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Physical Properties of Polymers

Third Edition

聚合物的物理性能 第3版

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PHYSICAL PROPERTIES OF POLYMERS

The third edition of this well-known textbook discusses the diverse physical states and associated properties of polymeric materials. The contents of the book have been conveniently divided into two general parts, "Physical states of polymers" and "Some characterization techniques."

This third edition, written by seven leading figures in the polymer-science community, has been thoroughly updated and expanded. As in the 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.

The third edition of *Physical Properties of Polymers* provides enough core material for a one-semester survey course at the advanced undergraduate or graduate level.

Professor James E. Mark is a consultative editor for the Cambridge polymer science list.

The authors wish to dedicate this volume to the memory of Paul J. Flory, whose intuitive grasp of the fundamentals of polymer science predicted and integrated much of the research described in their various contributions. Paul was an inspiring colleague to those of us who were fortunate enough to know him, and one whose influence is still very much in evidence in the field.

Preface

The first two editions of this book found considerable use either as a supplementary text or as sole textbook in introductory polymer courses, or simply as a book for self-study. It was therefore decided to bring out an expanded third edition. As before, 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. All chapters have been extensively updated and expanded. The authors are the same as those for the second edition, except for the authorship of the chapter "The glass transition and the glassy state" by Kia L. Ngai. For pedagogical purposes, the contents have been subdivided into two parts, "Physical states of polymers" and "Some characterization techniques."

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 readily be adapted to the classroom, each chapter is self-contained and may be used as an introductory source of material on the topics covered.

Contents

Part I

Physical states of polymers

1

The rubber elastic state

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1.1 Introduction

1.1.1 Basic concepts

The elastic properties of rubber-like materials are so strikingly unusual that it is essential to begin by defining rubber-like elasticity, and then to discuss what types of materials can exhibit it. Accordingly, this type of elasticity may be operationally defined as very large deformability with essentially complete recoverability. In order for a material to exhibit this type of elasticity, three molecular requirements must be met: (i) the material must consist of polymeric chains, (ii) the chains must have a high degree of flexibility and mobility, and (iii) the chains must be joined into a network structure [1–5].

The first requirement arises from the fact that the molecules in a rubber or 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 Fig. 1.1 [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 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 is the fact that rotational states are interdependent; what one rotational skeletal bond does depends on what the adjoining skeletal bonds are doing [6–8]. One important feature of this typical configuration is the relatively high spatial extension of some parts of the chain. This is due to the preference for the *trans* conformation, as has already been mentioned, which is essentially a planar zig-zag and thus of high extension. The

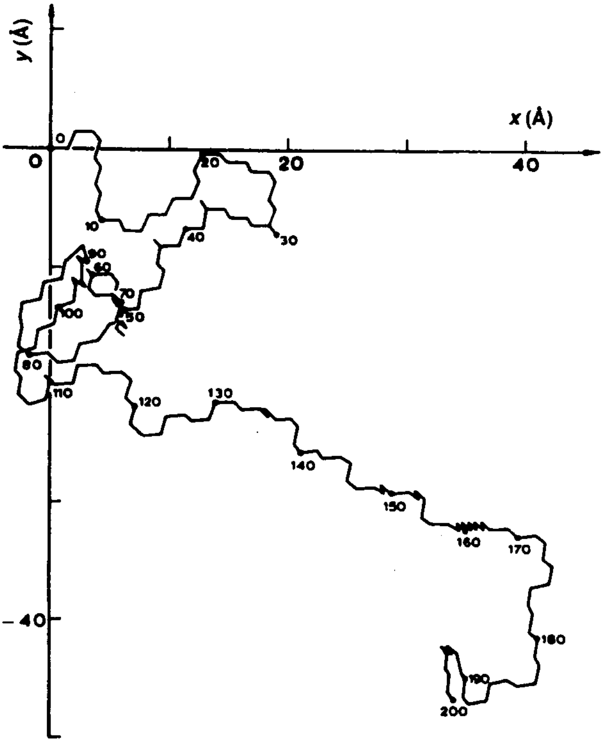

Fig. 1.1. A two-dimensional projection of an n-alkane chain having 200 skeletal bonds [3]. The end-to-end vector starts at the origin of the coordinate system and ends at carbon atom number 200.

second important feature is the fact that, in spite of these preferences, many sections of the chain are quite compact. Thus, the overall chain extension (measured in terms of the end-to-end separation) is quite small. Even for such a short chain, the extension could be increased approximately four-fold by simple rotations about skeletal bonds, without any need for distortions of bond angles or increases in bond lengths.

The second characteristic required for rubber-like elasticity specifies that the different spatial arrangements be *accessible*, i.e. changes in these arrangements should not be hindered by constraints such as might result from inherent rigidity of the chains, extensive chain crystallization, or the very high viscosity characteristic of the glassy state [1, 2, 9].

The last characteristic cited is required in order to obtain the elastomeric recoverability. It is obtained by joining together or "cross-linking" pairs of segments, approximately one out of a hundred, thereby preventing stretched polymer chains

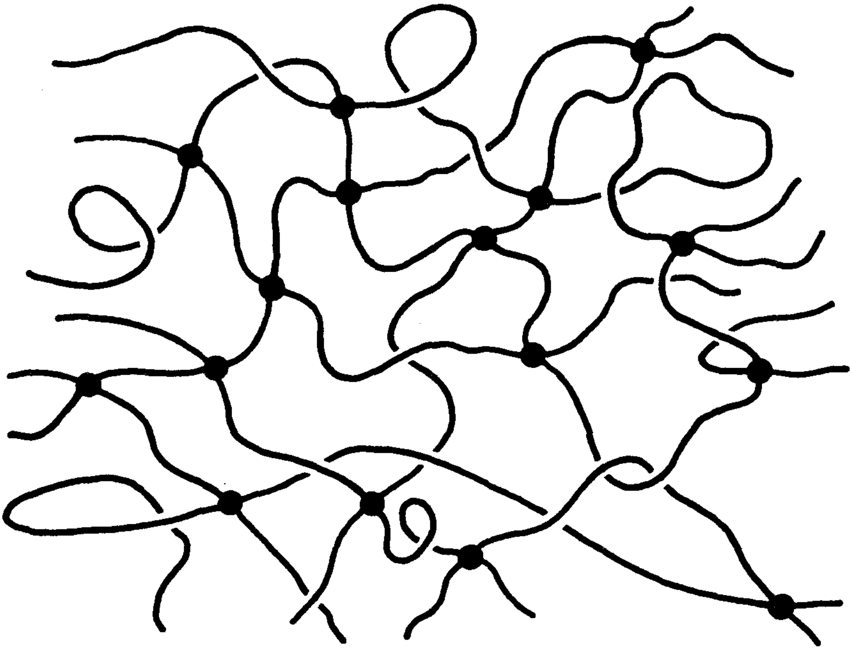

Fig. 1.2. A sketch of an elastomeric network, with the cross-links represented by dots [3].

from irreversibly sliding by one another. The network structure thus obtained is illustrated in Fig. 1.2 [9], in which 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 in Section 1.1.6.

1.1.2 The origin of the elastic retractive 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 at constant length L or the length at constant force [1, 3]. Consider first a thin metal strip stretched with a weight W to a point short of that giving permanent deformation, as is shown in Fig. 1.3 [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 purposes

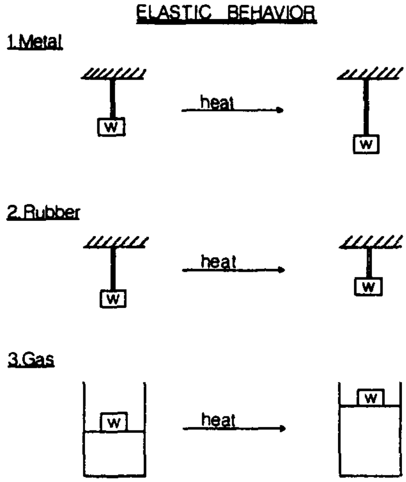

Fig. 1.3. Results of thermoelastic experiments carried out on a typical metal, rubber, and gas [3].

of comparison, the result observed for a gas at constant pressure is included in Fig. 1.3. Raising its temperature would of course cause an increase in volume V, as exemplified by the ideal-gas law.

The explanation for these observations is given in Fig. 1.4 [3]. The primary effect of stretching the metal is the increase ΔE in energy caused by changing the separation d between the metal atoms. The stretched strip retracts to its original length 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 an increase in 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 [1–3]. Thus, the retractive force arises primarily from the tendency of the system to increase its entropy toward the (maximum) value it had in the undeformed state. An increase in temperature increases the magnitude of the chaotic molecular motions of the chains and thus increases the tendency toward this 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 also largely entropically derived, with an increase in deformation (i.e. an 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

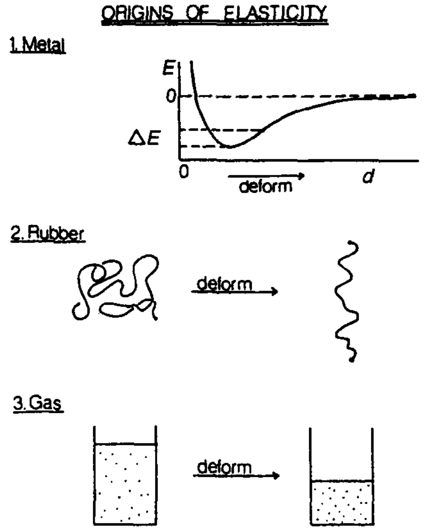

Fig. 1.4. Sketches explaining the observations described in Fig. 1.3 in terms of the molecular origin of the elastic force or pressure [3].

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 $\mathrm{d}w$ of deformation. In the case of a gas, $\mathrm{d}w$ is of course $-p\,\mathrm{d}V$. 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 now becomes $+f\,\mathrm{d}L$, where the difference in sign is due to the fact that positive $\mathrm{d}w$ corresponds not to a decrease in volume of a gas but to an increase in 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 during 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 closed related.

1.1.3 Some historical high points

The simplest of the thermoelastic experiments described above were first carried out many years ago, by J. Gough, back in 1805 [1, 2, 9, 10]. Gough was a clergyman,