polymer communications

Cooperative and self-diffusion of polymers in semidilute solutions by dynamic light scattering

Eric J. Amis and Charles C. Han
Polymer Science and Standards Division, Center for Materials Science, National Bureau of Standards, Washington, DC 20234, USA

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The quasielastic light scattering from semidilute solutions of polystyrene in tetrahydrofuran has been measured and we observe two distinct exponential decays separated by several orders of magnitude. The angular dependence of the decay constants is indicative of diffusive processes which we identify with the cooperative diffusion coefficient, D_c and the self diffusion coefficient D_s. It is found that D_c, identified with the fast decay, increases with polystyrene concentration and is independent of molecular weight. However, D_s decreases sharply with concentration and molecular weight. An explanation is given for the light scattering detection of these two diffusion coefficients which is based only on the assumptions inherent in the reptation model. In a limited region of molecular weight and concentration the experimental results appear to be consistent with the predictions of scaling theory.

Keywords Dynamic light scattering; semidilute solution; cooperative diffusion coefficient; self-diffusion coefficient; reptation; scaling

Introduction

Dynamic light scattering has been established in recent years as one of the major techniques for studying polymer chain statistics. For flexible synthetic polymers, dynamic light scattering has generally been limited to the study of dilute solutions[1] and of the short time diffusion (cooperative diffusion D_c) in semidilute solutions[2–6]. Recently, Amis *et al.*[7] have demonstrated that for semidilute solutions of gelatin above the gelling temperature, the centre of mass motion, D_s, as well as D_c can be measured by dynamic light scattering.

In this communication, we report experimental results of D_c and D_s for a series of well characterized polystyrenes with narrow molecular weight distribution in a good solvent. The experimental results for D_c and D_s are at least asymptotically consistent with theoretical predictions for both concentration and molecular weight dependence[8,9].

Background for dynamic light scattering

The intermediate scattering function $S(q,t)$ in a dynamic scattering experiment can be written as[1]:

$$S(q,t) = \langle \rho^*(0)\rho(t) \rangle \qquad (1)$$

with

$$\rho(t) = \sum_j e^{i\mathbf{q}\mathbf{R}_j(t)} \qquad (2)$$

where j sums over all scattering elements at $\mathbf{R}_j$ from an arbitrary origin and $\mathbf{q}$ is the usual scattering wave vector ($q = 4\pi\sin(\theta/2)/\lambda$). In semidilute solutions the density fluctuations measured by dynamic light scattering are complicated by considerable interchain interactions. It can be shown[10] that in the limit of small q and small correlation time, the scattering function has the form,

$$S(q,t) = Ae^{-q^2D_ct} + S_c(q) \qquad (3)$$

where $S_c(q)$ is a time independent function and D_c is the cooperative diffusion coefficient[2]. For semidilute solutions D_c is independent of molecular weight and is due to concentration fluctuations which dissipate on this time scale without overall motion of the centres of mass of the chains. In terms of the language of scaling theory D_c reflects the motion of strands the size of the screening length ξ.

Turning now to the self diffusion coefficient D_s, we are concerned with the centre of mass motion of the entire polymer chain in its surroundings. In the case of diffusive motion of a free polymer chain in a gel[11] and in concentrated solutions and melts where the motion of the chains are severely restricted[12,13], deGennes and Doi and Edwards have suggested that each polymer is confined, by the other chains, to move along its contour by reptation. In the reptation model, the time for a chain to completely redefine its configuration by reptating is t_R. For time longer than t_R the centre of mass of the chain actually diffuses in a three dimensional random walk over a distance related by the self diffusion coefficient D_s as,

$$6D_st_R = R^2 \qquad (4)$$

where R is the chain end-to-end distance. This motion is very slow and D_s is typically several orders of magnitude smaller than D_c.

Although each chain may be moving with respect to the other, the motions of the reptating chain and of the chains which restrict it are uncorrelated and can be considered statistically fixed. It is therefore reasonable to assume that for correlation times larger than t_R the centre of mass motions of different polymers are statistically independent. If this approximation is qualitatively correct[10],

$$S(q,t) = Ae^{-q^2D_st} + S_s(q). \qquad (5)$$

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Thus by equations (3) and (5) we see that D_c and D_s can be obtained by dynamic light scattering in the limits of $t \ll t_R$ and $t \gg t_R$ respectively.

A question could be raised as to the applicability of the reptation model for the centre of mass diffusion of a polymer in solutions with concentrations around or below that required for entanglement coupling to be evident in viscoelastic experiments. It has been suggested by the forced Rayleigh scattering experiments of Léger, Hervet and Rondelez[9] that, at least for centre of mass diffusion, reptation remains the important mechanism at these concentrations. Measurements at these semidilute concentrations will also alow us to investigate the excluded volume effect, predicted by deGennes' model, which may not be important for concentrated solutions and melts (and was therefore neglected by the Doi-Edwards model).

Experimental

Materials. All samples used for these studies were prepared gravimetrically from sharp molecular weight fractions of polystyrene in spectroscopic grade tetrahydrofuran which had been filtered through 0.5 μm teflon filters from Millipore Co.* For the concentration dependence study four molecular weight samples were used: 3.74×10^4 (NBS 1478); 1.79×10^5 (NBS 705); 1.05×10^6 (NBS 1479); 5.05×10^6 (Toya Soda). For most molecular weights 5 to 10 concentrations were prepared to extend from below the semidilute concentration, c^* (defined as $c^* = M/N_A R_g{}^3$) to above the entanglement concentration c_E (defined as $c_E = \rho M_c^0/M$ where M_c^0 is the critical entanglement spacing and is taken as 36000)[14]. The total range of concentration covered almost 3 orders of magnitude from 1 to 630 mg cm^{-3}.

To investigate the molecular weight dependence of the diffusion coefficients it was necessary to include a more closely spaced set of molecular weights. Samples of molecular weight: 1.11×10^5 (Pressure Chemical), 1.79×10^5 (NBS 705), 3.9×10^5 (Pressure Chemical), 4.98×10^5 (Pressure Chemical), 8.67×10^5 (Waters Associates) and 1.05×10^6 (NBS 1479) were all prepared at a concentration of 50 mg cm^{-3}. At this concentration two samples are above c_E, one is slightly below c^*. All preparations were dissolved with gentle agitation and equilibrated at 35°C for one to four weeks in sealed sample cells.

Methods. All dynamic light scattering measurements were performed at 30°C using a spectrometer and real time, multibit 128 channel autocorrelator (Malvern 7025) which has been described previously[15]. The light of a vertically polarized 488 nm Ar-Ion laser was measured at several angles in the range 30° to 120° for each sample. At each angle the intensity autocorrelation of the scattered light was measured with at least two widely different sample times (also called delay or lag times). These sample times were chosen so that the accumulated autocorrelation displayed a reasonable portion (perhaps 2 decay times or *e*-folds) of an apparent exponential decay. In general, the required sample times were separated by a factor of 10^2 to 10^6 with the short sample times in the range of 1–50 μseconds and long times typically 1–100 mseconds.

If a correlator could have provided several thousand delay channels (rather than 128) both processes could have been observed in a single experiment and both decay constants could have been extracted directly. Since this was not the case, each autocorrelation curve was independently analysed with a three parameter single exponential model function by nonlinear regression. Treating the data in this way involves two important approximations. First, in fitting fast decay (short sample time) data, the baseline value was allowed to float such that it included a sum of both the infinite time baseline and the initial value (essentially constant over the short time scale) of the slow decay.

The second approximation is that the contribution of the fast process to the experimental slow decay curve is assumed to be negligible after the first two or three sample times. It is found that in the worst case the contribution of the fast process to the correlation function of the slow process is less than 0.1% at the fourth delay point. The loss of data caused by deleting two or three points is acceptable.

Results and Discussion

In *Figure 1* the autocorrelation data for both the short time and long time measurements of a representative semidilute polystyrene solution are shown. *Figures 1a* and *1c* show the correlation data and the resulting independent fits to the three parameter model equation:

$$C(q,t) = A + B\,e^{-\Gamma t}. \tag{6}$$

To better indicate the quality of the fit and the sufficiency of the single exponential model function, the same data are reduced and plotted as $\ln(C(t) - A)$ vs. t in *Figures 1b* and *1d*. It is clear that a single exponential fit does not cause any major problem. Indeed, a second order cumulant fit yielded approximately the same decay constant and its additional parameter was not statistically justifiable.

The decay constant Γ of the short time correlation functions for a series of measurements varying from 30° to 120° were evaluated for their q^2 dependence. In the literature, the cooperative diffusion coefficient has been obtained by the equation $\Gamma \equiv 2q^2 D_c$ which implies the assumption of homodyne scattering. We believe it is more likely that heterodyne scattering (i.e. $\Gamma \equiv q^2 D_c$) is seen in measurements of D_c in semidilute solutions but to be consistent with previous workers we have calculated our values of D_c by $D_c \equiv \Gamma/2q^2$. The concentration and molecular weight dependence of D_c will of course not be changed by this distinction. Again, D_s is extracted from the long time decay constant. In these measurements, the small angle decay was interpreted as the heterodyne limit and the large angle decay as homodyne. The results were consistent with this analysis with very little ambiguity. The resulting diffusion coefficients are plotted in *Figure 2* as $\log D_c$ and $\log D_s$ vs. log concentration, for each of the four molecular weight samples from our broad range.

The only molecular model we know of which gives explicit predictions for diffusion in semidilute solutions and which considers the excluded volume effects is deGennes' scaling and reptation model. The details have

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* Disclaimer: Certain commercial materials and equipment are identified in this paper in order to specify adequately the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that the material or equipment identified is necessarily the best available for this purpose.

been given elsewhere[8] so we give only the final predictions here. As is usual in scaling descriptions only the dependence on c and N in terms of power laws are predicted not magnitudes. In both cases the good solvent prediction (i.e. $\nu = 0.6$) is given.

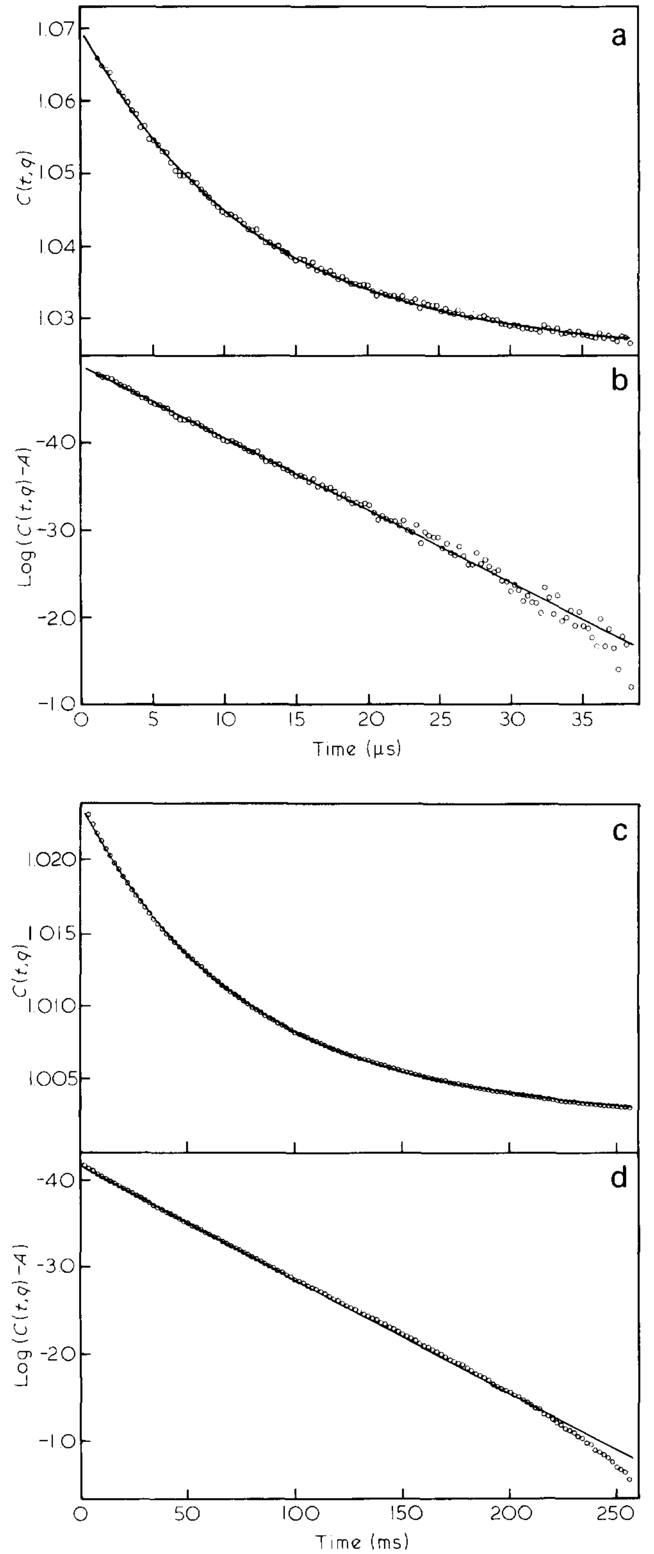

Figure 1 Correlation functions of scattered light, $C(t, q)$, from polystyrene with $M_w = 1.05 \times 10^6$ and scattering angle $\theta = 90°$. Short time (with sample time $\Delta t = 0.3$ µs) and long time ($\Delta t = 2$ ms) decay are shown separately in *Figures 1a* and *1c*. Also shown in *Figures 1b* and *1d* are the corresponding semilogarithmic plots for $\ln\,[C(t, q)-A]$ vs. t. Note that the magnitude of the base line for *Figure 1a* is approximately equal to the starting point of *Figure 1c*. Solid lines are single exponential fits

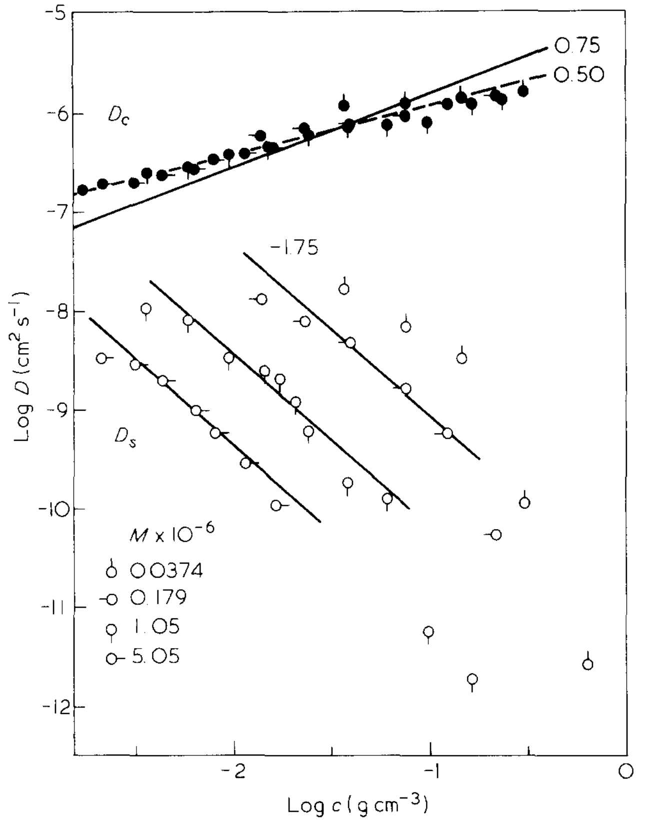

Figure 2 Variation of the cooperative diffusion coefficient (filled circle) D_c and the self diffusion coefficient (open circle) D_s for four different molecular weight polystyrenes are displayed. Solid lines are the scaling predictions of the -1.75 and 0.75 power law dependence of D_s and D_c on concentration. Also shown in dotted line is an estimated 0.5 exponent for the D_c data in this graph. Both D_c and D_s are reduced from their corresponding short time and long time decay rate Γ, with $D \equiv \Gamma/2q^2(1-\phi)$ and ϕ is the monomer volume fraction in the solution

(1) Cooperative diffusion coefficient, D_c

$$\begin{aligned} D_c &\propto N^0 c^{-\nu/(3\nu-1)} \\ &\propto N^0 c^{+0.75} \end{aligned} \tag{7}$$

(2) Self diffusion coefficient, D_s

$$\begin{aligned} D_s &\propto N^{-2} c^{\left(\frac{\nu-2}{3\nu-1}\right)} \\ &\propto N^{-2} c^{-1.75} \end{aligned} \tag{8}$$

In *Figure 2* lines are drawn showing these predictions of concentration dependence for D_c and D_s.

Several points of comparison should be made. First, while our measurements of D_c show a slope which is less than the predicted one (0.5 vs. 0.75), this is not unusual and has been reported by previous workers. In fact, in those experiments which have observed the 0.75 power law[2,5], it is usually valid only for a very limited range of concentration, molecular weight and solvent quality[3,4,6]. Next, in the self diffusion measurements there is agreement with the scaling prediction of $c^{-1.75}$ over a decade for only the 1.05×10^6 molecular weight sample. For the other molecular weights, scaling behaviour is only asympotic and certainly covers less than one decade of concentration.

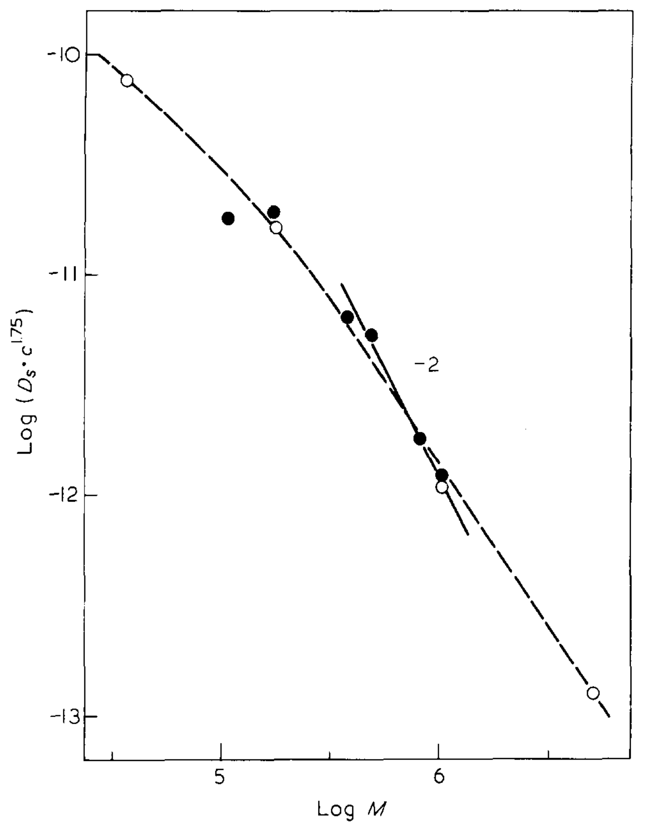

Figure 3 Self diffusion coefficient D_s for 6 different molecular weight polystyrenes (1.1×10^5, 1.79×10^5, 3.9×10^5, 4.98×10^5, 8.3×10^5 and 1.05×10^6) measured at c = 50 mg cm^{-3} are displayed in logarithmic scales with filled circles. Also the D_s values for each of the four molecular weights in *Figure 2* are scaled by $c^{1.75}$ and averaged. They are shown as open circles. Solid line with slope −2 is the scaling prediction and broken curve is drawn to connect experimental points

At lower concentrations, near c^*, the slope is less steep than −1.75 presumably because the solutions are too dilute for the diffusion of the chains to be defined by reptation. For higher concentrations the scaling model also breaks down as D_s drops off dramatically. This drop may be the result of the screening length becoming smaller than the 'temperature blob, N_τ' or even becoming comparable with the statistical segment length of the chain. It seems that the scaling region in this study is narrower than that observed by other techniques[9]. The explanation of this may be that our long time decay yields the self diffusion coefficient only when the condition of the statistical independence of the reptating chain and surrounding chains is strictly true. This extra criterion is not necessary in the forced Rayleigh scattering experiment.

The final point to be made about this figure is that the molecular weight and concentration ranges were chosen purposely to be much wider than is usual in many experiments which presume to test the scaling model. The attempt was to show two decades of molecular weight and for each of them to show two decades of concentration. We believe that through this perspective scaling predictions can be more realistically evaluated.

In *Figure 3* a plot of $\log(D_c c^{1.75})$ vs. log molecular weight is shown. This plot includes average values for the four molecular weights in *Figure 2* (open circles) as well as six additional samples (filled circles) which were measured independently at 50 mg cm^{-3}. The predicted slope of −2, shown by the line in the figure, may be observed over a decade of molecular weight (between 10^5 to 10^6) although there is substantial deviation at low molecular weight. The deviation from the M^{-2} line for the 5.05×10^6 molecular weight sample is more disturbing. For this sample we cannot rule out errors due to the very large concentration shift involved or the increased polydispersity. While all of these samples are within the semidilute region in terms of concentration scaling and c^* line, the deviations in *Figure 3* serve to point out that the region where scaling behaviour is observed will depend on the particular experiment and property which is studied. Even with the same dynamic light scattering technique, D_s can have a wider and more easily observable scaling region than D_c.

To summarize, we have demonstrated that both the cooperative and self diffusion coefficients can be measured by dynamic light scattering. Since no labelled species is involved, the compatibility between the measured species and the surrounding chains is not in question. This advantage is also a disadvantage because it is not possible to study the effects of different surroundings. We have also demonstrated that both the $c^{-1.75}$ and M^{-2} dependence of D_s can be observed as predicted by scaling theory, but only for a limited (about one decade) range. It is clear that the crossover behaviour is complicated and that interpolation formula for these wide regions would be very useful.

Acknowledgements

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