

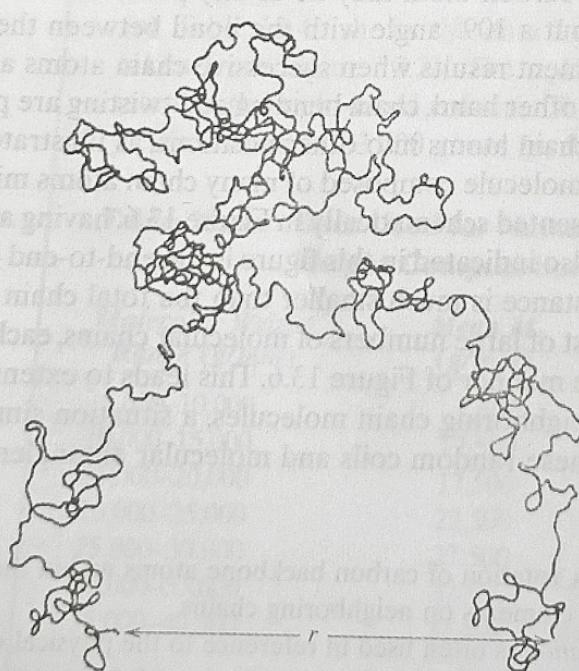
**Figure 13.5** Schematic representations of how polymer chain shape is influenced by the positioning of backbone carbon atoms (gray circles). For (a), the rightmost atom may lie anywhere on the dashed circle and still subtend a  $109^\circ$  angle with the bond between the other two atoms. Straight and twisted chain segments are generated when the backbone atoms are situated as in (b) and (c), respectively. (From *Science and Engineering of Materials*, 3rd edition by Askeland. © 1994. Reprinted with permission of Nelson, a division of Thomson Learning: [www.thomsonrights.com](http://www.thomsonrights.com). Fax 800 730-2215.)

for a number of important characteristics of polymers, to include the large elastic extensions displayed by the rubber materials.

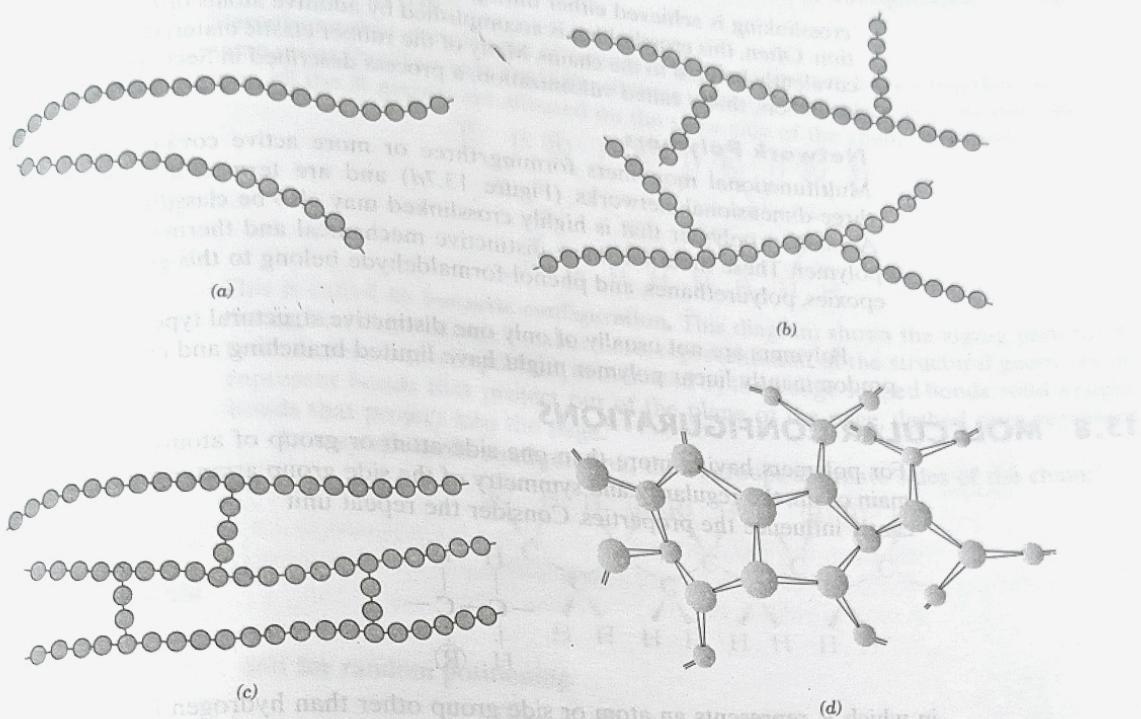
Some of the mechanical and thermal characteristics of polymers are a function of the ability of chain segments to experience rotation in response to applied stresses or thermal vibrations. Rotational flexibility is dependent on repeat unit structure and chemistry. For example, the region of a chain segment that has a double bond ( $C=C$ ) is rotationally rigid. Also, introduction of a bulky or large side group of atoms restricts rotational movement. For example, polystyrene molecules, which have a phenyl side group (Table 13.3), are more resistant to rotational motion than are polyethylene chains.

## 13.7 MOLECULAR STRUCTURE

The physical characteristics of a polymer depend not only on its molecular weight and shape but also on differences in the structure of the molecular chains. Modern polymer synthesis techniques permit considerable control over various structural possibilities. This section discusses several molecular structures including linear, branched, crosslinked, and network, in addition to various isomeric configurations.



**Figure 13.6** Schematic representation of a single polymer chain molecule that has numerous random kinks and coils produced by chain bond rotations. (From *The Physics of Rubber Elasticity*, 2nd edition, by Treloar (1958), Fig. 3.3, p. 47. By permission of Oxford University Press.)



**Figure 13.7** Schematic representations of (a) linear, (b) branched, (c) crosslinked, and (d) network (three-dimensional) molecular structures. Circles designate individual repeat units.

### Linear Polymers

**Linear polymers** are those in which the repeat units are joined together end to end in single chains. These long chains are flexible and may be thought of as a mass of spaghetti, as represented schematically in Figure 13.7a, where each circle represents a repeat unit. For linear polymers, there may be extensive van der Waals and hydrogen bonding between the chains. Some of the common polymers that form with linear structures are polyethylene, poly(vinyl chloride), polystyrene, poly(methyl methacrylate), nylon, and the fluorocarbons.

### Branched Polymers

Polymers may be synthesized in which side-chain chains are connected to the main ones, as indicated schematically in Figure 13.7b; these are fittingly called **branched polymers**. The branches, considered to be part of the main-chain molecule, may result from side reactions that occur during the synthesis of the polymer. The chain packing efficiency is reduced with the formation of side branches, which results in a lowering of the polymer density. Those polymers that form linear structures may also be branched. For example, high density polyethylene (HDPE) is primarily a linear polymer, while low density polyethylene (LDPE) contains short chain branches.

### Crosslinked Polymers

In **crosslinked polymers**, adjacent linear chains are joined one to another at various positions by covalent bonds, as represented in Figure 13.7c. The process of

crosslinking is achieved either during synthesis or by a nonreversible chemical reaction. Often, this crosslinking is accomplished by additive atoms or molecules that are covalently bonded to the chains. Many of the rubber elastic materials are crosslinked; in rubbers, this is called vulcanization, a process described in Section 14.9.

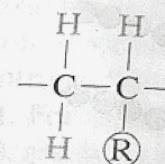
### Network Polymers

Multifunctional monomers forming three or more active covalent bonds, make three-dimensional networks (Figure 13.7d) and are termed **network polymers**. Actually, a polymer that is highly crosslinked may also be classified as a network polymer. These materials have distinctive mechanical and thermal properties; the epoxies, polyurethanes, and phenol-formaldehyde belong to this group.

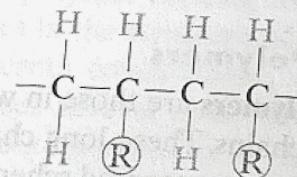
Polymers are not usually of only one distinctive structural type. For example, a predominantly linear polymer might have limited branching and crosslinking.

## 13.8 MOLECULAR CONFIGURATIONS

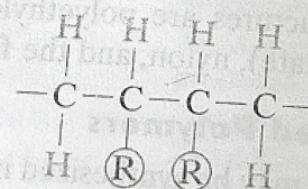
For polymers having more than one side atom or group of atoms bonded to the main chain, the regularity and symmetry of the side group arrangement can significantly influence the properties. Consider the repeat unit



in which R represents an atom or side group other than hydrogen (e.g., Cl, CH<sub>3</sub>). One arrangement is possible when the R side groups of successive repeat units are bound to alternate carbon atoms as follows:



This is designated as a head-to-tail configuration.<sup>7</sup> Its complement, the head-to-head configuration, occurs when R groups are bound to adjacent chain atoms:



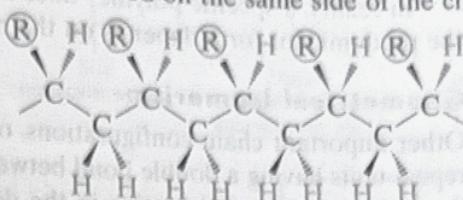
In most polymers, the head-to-tail configuration predominates; often a polar repulsion occurs between R groups for the head-to-head configuration.

Isomerism (Section 13.2) is also found in polymer molecules, wherein different atomic configurations are possible for the same composition. Two isomeric subclasses, stereoisomerism and geometrical isomerism, are topics of discussion in the succeeding sections.

<sup>7</sup> The term *configuration* is used in reference to arrangements of units along the axis of the chain, or atom positions that are not alterable except by the breaking and then reforming of primary bonds.

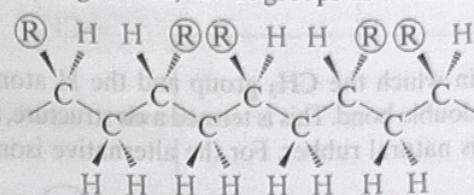
### Stereoisomerism

**Stereoisomerism** denotes the situation in which atoms are linked together in the same order (head-to-tail) but differ in their spatial arrangement. For one stereoisomer, all the R groups are situated on the same side of the chain as follows:

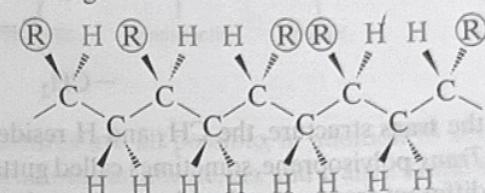


This is called an **isotactic configuration**. This diagram shows the zigzag pattern of the carbon chain atoms. Furthermore, representation of the structural geometry in three dimensions is important, as indicated by the wedge-shaped bonds; solid wedges represent bonds that project out of the plane of the page, dashed ones represent bonds that project into the page.<sup>8</sup>

In a **syndiotactic configuration**, the R groups alternate sides of the chain:<sup>9</sup>

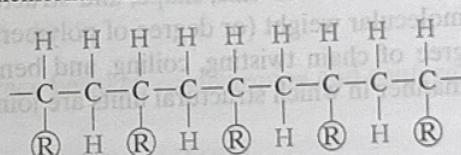


and for random positioning,

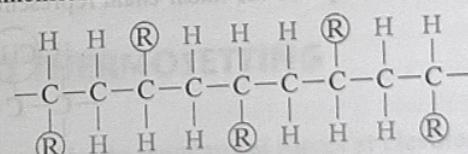


the term **atactic configuration** is used.<sup>10</sup>

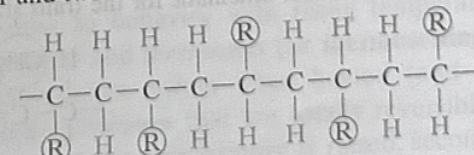
<sup>8</sup> The isotactic configuration is sometimes represented using the following linear (i.e., nonzigzag) and two-dimensional schematic:



<sup>9</sup> The linear and two-dimensional schematic for syndiotactic is represented as



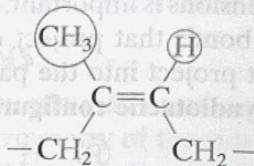
<sup>10</sup> For atactic the linear and two-dimensional schematic is



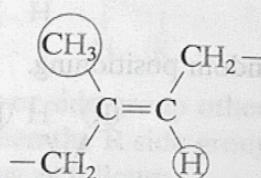
Conversion from one stereoisomer to another (e.g., isotactic to syndiotactic) is not possible by a simple rotation about single chain bonds; these bonds must first be severed, and then, after the appropriate rotation, they are reformed. In reality, a specific polymer does not exhibit just one of these configurations; the predominant form depends on the method of synthesis.

### Geometrical Isomerism

Other important chain configurations, or geometrical isomers, are possible within repeat units having a double bond between chain carbon atoms. Bonded to each of the carbon atoms participating in the double bond is a side group, which may be situated on one side of the chain or its opposite. Consider the isoprene repeat unit having the structure



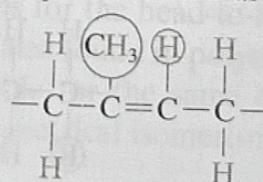
in which the  $\text{CH}_3$  group and the H atom are positioned on the same side of the double bond. This is termed a **cis** structure, and the resulting polymer, *cis*-polyisoprene, is natural rubber. For the alternative isomer



the **trans** structure, the  $\text{CH}_3$  and H reside on opposite sides of the double bond.<sup>11</sup> *Trans*-polyisoprene, sometimes called gutta percha, has properties that are distinctly different from natural rubber as a result of this configurational alteration. Conversion of trans to cis, or vice versa, is not possible by a simple chain bond rotation because the chain double bond is extremely rigid.

Summarizing the preceding sections, polymer molecules may be characterized in terms of their size, shape, and structure. Molecular size is specified in terms of molecular weight (or degree of polymerization). Molecular shape relates to the degree of chain twisting, coiling, and bending. Molecular structure depends on the manner in which structural units are joined together. Linear, branched, crosslinked,

<sup>11</sup> For cis-isoprene the linear chain representation is as follows:



whereas the linear schematic for the trans structure is

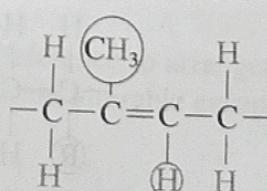
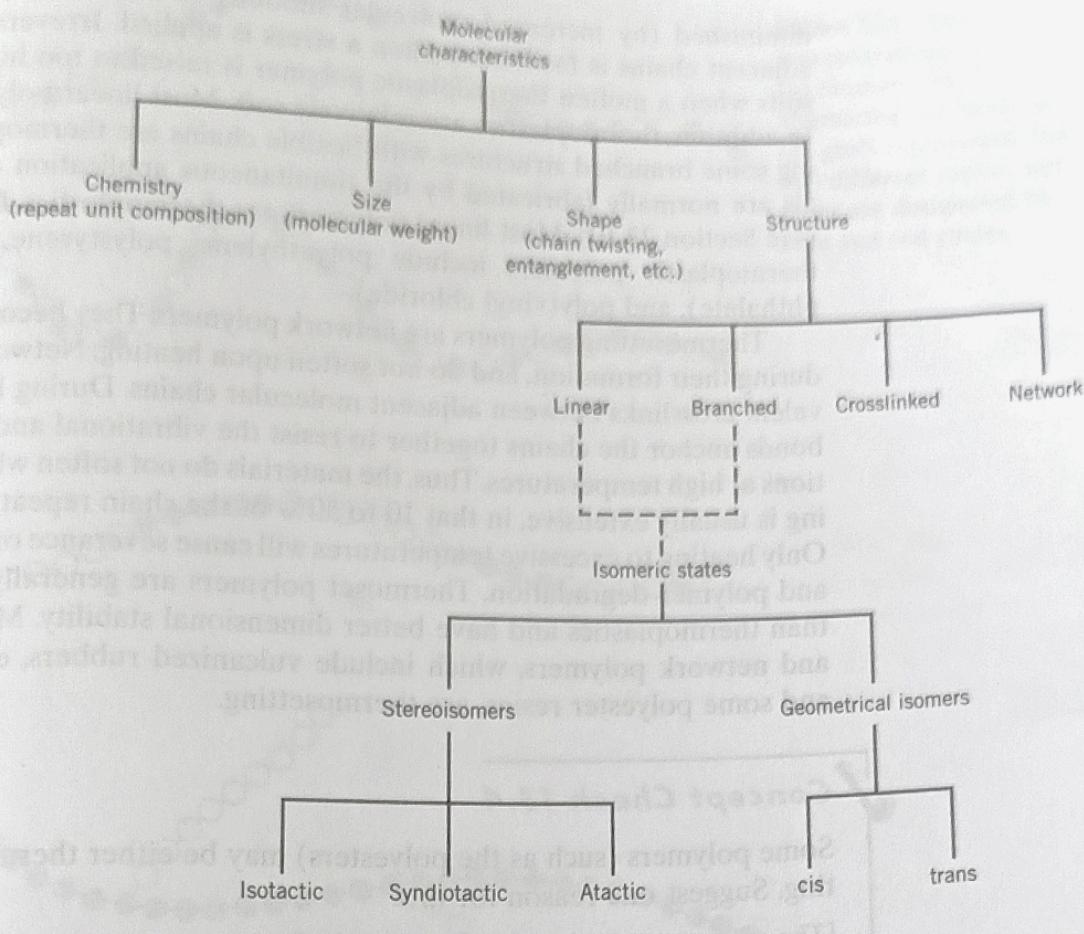


Figure 13.8  
Classification scheme for the characteristics of molecules.



and network structures are all possible, in addition to several isomeric configurations (isotactic, syndiotactic, atactic, cis, and trans). These molecular characteristics are presented in the taxonomic chart, Figure 13.8. Note that some of the structural elements are not mutually exclusive of one another, and, in fact, it may be necessary to specify molecular structure in terms of more than one. For example, a linear polymer may also be isotactic.

### Concept Check 13.3

What is the difference between *configuration* and *conformation* in relation to polymer chains?

[The answer may be found in enclosed CD.]

## TERMOPLASTIC AND THERMOSETTING POLYMERS

The response of a polymer to mechanical forces at elevated temperatures is related to its dominant molecular structure. In fact, one classification scheme for these materials is according to behavior with rising temperature. **Thermoplastics** (or **thermoplastic polymers**) and **thermosets** (or **thermosetting polymers**) are the two subdivisions. Thermoplastics soften when heated (and eventually liquefy) and harden when cooled—processes that are totally reversible and may be repeated. On a molecular level, as the temperature is raised, secondary bonding forces are