行政院國家科學委員會專題研究計畫成果報告

高分子動力學
Study of Polymer Dynamics

計畫編號：NSC 88-2113-M-009-004
執行期限：87 年 8 月 1 日至 89 年 3 月 31 日
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一、中文摘要

我們從事高分子動力學三方面的研究(1) 用光子相關譜觀測; (2) 和黏彈性之關係; 及(3) 鏈節運動的蒙地卡羅模擬。

關鍵詞：高分子鏈運動,光子相關譜,黏彈性,糾纏,勞斯節,蒙地卡羅模擬.

Abstract

Polymer chain dynamics have been studied in three aspects: (1) probing by the photon-correlation spectroscopy; (2) the relation with the viscoelastic properties; and (3) the Monte-Carlo simulation of chain motions.

Keywords: Polymer chain dynamics, photon-correlation spectroscopy, viscoelasticity, entanglement, Rouse segment, Monte-Carlo simulation.

二、緣由與目的

While involving quite a few fundamental aspects of physical science, the study of polymer dynamics is very unique because of the chain structure of the polymer molecule, and thus academically is an important research field. On the other hand it is related to a wide scope of applications of the polymer, such as viscoelastic properties, diffusion, glass/rubber transition, toughness of polymer blends and lubrication effect of polymers. In fact almost all polymer properties are related in various degrees to polymer dynamics. It has been our long-term research interest to combine theory and experiment to advance our understanding of polymer dynamics at the molecular level. Recently, we added to it the Monte-Carlo simulation. Based on our long-term research, we have recognized the central roles of two basic structural size scales in the universal behavior of polymer chain dynamics and viscoelasticity: that of the Rouse segment and that of an entanglement stand.

In our study of the polymer dynamics using the depolarized photon-correlation spectroscopy, a theoretical model was first developed showing that the observed dynamics is basically the reorientation motion associated with a Rouse segment. [1] Based on it, the experiment has been designed and carried out.[2, 3] Because the Langevin equation does not yield an analytic solution for the dynamic quantity associated with a single Rouse segment observed by the depolarized photon-correlation spectroscopy, the Monte-Carlo simulation is employed. The Monte-Carlo simulation has been first tested for the cases, where a comparison with the analytical solution is possible. Very good agreement between the measured depolarized photon-correlation functions and the simulation curves has been obtained. [4] The study has much advanced our understanding of the polymer chain dynamics at the Rouse segment level; at the same time it serves as a very good example demonstrating the interplay among theory, experiment and computer simulation in advancing scientific research.

From the analyses of the polymer viscoelasticity and diffusion data in terms of the extended reptation model,[5-8] it has been expected that the onset of entanglement occurs at M_e (=4ρRT/5G_N) rather at M_c as believed traditionally. This is confirmed by the study of a specially designed polymer blend solution system.[9] The viscoelastic spectra of the blend solutions from the entanglement-free region to the entanglement region have been analyzed in terms of the Rouse theory. The onset of entanglement M_e^o is determined from monitoring the beginning point of deviation from the theory. This analysis in terms of the Rouse theory, while confirming the expectation based on the extended reptation theory, is totally independent of the reptation model. The agreement of M_e and M_e^o is very significant in understanding the basic nature of chain entanglement.

三、研究報告應含的內容

(1) Chain Dynamics in Concentrated Polystyrene Solutions Studied by Depolarized Photon-Correlation and Viscosity Measurements (Ref. 3). Concentrated solutions of nearly monodisperse polystyrene samples in cyclohexane in the theta condition and in the entanglement-free region have been studied by means of the depolarized photon-correlation spectroscopy and viscosity measurements. It is shown that the viscoelastic behavior of the studied systems is described by the Rouse theory and that in agreement with the theoretical analysis the main polymer dynamic process probed by the depolarized Rayleigh scattering is basically the reorientation motion associated with a Rouse segment of the polymer chain, whose relaxation is independent of the scattering angle and the molecular weight. In addition to the main dynamic process, the tail region of a very fast process associated with the sub-Rouse-segmental motions can be observed, whose existence is expected from the theoretical analysis.

(2) Monte Carlo Simulations of the Motions Associated with a Single Rouse Segment (Ref. 4). The validity of the Monte Carlo simulation for studying the dynamics of a Rouse chain with a finite number of beads, N, is established by showing the close agreement between the simulation results and the analytical solutions for the time-correlation function of the end-to-end vector. Then, the Monte Carlo simulation is used to calculate the dynamic functions associated with the bond vector $\mathbf{b}(t)$ or direction $\mathbf{u}(t)=\mathbf{b}(t)/|\mathbf{b}(t)|$ of an elastic dumbbell and a Rouse segment in a chain. The effect of chain connectivity on the motions of a single Rouse segment is studied. In particular, it is shown that the dynamic function $<P_2[\mathbf{u}(0)\cdot\mathbf{u}(t)]>^2$ over a wide dynamic range, which is the main region probed by the depolarized photon-correlation spectroscopy, is basically independent of the values of $N \geqq 8$ in agreement with the experimental results. Furthermore, the line shape of the depolarized photon-correlation functions of the concentrated solutions (~60wt%) of polystyrene in cyclohexane at the theta point can be fully accounted for by including the effect of chain connectivity regardless of the crudeness of the Rouse segment relative to the chemical structure. From the study, the molecular weight for a Rouse segment of polystyrene in the concentrated solutions is estimated to be 1100, which is slightly larger than the values m=780~900 obtained for polystyrene in the melt state by other methods.

(3) Onset of Entanglement (Ref. 9). The onset of entanglement was determined from studying the viscoelastic spectra of the blends consisting of two nearly monodisperse polystyrene polymers: component one having a molecular weight slightly less than the entanglement molecular weight $M_e(=4\rho RT/5G_N)$, whereas that of component two being greater than M_e (such a blend is referred to as the blend solution). It is shown that because of the absence of the hydrodynamic interaction the viscoelastic spectrum of the blend solution can be described by applying the Rouse theory to both components in the entanglement-free region. As entanglements among the chains of component two occur, when its weight fraction, W_2, increases above a critical point, the viscoelastic response of component one remains described by the Rouse theory. With the Rouse viscoelastic response of component one as the internal reference, the onset of chain entanglement among the chains of component two can be determined by monitoring the deviation of the viscoelastic response of component two from being described by the Rouse theory as a function of W_2. According to the study, entanglement starts to occur in the close neighborhood of M_e' (the entanglement molecular weight of the blend solution and $M_e' = M_eW_2^{-1}$) for the polymer blend solution or equivalently M_e for the monodisperse polymer melt well below M_C' or M_C ($M_C'=M_CW_2^{-1}$, where M_C is the critical molecular weight of the zero shear viscosity of the polymer melt). The traditional idea of regarding the Rouse theory as being applicable below M_C' or M_C is thus incorrect.

四、結語

From our long-term research on the universality in polymer dynamics and viscoelasticity, the important roles of two basic structural size scales: that of a Rouse segment and that of an entanglement strand, have been recognized. We have made significant advances in both aspects. In the case of the Rouse segment, in addition to the obtained understanding as to its dynamics, which can be probed by the depolarized photon-correlation spectroscopy, we have demonstrated that a close interplay among theory, experiment and computer simulation can contribute greatly the advancement of a scientific research. As to chain entanglement, by studying the specially designed blend solutions, we illustratively show that the onset of entanglement occurs at M_e rather than at M_C. This clearly breaks the belief that the viscoelastic behavior of a polymer is described by the Rouse theory below M_C, which has been wrongly held for decades.

五、參考文獻

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