行政院國家科學委員會專題研究計畫 成果報告

高分子運動及黏彈性：電腦模擬,理論及實驗之互補互成 (第 3 年)
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行政院國家科學委員會補助專題研究計畫成果報告

高分子運動及黏彈性：電腦模擬,理論及實驗之互補互成

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Progress Report (2008 – 2010)
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Polymer Dynamics and Viscoelasticity: Interplay of Computer Simulations, Theories and Experiments

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My research in recent years had developed or discovered new concepts and effects in polymer viscoelasticity as summarized in the following:

(1) Demonstrate the interplays between theories, experiments and simulations in polymer viscoelasticity.

(2) Simulations on Fraenkel chains provide a theoretical basis resolving the paradox that the experimentally determined sizes of the Rouse and Kuhn segments are nearly the same.

(3) Concurrently, the simulations give a natural explanation for the coexistence of the energy-driven and entropy-driven modes in the relaxation modulus.

(4) The simulations also show that the stress-optical rule need not be based on the Gaussian chain model as done traditionally.

(5) Show the universality of the glass transition-related thermorheological complexity in the polystyrene system, entangled or not.

(6) Show that the thermorheological complexity in polystyrene and the breakdown of Stokes – Einstein relation in OTP share the same basic mechanism.

Although these results have all been published (see publications uploaded to NSC), their fundamental bases as well as importance are not yet widely understood and appreciated. Realizing this and anticipating my retirement—I retired from National Chiao Tung University at the end of January, 2010—I had focused on presenting these results in a systematic way and integrating them into my book on polymer viscoelasticity (published in 2003). On the eve of my retirement, the second edition of the book was completed. With a slightly changed title: "Polymer Viscoelasticity: Basics, Molecular Theories, Experiments and Simulations," the second edition is expected to be published in the near future. Here, I reproduce the "Preface to the Second Edition," which is also contained in the galley proof PDF file "Contents of the Second Edition of the Book: Polymer Viscoelasticity" uploaded to NSC. Basically the preface and the table of contents together have given an overview of the key aspects of my recent contributions to the field of polymer viscoelasticity. The details as presented in the book will be made available if requested.

The second edition has five additional chapters (Chapters 14–18), which further explore and extend the scope of the subjects that are covered in the first edition. These additional chapters incorporate new concepts and effects that have been developed or discovered in recent years, thanks to a large extent to the theories and experiments studied in the first edition. To more closely integrate the new and existing materials, modifications, insertions and additions have been made to the first thirteen chapters at appropriate places.

There are two main themes in the newly added portion, which are complementary to each other: The first (Chapters 14 and 15) are the studies of viscoelastic response functions over the full dynamic range. The quantitative line-shape analyses of viscoelastic responses of polystyrene melts over the entropic region (modulus values below $\sim 4\times10^7\,\mathrm{dyne/cm^2}$) covered in the first edition are extended to the energetic region (modulus values between $\sim 4\times10^7$ and $\sim 10^{10}\,\mathrm{dyne/cm^2}$). The full-range analyses are carried out using the consistently successful description of the entropic region by the extended reptation theory (ERT; for entangled systems) or the Rouse theory (for entanglement-free systems)—extensively illustrated in Chapters 10 and 11—as the frame of reference. The scheme allows the temperature dependence of dynamics in the energetic region being stronger than that in the entropic region of polystyrene samples to be analyzed consistently and systematically revealing universal aspects of the glass transition-related thermorheological complexity. The time and length scales of the glassy-relaxation process and the basic mechanism for the thermorheological complexity are evaluated or analyzed in terms of the molecular pictures as embodied in the ERT (Chapter 9) and the Rouse theory (Chapter 7). The second theme is the use of the Langevin equation-based Monte Carlo simulations to study fundamental issues at the "Rouse"-segmental level. Firstly the simulation method is introduced and illustrated by applying it to the Rouse chain case (Chapter 16), where quantitative comparisons with the theoretical results (Chapters 3 and 7) can be made. The simulations of Fraenkel chains reveal previously unknown mechanisms—unlike the traditional explanations based on the Gaussian chain—for the occurrence of the entropic Rouse process and the holding of the (rubbery) stress optical rule (Chapters 17 and 18). Concurrently, the Fraenkel chain model provides a theoretical basis for resolving the paradox that the experimentally determined sizes of the Rouse and Kuhn segments are nearly the same and gives a natural explanation for the coexistence of the energy-driven and entropy-driven modes.

I am grateful to Professors M. D. Ediger and T. Inoue for providing their data in digital form. The data from Professor Ediger are used in Fig. 15.1. The data from Professor Inoue allow the analyses of viscoelastic spectra to be a smooth process, as presented in Chapter 14.

I am thankful to my wife Ling-Hwa for her patience and support through my research career as well as the writing of this book.