

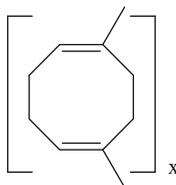
Chapter 1

Introduction and Nomenclature

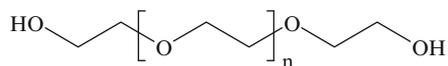
1.1 Brief Historical Introduction

The initial proof of the existence of very large organic molecules was supplied by Raoult [1] and van't Hoff [2], who carried out cryoscopic molecular weight determinations on rubber, starch, and cellulose nitrate. By the methods developed by Raoult and by van't Hoff and by the formulation of solution laws, molecular weights of 10,000–40,000 were demonstrated. Unfortunately, chemists of that day failed to appreciate this evidence and refused to accept it. The main reason for such a response was the inability to distinguish macromolecules from colloidal substances that could be obtained in low molecular weights. The opinion of the majority of that day was that “Raoul’s solution does not apply to materials in colloidal state.”

During the period 1890–1910, the idea of molecular complexes was generally accepted [3]. It was used to explain polymeric structures in terms of physical aggregates of small molecules. In fact, molecular association was considered polymerization. Thus rubber, for example, was assumed to be composed of short sequences of isoprene units, either as chains or as cyclic structures. The structure of isoprene itself was known, because it was isolated from natural rubber, in 1860. What added to the general confusion was the fact that no one was able to show the existence of end groups in the macromolecules studied. This enhanced the idea that rubber is a ring-like structure, a dimethyl cyclooctadiene. Large numbers of such rings were assumed to be held together by associations, giving rise to colloidal materials. This can be illustrated as follows:

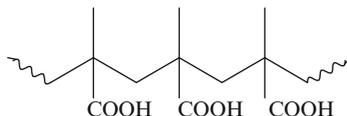


Early synthetic polymeric products were usually discarded as being oils or tars (“gooks”), and considered as useless. To be fair to the chemists of that period, however, one should not forget that in spite of the general attitude of the time, the structures of some polymers, like polyethylene glycol ($n = 6$), for instance,



was correctly assigned in 1860, and the concept of extending the structure to very large molecular weights by continued condensation was understood [4–6].

At approximately the same time, poly(methacrylic acid), which we now know to be a linear molecule



was prepared in 1880 [7]. But, here too, a cyclic structure was assigned which was believed to be attached to other cyclic structures by “partial valences,” thereby forming gels. What is more noteworthy is that Emil Fischer and his coworkers studied many natural polymers, such as rubber, starch, polypeptides, cellulose, and lignin. His work probably entitles him to be called the spiritual father of polymer chemistry. During that period, Willstätter worked on the synthesis of polysaccharides, and studied lignin and enzymes [8].

One should also acknowledge the fact that in spite of ignorance of structure, many inventors developed ways to convert cellulose into cellulose acetate and then to use the products to form fibers, films, and coatings. Cellulose was also converted to cellulose nitrate and was used to prepare explosives and other products. At the turn of the century, Baekeland formed a hard resin by condensing phenol with formaldehyde [9].

The evolution of our present-day understanding of polymeric structures occurred in the early 1920s. Thus, Staudinger et al. firmly established the existence of macromolecules [10–15]. Others, by X-ray analyses and careful use of molecular weight determinations, confirmed his findings [16]. In 1929, a series of outstanding investigations were carried out by Carothers on other polymeric materials. This resulted in much of today’s knowledge and understanding [17].

Now, we know that a typical molecule such as polyethylene can have a contour length of 25,000 Å, but a diameter of only 4.9 Å. Such a molecule can be compared in dimensions to a long, snarled clothesline, 75 ft long and 1 in. in diameter. Furthermore, work with naturally occurring macromolecules, such as nucleic acids, for instance, revealed even more startling dimensions. When molecules of virus dinucleic acids were tritium-labeled (whose nuclear emission is less than 1 μm) and then autoradiographs prepared, these showed molecules that were about 50 μm long [18]. Such length would signify a molecular weight of 100 million. Similar work carried out on dinucleic acids of bacteria revealed molecular weights of approximately 200 million.

The above figures are, of course, extremes in molecular dimensions. Typical synthetic polymers will range in molecular weights anywhere from ten to several hundred thousand, although synthetic polymers in molecular weight ranges of several million are well known and some are used commercially. Interestingly enough, many of these polymers are prepared through the use of organic reactions that have been known for a long time. Also, new reactions and catalysts are still being discovered and applied to polymer syntheses. It is probably safe to predict that this situation will undoubtedly continue into the distant future.

1.2 Definitions

The word polymer is commonly understood to mean a large molecule composed of repeating units, or mers (from the Greek word *meros*—part), connected by covalent bonds. Such units may be connected in a variety of ways. The simplest is a linear polymer, or a polymer in which the units are connected to

each other in a linear sequence, like beads on a string. Many examples of such linear polymers are possible, as, for instance, linear polyethylene:



The terminal units in such molecules must be different from the internal ones to satisfy valence requirements. Polyethylene, like all other polymers, can be written to show the number of repeat units, $-\text{[CH}_2\text{-CH}_2\text{-]}_n-$, by using a number or a letter, like in this case n . It represents the *average* quantity of mers present in the polymer and is called *the degree of polymerization* or *DP*, or the average number of repeat units in the polymeric chain. Thus the average molecular weight of polystyrene with a DP of 100 is 104×100 or 10,400. (There are actually several ways of expressing the average molecular weights of polymers. This is discussed further in this chapter).

An alternative to a linear polymer is a branched one. The branches can be long or short. Low-density polyethylene, for instance, can have both short and long branches. Linear and branched molecules are shown in Fig. 1.1a, b. Branched polymers can also be star- or comb-shaped (Fig. 1.1c, d). In addition to the above, polymer molecules can also be double-stranded. Such polymers are called ladder polymers (Fig. 1.1e). It is also possible for polymers to have semi-ladder structures (Fig. 1.1f).

When branches of different polymers become interconnected, *network* structures form. Planar networks resemble the structure of graphite. Three-dimensional networks, or space networks, however, can be compared with diamonds. A network polymer is shown in Fig. 1.1g.

The term polymer can be applied to molecules made up from either single repeating structural units, like in the above shown polyethylene, or from different ones. If there are two or more structural units then the term *copolymer* is used. An example would be a copolymer of ethyl methacrylate and styrene:

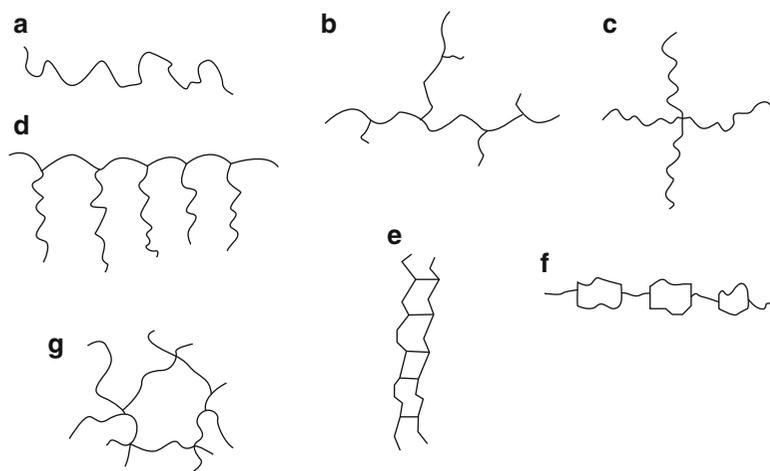
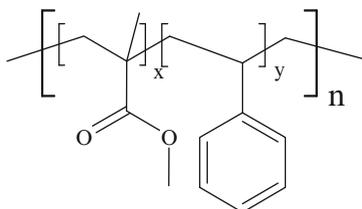


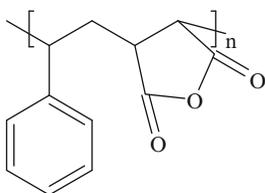
Fig. 1.1 Shapes of polymer molecules. (a) Linear polymer, (b) branched polymer, (c) star-shaped polymer, (d) comb shaped polymer, (e) ladder polymer, (f) semiladder polymer, and (g) network structure



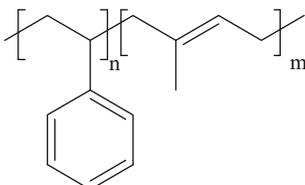
methyl methacrylate unit styrene unit

A copolymer can also be linear or branched. Should there be regularity in the repetition of the structural units and should this repetition alternate, then the copolymer is called an **alternating copolymer**. An absence of such regularity would make it a **random copolymer**.

An example of an alternating copolymer can be a copolymer of styrene with maleic anhydride:

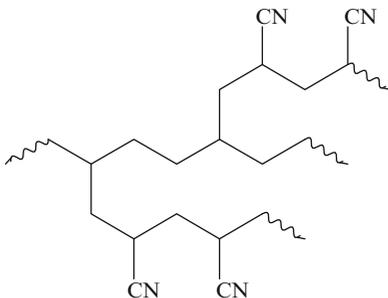


In addition to the random-sequence and an alternating one, sometimes called ordered-sequence, there are also **block copolymers**. These are copolymers made up of blocks of individual polymers joined by covalent bonds. An example can be a block copolymer of styrene and isoprene:



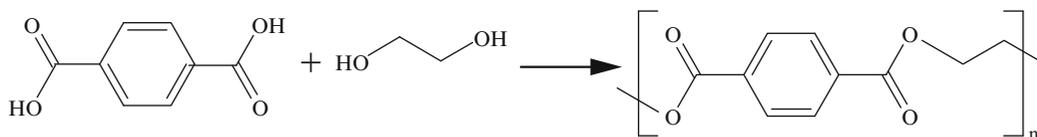
polystyrene block-polyisoprene block

Still another type of a copolymer is one that possesses backbones composed of one individual polymer and the branches from another one. It is called a **graft copolymer**, because many such materials were formed by grafting the branch polymers to the polymer backbone. This, however, is not always the case and many graft copolymers were formed by polymerizing the branch copolymer from a different polymer backbone. (The subject of block and graft copolymers is discussed in Chap. 9) A graft copolymer of polyacrylonitrile on polyethylene can serve as an example:

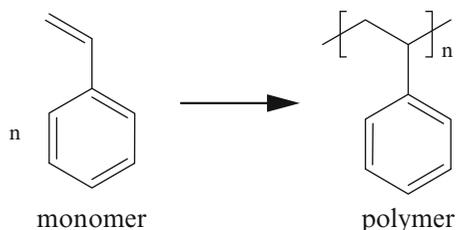


In both block and graft copolymers the length of the uninterrupted sequences may vary.

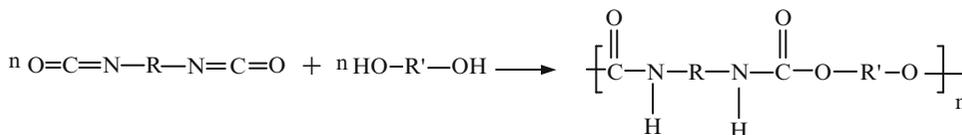
In 1929, Carothers [19] suggested a separation of all polymers into two classes, **condensation** and **addition** polymers. By condensation polymers he defined those polymers that lack certain atoms from the monomer units from which they were formed or to which they may be degraded by chemical means. An example would be a polyester:



He also defined addition polymers as polymers with identical structures of the repeat units to the monomers from which they are derived. According to the above definition, an example of an addition polymer can be polystyrene that is formed by addition of styrene monomers:



Note: The definition ignores loss of double bonds. The Carothers definition fails to describe all the polymers that can fit into the category of condensation polymers, yet form without an evolution of a byproduct. An example is polyurethane that can form from a reaction of a glycol with a diisocyanate:



Flory proposed a superior definition [20]. It is based on the reaction mechanism involved in the formation of the two classes of polymers. Into the first category (it includes all the condensation polymers) falls the macromolecules that form through reactions that occur in **discreet steps**. They are, therefore, called **step-growth** polymers. Such polymerizations require long periods of time for each macromolecule to form, usually measured in hours. Into the second category belong all polymers that form by **chain propagating reactions**. They are, therefore, called **chain-growth polymers**, as one might expect. Such reactions depend upon the presence of active centers on the ends of the growing chains. The chains grow by propagating these reactive sites through inclusion of monomers at such sites. These inclusions are very rapid and chain-growth can take place in a fraction of a second, as the chains successively add monomers.

The important features of step-growth polymerizations are:

1. The monomer is consumed early in the beginning of the reaction while the increase in molecular weight occurs only slowly.
2. The growth of polymeric chains takes place by reactions between monomers, oligomers, and polymers.

3. There is no termination step, and the end groups of the polymers are reactive throughout the process of polymerization.
4. The same reaction mechanism functions throughout the process of polymerization.

The important features of chain-growth polymerizations are:

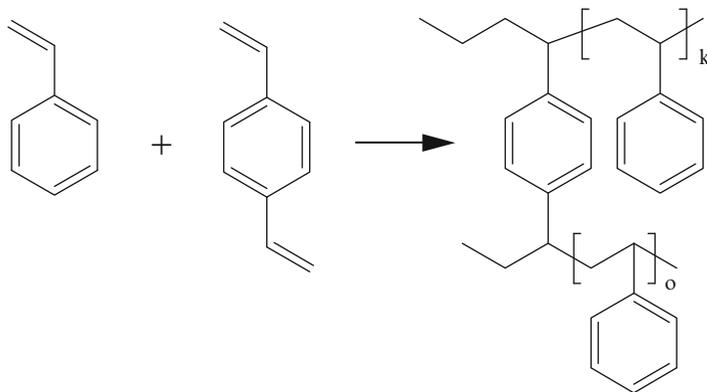
1. Chain-growth takes place by repeated additions of monomers to the growing chains at the reactive sites.
2. The monomer is consumed slowly and is present throughout the process of polymerization.
3. There are two distinct mechanisms during polymer formations. These are initiation and propagation.
4. In the majority of cases, there is also a termination step.

When the polymerization reaction takes place in three dimensions, after it has progressed to a certain point, gelation occurs. This well-defined change during polymerization is known as the *gel point*. At this point the reaction mixture changes from a viscous liquid to an elastic gel.

Before gelation, the polymer is soluble and fusible. After it, however, it is neither soluble nor fusible. This is a result of restraining effects of three-dimensional space networks. Another classification of polymers is also possible. It is based on whether the material can form crosslinked or gelled networks. The polymers that eventually reach gelation are called **thermosetting**. Such polymers are also called **crosslinkable** polymers. Once past gelation, raising the temperature will no longer attain plasticity as the molecules can no longer move past each other. For the same reason they can no longer be dissolved in any solvent.

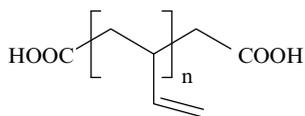
Polymers that never gel or become crosslinked are called **thermoplastic**. Such polymers can always be reflowed upon application of heat. They can also be dissolved again in appropriate solvents.

The wiggly lines in the above illustration imply that the polymer extends further in their directions. The above illustration is one of a thermoset polymer that is formed by the step-growth mechanism. It is also possible to form crosslinked polymers by the chain-growth mechanism. This requires presence in the polymerization mixture of a comonomer that possesses multiple functionality. Copolymerization of styrene with a comonomer like divinyl benzene can serve as an example:



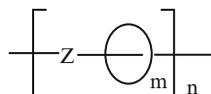
An **oligomer** is a very low molecular weight polymer. It consists of only a small number of mers. The definition of a **telomer** is that of a chain-growth polymer that is composed of molecules with end groups consisting of different species from the monomer units. Telomers can form by either free radical or by ionic chain-growth polymerization mechanism.

Telechelic polymers are macromolecules with reactive functional groups at the terminal ends of the chains. An example of telechelic polymer is polybutadiene with carboxylic acid end groups



Into a special category should be placed starburst **dendrimer polymers**. These molecules are formed by growing them in three dimensions. These materials often possess radially symmetrical star-shaped structures with successive cascades of branched polymer structures. For additional discussions see Chap. 6.

Another group of polymers are the **rotaxanes**. They too are discussed in Chap. 7. The materials consist of polymeric chains that are threaded through macrocycles:



Tables 1.1 and 1.2 illustrate some common chain-growth and step-growth polymers as well as monomers used in their preparations.

1.3 Nomenclature of Polymers

The names of many polymers are based on the monomers from which they were prepared. There is, however, frequent variation in the format. A nomenclature of polymers was recommended by IUPAC [21–23] and is used in some publications. Strict adherence to the recommendation, however, is mainly found in reference works. Also, problems are often encountered with complex polymeric structures that are crosslinked or have branches. In addition some polymers derive their names from trade names. For instance, a large family of polyamides is known as nylons. Also, when more than one functional group is present in the structure, the material may be called according to all functional groups in the structure. An example is a polyesteramide. A thermoset polymer prepared from two different materials may be called by both names. For instance, a condensation product of melamine and formaldehyde is called melamine–formaldehyde polymer.

1.3.1 Nomenclature of Chain-Growth Polymers

1. A polymer of unspecified chain length is named with a prefix *poly*. The prefix is then followed by the name of the monomer. Also, it is customary to use the common names of monomers and polymers. For instance, common names for phenylethene and polyphenylethene are styrene and polystyrene. This, however, is not an inflexible rule. When the monomer is named by a single word then the prefix *poly* is simply added like polyethylene for a polymer of ethylene or polystyrene for a polymer of styrene. If, however, the monomer is named by two words or is preceded by a number, like methyl methacrylate, parentheses are used. Examples are poly(methyl methacrylate) or poly(1-hexene).
2. End groups are usually not specified in high polymers. End groups, however, can be known parts of the structure. This can be the case with telomers. Here, the end groups are named as radicals,

Table 1.1 Illustration of common chain-growth polymers

Name	Monomer	Polymer
Polyethylene		
Polyisobutylene		
Polystyrene		
Poly(vinyl chloride)		
Poly(vinyl acetate)		
Poly(methyl methacrylate)		
Polyisoprene		

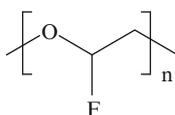
prefixed by Greek letters, α and ω . They appear before and after the name of the polymer. The structure of a telomer, like $\text{Cl}-(\text{CH}_2)_n-\text{CCl}_3$, is, therefore, called α -chloro- ω -trichloromethyl poly(methylene).

- In naming the polymer the following steps are recommended by IUPAC: (1) identify the constitutional repeating unit, (2) orient the **constitutional repeating unit**, and (3) name the constitutional repeating unit.
- Random copolymers are designated by the prefix *co*, as in poly(butadiene-*co* styrene) and poly(vinyl chloride-*co* vinyl acetate). Alternating copolymers can be differentiated by substituting *alt* for *co*, as in poly(ethylene-*alt*-carbon monoxide).
- The prefix *g* describes graft copolymers and the prefix *b* describes block copolymers. In this system of nomenclature, the first polymer segment corresponds to the homopolymer or copolymer that was formed during the first stage of the synthesis. Should this be a graft copolymer then this will represent the backbone polymer. For instance, if polystyrene is graft copolymerized with polyethylene, the product is called poly(ethylene-*g*-styrene). A more complex example can be poly(butadiene-*co*-styrene-*g*-acrylonitrile-*co*-vinylidene chloride). Similarly, examples of block copolymers would be poly(acrylonitrile-*b*-methyl methacrylate) or poly(methyl methacrylate-*b*-acrylonitrile).
- Conventional prefixes indicating *cis* and *trans* isomers are placed in front of the polymer name. An example is *cis*-1,4-polybutadiene, or in *trans*-1,4-polyisoprene.

Table 1.2 Illustration of some step-growth polymers and monomers used in their preparation

Poly(ethylene terephthalate)	
Poly(hexamethylene adipate); nylon 6,6	
Polycaprolactam; nylon 6	
Poly(ethylene oxide)	
Poly(lactic acid)	
Poly(benzimidazole)	
Poly(p-xylylene)	
Poly(butylolactone)	

7. The nomenclature adopted by IUPAC rests upon selection of preferred *constitutional repeating units* [5] from which the polymer is a multiple. The unit is named wherever possible according to the definitive rules for nomenclature of organic chemistry [24]. For single-stranded polymers this unit is a bivalent group. An example is a polymer with oxy(1-fluoroethylene) constitutional repeat unit:

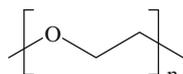


poly [oxy(1-fluoroethylene)]

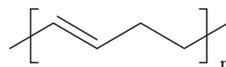
The following are examples of simple constitutional repeat units:



polymethylene

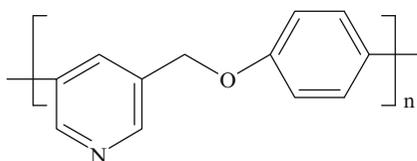


polyoxyethylene

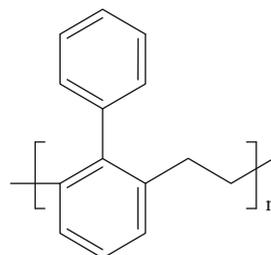


poly(1-butenylene)

8. Polymers with repeating units consisting of more than one simple bivalent radical should be named according to the order of seniority among the types of bivalent radicals: (a) heterocyclic rings, (b) chains containing hetero atoms, (c) carbocyclic rings, and (d) chains containing only carbons. This is illustrated below:

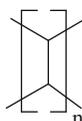


poly(3,5-pyridinediylmethylenoxy-1,4-phenylene)

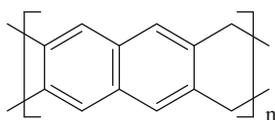


poly(2,6-biphenyleneethylene)

9. Double-stranded or “ladder” polymers that have tetravalent repeat units are named similarly to bivalent units. The relation of the four free valences is denoted by pairs of locants separated by a chain:

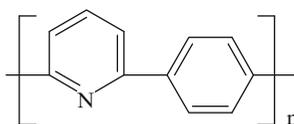


poly(1,2:1,2-ethane diylidene)



poly(2,3,6,7-naphthalenetetrayl-6,7-dimethylene)

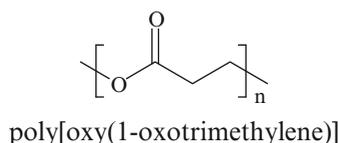
10. For polymers that contain heteroatoms or acyclic subunits containing heteroatoms there is a decreasing seniority in naming. It is in the following order, O, S, Se, Te, N, , Sb, Bi, Si, Ge, Sn, Pb, B. Similarly, for polymers containing ring structures, the seniority if for the heterocyclic ring to have greater seniority that heteroatoms or acyclic subunits. Similarly, heterocyclic subunits have greater seniority than do carbocyclic ring and they in turn have greater seniority than acyclic substructures. An example would be,



poly(2,4-pyridinediyl-1,4-phenylene)

1.3.2 Nomenclature of Step-Growth Polymers

The nomenclature for step-growth polymers is more complicated due to the possibility of having many different repeat units. Usually, the polymers are referred to according to their functional units. A polyester from ethylene glycol and terephthalic acid is called poly(ethylene terephthalate). A product from ring opening polymerization, like, for instance, a polymer of caprolactam might be called polycaprolactam. Here, it is based on the source. The repeat unit is actually not a lactam but rather an open chain polyamide. Because it is derived from a lactam, it may still carry that name. In this particular instance, however, it is more common to call the polymer by its generic name, namely, nylon 6. The same would be true for a polymer from a lactone, like poly(β -propiolactone). The IUPAC name for this polymer, however, is:



The name is based on a presence of two subunits. Note that the carbonyl oxygen is called an *oxo* substituent. In addition, the presence of a 1-oxo substituent requires that parentheses enclose the subunit.

1.4 Steric Arrangement in Macromolecules

In linear polymers, due to the polymerization process, the pendant groups can be arranged into orderly configurations or they can lack such orderliness. Propylene, for instance, can be polymerized into two types of orderly steric arrangement. It can also be polymerized into one lacking steric order. The same can be true of other monosubstituted vinyl monomers. The steric arrangement in macromolecules is called *tacticity*. Polymers can be *isotactic*, where all the chiral centers have the same configuration (see Fig. 1.2). By picturing the chain backbone as drawn in the plane of the paper and by picturing all the phenyl groups as oriented above the plane (Fig. 1.2a), isotactic polystyrene can then be visualized. The orderliness can also be of the type where every other chiral center has the same configuration. Such an arrangement is called *syndiotactic* (Fig. 1.2b). A lack of orderliness or randomness in the steric arrangement is called *atactic* or *heterotactic*. Stereospecific polymers can also be prepared from 1,2 disubstituted olefins. These macromolecules can be distereoisomers, or ditactic polymers. To describe the arrangement of such polymers, a *threo-erythro* terminology is used. An erythrodiisotactic polymer is one possessing alternating substituents—(–CHR'CHR–)_n. If we draw the carbon chain backbone in the plane of the paper, then all the R groups would find themselves on one side of the chain and all the R' groups on the other. They would, however, all be on the same side of the chain in a Fischer or in a Newman projection (Fig. 1.2c). A threo isomer or a threodiisotactic polymer is illustrated in Fig. 1.2d.

Polymerization of 1,4-disubstituted butadienes can lead to products that possess two asymmetric carbon atoms and one double bond in each repeat unit. Such *triatctic* polymers are named with prefixes of *cis* or *trans* together with *erythro* or *threo* (see Fig. 1.3).

In polymers with single carbon to carbon bonds, there is free rotation, provided that steric hindrance does not interfere. This allows the molecules to assume different spatial arrangements or *conformations*. Most of the possible isomers, however, represent prohibitively high-energy states. The three lowest energy states that are most probable [8] are one *trans* and two *gauche*.

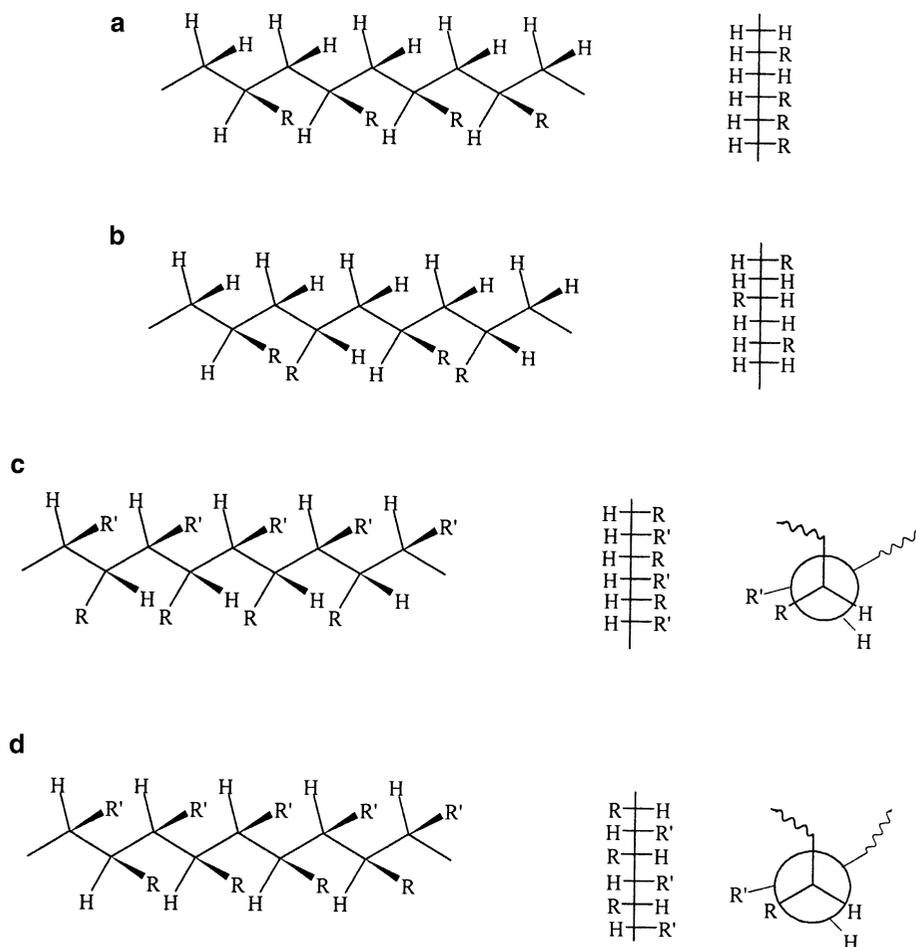


Fig. 1.2 Steric arrangement in macromolecules ($R = \text{phenyl}$). (a) Isotactic polymer, (b) syndiotactic polymer (c) erythrodiisotactic polymer, and (d) threodiisotactic polymer

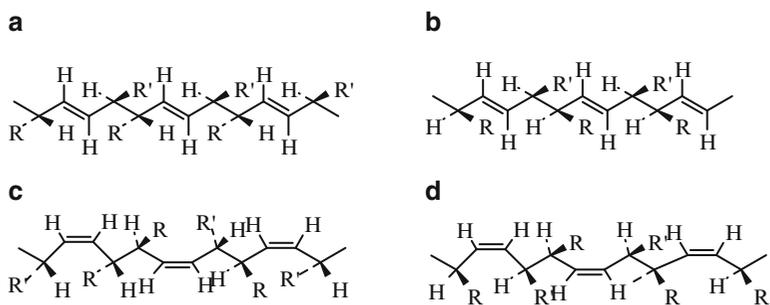


Fig. 1.3 Tritactic polymers. (a) *Trans-erythro* tritactic polymer, (b) *trans-threo* tritactic polymer, (c) *cis-erythro* tritactic polymer, and (d) *cis-threo* tritactic polymer

Several rules that govern the configuration of repeat units along the polymeric chains were elucidated by Natta and Carradini [24]. A basic assumption is used to predict the lowest energy conformation. This assumption is known as the *equivalence postulate*. It says that all the structural units along the chain are geometrically equivalent with regard to the axis of the chain. All stereoregular polymers appear to meet this condition, with a few exceptions [25].

It should be possible to calculate (in principle) the lowest internal conformational energy of a given polymer molecule. To do that it is necessary to know: (1) the energy vs. the bond rotation curve that relates the interactions within the structural units; and (2) the interaction energy vs. the distance curve for the neighboring pendant groups of the adjacent structural units. It should be noted that the neighboring units approach each other close enough for substantial interaction. As a result, the interaction energies between the groups may distort the basic energy–rotation curves. The core electron repulsion between the units contributes most significantly to the deviations from the simple *trans* or *gauche* conformation. The specific chain conformation, therefore, is very dependent upon the exact nature of the repulsive potential. A contour plot, which represents the internal energy per mole of the polymer, can be prepared. The variables in such a plot are the relative bond rotations of the successive bonds.

Appendix

Additional Definitions:

Term	Definition
Tensile strength	Ability to resist stretching
Flexural strength	Resistance to breaking or snapping
Tensile stress (σ)	$\sigma = \text{force/cross-section area } \sigma = F/A$
Tensile strain (ϵ)	Change in sample length (when stretched) divided by the original length $\epsilon = \Delta l/l$
Tensile modulus (E)	Ratio of stress to strain $E = \sigma/\epsilon$

Recommended Reading

R.B. Seymour, *History of Polymer Science and Technology*, Dekker, New York, 1982
 H. Morawetz, *The Origin and Growth of a Science*, Wiley-Interscience, New York, 1982
 M.P. Stevens, *Polymer Chemistry*, 3rd Ed., Oxford University Press, 1998, (Chapter 1)
 G. Odian, *Principles of Polymerization*, 3rd Ed. Wiley, New York, 1991, (Introduction)

Review Questions

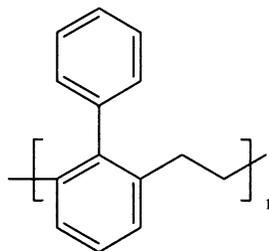
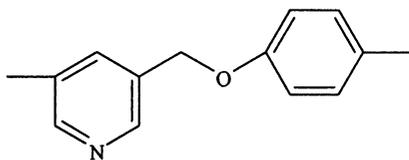
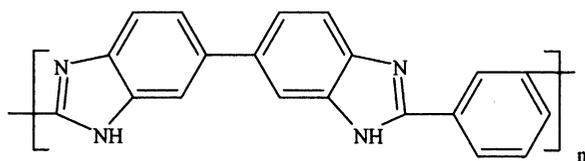
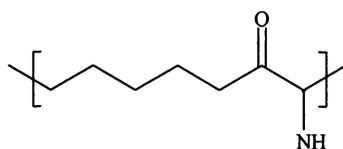
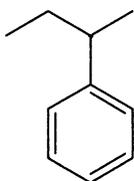
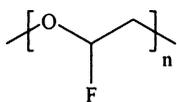
Section 1.2

1. Define the degree of polymerization.
2. Polystyrene has a DP of 300. What is the molecular weight of the polymer?
3. What is a linear, a branched, a star-shaped, a comb-shaped, and a ladder polymer? Explain.
4. What is a network structure?
5. How can a network structure be formed by step-growth polymerization and also by chain-growth polymerization?
6. What is the difference between random and alternating copolymers?
7. What is meant by graft and block copolymers? Illustrate such copolymers of styrene and methyl methacrylate?

8. What are the important features of chain-growth and step-growth polymerizations. Explain the difference between the two? Can you suggest an analytical procedure to determine by what mechanism a particular polymerization reaction takes place?
9. What is the DP of polystyrene with molecular weight of 104,000 and poly(vinyl chloride) with molecular weight of 63,000?
10. Explain the differences between thermosetting and thermoplastic polymers and define gel point. How would you determine the gel point of a thermoset polymer?
11. Give the definitions of oligomer, telomer, and telechelic polymers.
12. What is a dendrimer polymer and what is a rotaxane polymer?
13. Illustrate three chain-growth polymers and three step-growth polymers.

Section 1.3

1. Name the following chain-growth polymers by the IUPAC system and by giving them trivial names:



Section 1.4

1. What is meant by tacticity?
2. Give a definition of and illustrate by examples on polystyrene, isotactic, syndiotactic, and atactic arrangement of the macromolecules. This should include Fischer and Newman projections.
3. Explain what is meant by erythrodiisotactic, threodiisotactic polymers. Illustrate. Do the same for erythrodisyndiotactic and threodisyndiotactic.
4. What are tritactic polymers? Draw *cis* and *trans* tritactic polymers.

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