COMPUTATIONAL MODELING OF POLYMERS

EDITED BY
JOZEF BICERANO

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JOZEF BICERANO
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Preface

The use of computational modeling to study the structures and properties of polymers is reviewed in this book, with particular emphasis on non-crystalline polymers. Both the computational techniques and their applications to specific types of polymers are covered in detail. The book is intended for those interested in understanding the structures and properties of polymers—including workers and students in the fields of polymer science, plastics engineering, materials science, organic chemistry, chemical engineering, theoretical chemistry, and theoretical solid-state physics.

The contributors have attempted to (a) present the similarities and differences among various types of techniques, (b) explore how these techniques can be combined with one another and with experimental results to provide more complete descriptions of the structures and properties of specific materials, (c) bridge the gap between molecular-level calculations and techniques for the prediction of the properties of bulk materials, (d) present critical state-of-the-art reviews of their topics, and (e) indicate what they perceive to be the most promising directions for future research.

Emphasis is placed on the contribution of molecular-level theory to understanding the structures and physical and mechanical properties of *synthetic amorphous polymers* used in or intended for plastics technology.

The following topics have, therefore, either been excluded or are not discussed in great detail: (a) detailed treatment of the effects of semicrystallinity in polymers, (b) the modeling of biological polymers, such as proteins and nucleic acids, (c) the properties of conducting polymers, such as polyacetylene and its derivatives, (d) the computational techniques used only for these three types of polymers or problems, and (e) computer-aided design and manufacture of plastics by the techniques of plastics engineering not involving molecular-level descriptions.

The introductory chapter is an overview that provides a perspective of certain aspects of the field, both as a subfield of polymer science and within its own historical context. Each successive part of the book discusses computational techniques more complex than those covered in the preceding parts. This increasing "complexity" can be due to the increasing sophistication of the formalisms used, or to more computer time being required to solve the equations of the formalisms, or to a combination of these two factors.

Several types of computational techniques are often combined in order to provide schemes that enable the study of complicated polymer structures and properties. The partitioning of the book into five parts should therefore be viewed mainly as a heuristic device, rather than as a reflection of a real division of the techniques into different classes.

In Part One, Chapter 1, the application of group contribution techniques for the correlation of the properties of polymers with their chemical structures is reviewed. The very simple but useful group contribution techniques are based on the empirical observation that the values of certain important properties can be approximated by additive contributions from structural subunits of the polymer.

The use of force-field techniques is covered in Part Two. These techniques are all based on a simple classic mechanical model of molecular structure, in which atoms are treated as point masses connected by springs. Chapter 2 begins with a general introduction to force-field techniques. It then goes on to describe the force-field hamiltonians most commonly used, and to give examples of their use in calculating the conformational stabilities of polymers. In Chapter 3, a detailed example of the use of rotational isomeric state theory for conformational analysis and for calculating configurational properties is presented. The placement of this chapter in Part Two is simply in recognition of the fact that rotational isomeric-state calculations most often start from the results of conformational-energy calculations performed by force-field techniques on model molecules representing polymer-chain segments. The "Strophon" model for deformation of glassy amorphous polymers is presented in Chapter 4. This model is based on a force-field description of intrachain and interchain interactions in polymers. It has been quite successful in spite of its apparent simplicity.

Thermodynamic and statistical mechanical techniques are covered in Part Three. Chapter 5 discusses Monte Carlo and molecular dynamics simulations of amorphous polymers, giving several examples of the applications of such simulations. Free volume, the relationship between free-volume fluctuations and localized molecular rearrangements, and the application of free-volume theory to polymer relaxation in the glassy state, are discussed in Chapter 6. In Chapter 7, an example is given of the utilization of a combination of force-field, free-volume, and statistical mechanical techniques to study the structures of a family of semicrystalline copolymers in relation to a technologically important property, namely the transport of penetrant molecules through plastics. In Chapter 8, an atomistic model is presented for the structure and mechanical properties of polymeric glasses.

In Part Four, Chapter 9 treats the modeling of polymer-surface interactions, which are extremely important in many technological applications. These interactions are most easily modeled using crystalline systems. Much can be learned from the results of calculations such as those reported in Chapter 9, justifying the inclusion of a chapter on crystalline polymers in a book whose main emphasis is on noncrystalline polymers.

The use of quantum mechanical techniques to study noncrystalline polymers is covered in Part Five. It is only in recent years that the increase in speed, available storage space, and reliability, and the decrease in size and price of computers, coupled with the development of powerful new integrated software packages, have enabled these techniques to begin making significant contributions to understanding the structures and properties of polymers. Although this field is still in its infancy, it holds great promise for the future. Chapter 10 provides a general introduction to quantum mechanical techniques, including brief discussions of some of the specific quantum mechanical techniques useful for studying noncrystalline polymers. Some of the specific applications of quantum mechanical techniques to the study of noncrystalline polymers are presented in Chapters 11 to 13.

I thank the authors whose contributions made this book possible, and the management of The Dow Chemical Company for allowing me to edit this book.

Jozef Bicerano

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Contents

Multiple Transitions and Relaxation in Synthetic Organic Amorphous Polymers and Copolymers: An Overview

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The general subject matter of this review began appearing in the world literature—England, Europe, the Soviet Union, Japan, and the United States—with increasing frequency for at least 25 years prior to the beginning of our following account. Dielectric and dynamic mechanical loss, ultrasonic attenuation, and, more recently, NMR, became familiar topics. Suddenly there was an apparent uncoordinated implosion of widely scattered publications into a proliferation of highly coordinated reviews, starting in 1963. Their specific subject matter and sequence appears in the introduction.

Our single directive from the editor was to be concerned with amorphous polymers. This has been interpreted broadly as covering amorphous polymers and copolymers, the amorphous phase of semicrystalline polymers, and the amorphous material above T_m in crystalline polymers. Thus, crystalline melting points per se, the kinetics of crystallization and melting, and crystal morphology have been avoided, and yet the ratio of T_g/T_m, is included. The existence of local structure in amorphous polymers is reviewed in some detail. We differ with conventional opinion and cite diverse evidence supporting the presence of local structure in amorphous polymers.

We consider three amorphous phase events, T_g, T_{ll} at $1.2T_g$, and T_u at $1.2T_m$, as indicative of local structure in amorphous polymers.

Considerable attention focuses on the three common $T < T_g$ transitions, T_β, T_γ, T_δ; T_g itself; and the four liquid state transitions: T_{ll}, $T_{l\rho}$, and $T_{l\phi} > T_g$; and $T_u > T_m$: their positions along the temperature scale; their relative intensities; apparent activation energies; and, still largely speculative, their molecular origins. A possible general phenomenon, designated the *triumvirate* concerns T_β at $0.75T_g$; T_g as a dominant amorphous phase event; and T_{ll} at $1.2T_g$, with T_β and T_{ll} being weak satellites of T_g. Double glass temperatures in semicrystalline polymers, block copolymers, and incompatible polyblends are not covered.

The use of relaxation maps, log frequency in hertz versus T^{-1}, are considered for representing the frequency dependence of each of the several common multiple transitions as used by McCrumm et al. and by McCall. The use of apparent activation energies, ΔH_a, in kcal/mole or kJ/mole for the same purpose, is also used but questioned by some.

We finally list some typical group motions which are common to several polymers. Also given are some common empirical equations that have emerged in connection with polymer transitions. We are possibly derelict in not distinguishing between transitions such as melting, and relaxations such as T_g. Once T_g was dignified with the title of a transition when, in fact, it exhibited rate effects like a relaxation, we settled for transitions until nomenclature experts decided otherwise.

INTRODUCTION: HISTORY: THE 1963–1967 IMPLOSION

Two unrelated reviews on the named subject matter appeared in 1963. The one by Saito et al. [1], "Molecular Motion in Solid State Polymers," covered amorphous and semicrystalline polymers. The four authors were active in various aspects of the related subject matter and familiar with relevant world literature. Saito, for example, played a key role in developing a theory for local mode motion in the glassy state below T_g.

The author of the second paper [2], "The Relation of Transition Temperatures to Chemical Structure in High Polymers," was, by contrast, an amateur except with regard to glass-transition phenomena [3], which subject bridged a path for him into this new field. Still a third manuscript by Allen [4] was essentially ready for publication but was withdrawn after Ref. 2 appeared in print.

Our own interest arose as a result of a main lecture at the 1960 Gordon Conference on Polymers by the late polymer physicist, Dr. Karl Wolf, then from BASF in Ludwigshafen, Germany. He first discussed the torsion pendulum developed by Schmieder and himself [5a] and then reviewed extensive measurements on a wide variety of elastomers, amorphous polymers, copolymers, and crystalline polymers [5b]. As numerous "spectra" showing tan δ or $\lambda = \pi \tan \delta$, and shear modulus G, flashed on the screen in rapid succession, our familiarity with T_g for most of these polymers allowed us to concentrate on T_g as the dominant amorphous phase transition and thence to compare the location and intensity of secondary transitions in the glassy state with the T_g loss peak.

The following morning we awoke with a clear conception that if different "spectra" were superimposed, with T_g's overlapping, the spectra became remarkably similar, differing only in fine details. Dr. Wolf lectured the following week at the Dow Chemical Company in Midland, MI [6]. This gave us a second opportunity to review his extensive presentation of torsion pendulum data. This reinforced the earlier conclusion.

Subsequent to the July 1960 Gordon Conference, we began an in-depth review of all pertinent subject matter:

1. Dynamic mechanical loss, both torsion pendulum and other techniques
2. Dielectric and NMR data
3. Ultrasonic loss
4. Volume-temperature and specific heat–temperature

This was supplemented by discussions with scientists active in the field, primarily American and British polymer scientists. The practice of plotting loss data on a relative temperature scale was pursued. A provisional 100-page typed report was circulated to peer groups for comments and became the basis for an IUPAC lecture [7], which was the precursor to Ref. 2.

The T/T_g plotting technique quickly led to the recognition that there was evidence for a loss process lying above T_g and hence in the liquid state [2]. This new event was considered to represent a transition between two liquid states, liquid$_1$ ↔ liquid$_2$, both of unknown nature. We designated this transition event as T_{ll}, with evidence for it from thermal expansion, torsion pendulum, penetrometry, x-ray diffraction, and NMR data [2]. The transition $T_\beta < T_g$ was widely believed to represent a local motion of 1 to 2 monomers, and T_g the micro-Brownian motion of 10–20 monomers. It was natural to postulate that T_{ll} involved the motion of the entire polymer chain in an unspecified manner.

The T_{ll} concept was to encounter resistance on several grounds:

1. T_{ll} was a new concept not hitherto noted by peer groups.
2. T_{ll} was very weak, generally 5–20% of the strength of T_g, as we were to discover much later. Its detection was therefore prone to artifacts inherent in the several test methods used to show T_{ll}.
3. We overlooked some of the best evidence for it, widely dispersed in the literature.