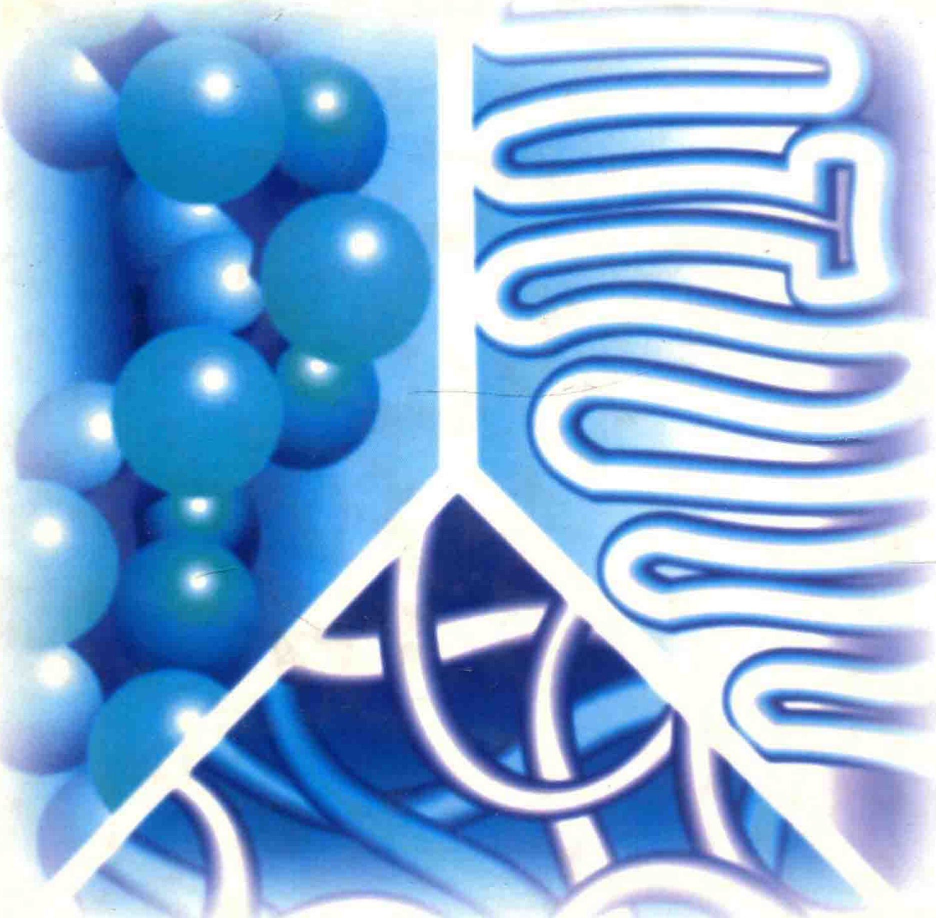
Fundamentals of Polymer Physics

Bincai (Pun Choi) LI



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PREFACE TO THE ENGLISH EDITION

The Chinese Edition of the Book was published by the Science Press, Beijing, in the late of 1989, entitled "Structure and Physical Properties of High Polymers". Since then, the Book was rewritten in English with revisions and enlargements. In the writings, emphases have been laid on improving the deepness and comprehensibility of the Book and adding new contents to keep up with the developments in polymer science. Some essential contents are cited as examples: Discussions on NMR begin with basic principles and the advanced techniques, pFT and MAS, are introduced. In the descriptions of amorphous bulk polymers, the method of RDF, in addition to SANS, is also described so that different scalings can be compared. The application of SALS to the studies of crystal structure and birefringence is set forth. Recent progresses in the field of polymer blends are discussed. Comprehensive discussions on the molecular theory of rubber elasticity are set forth; besides the classical affine network, the phantom and the constrained junction models are also expounded, moreover, birefringence and SANS of deformed networks are described. Two molecular theories of viscoelasticity, the bead and spring and the reptation models, are discussed, which concern with the rheological behavior of polymers. Fractography is introduced associated with fracture of polymers. Most of the key Equations in the Text are derived in details for instructive purpose, e. g., the radial distribution function of chain coils, the kinetic equation of crystallization, the elastic equation of state for polymer networks, etc. Furthermore, Study Problems appended to the end of each Chap. are instructive and helpful to reviewing.

Since the Book covers almost the entire field of polymer physics, expounding most of the basic principles, and moreover, it is addressed to students of polymer science, the change of the Title to the present one, "Fundamentals of Polymer Physics", is appropriate. The treatment of the Book is at the first year graduate (or last year undergraduate) level as a textbook. However, a reminiscence of the fundamental concepts and basic principles would also be helpful to research workers and engineers in the field of polymer science and industry.

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PREFACE TO THE CHINESE EDITION

The importance of the subject, structure and physical properties of high polymers, in the field of polymer science should be stressed unambiguously since this subject concerns with almost every aspect of the field: from the monitoring of polymerization reactions to the characterization of the products, from the control of the processability of raw materials to the prediction and judgement of the quality of finished articles; all of these courses involve the studies of the relationships between structure and properties. Moreover, research works in this subject contribute to the advances of the theories of polymer science. However, the concerned works published in our country in the seventies were rare. At the beginning of the eighties, the author had written a series of papers of the same title, published successively in the Journal of Synthetic Rubber Industry [1]. Afterwards, some books of similar kind were published [2 ~ 8]. Beginning from 1983, the author opened the course, "Structure and Behavior of High Polymers", in South China University of Science and Technology to graduate students of polymer science. The same course was also offered twice to Qing Tao College of Chemical Engineering in Summer vacations. Then, stemming from some monographs of polymer physics and following the advances in polymer science, the book was begun to prepare for the purpose of providing a new text for graduate students as well as a reference for research workers and engineers in the field of polymer science and industry. In view of that students in their undergraduate studies would be in contact with all the basic knowledges of polymer science, the author had no attempt to write a book of all-embracing but rather more insight and detailed discussions on key topics.

A high polymer consists of macromolecules each of which is formed by linking together one kind (or two or three kinds in copolymer) of monomeric (structural) units of the same chemical structure but not necessarily the same configuration. Therefore, the studies of the chemical structure, configuration, and arrangement of monomeric units have become the foundation of polymer science. Studies in this respect have been greatly promoted by the method of nuclear magnetic resonance since the seventies, so that detailed discussions on NMR spectroscopy are given in Chapter 2. The variations of the conformations of molecular chains due to internal rotations about single bonds relate in many respects to the behavior of polymers such as crystallization, properties of solution and molecular mass determination, long range elasticity, as well as the viscoelastic flow of the bulk. Details of conformations are described in Chaps. 3 and 4. The manifestations of bulk properties in the performances of polymers depend on the structure of aggregation states and the molecular motions in different physical states. Orientation of molecular chains in the aggregation state and the glassy-rubbery transition of the physical state are two characteristics of high polymers which are not displayed by low molecular substances; and the two transition temperatuares, T_g and T_m, are particularly important in the commercial applications of polymers. These phenomena are discussed in Chaps. 6 and 8. Long range elasticity arising from the change of conformational entropy of molecular chains, which is indispensable for rubbers, is introduced in Chap. 9. The properties most closely related to the practical applications of high polymers are mechanical properties which, according to the author's idea, are best divided into two parts: 1) visco-elastic properties and flow behavior governing the processability of polymeric materials [Chap. 10] and 2) strength and failure of polymer products including fracture mechanics and the micromechanism of failure such as shear yielding and crazing [Chap. 11]. For many years, polymer blends because of their variety and versatility have played an important role in open up the uses of polymers, a review is given in Chapter 7. However, the book is no more inclusive, some important topics have been omitted, for example, electric and optical properties.

In view of that the uses of units for the expressions of the magnitudes of physical quantities have not reached to the common standards of SI and many non-SI units are also prevaling in recent literatures, conversion tables for non-SI and SI units are given in Appendix I. Appendix II is a list of abbreviations for polymers.

The author is especially indebted to Professor Jianyuan Pan of Zhong Shan University, Professor Min Zhu and Professor Yuanlan Jiang of South China University of Science and Technology for their readings and valuable criticisms to the manuscripts, and Mr. Licheng Jia and Miss Ying Liu for their transcription of the manuscripts.

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1. Introduction

Polymer chemistry has been stemming from organic chemistry. High polymers, most of which are organic compounds with chain-like molecules, may simply be classified according to the chemical nature of their molecular chains, see Table 1.1. Thus, the nomenclature of high polymers is based on the structure of their macromolecular chains. For homopolymers, each chain is formed by linking together structural units of the same chemical structure know as MONOMERIC UNITS, but a monomeric unit may assume different configurations. For example, there are three stereo-isomers for monomeric units of polybutadiene: *cis*-, *trans*-, and 1,2-. For copolymers, a chain is formed by two or three kinds of monomeric units. The studies of the structure, configuration, and arrangement of monomeric units have become the foundation of polymer science. Refer to Chap. 2.

Table 1.1 Classification of High Polymers

Type		Example
Carbon Chain Polymer	Saturated Unsaturated	Polyethylene $\left(CH_2-CH_2 \right)_n$ Polybutadiene $\left(CH_2-CH=CH-CH_2 \right)_n$
Hetero-chain Polymer		Nylon-6,6 $\left(CO(CH_2)_4CO-NH(CH_2)_6NH \right)_n$

The most important characteristic of high polymers is the great magnitude and inhomogeneity of their molecular masses which can only be expressed as average quantities. The molecular mass must reach a certain value for a high polymer to possess physical properties which low molecular mass substances do not display, particularly mechanical properties. This TRANSITIOIN MOLECULAR MASS is about 150000 ~ 200000 for non-polar carbon chain polymers. For example, the molecular mass of butyl rubber has to exceed 200000 for a vulcanizate to have a usable break strength, see Fig. 1.1. For polar hetero-chain polymers, the transition molecular mass can be much lower, being 15000 ~ 20000, because the interactions between molecular chains are strengthened by polar groups or hydrogen bondings.

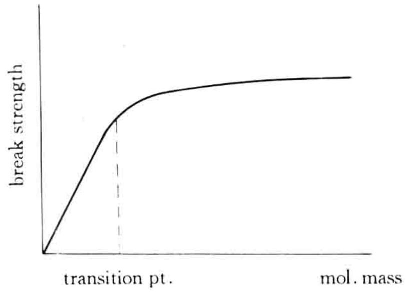
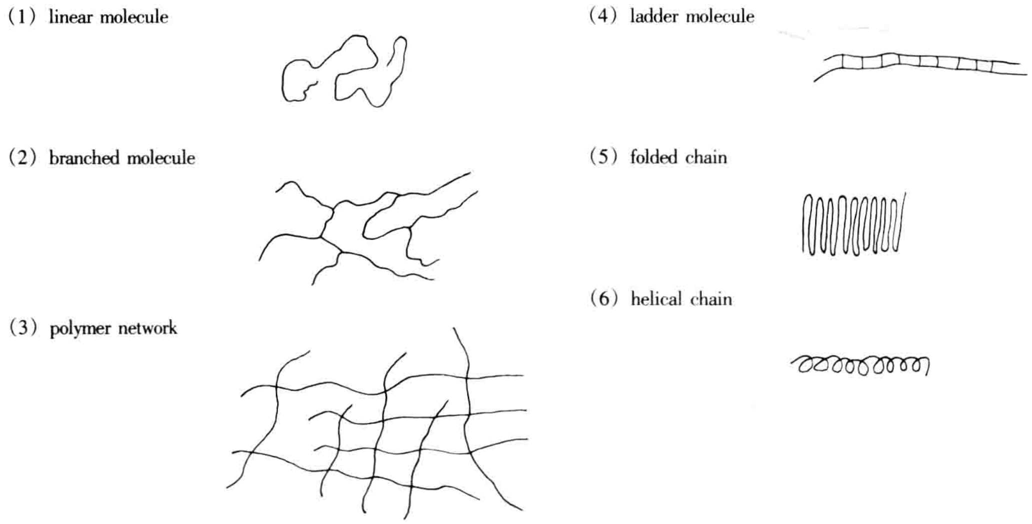


Fig. 1.1 Relationship between molecular mass of butyl rubber and the break strength of its vulcanizate.

Macromolecular chains are not necessarily linear, some of them assume branched or other shapes. Fig. 1.2 presents different shapes of polymer molecules, therein (3) is a polymer stereo-network which is formed by cross-linking together many molecular chains. Such a network is insoluble in any solvent, molecular mass is not determinable by usual methods so that the concept of molecule is no more applicable. (5) and (6) in the Fig. are folded and helical chains, respectively, existing in the crystalline regions of some polymer bulks; they will become randomly coiled linear molecules when melted or dissolved in solvents.

Most polymers are soluble in certain solvents. Therefore, informations concerning the structure of individual molecules such as molecular mass, molecular mass distribution, molecular shapes (e. g., branching), etc., can be obtained from the studies of the properties of dilute polymer solutions. These studies have become an important field in polymer science, see Chaps. (4) and (5).


(1) linear molecule

(2) branched molecule

(3) polymer network

(4) ladder molecule

(5) folded chain

(6) helical chain

Fig. 1.2 Some geometrical shapes of polymer molecules [(3) is an infinite network, the concept of molecule is not applicable].

Practically, polymers are used in the form of bulks; it is necessary to study the relationship between structure and bulk properties. Of course, the structures of monomeric units and individual molecules are of fundamental. For example, poly(α-methylstyrene) has a much higher glass transition temperature T_g than polystyrene, since the methyl groups in the monomeric units increase the stiffness of the chain. Rubber of too low a molecular mass couldn't yield a vulcanizate with sufficient strength because of the incompleteness of the network, see Fig. 1.1. However, the aggregation state (amorphous or crystalline) of the bulk plays an important role; in many cases, the effect of the structure of monomeric unit on bulk properties is via its effect on the aggregation state. The example of polyethylene is cited. Its molecular chains are regular with no substituents so that liable to close together for crystallization, and high crystallinity in the bulk prevents PE for application as rubber. Copolymerization of ethylene and propylene results in molecular chains of irregular structure which prohibit crystallization, and the copolymer produced (with low T_g) has become a famous commercial rubber. For some crystalline polymers used as plastics such as PE and PP, molecular mass and its distribution may influence the rate and degree of crystallization, while the structure of the crystalline region would in turn influence the mechanical properties of the bulk. Therefore, structure of aggregation state is directly related to bulk properties, its importance is unquestionable.

Most polymers consist of chain molecules. But some of them have to be transformed into stereo-networks for commercial applications. A typical example is rubber which must be vulcanized in order to possess long range elasticity and strength. other examples are phenol-formaldehyde resin and epoxides.

The role of molecular motion in the relationship between stucture and physical properties should not be ignored. For a rubber in the course of processing, the molecular mass of which should not be too high and process oil has to be added in order to promote molecular flow so that the 'compound' would have sufficient plasticity for fabrication. However, once network is formed by vulcanization, no relative motions among molecules take place so that the product is stable in shape; but chain segments in the network can be set into motion for elasticity.

Thermoplastics melt and relative molecular motions (flow) can be set in at high temperature for processing such as extrusion or moulding. Once cooling down to room temperature, the properties of the products depend on the nature of the monomeric units of the polymers. For polymers with monomeric units forming irregular chain structure and T_g higher than room temperature, such as atactic polystyrene and poly(methyl methacrylate), they are in a state of amorphous glass with molecular motions frozen, displaying a hard and brittle property. For crystalline polymers (whose monomeric units form regular chain structure) such as PE and PP, crystallites of high melting point are dispersed in amorphous matrix which is rubbery at room temperature due to low T_g. There would be no molecular motion in the crystalline region, but motions of chain segments in the rubbery matrix can be set in. Therefore, impact energy could be transformed into energy of molecular motions when the bulk is under the action of impact. These polymers display a property of toughness.

The scope of polymer structure is demonstrated in Fig. 1.3.

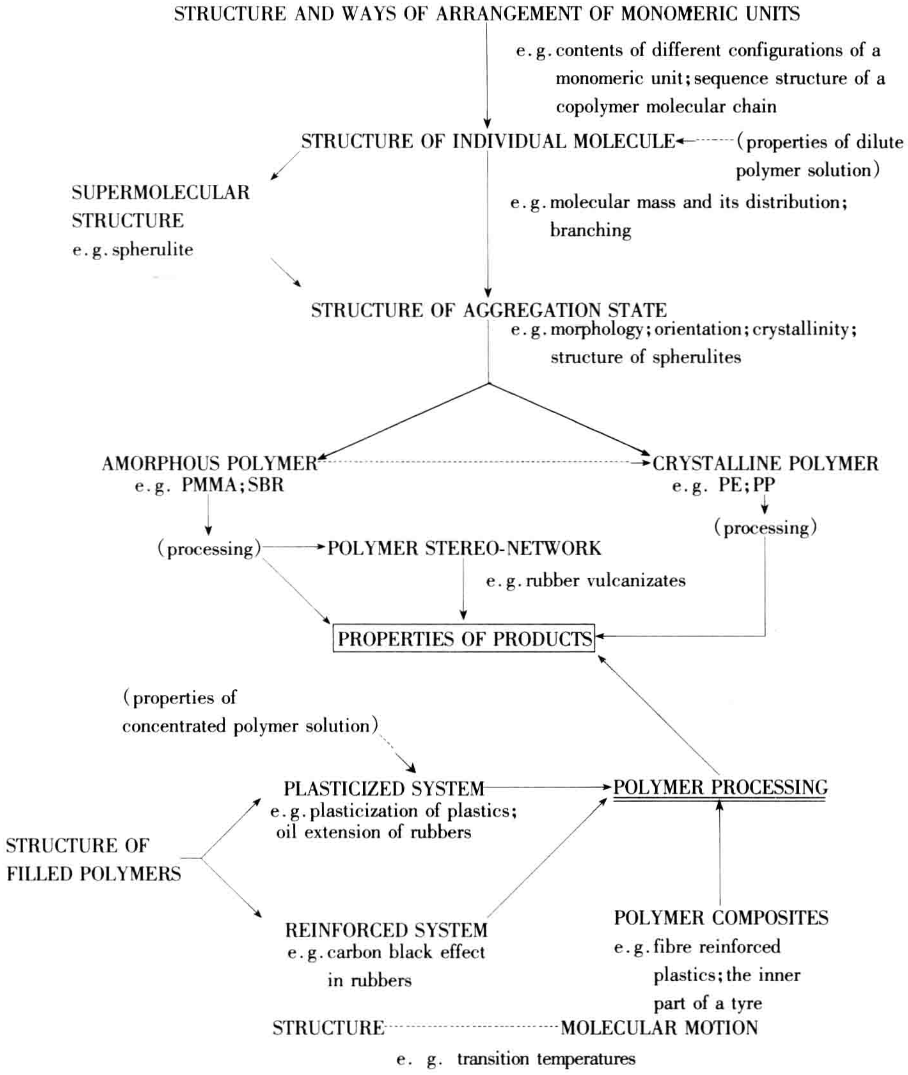


Fig. 1.3 Aspects in the studies of polymer structure, (PMMA, poly(methyl methacrylate); SBR, styrene-butadiene rubber; PE, polyethylene; PP, polypropylene).

The physical properties of polymer bulks have to be interpreted in terms of structures. For example, glass transition temperature and melting point are related to the structure of molecular chains and that of the aggregation state. But in turn, the result of the study of structure needs demonstration and proof from physical properties. The structure of the aggregation state revealed by X-ray diffraction, electron microscopy, etc. should be expounded via physical properties. For example, crystallinity must be associated with melting point. Thus, structure and physical properties are always correlated.

Problems in the production of polymers lie on the studies of structure and physical properties, such as to establish various methods of characterization to monitor the processing behavior of raw materials and the qualities of final products. These studies at the same time, promote the advancement of the theories of polymer science. The relationships are shown in Fig. 1.4.

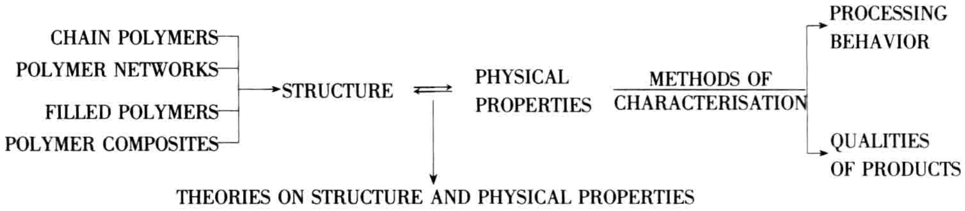


Fig. 1.4 Relationships between structure and physical properties.

Study Problems

I-1 What is meant by transition molecular mass? The transition molecular mass for Nylon-6,6 is much lower than that for polybutadiene, why?

I-2 Give one example to illustrate how the structure of aggregation state is related to the mechanical properties of the polymer.