Part I

Fundamentals

1

Introduction

General comments

The materials to be discussed in this book are known by a variety of names. The oldest, *rubbers*, is not very illuminating since it refers to their relatively unimportant ability to remove pencil or ink marks from paper by an abrasive rubbing action (Treloar, 1975; Eichinger, 1983; Mark, 2005a). Of much greater importance are their elastic properties, and the term *elastomers* is now much in use. So also is *rubberlike materials*, which emphasizes the similarities between such substances and natural rubber, which is obtained from the Hevea tree.

Rubberlike materials have long been of extraordinary interest and importance. They find usage in items ranging from automobile tires and conveyor belts to heart valves and gaskets in supersonic jet planes (Gent, 1992). The striking nature of their elastic properties and their relationships to molecular structure has attracted the attention of numerous physical chemists and chemical physicists interested in structure–property relationships, particularly those involving polymeric materials (Flory, 1953; Treloar, 1975; Mark and Erman, 1992; Erman and Mark, 1997; Graessley, 2003; Witten, 2004).

Rubberlike elasticity and its molecular requirements

A useful way to begin a discussion of rubberlike elasticity is to define it and then to list the molecular characteristics required to achieve the very unusual behavior described. This is done in Table 1.1. The definition has two parts: very high deformability and essentially complete recoverability. In order for a material to exhibit this type of elasticity, three molecular requirements must be met: (1) the material must consist of polymeric chains; (2) the chains must have a high degree of flexibility and mobility; and (3) the chains must be joined into a network structure (Mark *et al.*, 1993; Mark, 2002a, 2003).

Table 1.1 *Definitions and molecular requirements for rubberlike elasticity*

Two-part definition	Molecular requirements
1. Very high deformability	1. Materials that are constituted of molecules that are: (a) long chains (polymers) (b) highly flexible and mobile
2. Essentially complete recoverability	2. Network structure from cross linking of molecules

The first requirement is associated with the very high deformability. It arises from the fact that the molecules in an elastomeric material must be able to alter their arrangements and extensions in space dramatically in response to an imposed stress, and only a long-chain molecule has the required very large number of spatial arrangements of very different extensions. This versatility is illustrated in Figure 1.1, which depicts a two-dimensional projection of a random spatial arrangement of a relatively short polyethylene chain in the undeformed amorphous state. The spatial configuration shown was computer generated using a Monte Carlo technique in as realistic a manner as possible. The correct bond lengths and bond angles were employed, as was the known preference for *trans* rotational states about the skeletal bonds in any *n*-alkane molecule. A final feature taken into account was the fact that rotational states are interdependent; what one rotatable skeletal bond does depends on what the adjoining skeletal bonds are doing (Flory, 1969; Mattice and Suter, 1994; Rehahn *et al.*, 1997). One important feature of this typical configuration is the relatively high spatial extension of some parts of the chain. This is due to the already mentioned preference for *trans* conformations, which are essentially planar zigzag and therefore of high extension. A feature that is more important in the present context is the fact that, in spite of these preferences, many sections of the chain are quite random and compact. As a result, the chain extension (as measured by the end-to-end separation) is quite small. For even such a short chain, the extension could be increased approximately fourfold by simple rotations about skeletal bonds, without any need for the more energy-demanding distortions of bond angles or increases in bond lengths.

The second characteristic required for rubberlike elasticity also relates to the high deformability. It specifies that the chains be flexible and mobile enough that the different spatial arrangements of the chains are accessible. That is, changes in these arrangements should not be hindered by such constraints as might result from inherent rigidity of the chains, or by decreased mobility as would result from extensive chain crystallization, or from the very high viscosity characteristic of
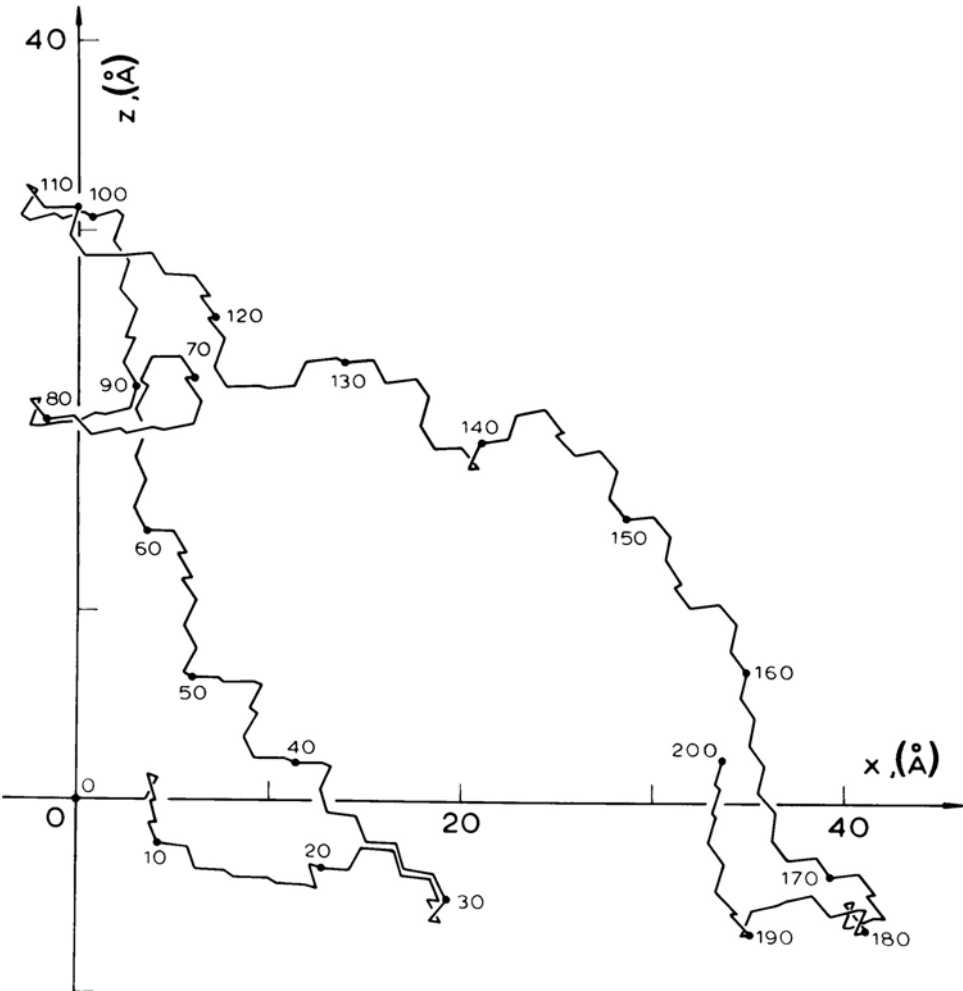
Figure 1.1 A two-dimensional projection of the backbone of an undeformed *n*-alkane chain (or sequence from a longer polyethylene chain) which consists of 200 skeletal bonds (Mark, 1981; Mark *et al*., 1993). This representative arrangement or spatial configuration was computer generated using known values of the bond lengths, bond angles, rotational angles about skeletal bonds, and preferences among the corresponding rotational states. (Reprinted with permission from J. E. Mark *et al*., Eds., *Physical Properties of Polymers*. Copyright 1984, American Chemical Society.)

the glassy state. These two requirements are further discussed in Chapter 2, using specific examples of elastomeric and non-elastomeric materials.

The last characteristic cited is required in order to obtain the recoverability part of the definition. The network structure is obtained by joining together, or cross linking, pairs of segments, approximately one out of every 100, thereby preventing
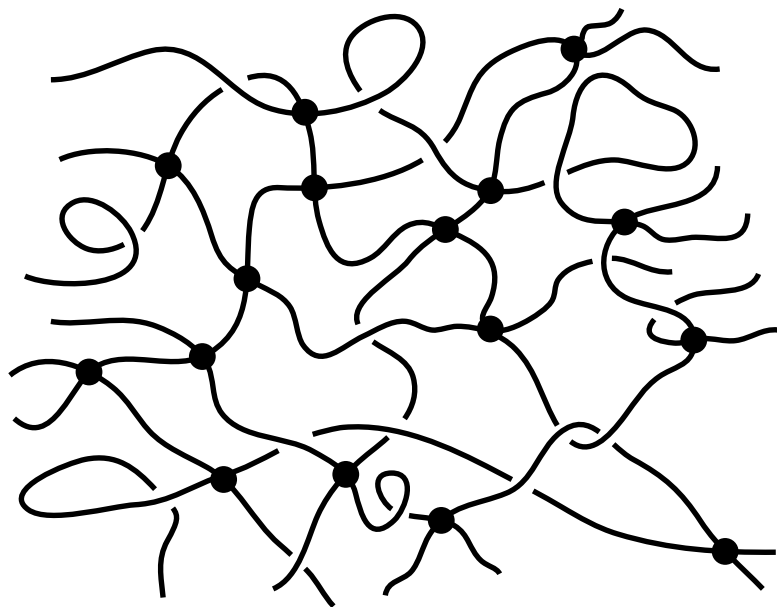
Figure 1.2 Sketch of part of a typical elastomeric network.

stretched polymer chains from irreversibly sliding by one another. The structure obtained in this way is illustrated in Figure 1.2, in which the cross links may be either chemical bonds (as is illustrated by sulfur-vulcanized natural rubber) or physical aggregates, like the small crystallites in a partially crystalline polymer or the glassy domains in a multiphase triblock copolymer (Mark, 2000). Different types of cross linking are discussed in more detail in Chapter 4.

Origin of the elastic force

The molecular origin of the elastic force f exhibited by a deformed elastomeric network can be elucidated through thermoelastic experiments, which involve the temperature dependence of either the force f at constant length L or the length at constant force. Consider first a thin metal strip stretched with a weight W to a point short of that giving permanent deformation, as is shown in Figure 1.3. Increase in temperature (at constant force) would increase the length of the stretched metal strip in what would be considered the usual behavior. Exactly the opposite result, a shrinkage, is observed in the case of a stretched elastomer! For purposes of comparison, the result observed for a gas at constant pressure is included in the figure. Raising its temperature would of course cause an increase in its volume V, as is illustrated by the well-known ideal gas law $pV = nRT$ (Atkins, 1990).
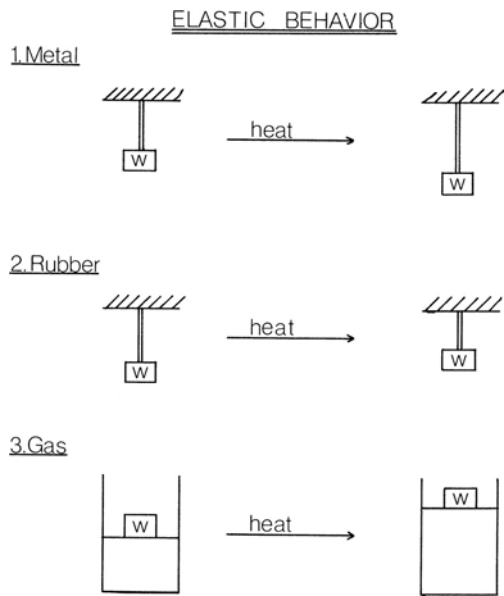
Figure 1.3 Results of thermoelastic experiments carried out on a typical metal, rubber, and gas (Mark, 1981).

The explanation for these observations is given in Figure 1.4 (Mark, 1981). The primary effect of stretching the metal is the increase ΔE in energy caused by changing the values of the distance d of separation between the metal atoms. The stretched strip retracts to its original dimensions upon removal of the force since this is associated with a decrease in energy. Similarly, heating the strip at constant force causes the usual expansion arising from increased oscillations about the minimum in the asymmetric potential energy curve. In the case of the elastomer, however, the major effect of the deformation is the stretching out of the network chains, which substantially reduces their entropy. Therefore the retractive force arises primarily from the tendency of the system to increase its entropy toward the (maximum) value that it had in the undeformed state. Increase in temperature increases the chaotic molecular motions of the chains, which increases the tendency toward the more random state. As a result there is a decrease in length at constant force, or an increase in force at constant length. This is strikingly similar to the behavior of a compressed gas, in which the extent of deformation is given by the reciprocal volume $1/V$. The pressure of the gas is largely entropically derived, with increase in deformation (i.e., increase in $1/V$) also corresponding to a decrease in entropy. Heating the gas increases the driving force toward the state of maximum entropy (infinite volume or zero deformation). Therefore, increasing the temperature increases the volume at constant pressure, or increases the pressure at constant volume.
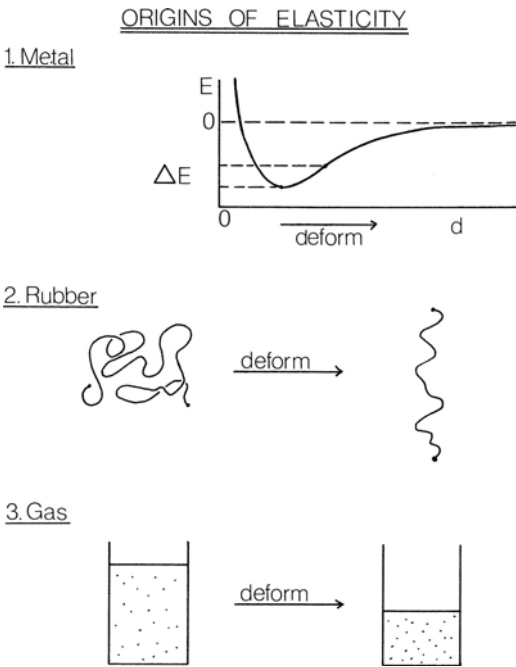
Figure 1.4 Sketches explaining the observations described in Figure 1.3 in terms
of the molecular origin of the elastic force or pressure (Mark, 1981).

Some other analogies

The surprising analogy between a gas and an elastomer (which after all is a con-
densed phase) carries over into the expressions for the work dw of deformation.
In the case of a gas, dw is of course $-p\,dV$. For an elastomer, however, this
term is essentially negligible since network deformation (except for swelling)
takes place at very nearly constant volume. The corresponding work term now
becomes $f\,dL$, where the difference in sign is due to the fact that positive w cor-
responds to a decrease in volume of a gas but to an increase in length of an
elastomer.

Similarly, adiabatically stretching an elastomer increases its temperature in the
same way that adiabatically compressing a gas (for example, in a diesel engine)
will increase its temperature. The situation in the case of the elastomer is somewhat
more complicated in that if some crystallization is induced by the stretching, then
part of the temperature increase would be due to the latent heat of crystallization.
In any case, for both the elastomer and the gas, the total entropy change for the
reversible process

$$\Delta S = \Delta S(\text{deformation}) + \Delta S(\text{temperature change}) \geq 0 \qquad (1.1)$$

must be positive or zero since the systems are acting as though they are (temporarily) isolated. Therefore, since ΔS(deformation) must be negative, ΔS(temperature change) must be positive, and this has to correspond to a temperature increase. The basic point here is the fact that the retractive force of an elastomer and the pressure of a gas are both primarily entropically derived, and as a result the thermodynamic and molecular descriptions of these otherwise dissimilar systems are very closely related.

As would be expected, letting a stretched elastomer contract adiabatically causes its temperature to decrease. These increases and decreases in temperature can, in fact, be used to construct heat-transfer devices such as refrigerators and air conditioners (DeGregoria, 1994; DeGregoria and Kaminski, 1997). An analogy of this effect in elastomers is provided by adiabatic demagnetization, a technique used to reach very low temperatures (Atkins, 1990). A suitable salt is magnetized isothermally by the application of a strong field, thereby aligning its magnetic moments with an associated decrease in entropy. The field is then removed adiabatically (which is analogous to letting the elastomer snap back), and the moments again spontaneously become disordered. In both cases ΔS(disordering) is positive and is offset by a negative ΔS(temperature change), which of course corresponds to a decrease in temperature.

The fact that heat is given off in the stretching of an elastomer can be used to provide a thermodynamic explanation of the observed shrinkage of a stretched elastomer when its temperature is increased. According to Le Chatelier's principle, "A system at equilibrium, when subjected to a perturbation, responds in a way that tends to eliminate the effect" (Atkins, 1990). Since heat is given off during stretching, adding heat has to cause a contraction. The temperature increase observed upon stretching an elastomer is augmented by heat generated by the wasteful conversion of part of the deformation energy through frictional effects. As a result, the temperature increase during the stretching process is not completely offset by the temperature decrease during the retraction phase. There is therefore a hysteretic buildup in temperature that is highly disadvantageous. Not only does it represent wastage of mechanical energy, but the heat buildup can have a degradative effect on the elastomer. Probably the most important example here is the flexing of an automobile tire as it rotates through its bending–recovery cycles.

Some historical high points

Table 1.2 summarizes some important contributions from early experiments on rubberlike elasticity. The earliest experiments, by Gough in 1805 (Flory, 1953; Treloar, 1975; Mason, 1979), demonstrated the heat effects described in the preceding few paragraphs and also the phenomenon of strain-induced crystallization, which is

Table 1.2 *Some early contributions in the experimental area*

Contribution	Scientists	Date
Heat effects, strain-induced crystallization	Gough	1805
Vulcanization (cross linking)	Goodyear and Hayward	1839
Thermoelasticity	Joule	1859
Volume changes accompanying deformation	Several	*c.* 1930
Physically cross-linked networks such as the thermoplastic elastomers	Numerous	—
Insights from studies of bioelastomers	Numerous	—

discussed in Chapter 12. The discovery of vulcanization (sulfur-based cross linking) by Goodyear and Hayward in 1839 greatly facilitated experimental investigations since cross-linked elastomers could now be brought close to elastic equilibrium (Morawetz, 1985). The more quantitative thermoelasticity experiments described above were first carried out by Joule back in 1859. This was in fact only a few years after the entropy S was introduced as a thermodynamic function. Another important experimental contribution was the observation by several workers that deformations (other than swelling) of rubberlike materials occurred essentially at constant volume, so long as crystallization was not induced (Gee *et al.*, 1950). (In this sense, the deformations of an elastomer and a gas are very different.) Some more recent milestones are physically cross-linked networks such as the thermo-plastic elastomers (discussed primarily in Chapter 4), and biomimetic insights from studies of bioelastomers (covered in Chapter 17).

Some early contributions on the theoretical side are described in Table 1.3. A molecular interpretation of the fact that rubberlike elasticity is primarily entropic in origin had to await Hermann Staudinger's later demonstration that polymers were covalently bonded molecules and not some type of association complex best studied by colloid chemists (Morawetz, 1985). Meyer, von Susich, and Valko in 1932 correctly interpreted the observed near constancy in volume to indicate that the changes in entropy must therefore involve changes in the spatial configurations of the network chains. These workers also concluded that the elastic force should be proportional to the absolute temperature (Treloar, 1975). These basic qualitative ideas are shown in the sketch in Figure 1.5, where the arrows represent some typical end-to-end vectors of the network chains. The first step toward making these ideas more quantitative, in the form of an elastic equation of state, was the idea, proposed

Table 1.3 *Some early contributions in the theoretical area*

Contribution	Scientists	Date
Chainlike nature of polymers	Staudinger	*c.* 1920
Chain orientation upon network deformation; elastic force proportional to absolute temperature	Meyer, von Susich, and Valko	1932
Elastic force proportional to number of "molecules"	Kuhn	1936
Elastic force proportional to absolute temperature and to sample length	Guth and Mark	1934
Phantom network theory	James and Guth	1941
Affine network theory	Wall	1942
	Flory and Rehner	1943
Theories with constraints on junctions	Allegra and Ronca	1975
	Flory and Erman	1977
Slip-link theories	Ball, Doi, and Edwards	1981

by Werner Kuhn in 1936, that the elastic force f should be proportional to the number of "molecules" in the elastomer. In the 1930s, Kuhn, Eugene Guth, and Herman Mark first began to develop quantitative theories based on this idea that the network chains undergo configurational changes, by skeletal bond rotations, in response to an imposed stress. Guth and Mark (Guth and Mark, 1934) also concluded from this picture that f should be proportional to the absolute temperature, which turns out to be approximately correct. They also concluded, however, that f should be proportional to the length of the stretched elastomer. This is incorrect since the constant-volume nature of the elongation process requires that the sample dimensions perpendicular to the stretching direction decrease proportionally. Some chains are therefore compressed in an elongation experiment, as is illustrated by the horizontal end-to-end vector shown in the middle of the sample strip in Figure 1.5. As a result, f is not proportional to L or to the elongation $\alpha = L/L_i$; (L_i being the initial length), but to $(\alpha - \alpha^{-2})$, where the subtractive term α^{-2} results from these compressive effects.

Guth, in collaboration with Hubert James, began development of the phantom network theory of rubberlike elasticity around 1941. Fred Wall, Paul Flory, and John Rehner in 1942 and 1943 then began development of the alternative affine network theory. Later refinements include theories with constraints on junctions, and the slip-link theories. All these developments are described in Chapters 5 and 6.