounds. They also define the solubility of organic substances in polar and non-polar media. Van der Waals–London forces increase with the length of the non-polar part of the substance.

1.3.3.1 Dipole Forces

When different atoms in a molecule carry equal and opposite electric charges, the molecule is said to be *polar* or to have a *dipole moment*. At large distances such a molecule acts like an electrically neutral system, but at molecular distances the charge separation becomes significant and leads to a net intermolecular force of attraction. The magnitude of interaction energy depends on the mutual alignment of the dipoles. Molecular orientation of this sort is always opposed by thermal agitation; hence the dipole force is strongly dependent upon temperature.

1.3.3.2 Hydrogen Bonds

The bond in which a hydrogen atom is associated with two other atoms is particularly important in many polymers, including proteins, and is held by many to be essential to life processes. Since the classical concepts of chemical bonding allow hydrogen to form only one covalent bond, the hydrogen bond can be considered electrostatic or ionic in character. This model does not, however, account for all the properties of the hydrogen bond; it is appealing to consider the bond covalent in some cases. The hydrogen bond occurs between two functional groups in the same or different molecules. The hydrogen is usually attached to an acidic group (a proton donor), typically a hydroxyl, carboxyl, amine, or amide group. The other group must be basic, usually oxygen (e.g., carbonyls, ethers, or hydroxyls), nitrogen (e.g., amines and amides), and occasionally halogens. The association of such polar liquid molecules as water, alcohols, and hydrofluoric acid, the formation of dimers of simple organic acids, and important structural effects in polar polymers such as Nylon, cellulose, and proteins are due to hydrogen bonding.

Typically, hydrogen bonds range between 2.4 and 3.2 Å in length and between 12 and 30 kJ/mol in dissociation energy. Only fluorine, nitrogen, oxygen, and (occasionally) chlorine are electronegative enough to form hydrogen bonds.

At the same time, the energy of the van der Waals forces is between 4 and 8 kJ/mol. One can easily conclude that the energy of the intermolecular interactions is by magnitude of order weaker than the chemical bonds. For example, the energy of the chemical O—H bond in a water molecule is 457 kJ/mol, of the C—C bond in paraffins –412 kJ/mol, and of the C—H bond – 331 kJ/mol. The dissociation energy between water molecules amounts 42 kJ/mol and that between chemically non-bonded CH₃ groups in paraffins is only 4.2 kJ/mol.

The formation of hydrogen bonds in polymers plays an exclusive role for their properties and functions, particularly in the case of natural polymers such as cellulose and proteins. The existence of the famous double helix of DNA is possible only due to the formation of hydrogen bonds. What is more, the helix is the only spatial arrangement of the chain molecules which allows the formation of maximum number of hydrogen bonds.

Hydrogen bonding is very useful in preparation of polymer blends because, as a rule, the polymers are not miscible. The hydrogen bonding makes the two partners at least compatible which improves significantly the properties of polymer blend. Examples are shown in Figure 1.9.

1.3.3.3 Interrelation of Intermolecular Forces

The energy of the intermolecular attractive forces varies as the inverse sixth power of the intermolecular distance. As is the case with primary bond forces, repulsion arises when the atoms approach more closely than an equilibrium distance of 3–5 Å. The energy of typical secondary bond attractive forces is 8–40 kJ/mol, divided among the three secondary-bond types according to the polarizability and dipole moment of the bonding molecules.

After reading these introductory remarks, we should understand the following concepts:

- 1) The macromolecules are giant molecules with large structures and high molecular weights. In spite of their varieties, they are governed by the same laws that apply to small molecules.
- 2) If we disregard metals and some inorganic compounds, practically everything else in this world is polymeric. Polymers form the basis for life itself and for our communications, transportation, buildings, food, and so on. Polymers include protein and nucleic acids in our bodies, the fibers (natural and synthetic) we use for clothing, the protein and starch we eat, the elastomers in our automotive tires, the paint, plastic wall and floor coverings, foam insulation, dishes, furniture, and pipes.
- 3) Early developments in polymers were largely empirical because of a lack of knowledge of polymer science. Advancements in polymers were rapid in the 1930s and 1940s because of the theories developed by Staudinger, Carothers, Mark, and many other scientists.
- 4) This is truly the age of the macromolecule. Essentially every important problem and advance includes polymers including synthetic (such as carbon nanotubes) and biological (such as the human genome and proteins). There are more chemists working with synthetic polymers than in all of the other areas of chemistry combined.

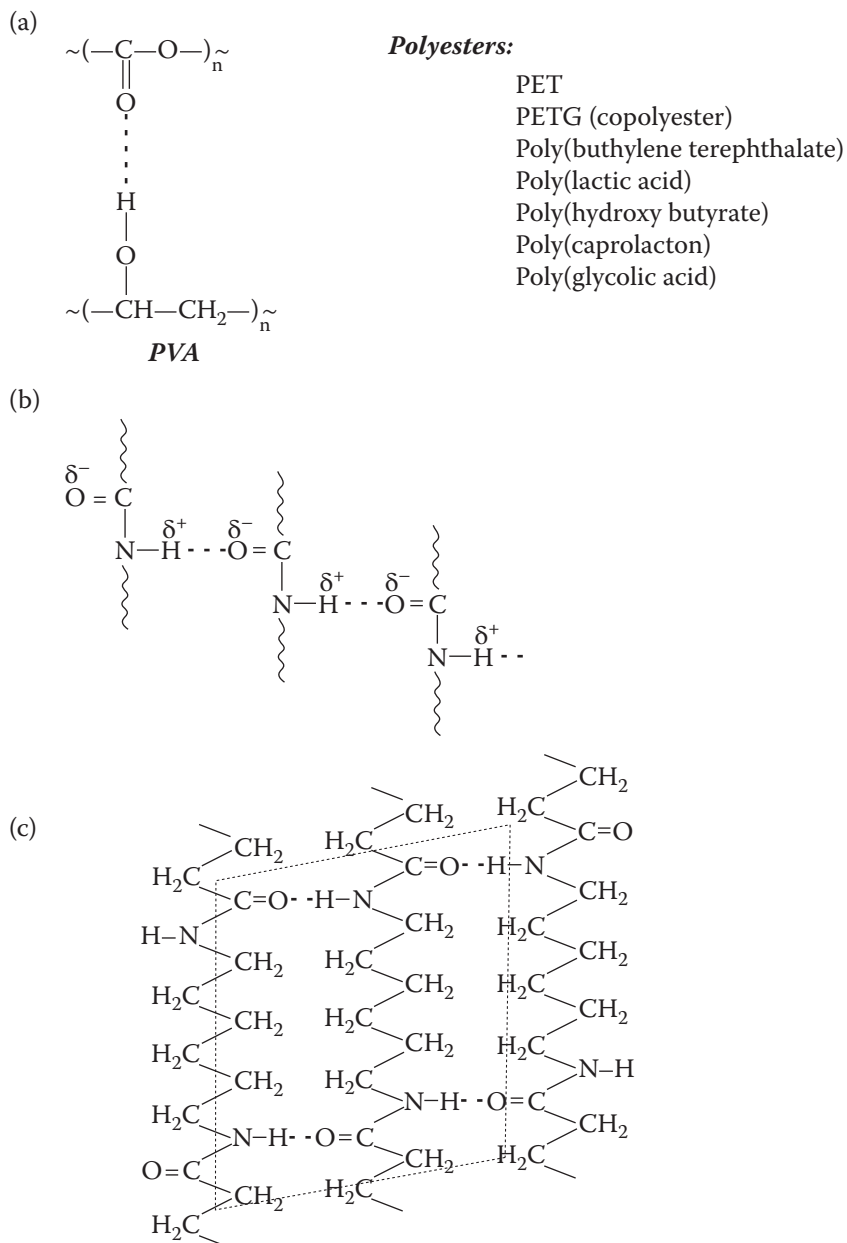


Figure 1.9 Hydrogen bonds between: (a) polyesters and alcohols [poly(vinyl alcohol) in the present case], (b) hydrogen bonds between neighboring chains of polyamide, and (c) alignment of chains in hydrogen-bonded sheets in the crystal structure of Nylon-6,6.

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