

Physical Properties of Polymers

Second Edition

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William W. Graessley
Leo Mandelkern
Edward T. Samulski
Jack L. Koenig
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George D. Wignall

Preface

When we noticed that the first edition of this book (published in 1984) was being used either as a supplementary text or as the sole textbook in introductory polymer courses, we decided it was time to bring out an expanded second edition. All of the chapters contain general introductory material and comprehensive literature citations designed to give newcomers to the field an appreciation of the subject and how it fits into the general context of polymer science. For pedagogical purposes, the contents have been subdivided into two parts, "Physical States of Polymers" and "Some Characterization Techniques". A new chapter has been added to each part: "The Mesomorphic State" (Samulski) covers the rapidly developing subject of liquid-crystalline polymers; "Scattering Techniques" (Wignall) emphasizes the potential of small-angle neutron scattering in contemporary characterization of bulk polymers. The original five chapters: "The Rubber Elastic State" (Mark), "The Glassy State and the Glass Transition" (Eisenberg), "Viscoelasticity and Flow in Polymer Melts and Concentrated Solutions" (Graessley), "The Crystalline State" (Mandelkern), and "Molecular Spectroscopy" (Koenig), have been revised and updated. This expanded edition should provide ample core material for a one-term survey course at the graduate or advanced undergraduate level. Although the chapters have been arranged in a sequence that may be readily adapted to the classroom, each chapter is self-contained and may be used as an introductory source for these seven topics.

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Physical States of Polymers

The Rubber Elastic State

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Basic Concepts

The most useful way to begin an article on rubberlike elasticity is to define it and then to discuss what types of materials can exhibit this very unusual behavior. Accordingly, rubber elasticity may be defined operationally as very large deformability with essentially complete recoverability. 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 (3) the chains must be joined into a network structure (1-3).

The first requirement arises from the fact that the molecules in a rubber or elastomeric material must be able to alter dramatically their arrangements and extensions in space 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 (3), which depicts a two-dimensional projection of a random spatial arrangement of a relatively short polyethylene chain in the amorphous state. The spatial configuration shown was computer-generated, in as realistic a manner as possible. The correct bond lengths and bond angles were used, as was the known preference for *trans* rotational states about the skeletal bonds in any *n*-alkane molecule. A final feature taken into account is the fact that rotational states are interdependent; what one rotational skeletal bond does, depends on what the adjoining skeletal bonds are doing (4). One important feature of this typical configuration is the relatively high spatial extension of some parts of the chain. This feature is due to the preference for the *trans* rotational states, already mentioned, which are essentially planar zigzag and thus of high extension. The second important feature is the fact that, despite these

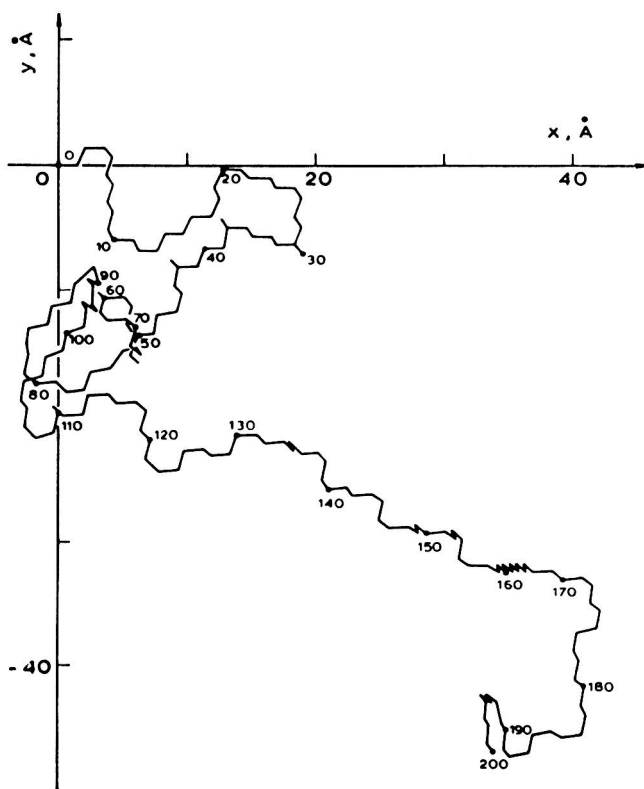


FIGURE 1. A two-dimensional projection of an n -alkane chain having 200 skeletal bonds (3). The end-to-end vector starts at the origin of the coordinate system and ends at carbon atom number 200.

preferences, many sections of the chain are quite compact. Thus, the overall 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 distortions of bond angles or increases in bond lengths.

The second requirement for rubberlike elasticity specifies that the different spatial arrangements be *accessible*; that is, changes in these arrangements should not be hindered by constraints that might result from inherent chain rigidity, extensive chain crystallization, or the very highly viscous nature of the glassy state (1, 2, 5).

The third requirement allows elastomeric recoverability. A network structure is obtained by joining together or cross-linking pairs of segments, approximately one out of a hundred; the cross-linked segments prevent stretched polymer chains from irreversibly sliding by one another. In a network structure (Figure 2; 5), the cross-links may be either chemical bonds (as would occur in sulfur-vulcanized natural rubber) or physical aggregates (for example, the small crystallites in a partially crystalline polymer or the glassy domains in a multiphase block copolymer; 3). Additional information on the cross-linking of chains is given later in *Preparation of Networks*.

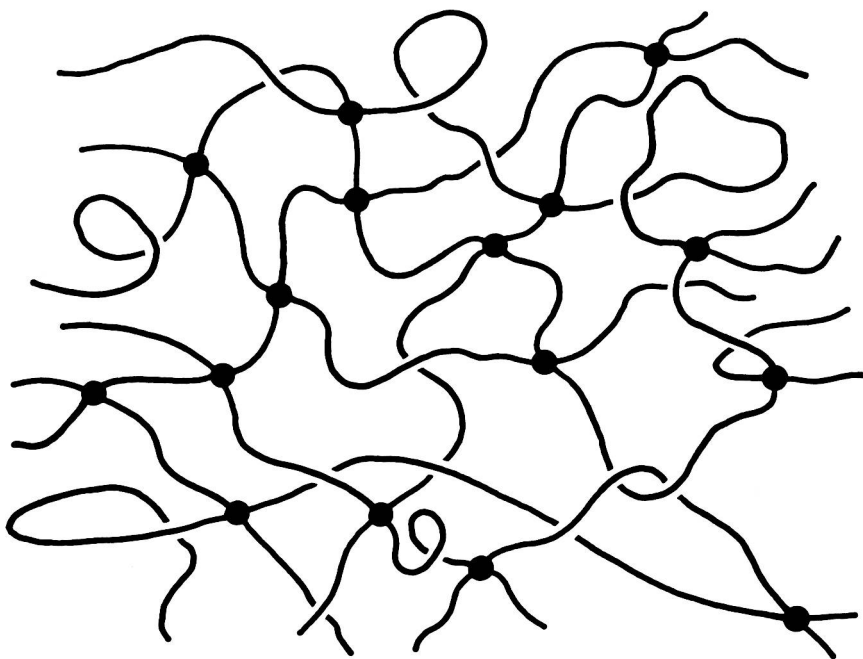


FIGURE 2. Schematic sketch of a typical elastomeric network. (Reproduced with permission from reference 5. Copyright 1988 John Wiley and Sons, Inc.)

Origin of Elastic Retractive Force

The molecular origin of the elastic force (f) exhibited by a deformed elastomeric network can be elucidated through thermoelastic experiments, which examine the temperature dependence of either the force at constant length (L) or the length at constant force (l , 3). Consider a thin metal strip stretched with a weight W to a point short of that giving permanent deformation, as shown in Figure 3 (3). An increase in temperature (at constant force) would increase the length of the stretched strip in what would be considered the “usual” behavior. Exactly the opposite, a *shrinkage*, is observed in the case of a stretched elastomer! For purpose of comparison, the result observed for a gas at constant pressure is included in the figure. Raising the gas temperature would, of course, cause an increase in volume (V), as required by the ideal gas law.

The explanation for these observations is given in Figure 4 (3). The primary effect of stretching the metal is the increase in energy (ΔE) caused by changing the distance (d) of separation between the metal atoms. The stretched strip retracts to its original dimension upon removal of the force, because this retraction 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. For the elastomer, however, the major effect of the deformation is the stretching out of the network chains, which substantially reduces their entropy (1–3). Thus, the retractive force arises primarily from the tendency of the system to increase its entropy toward

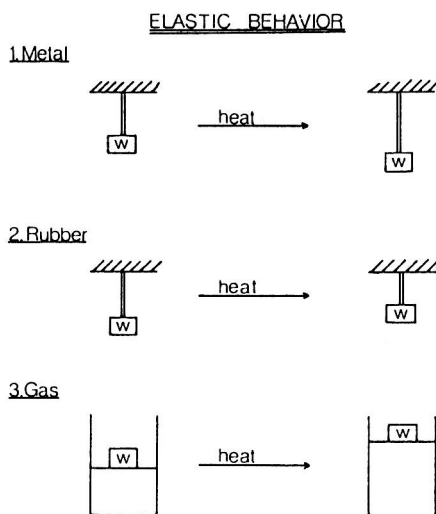


FIGURE 3. Results of thermoelastic experiments carried out on a typical metal, rubber, and gas (3).

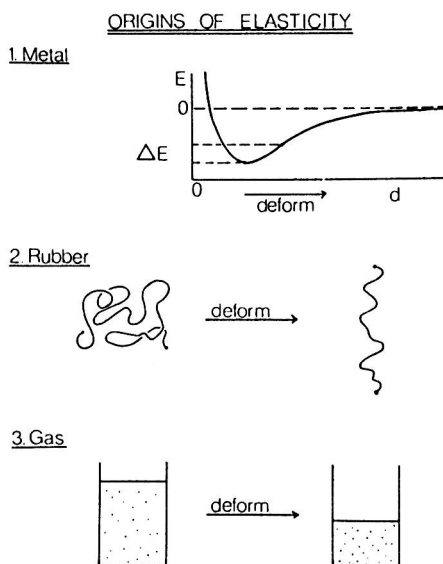


FIGURE 4. Sketches explaining the observations described in Figure 3 in terms of the molecular origin of the elastic force or pressure (3).

the (maximum) value it had in the undeformed state. An increase in temperature increases the chaotic molecular motions of the chains and thus increases the tendency toward this more-random state. As a result, the length decreases at constant force, or the force increases at constant length. This behavior is strikingly similar to that of a compressed gas, in which the extent of deformation is given by the reciprocal volume ($1/V$). The pressure of the gas is also largely entropically derived, with an in-

crease 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). Thus, increasing the temperature increases the volume at constant pressure or increases the pressure at constant volume.

This surprising analogy between a gas and an elastomer (which is a condensed phase) carries over into the expressions for the work of deformation (dw). For a gas, dw is, of course, $-pdV$, in which p is pressure. For an elastomer, however, this pressure-volume term is generally essentially negligible. For example, network elongation is known to take place at very nearly constant volume (1, 3). The corresponding work term (dw) now becomes $+fdL$; the difference in sign is due to the fact that a positive w corresponds to a decrease in the volume of a gas but to an increase in the length of an elastomer. 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. Similarly, an elastomer cools on adiabatic retraction, just as a compressed gas cools in the corresponding expansion. 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.

Some Historical High Points

Experimental Approaches

The simplest of the thermoelastic experiments described earlier were first carried out many years ago, by J. Gough, back in 1805 (1, 2, 5, 6). The discovery of vulcanization (i.e., curing of rubber into network structures) by C. Goodyear and N. Hayward in 1839 was important in this regard, because it permitted the preparation of samples that could be investigated in this regard with much greater reliability. Such more-quantitative experiments were carried out by J. P. Joule, in 1859, in fact, only a few years after entropy was introduced as a concept in thermodynamics in general! Another important experimental finding relevant to the development of these molecular ideas was the fact that deformations of rubberlike materials, other than swelling, occurred essentially at constant volume as long as crystallization was not induced (1). (In this sense, the deformation of an elastomer differs from that of a gas.)

Theoretical Approaches

A molecular interpretation of the fact that rubberlike elasticity is primarily entropic in origin had to await H. Staudinger's demonstration in the 1920s that polymers were covalently bonded molecules and not some type of association complex best studied by the colloid chemists (1). In 1932, W. Kuhn used this observed constancy in volume to point out that the changes in entropy must therefore involve changes in orientation or configuration of the network chains. These basic qualitative ideas are