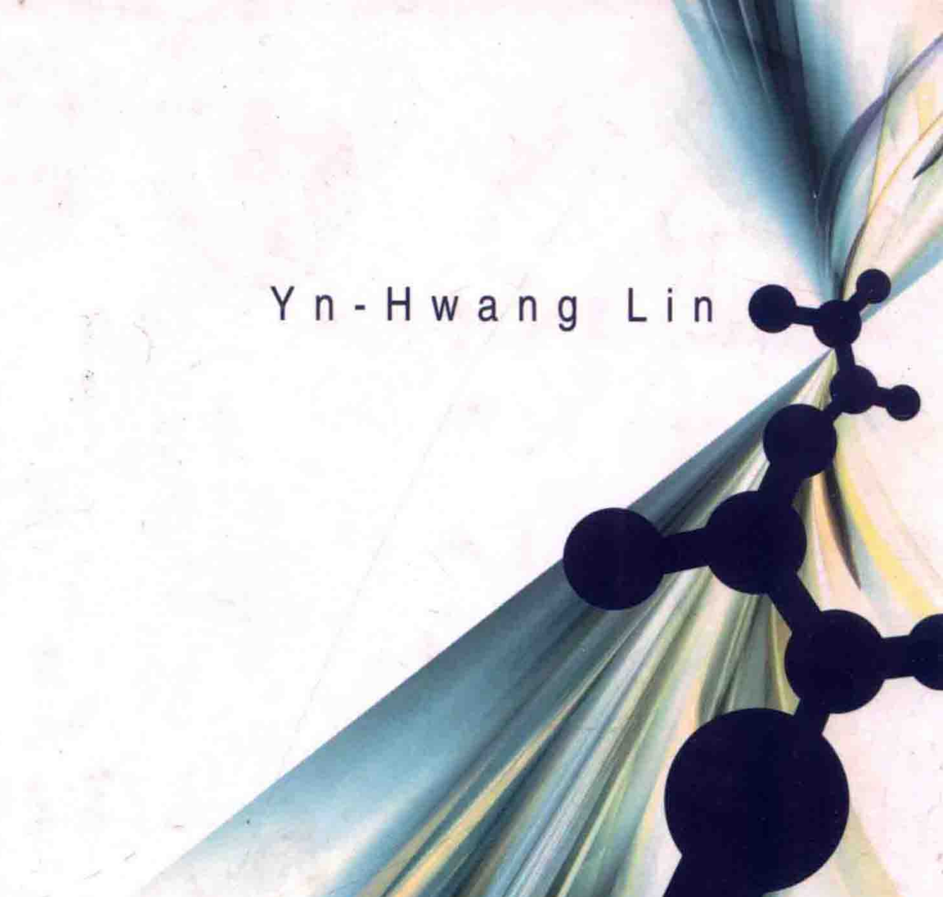
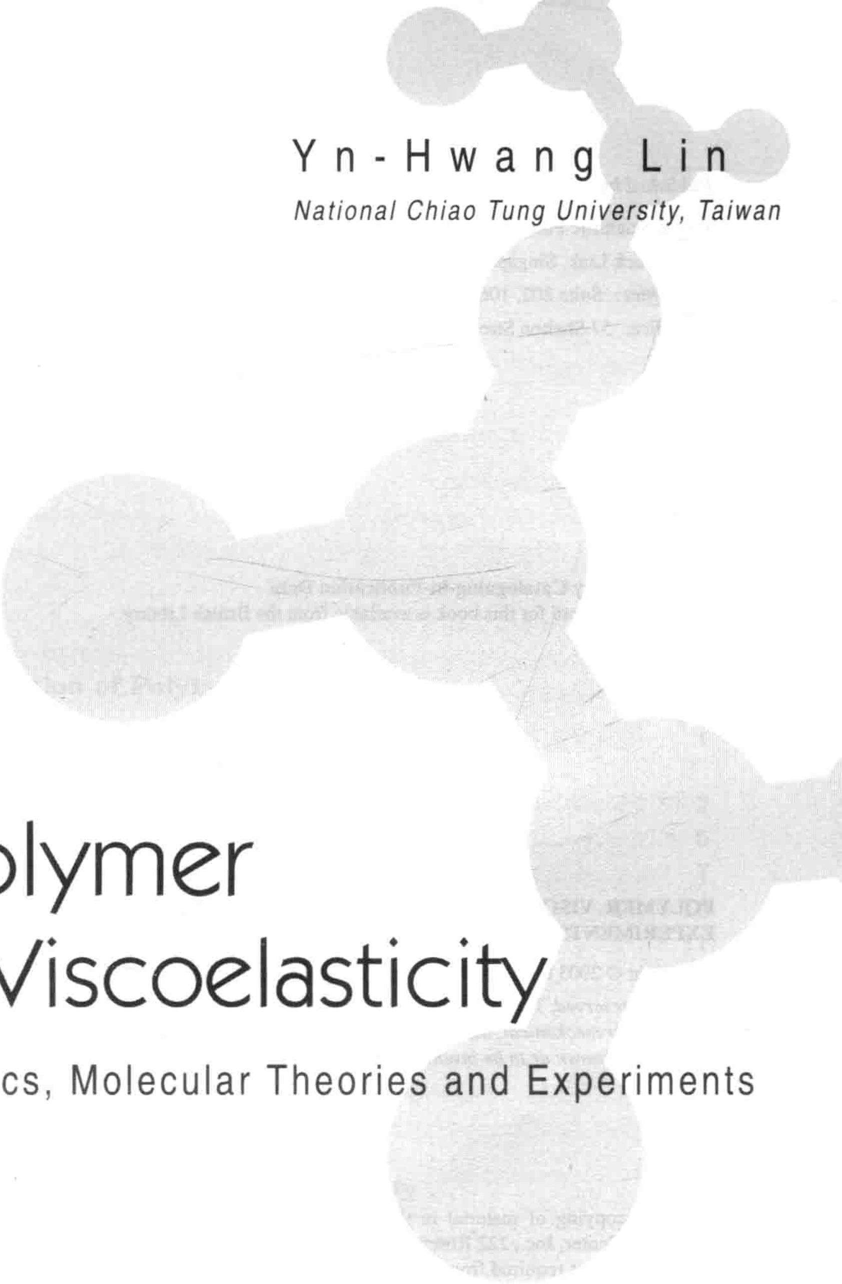
Yn-Hwang Lin



Polymer Viscoelasticity

Basics, Molecular Theories and Experiments



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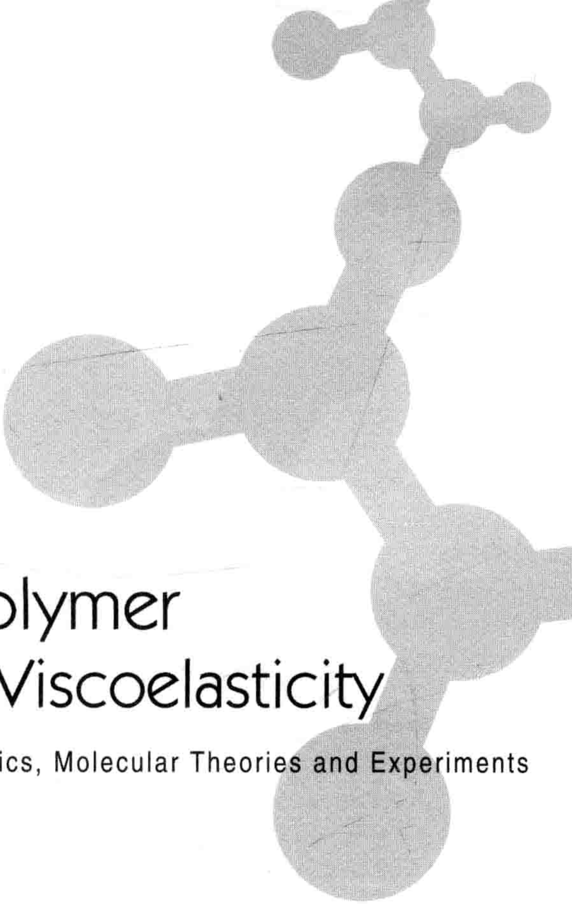

Polymer Viscoelasticity

Basics, Molecular Theories and Experiments

Preface

I became involved in the research of polymer viscoelasticity shortly after I began to work in the Exxon Chemical Company in 1980, two years after the landmark papers of Doi and Edwards were published. Even though there was a great deal of hope and excitement among polymer researchers regarding the Doi–Edwards theory, at the time I did not foresee that I would come to accept the theory so completely, as eventually the supporting evidence, a great deal of my own research over the years, convinced me. This book is an account of how the universal viscoelastic phenomena of nearly monodisperse polymers are explained quantitatively by the Doi–Edwards (reptation) theory and the extended reptation theory, developed on the framework of the Doi–Edwards theory. These include the transformation of the characteristic viscoelastic spectrum with molecular-weight change and/or dilution; the molecular-weight dependence of the zero-shear viscosity and of the steady-state compliance, and their respective transition points, M_c and M_c'; the relation between viscoelasticity and diffusion; the damping function; and the slip-stick melt fracture phenomenon. The consistently quantitative agreements between theory and experiment led to the proposition that the number of entanglement strands per cubed tube diameter (or cubed entanglement distance) be a universal constant, which is now well supported by a large collection of data (Chapter 13). The ultimate significance of these results is that the basic mean-field assumption in the Doi–Edwards theory: $aL = \langle R^2 \rangle$ (a, the tube diameter; L, the primitive chain length; $\langle R^2 \rangle$, mean square end-to-end distance of the polymer chain) is valid for a (nearly) monodisperse system. Here the mean field is assumed rather than derived. The proposition of the characteristic length "a" for an entanglement system is as important as the conceiving of the Rouse segment twenty five years earlier. From the study of blend-solution systems, it is shown in Chapter 11 that the extended reptation theory has bridged the gap between the Doi–Edwards theory and the Rouse theory. As shown in the same chapter, the tube dilation effect, which is found occurring in the long-time region of a binary-blend's relaxation, indicates that the mean-field length $a = \langle R^2 \rangle / L$ has a dynamic aspect. It is hoped that the readers will recognize the far-reaching insight of Doi and Edwards' assumption $aL = \langle R^2 \rangle$ in this book.

The first part of this book explains the basics of polymer conformation, rubber elasticity, viscoelasticity, and chain dynamics (Chapters 1–5). Knowledge of these basics is not only generally useful but is quite essential in understanding the molecular theories studied after Chapter 6. This book starts from a very fundamental level. Each chapter is built upon the contents of the previous chapters. The elastic-dumbbell model is introduced in Chapter 6 as a prerequisite for the Rouse model, studied in Chapter 7. Although the final theme of this book is about entanglement (Chapters 8–13), there are several essential reasons to include the Rouse model: Firstly, the Rouse theory is the foundation for modern theories of polymer dynamics and viscoelasticity. Without it this book would be quite incomplete. Secondly, in spite of its original intention for a dilute polymer solution, the Rouse theory has been generally accepted as valid for describing the viscoelastic behavior of an entanglement-free polymer melt system. A further in-depth experimental study supporting the validity of the Rouse theory is presented in Chapter 11. It is desirable to compare the Rouse theory with the Doi–Edwards theory and the extended reptation theory so that both the entanglement-free and entanglement regions can be studied in perspective. It is shown in Chapter 11 that the onset molecular weight of entanglement is equivalent to the entanglement molecular weight M_e determined from the plateau modulus ($G_N = 4\rho RT/5M_e$). Thirdly, the extended reptation theory is developed by incorporating the Rouse motions in the Doi–Edwards theory. Thus, for discussing this topic, it is quite essential to know the basic elements of the Rouse model.

This book includes a broad range of studies of polymer viscoelastic properties: basics, molecular theories, and experiments. It also covers both the entanglement and entanglement-free regions. Moving from one region to the other is made by either molecular-weight change or concentration change. The linear viscoelastic behavior is studied in Chapters 8–11; the nonlinear behavior is studied in Chapter 12. And a newly discovered law is discussed in Chapter 13. On the other hand, this book is limited mainly to the studies of polystyrene; viscoelastic-spectrum results of nearly monodisperse polystyrene samples and their blends predominantly used in part of this book (Chapters 10–12) have been obtained and published by myself. Polystyrene is the most accessible system for study. In view of the universality existing among the flexible polymers as evidenced in several important cases, the ideas and theories presented in this book, which have been consistently and quantitatively tested by the experimental results of polystyrene, should be applicable to other kinds of polymers. To my knowledge, besides those studies of viscoelastic spectra reported by myself, there are few other studies of such a quantitative nature. It may strike the reader that the new theories and experimental spectrum results come mainly from my own work; this is due to the pioneering aspect of this field, to which I have devoted years of research, as well as the relative scarcity of parallel in-depth studies. Nevertheless, the agreement between theory and experiment has been further supported by experimental data obtained by Plazek and O'Rourke, Kramer *et al.*, Lodge *et al.*, Watanabe *et al.* and others at various key points.

In terms of the theories based on the tube assumption ($aL = \langle R^2 \rangle$), quantitative study is only possible for nearly monodisperse systems, due to the complexity caused by the tube dilation effect, which occurs in the system of broad molecular-weight distribution. As a result, the theories presented in the book may be limited from being directly applied to commercial polymers, whose molecular-weight distribution is broad in general. However, the theories and analyses presented in this book should be useful and valuable in many aspects of polymer research and development work. A unique problem in industry is the slip-stick melt fracture phenomenon that occurs in extrusion. The basic dynamic processes related to the phenomenon are discussed in Chapter 12. Because of the limited space of this book, the reader is referred to the original work for an explanation of the phenomenon in terms of the molecular dynamic processes. Since the viscoelastic properties of nearly monodisperse polymers can be analyzed quantitatively in terms of the molecular theories, dynamic mechanical measurement can be used very effectively to study the chain motions that correspond to various length-scales above the Rouse-segment size. Thus, very rich dynamic information can be obtained from the viscoelastic spectra for comparing studies with other spectroscopies, such as NMR, dielectric relaxation, dynamic light scattering, and neutron spin-echo spectroscopy, etc. Such interplay among different probing techniques should greatly enhance the studies and applications of chain dynamics.

Last but not least, I should mention that important concepts from early studies of polymer viscoelasticity have not been used and described according to their historical developments. Here, I should like to refer to the review by J. D. Ferry,[a] which covers the key research works in the period from 1930 to 1970.

Y.-H. Lin
July 2002

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[a] Ferry, J. D., *Macromolecules* **24**, 5237 (1991).

Contents

Chapter 1

Conformation of Polymer Chains

1.1 Introduction

A polymer is formed by connecting many small molecules. For example, with the help of the catalyst, ethylene $CH_2{=}CH_2$ molecules can form long strings of polyethylene molecules $-CH_2-CH_2-CH_2 \cdots CH_2-$. We refer to $CH_2{=}CH_2$ as the monomer, a structural unit CH_2- in the polymer chain as the chemical segment, and CH_2-CH_2- as the monomeric segment. A large number of different kinds of flexible polymers can be formed from different monomers. The chemical structure of the monomeric segment is generally referred to as the microstructure of the polymer. If all the monomers are the same, the formed polymer is called a homopolymer, such as polystyrene, poly(α-methyl styrene), etc. If more than two kinds of monomers are used, the formed polymer can be a random copolymer or a block copolymer. If a linking agent with multiple arms is added to the monomer in polymerization, a polymer with a "star shape" can be formed. The kind of polymer materials whose viscoelastic properties will be the main subject of study in this book are the linear flexible polymers, including homopolymers and random copolymers. As required for making quantitative comparisons with theories, the samples chosen for study are exclusively well-characterized nearly monodisperse polymers ($M_w/M_n < 1.1$), obtained mainly from anionic polymerization. When the word "polymer" is used in this book, it means this kind of polymer if no further specification is made. Although some of the derived conclusions and concepts from the study can be applied to star polymers and block copolymers, no discussion of them will be made in this book.

In a melt or solution, a polymer chain can take up an enormous number of configurations, as each chemical segment has the probability of pointing in many different directions. In addition, because of the thermal fluctuation effect, the chain configuration is changing continuously. Thus, to describe the physical properties of the polymer chain, we can only consider the probability distribution function for the configuration and calculate the average value. The static properties of the polymer are studied if it is in the equilibrium state. The changing behavior of chain configuration with time is generally referred to as polymer chain dynamics. A large portion of this book is devoted to the study of chain dynamics and how the polymer viscoelastic properties are affected by them. In the first chapter, we shall study the polymer chain conformation in the equilibrium state. The basic theoretical assumptions used to treat the problem also play a fundamental role in the theories developed for describing various static and dynamic properties of the polymers. In this chapter, we will study two chain models: the freely jointed chain model and the Gaussian chain model. The importance of the latter model will become particularly apparent in the later chapters. In these models, the microstructural details are ignored. It is also understood that when a model chain of these two types is compared with a real chain, the length of each segment of the model is much longer than the microstructural length-scale. These chain models are applicable mainly when the polymer chain is long, i.e. the molecular weight of the polymer is large. The physical properties that can be described by the models (such as low-frequency viscoelasticity of a polymer and the scattering structure factor in the small scattering vector region) exhibit universal behavior. That is, different kinds of polymers have the same kind of physical properties regardless of their different microstructure. Theoretically, this is a consequence of the central limit theorem.[1,2] The freely jointed chain model and the Gaussian chain model have simplified the problem greatly and have allowed us to grasp the essential and universal aspects of the physical properties. Before studying these models in this chapter, we shall review several basic theories in statistics, which are not only needed here but also in studying the chain dynamic behavior in the later chapters.

1.2 Probability Distribution Functions, Moments and Characteristic Functions

Consider a stochastic variable X. If X has a countable set of realizations, $\{x_i\}$, where $i = 1, 2, \ldots, n$ (n is either a finite integer or $n = \infty$), a probability distribution function $P_X(x)$ can be defined as

$$P_X(x) = \sum_{i=1}^{n} p_i \delta(x - x_i) \tag{1.1}$$

where $\delta(x - x_i)$ is the Dirac delta function (see Appendix 1.A); and p_i is the probability for finding the variable X at x_i, which must satisfy the conditions $p_i \geq 0$ and $\Sigma_{i=1}^{n} p_i = 1$. If X can take on a continuous set of values, such as an interval on the real axis, we assume that there exists a piecewise continuous function, $P_X(x)$, such that the probability that X has a value in the interval $\{a \leq x \leq b\}$ is given by

$$\text{Prob}(a \leq x \leq b) = \int_a^b dx\, P_X(x). \tag{1.2}$$

Then $P_X(x)$ is the probability distribution for the stochastic variable, and $P_X(x)\, dx$ is the probability of finding the stochastic variable in the interval $x \to x + dx$. The probability distribution must satisfy the condition $P_X(x) \geq 0$ and $\int_{-\infty}^{\infty} P_X(x)\, dx = 1$.

Often we wish to find the probability distribution for another stochastic variable, $Y = H(X)$, where $H(X)$ is a known function of X. The probability distribution, $P_Y(y)$, for the stochastic variable Y, is given by

$$P_Y(y) = \int_{-\infty}^{\infty} dx\, \delta(y - H(x)) P_X(x). \tag{1.3}$$

If we can determine the probability distribution function $P_X(x)$ for the stochastic variable X, then we have all the information needed to characterize it. This sometimes cannot be obtained. However, in that case, we can often obtain the moments of X. The nth moment of X is defined by

$$\langle x^n \rangle = \int_{-\infty}^{\infty} dx\, x^n P_X(x). \tag{1.4}$$

The moment, $\langle x \rangle$, is also called the mean value of X; the combination, $\langle x^2 \rangle - \langle x \rangle^2$, is referred to as the variance of X; and the standard deviation of X, σ_X, is defined by

$$\sigma_X \equiv (\langle x^2 \rangle - \langle x \rangle^2)^{1/2}. \tag{1.5}$$

The moments give us information about the spread and shape of the probability distribution $P_X(x)$. The most important moments are the lower-order ones since they contain the information about the overall shape of the probability distribution.

The characteristic function $f_X(k)$, corresponding to the stochastic variable X, is defined by

$$f_X(k) = \langle \exp(ikx) \rangle = \int_{-\infty}^{\infty} dx \exp(ikx) P_X(x)$$
$$= \sum_{n=0}^{\infty} (ik)^n \frac{\langle x^n \rangle}{n!}. \tag{1.6}$$

The series expansion in the equation above is meaningful only if the higher moments, $\langle x^n \rangle$, are small so that the series converges. From the series expansion, we see that it requires all the moments to completely determine the probability distribution, $P_X(x)$. The characteristic function is a continuous function of k and has the properties that $f_X(0) = 1$, $|f_X(k)| \leq 1$, and $f_X(-k) = f_X^*(k)$ ($*$ denote complex conjugation). The product of two characteristic function is always a characteristic function. If the characteristic function is known, the probability distribution, $P_X(x)$, is given by the inverse Fourier transform

$$P_X(x) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dk \exp(-ikx) f_X(k). \tag{1.7}$$

Furthermore, if we know the characteristic function, we can obtain moments by differentiating:

$$\langle x^n \rangle = \lim_{k \to 0} (-i)^n \left[\frac{d^n}{dk^n} f_X(k) \right] \tag{1.8}$$

The probability distribution function can be generalized for more than one stochastic variable. For simplicity, let us consider two stochastic variables, X and Y. The joint probability of finding X and Y in the interval $x \to x + dx$ and $y \to y + dy$, respectively, is denoted as $P_{X,Y}(x, y)\, dx\, dy$, which must satisfy the condition $P_{X,Y}(x, y) \geq 0$ and

$$\int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy\, P_{X,Y}(x, y) = 1. \tag{1.9}$$

The reduced probability distribution $P_X(x)$ for the stochastic variable X is defined by

$$P_X(x) = \int_{-\infty}^{\infty} dy\, P_{X,Y}(x, y). \tag{1.10}$$

The reduced probability distribution, $P_Y(y)$, is obtained in a similar manner.

If $Z = G(X, Y)$, where $G(X, Y)$ is a known function of X and Y, the probability distribution $P_Z(z)$ for the stochastic variable Z is given as

$$P_Z(z) = \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy\, \delta(z - G(x, y)) P_{X,Y}(x, y). \tag{1.11}$$

Corresponding to the equation above, the characteristic function for the stochastic variable Z is then

$$\begin{aligned} f_Z(k) &= \int_{-\infty}^{\infty} dz \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy \exp(izk)\delta(z - G(x, y)) P_{X,Y}(x, y) \\ &= \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy \exp(ikG(x, y)) P_{X,Y}(x, y). \end{aligned} \tag{1.12}$$

If X and Y are two independent stochastic variables, then

$$P_{X,Y}(x, y) = P_X(x) P_Y(y). \tag{1.13}$$

1.3 A Central Limit Theorem[1,2]

Let us consider a stochastic variable, Y_N, which is the deviation from the average of the arithmetic mean of N statistically *independent* measurements of a stochastic variable, X. Y_N may be written as

$$Y_N = \frac{(X_1 + X_2 + \cdots + X_N)}{N} - \langle x \rangle = Z_1 + Z_2 + \cdots + Z_N \tag{1.14}$$

where

$$Z_i = \frac{(X_i - \langle x \rangle)}{N}. \tag{1.15}$$

We want to obtain the probability distribution function of Y_N, $P_{Y,N}(y)$. First, the characteristic function, $f_Z(k; N)$, for the stochastic variable, $Z_{i,N}$, can be written as

$$\begin{aligned} f_Z(k; N) &= \int_{-\infty}^{\infty} dz \int_{-\infty}^{\infty} dx \exp(ikz)\delta\left(z - \frac{(x - \langle x \rangle)}{N}\right) P_X(x) \\ &= \int_{-\infty}^{\infty} dx \exp\left(ik\frac{(x - \langle x \rangle)}{N}\right) P_X(x) \\ &= 1 - \frac{k^2 \sigma_X^2}{2N^2} + \cdots \end{aligned} \tag{1.16}$$