Self-Diffusion in Polymer Solutions: A Test for Scaling and Reptation

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We present preliminary results on the self-diffusion coefficient D_{self} of polystyrene chains (molecular weight $M_n = 245\,000$ and $123\,000$) in benzene, obtained by forced Rayleigh scattering. In the semidilute regime where the chains overlap, D_{self} decreases with the polymer concentration c as $c^{-1.7\pm0.1}$. This behavior is compatible with scaling-law predictions and is the first experimental evidence for the existence of reptation in this regime.

The static properties of polymer solutions in good solvent are now well understood since the discovery by des Cloizeaux[1] and de Gennes[2] of the analogy between chain statistics and magnetic phase transitions. Scaling predictions for molecular weight and concentration dependences are in good agreement with experimental observations.[3-5] On the other hand, the problem of chain dynamics seems more delicate: The diffusion coefficient of concentration fluctuations obtained from Rayleigh light scattering[6] and the disentanglement time T_R observed in viscoelastic experiments[7,8] do not scale exactly with molecular weight and concentration as predicted by de Gennes.[9] The self-diffusion coefficient of the chains, D_{self}, is another dynamical parameter which should provide a straightforward test of both scaling[9] and reptation[10] concepts. However, its measurement has been impeded so far in polymeric solutions by the lack of an adequate experimental technique.

In this Letter we present preliminary results on the concentration and molecular-weight dependences of D_{self} for polystyrene in benzene, obtained using a modified form of the forced Rayleigh light-scattering technique.[11,12] We make comparisons with scaling-law predictions and give, for the first time, a direct evaluation of T_R in the semidilute regime of concentration where the chains overlap.

We shall first recall the main features of the scaling description of polymer solutions in good solvent.[3,9] Increasing the concentration, we distinguish (1) the dilute regime, where the chains are independent coils, with a radius of gyration $R_G \sim aN^{\nu}$ (a is the effective monomer length, N the polymerization index, and $\nu = \frac{3}{5}$); (2) the semidilute regime, where the chains interpenetrate, for concentrations larger than $c^* = M/R_G^3$, and which can be viewed as a transient network. The relevant length is the average distance between entanglements $\xi(c) \sim c^{-3/4}$, which corresponds to the spatial range of the concentration fluctuations. For distances larger than ξ, both excluded volume and hydrodynamic interactions between monomers of the same chain are screened out by the other chains in the medium.

Following Ref. 9, the dynamic properties of the semidilute regime can be discussed in terms of collective or individual chains motions. Collective motions are described by the cooperative diffusion coefficient

$$D_{\mathrm{coop}} = kT/6\pi\eta_s\,\xi, \tag{1}$$

associated with the relaxation of concentration fluctuations. (η_s is the solvent viscosity.) D_{coop} is the diffusion coefficient of one sphere of size ξ, the "blob," considered as independent of its neighbors. Individual chain motions are described by introducing the reptation concept[10]: To renew its configuration, the chain has to slip in a tube of diameter ξ defined by its neighbors. The diffusion coefficient along the tube is

$$D_{\mathrm{tube}} = kT[6\pi\eta_s(N/g)\,\xi]^{-1} \tag{2}$$

as the friction coefficient of the chain is N/g larger than for one blob (g is the number of monomers in one blob, $g = n\xi^3$, where n is the monomer concentration, proportional to the mass concentration c in grams per cubic centimeter). The reptation time T_R is the time taken by the chain to define a completely new tube, and is related to the curvilinear length of the tube $L = (N/g)\xi$ by a one-dimensional diffusion law: $2D_{\mathrm{tube}} = L^2$. The above expressions for $D_{\mathrm{tube}} = L^2$. The above expressions for D_{tube} and L lead to

$$T_R \sim N^3 c^{3/2}. \tag{3}$$

The self-diffusion coefficient D_{self} measured in a macroscopic experiment corresponds to a three-dimensional random walk. The elementary step of time is T_R, and the elementary step of length is the end-to-end distance of the chain $R(c) = (N/g)^{1/2}\xi$ (ideal chain of blobs). Then $6D_{\mathrm{self}}\,T_R$

$=R^2(c)$, and

$$D_{\text{self}}=\frac{kT}{18\pi\eta_s(N/g)^2\xi}\sim N^{-2}c^{-1.75}. \tag{4}$$

An evaluation of D_{self} from Eq. (4) for polystyrene chains of molecular weight 10^5 and concentration $c\sim 10^{-1}$ g/cm^3 gives $D_{\text{self}}\sim 10^{-8}$ cm^2/sec. To follow such a slow diffusion process, conventional tracer techniques are time consuming: Diffusion over 1 mm is achieved in several days![13] We have bypassed that problem by using the force Rayleigh light-scattering technique[14] (FRS) which allows one to reduce the diffusion length down to a few microns, and that we shall now briefly describe.

The application of FRS to mass diffusion measurements necessitates that a few molecules be labeled with a photochromic probe. A periodic concentration fluctuation (wave vector $\vec{q}$) of photoexcited molecules is created by illuminating the sample cell with a pulsed interference pattern (see block diagram on Fig. 1). Following the flash excitation, the concentration distribution of photoexcited molecules is progressively relaxed by diffusion, provided, of course, that the deexcitation time τ_e is longer than the diffusion time over one fringe spacing. A laser beam, with a wavelength chosen in the absorption range of the photoexcited species, sees in the sample an absorption grating, and is diffracted. The diffracted amplitude decreases exponentially with a time constant τ_D related to the self-diffusion coefficient of the labeled molecules by[14]

$$\tau_D=(D_{\text{self}}q^2)^{-1}. \tag{5}$$

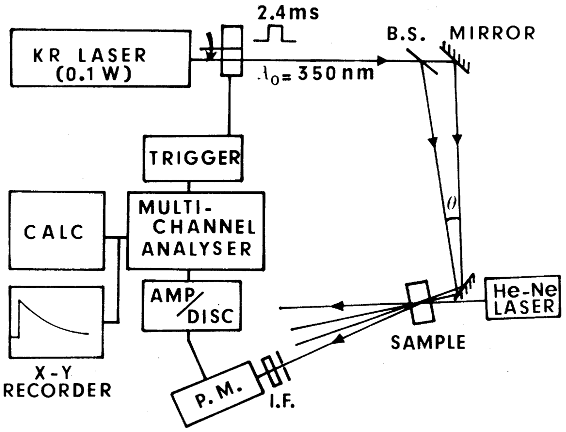

FIG. 1. Block diagram of the experimental setup: The exciting laser is a Coherent Inc. 500-K krypton laser delivering 100 mW at 350 nm. The fringe spacing can be adjusted from 5 to 100 μm, by varying the angle θ between the two interfering beams. The mechanical chopper gives light pulses of 2.4 ms duration, with a repetition rate adjustable from 200 msec to 200 sec. The diffracted intensity is collected with a cooled Philips "56 T. V. P." photomultiplier. The phototube output pulses are amplified and feed into a 50-nsec correlator (manufactured by "A. T. N. E.", Avenue de l'Atlantique, Courtaboeuf, 91400 Orsay, France) used as a multichannel analyzer. The data are then processed with a Hewlett-Packard model 9825 calculator.

The polymer we have used is anionic polystyrene ($M_n=123\,000$; $M_w/M_n=1.12$; $M_n=245\,000$; $M_w/M_n=1.10$), and the labeled molecules are obtained by a termination reaction on a spiropyran molecule.[15] This particular photochrome has been chosen for its high absorption coefficient in the excited state, and for its long lifetime ($\tau_e=10$ sec). Concentrations of spiropyran molecules smaller than 10^{-8} mole per liter can currently be detected by our technique. This necessitates the use of thick samples cells (~5 m/m) to absorb a sizable fraction of the exciting beam ($\lesssim 10\%$). We are then in thick holographic grating conditions[16] and Bragg diffraction angles have to be adjusted within 2 arc min.

For all the present experiments, we have observed an exponential decay of the diffracted intensity, and checked that the decay time τ_D was a linear function of q^{-2} for $\tau_D\leqslant 2$ sec. We are thus dealing with a purely diffusive process, and we can deduce D_{self} through Eq. (5) with a relative accuracy of 10% (the wave vector is independently measured by projection of the interference pattern on a distant screen).

A log-log plot of D_{self} vs c is shown in Fig. 2 for the two studied molecular weights. Let us first focus our attention on the results obtained with molecular weight 245 000. Two concentration regimes can easily be distinguished: A low-concentration range, for $c<2\times10^{-2}$ g/cm^3 in which D_{self} increases slightly with c, and the semidilute regime, for $c>2\times10^{-2}$ g/cm^3, where D_{self} rapidly decreases as the motion of any one chain is more and more hindered by the presence of the others. In the dilute regime, our results from FRS are quite close to the values from ordinary Rayleigh light scattering (ORS) of Ref. 6 calculated for $M_n=245\,000$. When the coils are isolated, the two methods should indeed give the same answer. This agreement confirms the validity of FRS to follow mass diffusion. In the semidilute regime, the two methods (ORS and FRS) are not equivalent. ORS is sensitive to collective concentration fluctuations and gives the

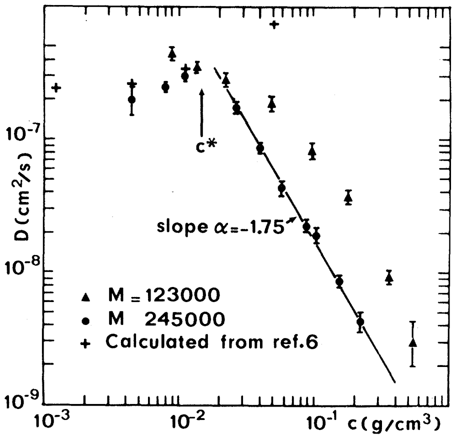

FIG. 2. Log-log plot of the self-diffusion coefficient D_{self} vs concentration c of polystyrene-benzene solutions, for two molecular weights. The solid line corresponds to the scaling-law prediction $D_{\text{self}} \propto c^{-1.75}$ in the semidilute regime. In the dilute range of concentration our results (circles) are compared to calculated values from Ref. 6 (plus). The cross-over concentration c^* $\sim$15 mg/cm^3 for $M = 245\,000$ is in good agreement with evaluations from $c^* = M/R_G^3$.

cooperative diffusion coefficient $D_{\text{coop}} \sim 1/\xi$, which increases with c (the mean distance between entanglements decreases with c). On the contrary, D_{self} decreases with c, with a linear behavior observed over about two decades in logarithmic scales, and corresponding to a power law $D_{\text{self}} \sim c^{-\alpha}$ with $\alpha = 1.7 \pm 0.1$, in good agreement with de Gennes's prediction of $\alpha = 1.75$.[9] The rather abrupt change in behavior from dilute to semidilute regime allows for a sharp determination of the critical concentration c^* and represents an advantage of FRS compared to other dynamical methods such as ORS or sedimentation[17] in which the crossover is smooth. The value $c^* \sim 1.6 \times 10^{-2}$ g/cm^3 for $M_n = 245\,000$ is half that obtained from $c^* = M/R_G^3$. The agreement is reasonable since all numerical factors are omitted in scaling arguments.

For $M_n = 123\,000$ the same behavior is qualitatively observed. However, the linear semidilute region of the $\ln D_{\text{self}}$ versus $\ln c$ diagram is reduced to one decade since (1) the crossover concentration c^* is higher for low-molecular-weight materials ($c^* \sim M^{-0.8}$), (2) a departure from linearity is observed for high concentrations ($c > 0.3$ g/cm^3) where monomer-monomer frictions may become important.

As far as the molecular-weight dependence of D_{self} is concerned, we can only say at this stage that we cannot distinguish between the usual results of viscoelastic measurements (exponent value 3.4 for T_R and 2.4 for D_{self}) and the N^{-2} prediction of Ref. 9. Recent diffusion experiments in the molten state[18] seem to support this last power law, but may be questionable because of polydispersity. Indeed, we have preliminary hints that, even with our anionically prepared samples, an accurate knowledge of the molecular-weight distribution is required to reliably compare data from different-molecular-weight samples. A complete set of experiments on various molecular weights, including polydispersity corrections in the data processing, will be published in a forthcoming paper.

To conclude, we have shown that the concentration dependence for self-diffusion of polystyrene chains in benzene is compatible with scaling and reptation predictions. More experiments are of course necessary, using longer chains, to check more precisely the molecular-weight dependence, and to extend the accessible concentration range of the semidilute regime. Nevertheless, the self-diffusion coefficient reveals itself an interesting dynamical quantity: (1) The abrupt change in behavior from dilute to semidilute regime provides dynamical critical-concentration measurements. (2) In the semidilute regime, our experiments yield a direct evaluation of the reptation time T_R of one molecule among the others—typically, for $M = 123\,000$ and $c = 0.1$ g/cm^3, the radius of gyration of one chain from neutron scattering data[4] is $R_G(c) \sim 100$ Å. Then $T_R \sim 10^{-5}$ sec, where T_R is defined as the time required for the chain to diffuse over its end-to-end distance.

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Ultrasonic Investigation of the Piezoelectric Ionic Crystal β-AgI

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Ultrasonic attenuation and phase velocity measurements as a function of temperature and frequency are reported in the β phase of AgI. Below about 50 MHz the dominant effect is the piezoelectric coupling between the mobile ions and the ultrasonic waves; an analysis similar to that of Hutson and White for piezoelectric semiconductors gives good agreement. Above 50 MHz this interaction becomes screened. An additional attenuation mechanism is observed at 540 MHz.

AgI has received considerable attention in recent years, largely because of its superionic properties. At $T_c = 420$ K, the material undergoes a first-order phase transition from the hexagonal wurtzite (β) structure[1] ($C_{6v}{}^4$-$P6_3mc$), which is the stable form at room temperature, to the body-centered-cubic (α) phase ($O_h{}^9$-$Im3m$). This structural phase transition is accompanied by a jump in the ionic conductivity of nearly four orders of magnitude from about 3×10^{-4} to over 1 $(\Omega\ \mathrm{cm})^{-1}$, the conductivity in the high-temperature phase being comparable to that in liquid electrolytes. However, even in the low-temperature β phase, the ionic conductivity of silver iodide is higher than in many ionic compounds.

Previous ultrasonic work[2] on β-AgI has been concerned with the effect on the elastic constants of the ionicity of the Ag-I bonds. The purpose of this Letter is to show that ultrasonic measurements can give information not only on lattice force constants, but also on quantities such as the dc ionic conductivity, the activation energy, and the frequency dependence of the ionic conductivity in a range not normally accessible by direct methods.

We have measured the temperature dependence of the variation in the attenuation and phase velocity of longitudinal ultrasonic waves propagating along the c axis of a number of β-AgI specimens. A standard pulse-echo transmission technique[3] was used in the frequency range of 7.5 to 540 MHz. The temperature was varied between room temperature and a few degrees below T_c. Measurements could not be made above T_c since single crystals of AgI invariably crack on crossing the first-order phase boundary. The crystals were grown at the University of California (Irvine) by M. J. Delaney using a method developed by Mills.[4] Specimens suitable for making ultrasonic measurements were formed by cleaving sections with faces perpendicular to the c axis of the as-grown crystals so that the samples were about 1 mm thick, the width being 2 to 3 mm. The results for the attenuation are shown in Fig. 1 and for the elastic constant in Fig. 2. The variation of the attenuation was measured to an accuracy of