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Diffusion and Relaxation in Polymer–Solvent Systems. 2. Poly(methyl methacrylate)/Methyl Ethyl Ketone

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ABSTRACT: The results of light scattering photon correlations from poly(methyl methacrylate) in methyl ethyl ketone are examined over a very wide range of polymer concentration (from 1 to 75 wt % in polymer). The isotropic binary diffusion coefficient which is observed below c^* splits into two components above c^*, a phenomenon which we have previously interpreted to be due to the anisotropic nature of macromolecular diffusion above the overlap concentration. At high polymer concentrations (>55%), the coupling between the cooperative (fast) diffusion mode and the internal mode dynamics of the chains is interpreted with reasonable success in terms of the analysis of Akcasu et al. The initial slope Ω of the correlation exhibits hydrodynamic interaction effects (Zimm dynamics) in the form of a q^3 dependence at 55% polymer concentration, where q is the scattering wave vector. A trend toward the screening of hydrodynamic interactions (Rouse dynamics) occurs at higher concentrations.

Introduction

A number of photon correlation experiments on polymer solutions above the macromolecular overlap concentration c^* have detected two diffusion modes.[1] We have recently interpreted these two modes in terms of the anisotropy of macromolecular diffusion that occurs at these concentrations and presented results on poly(*n*-butyl methacrylate) in methyl ethyl ketone which indicate that the two diffusion modes, slow and fast, appear to merge into the single isotropic diffusion mode that is observed in dilute solutions.[2] The slow mode was recently thought to be the self-diffusion of the chains;[3] further experiments by nuclear magnetic resonance (NMR) and forced Rayleigh spectroscopy (FRS) indicated that although the behavior of the slow mode as a function of concentration is parallel to that of the self-diffusion, the two are not identical.[4] Unlike the NMR and FRS techniques that measure self-diffusion coefficients which essentially reflect the friction encountered in the motion of the tagged particles, the light scattering experiment measures binary diffusion coefficients which are also affected by the thermodynamic interactions between the particles in the form of second and higher virial coefficients.[5] We report here measurements on D_c, D_{CM}, and $D_S{}^*$ in the poly(methyl methacrylate) (PMMA)/methyl ethyl ketone (MEK) system, where D_c is the cooperative or fast diffusion mode, D_{CM} is the center-of-mass or "slow" diffusion mode, and $D_S{}^*$ is the self-diffusion of the solvent measured by NMR. We again see a splitting of the isotropic diffusion coefficient into two components above c^*, and although initially the two must be coupled because of the closeness of their time scale, they develop at higher concentration into the cooperative diffusion and a diffusion essentially along the chain.[6]

We shall emphasize in this paper the results at very high polymer concentrations when D_{CM} becomes too slow to observe by photon correlation and when D_c is coupled to the internal mode relaxations of the chain (see Figure 1 of paper 1). The shape of the photon correlation function is no longer exponential at the shortest time scale monitored by the correlator and the simple analysis in terms of diffusive q^2-dependent modes applicable at lower concentrations is no longer possible. There are no available models describing the coupling of segmental diffusion and internal mode relaxations at very high concentrations, but several analyses[7–9] for the single unperturbed Gaussian chain have been presented in which the coupling between the translation diffusion and the internal chain dynamics is taken into account. Akcasu et al.[9] have obtained expressions for the correlation function in the infinite-chain limit with and without hydrodynamic interactions corresponding to the Zimm and the Rouse representations of the dynamics of the chain. Concentrated polymer solutions present some similarity to the infinite-chain limit in the sense that the cooperative diffusion coefficient is expected to be molecular weight independent and one may assume that its coupling to local internal modes be also independent of molecular weight. We shall show here that an interpretation of the photon correlation results in very concentrated solutions in terms of the theoretical results obtained for the single infinite chain can indeed be instructive. We have analyzed the behavior of the initial slope Ω of the time correlation function defined by

$$\Omega(q) = \lim_{t\to 0} \frac{\mathrm{d} \ln \mathcal{C}(q,t)}{\mathrm{d}t} \qquad (1)$$

where $\mathcal{C}(q,t)$ is the normalized correlation function ($\mathcal{C}(q,t) = C(q,t)/C(q,0)$) in terms of the interpretation proposed by Akcasu, Benmouna, and Han.[9] We find that the draining parameter B which we used as a fitting parameter to our results of $\ln \mathcal{C}(q,t)$ vs. Ωt decreases from $B \geq 0.38$ for the 55% PMMA solution to a value of $B \simeq 0.1$ for the 65% PMMA solution, indicating, as expected, an increase in screening of hydrodynamic interactions as a function of concentration and a trend from a Zimm-like behavior to a Rouse behavior of the chain dynamics. The theoretical results on the infinitely long chain show that in the regime where hydrodynamic interactions influence the dynamics of the macromolecule, the initial slope Ω is q^3 dependent and is independent of the segment size.[8,9] On the other hand, in the Rouse limit of totally screened hydrodynamic interactions, Ω goes like q^4a^2, where a^2 is the mean square end-to-end dimension of the segment. To observe the q^4 behavior of the Rouse limit, one has to go to the very high wave vectors of neutron scattering. The frequency regime in which a tendency toward q^4 behavior is predicted and has been observed is in the range of 10^{14} Hz[7,10] and is quite inaccessible to the photon correlation experiment. For the wave vectors of the light scattering experiments, one observes no angular (i.e., q) dependence of the correlation functions obtained from pure bulk polymer where the Rouse limit is satisfied.[11] We find therefore that the q^3 dependence that we observe for the 55% PMMA solution goes into a q^0 dependence for the 75% PMMA solution, passing by an intermediate regime at 65% polymer. The q behavior of Ω will depend not only on the concentration but, as mentioned above, also on the q regime examined.

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As one goes to smaller and smaller q, one would again separate and decouple the diffusion relaxation time from the internal relaxation times (see Figure 1 of paper 1). One would expect to see the diffusion q^2 dependence even for our highly concentrated solution if one goes to very small q values which are usually inaccessible or hard to achieve by the light scattering technique.

Experimental Section

Solutions with 40% or less by weight of polymer are prepared from linear poly(methyl methacrylate) obtained by suspension polymerization at 70 °C. The molecular weight and polydispersity of the polymer were determined by gel permeation chromatography, which gave $M_w = 9.6 \times 10^4$ and $M_w/M_n \simeq 1.85$. The highly concentrated solutions (≥55%) were prepared directly in the scattering cells from vacuum-distilled and degassed monomer (MMA) and solvent (MEK). The molecular weight characteristics of these solutions are $M_w = 2.7 \times 10^5$, 2.2×10^5, and 4.8×10^5 and $M_w/M_n = 1.6$, 1.7, and 1.7 for the 55, 65, and 75% polymer, respectively. The setup and preparation procedures of these solutions are as described in paper 1 for the PBMA/MEK samples.

The light scattering spectrometer consisted of a Lexel argon ion laser ($\lambda = 4880$ Å) in conjunction with an EMI 9789B photomultiplier tube and a Birnboim correlator. The light scattering experiments were performed at 19 °C. The pulsed field gradient spin-echo measurements of solvent self-diffusion were obtained at 26 °C by using the Carr–Purcell pulse sequence on a CFT-20 Varian NMR spectrometer. More details on the spectrometers and the preparation steps may be found in paper 1.

Measurements of Diffusion Coefficients

We performed an analysis of the correlation functions in terms of q^2-dependent diffusive modes up to a concentration of 40% polymer. In dilute solutions below c^*, a single-exponential fit of the correlation function

$$C(t) = A + Be^{-2\Gamma t}$$

gave the isotropic center-of-mass diffusion of the macromolecule $D = \Gamma/q^2$. The data from the 10% and 20% solutions where two diffusive processes were observed were fitted to

$$C(t) = A + (B_1 e^{-\Gamma_f t} + B_2 e^{-\Gamma_s t})^2$$

where A is a nonzero background and B_1, B_2, Γ_f, and Γ_s are the amplitude and decay constants of the fast (cooperative diffusion) and slow (center-of-mass diffusion) relaxation processes. When these two processes are well separated in time scale and give rise to a weak and strong scattering amplitudes for the fast and slow modes, respectively, such as for the 30% and 40% solutions, we used

$$C(t) = A + B_1 e^{-\Gamma_f t} + B_2 e^{-2\Gamma_s t}$$

with the assumption that the fast process is detected by heterodyne scattering whereas the slow one is detected by homodyne scattering.[2,3] Although this last assumption is supported by calculations of various contributions to the intensity correlation function, future work may necessitate an optical heterodyne mixing experiment to ensure correct values of the relaxation times.

Figure 1 shows the cooperative diffusion coefficient (D_c) variation with concentration. After the correction transforming the results of D_c obtained by light scattering in a frame of reference relative to volume velocity into D_c^S, the cooperative diffusion coefficient calculated in a frame of reference relative to solvent velocity,[12] we find for $c > c^*$ an exponent of concentration of ~0.4, a value which has also been reported for other systems.[2,3] We suspect that for our rather low molecular weight samples (in the range of 10^5) we may not have achieved the condition of molecular weight independent D_c in semidilute solutions which is required for the scaling prediction of an exponent equal to 0.75.[12] By increasing the concentration further, we probably enter into the concentrated regime before satisfying that condition.

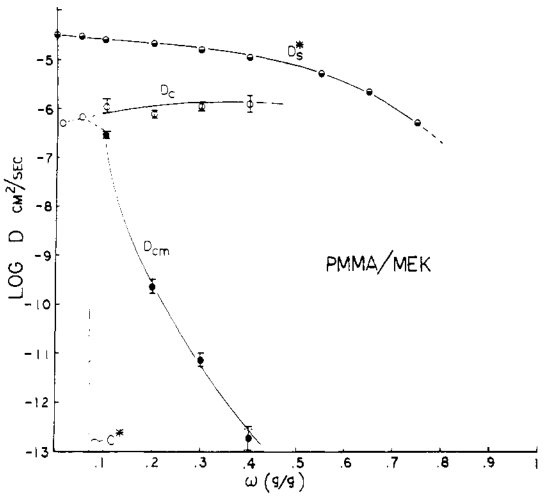

Figure 1. Diffusion coefficients vs. concentration for PMMA/MEK systems at 19 °C. $D_S{}^*$ is the self-diffusion of MEK obtained by NMR at 26 °C and reduced to 19 °C. The cooperative diffusion coefficient, D_c, and the center-of-mass diffusion D_{CM} are obtained by photon correlation.

Table I
Values of $D_S{}^*$, D_c, and D_{CM} in PMMA/MEK Systems

wt %, g/g	$D_S{}^{*26°C}$, cm²/s	$D_c{}^{19°C}$, cm²/s	$D_{CM}{}^{19°C}$, cm²/s
0	3.11×10^{-5}		
1		5.2×10^{-7}	
5	2.95×10^{-5}	7.0×10^{-7}	
10	2.51×10^{-5}	1.1×10^{-6}	2.9×10^{-7}
20	2.15×10^{-5}	7.6×10^{-7}	2.1×10^{-10}
30	1.57×10^{-5}	1.2×10^{-6}	7.2×10^{-12}
40	1.16×10^{-5}	1.3×10^{-6}	1.8×10^{-13}
55	5.35×10^{-6}		
65	2.31×10^{-6}		
75	5.34×10^{-7}		

The values of D_c measured by light scattering are listed in Table I along with those of $D_S{}^*$, the solvent self-diffusion, measured by the NMR spin-echo technique. These values are lower in the PMMA/MEK system than in the PBMA/MEK systems studied previously;[2] they suggest that the "softer" PBMA, with a glass transition temperature $T_g \simeq 20$ °C, provides more "free volume" for the motion of its own segments and of the solvent molecules compared to the "harder" PMMA with its glass transition temperature of $T_g \simeq 105$ °C. We have made no attempt to extrapolate $D_S{}^*$ (or D_c) to zero solvent concentration for the case of PMMA/MEK as was done for the PBMA system because our experimental temperature was below the glass transition temperature of highly concentrated PMMA solutions (>75%). Due to experimental limitations of the NMR spectrometer, we could not obtain $D_S{}^*$ at polymer concentrations higher than 75%; it is suspected however that the activation energy of diffusion differs at temperatures below the glass transition from those above it[13] and thus precludes an extrapolation of our data.

The results of the "slow" diffusion coefficient D_{CM} are listed in Table I and are shown in Figure 1. As for the PBMA system,[2] we observe, on one hand, the very fast drop of D_{CM} as a function of concentration at high concentrations and, on the other hand, its merging with the fast diffusion process below the overlap concentration in dilute solutions. The drop of D_{CM} in the PMMA system is more pronounced than in the PBMA case although the molecular weight of the latter was in fact higher. At 40% polymer, D_{CM} is of the order of 10^{-12} cm^2/s in PBMA/MEK and 10^{-13} cm^2/s in PMMA/MEK. Empirically, one can again attribute this effect to the "harder" nature of PMMA with its lower "free volume" as compared to the PBMA. On a molecular level, the observations made by Ferry[11] on the extent of entanglements in PMMA as compared to that in PBMA are pertinent to our results. PMMA was found to have twice as many entanglements as PBMA of the same molecular weight as reflected in their respective solution viscosity. This effect must contribute to the observed sharper decrease of D_{CM} in PMMA as compared to PBMA.

Coupling of the Cooperative Diffusion to Internal Modes Dynamics

Akcasu et al. have presented expressions for the scattering function from a single Gaussian chain based on linear response theory and an eigenfunction expansion method. Their approach led to a framework with which highly nonexponential correlation functions caused by the coupling of translation diffusion and internal modes dynamics could be analyzed. Their results have forms which are convenient for numerical calculations and have been demonstrated to be good representations of correlation functions for dilute polymer solutions.[14] In the absence of any theory applicable to highly concentrated solutions we have used Akcasu et al.'s framework of analysis for our experimental data of the 55, 65, and 75% PMMA/MEK solutions. We do not claim that their approach should apply to these concentrated solutions but that it provides a method of data analysis which we have found to be instructive. As we have suggested in the Introduction, it is believed that there are similarities in local macromolecular dynamics of an infinitely long chain and of a very highly concentrated solution.

In the infinitely long chain limit (for either closed or open chain[9]) and including the effects of hydrodynamic interactions in terms of the preaveraged Oseen tensor, Akcasu et al. obtained for the normalized correlation function

$$\mathcal{C}(q,t) = [e^{-\alpha\Psi_0(t)} + 2\sum_{s=1}^{\infty} e^{-\alpha\Psi_s(t)}][1 + 2\sum_{s=1}^{\infty} e^{-\alpha s}]^{-1} \quad (2)$$

where

$$\Psi_s(t) = s + \frac{1}{2\pi}\int_{-\pi}^{\pi} \mathrm{d}p\, \frac{1 - \exp(-\alpha_p t)}{1 - \cos p} \cos(ps)$$

$$\alpha_p = 2W(1 - \cos p)[1 + 2BZ(p)]$$

$$Z(p) = \sum_{n=1}^{\infty} \cos(pn)/n^{1/2}$$

$$B = \frac{\xi_0/\eta_0 a}{\pi(6\pi)^{1/2}}$$

$$\alpha = q^2a^2/6$$

$$W = (3/a^2)D_{\mathrm{m}}$$

η_0 is the solvent viscosity, a is the statistical polymer segment length, ξ_0 its friction factor, and $D_{\mathrm{m}} = kT/\xi_0$. The initial slope of $\mathcal{C}(q,t)$ is given by[9]

$$\Omega(q) = D_{\mathrm{m}}q^2\left[1 + 2B\sum_{s=1}^{\infty}\frac{1}{s^{1/2}}e^{-\alpha s}\right][1 + 2\sum_{s=1}^{\infty} e^{-\alpha s}]^{-1} \quad (3)$$

In the limit $\alpha \to 0$ but $B/\alpha^{1/2}$ finite, $\mathcal{C}(q,t)$ can be cast in the following form in the intermediate-q regime where $qa \ll 1$ and $qR_G \gg 1$:

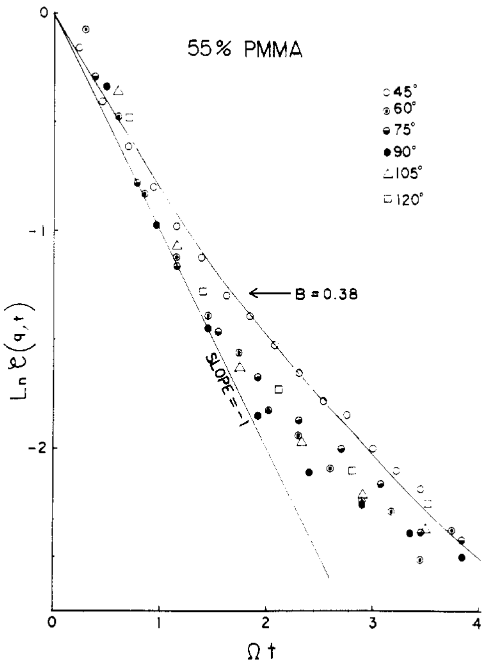

Figure 2. Correlation functions at different angles for 55% PMMA vs. Ωt, where Ω is the initial slope. The solid line, B = 0.38, is the theoretical curve based on eq 2.

$$\mathcal{C}(q,t) = \int_0^{\infty} \mathrm{d}u\, \exp[-u - J(u,\Omega t,B/\alpha^{1/2})] \quad (4)$$

where

$$J(u,\Omega t,B/\alpha^{1/2}) = \frac{2}{\pi}\int_0^{\infty} \mathrm{d}x\, \frac{\cos(xu)}{x^2}\left\{1 - \exp\left[-\Omega t x^2 \frac{1 + B(2\pi/\alpha x)^{1/2}}{1 + 2B(\pi/\alpha)^{1/2}}\right]\right\}$$

The corresponding initial slope is given by[9]

$$\Omega(q) = \frac{1}{12}\frac{kT}{\xi_0}q^4a^2\left[1 + \frac{2\pi^{1/2}B}{\alpha^{1/2}}\right] \quad (5)$$

In the Rouse model, where $B = 0$, eq 5 reduces to

$$\Omega_{\mathrm{R}} = \frac{1}{12}\frac{kT}{\xi_0}q^4a^2 \quad (6)$$

whereas in the Zimm limit

$$\Omega_{\mathrm{Z}} = \frac{1}{6\pi}\frac{kT}{\eta_0}q^3 \quad (7)$$

and corresponds to the case where $2\pi^{1/2}B/\alpha^{1/2} \gg 1$. The results of eq 6 and 7 have been used to interpret scattering experiments in the appropriate regimes.[10,15]

To obtain the initial slope of our highly nonexponential correlation functions obtained at high polymer concentrations, we fitted our experimental results of ln $C(t)$ to a polynomial of third order in time:[9]

$$\ln C(t) = -\Omega t[1 + C_1(\Omega t) + C_2(\Omega t)^2] + C_3$$

for the initial 25 points (channels) of our correlations with the shortest time interval Δt = 6.4 μs. The constant C_3 represents the amplitude of the correlation function, C_3 = ln $C(0)$. Figure 2 shows the experimental value of *ln* $\mathcal{C}(t)$ for the 55% solution as a function of Ωt for different

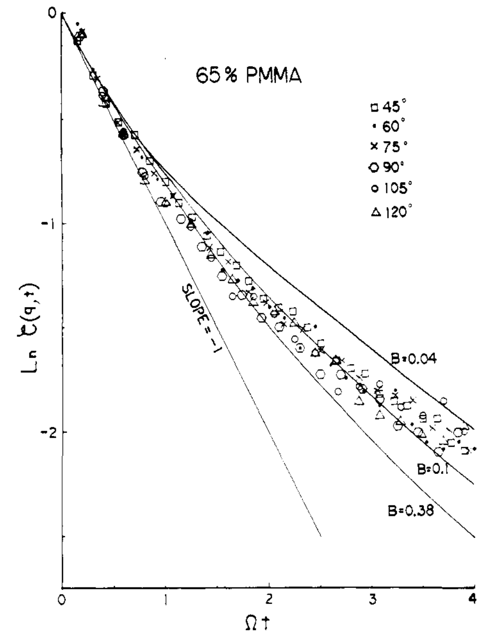

Figure 3. Correlation functions at different angles for 65% PMMA vs. Ωt. The solid lines are theoretical curves based on eq 2 for different values of B.

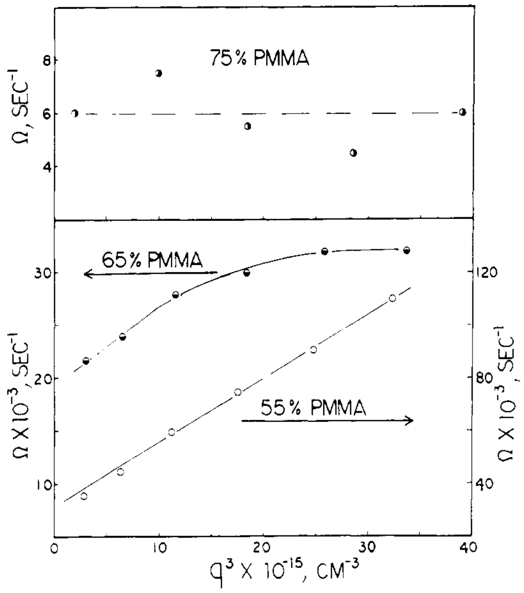

Figure 4. Initial slopes, Ω, of the correlation functions vs. q^3 for 55%, 65%, and 75% PMMA in MEK.

scattering angles. The experimental results fall generally below the theoretical curve based on eq 2 with a value of $B = 0.38$ also shown in the figure. This theoretical curve is practically independent of qa for qa values less than one,[9] which is certainly the case for the light scattering experiment. The value of qa, which was taken to be 0.3 for the computation of the curve based on eq 2, is therefore inconsequential. The experimental data points thus indicate a draining parameter B with a value of 0.38 or higher. For these values of B, the Zimm limit is achieved and eq 7 should be obeyed. We show in Figure 4 that the q^3 dependence of Ω is indeed well obeyed in this case. Figure 3 presents the experimental results for the 65% solution and a few theoretical shape functions calculated for $B = 0.38$, 0.1, and 0.04. All the experimental curves fall very close to each other in the region of $B \simeq 0.1$. For values of B smaller than approximately 0.3, Ω begins to deviate from the q^3 dependence to follow the more general equation, eq 5. In the limit where all experimental curves fall on a master curve, $B = 0$ and the Rouse limit is reached.[9] The q^4 dependence on the Rouse limit cannot however be observed by light scattering since the regime of wave vector and frequency needed to achieve the q^4 dependence of Ω is out of reach of the light scattering experiment but is rather in the domain of neutron scattering.[7,10] In light scattering the Rouse limit leads to q-independent correlation functions as observed in polymer melts.[16] We expect therefore that the Zimm behavior seen in the 55% solution with its associated q^3 dependence will go into a q-independent correlation at higher concentration. The results of Ω vs. q^3 for the 65% and 75% solutions are also shown in Figure 4. For the 65% solution the q^3 dependence of Ω is still obeyed at small q but goes into q^0 dependence at higher q. For the 75% solutions, q-independent Ω is obtained over the whole range of scattering angles employed.

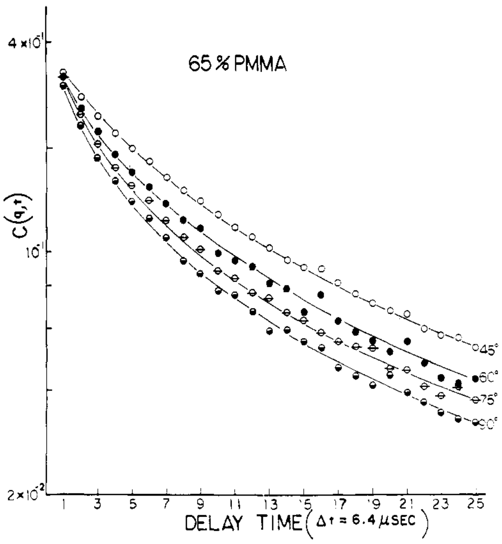

Figure 5. Correlation functions at four scattering angles for 65% PMMA for short delay times. The correlations at the higher angles of 105° and 120° coincide practically with that at 90° and are not shown. Solid lines are for visualization.

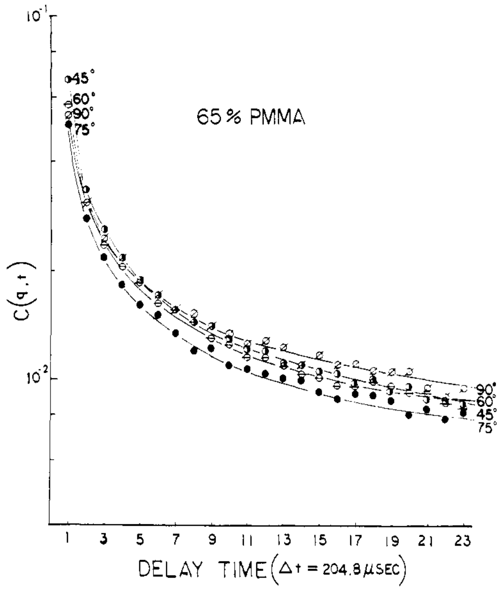

Figure 6. Correlation functions at four scattering angles for 65% PMMA for long delay times. Solid lines are for visualization.

In the regime where the photon correlation experiments monitor both the cooperative diffusion and the internal mode relaxations, a change in q affects only the relaxation time associated with D_c but not that of the internal modes.

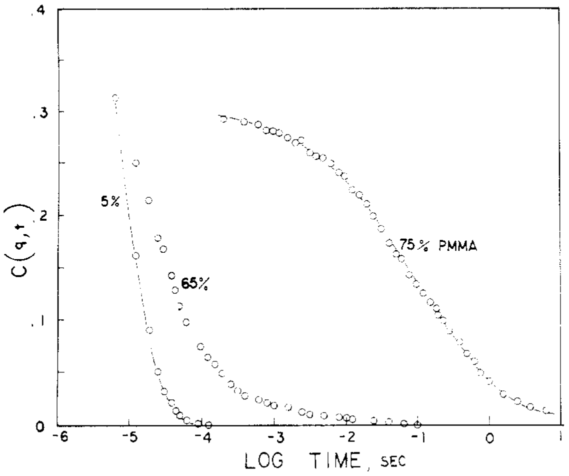

Figure 7. Different character of the correlation function at 75% PMMA compared to those at lower polymer concentrations obtained at a scattering angle of 90°.

Hence as q is increased, $(D_c q^2)^{-1}$ falls below the slower internal relaxation modes observed such that these internal modes dominate the long-time behavior of $C(q,t)$ whereas the diffusion mode and the faster internal modes appear at short times (refer to Figure 1 of paper 1). Figures 5 and 6 show this effect for the 65% PMMA/MEK solution where a strong q dependence is observed for short delay times (Figure 5) but diminishes for long delay times (Figure 6). For the short delay times of Figure 5, the correlations at the higher scattering angles of 105° and 120°, which are not shown, are almost superimposable on that obtained at 90°. These results indicate that, at these wave vectors, the amplitude of the internal relaxation modes becomes dominant relative to the cooperative diffusion relaxation mode. The latter is also becoming faster as it goes like q^{-2}. At 75% polymer, the amplitude of the cooperative diffusion is becoming still weaker as it must scale like some positive power of solvent concentration. The q^0 dependence of Ω observed by light scattering at this very high polymer concentration (see Figure 4) appears then as the result of the diminishing amplitude of the cooperative diffusion mode and the fact that the diffusion–internal mode coupling occurs at very high frequencies (10^{14} Hz) accessible only to neutron scattering. Since the diffusion effects are expected to die away extremely rapidly, we are left in light scattering with only the q-independent internal relaxation modes of the type observed in pure polymer melts.[2,17] The results of the 75% solution shown in Figure 7 are obtained by matching photon correlations observed with different time delays covering several decades of times.[17] This behavior is typical of polymer melts and implies therefore Rouse-like dynamics; it is very different from that at lower polymer concentrations shown in the same figure.

Discussion and Conclusion

In semidilute solutions and for concentrations of up to 40% PMMA in MEK we have determined a fast and a slow diffusion mode. The two diffusion coefficients appear to merge into the single classical binary diffusion in dilute solution below c^*. As we have proposed in paper 1, we link the presence of two diffusion coefficients to the inherent anisotropy of macromolecular diffusion past the overlap concentration and associate the "slow" mode to a diffusion of the whole chain in a path confined by the presence of contacts or entanglements with neighboring chains. The "slow" diffusion does not correspond to the self-diffusion of the polymer chain because the nature of the light scattering experiment incorporates into the binary diffusion measurement the thermodynamic effects of second and higher virial coefficients.

In highly concentrated solutions (≥55% PMMA in MEK) we have analyzed the coupling that occurs between the "fast" cooperative diffusion and the internal mode relaxations in terms of the framework proposed by Akcasu et al. for an infinitely long chain.[9] In terms of this analysis the results are quite instructive; we observe a q^3 dependence (Zimm dynamics) of the initial slope Ω of the correlation functions obtained with the 55% PMMA solution. As the polymer concentration is increased, we observe a decrease in the draining parameter and thus a trend toward Rouse dynamics. At 75% polymer, the initial slope Ω of the correlation function is q independent. Two reasons appear as the cause of this independence on wave vector: in the regime of Rouse dynamics, the coupling of the diffusion to internal relaxation modes occurs at frequencies inaccessible to light scattering and the amplitude of the cooperative diffusion mode which depends on solvent concentration is becoming too small to be detectable.

Although the analysis developed for the single infinite chain appears to be quite useful when applied to highly concentrated solutions, it does not of course provide all the answers. We shall raise here a few questions that can be elucidated only by a more complete theory. Despite the interesting q^3 dependence of Ω observed for the 55% solution over a wide range of light scattering wave vectors and for the 65% solution at small scattering angles, eq 7 obtained for the single infinite chain is not quantitatively obeyed. Thus, by examining the data of Figure 4 for 55% PMMA and the first three points (which possibly obey a q^3 law) for the 65% PMMA and using eq 7, one obtains from the slope of these curves an "effective" viscosity of approximately 0.09 and 0.30 cP, respectively. The viscosity of the pure solvent (MEK) is 0.43 cP at 20 °C, and for the length scale being probed (~1000 Å), one would have expected a higher viscosity for the very concentrated polymer solutions considered. The results suggest therefore that although the q^3 dependence of Ω is observed for light scattering in a regime corresponding to Zimm dynamics for the chains, the quantitative expression itself is incorrect for concentrated solution and will have to involve a function of concentration and frequency. The results of Figures 5 and 6 raise another question. At short times, the angular dependence ($\sim q^3$) of the correlation is demonstrated in Figure 5 whereas for the longer times of Figure 6, no angular (or q) dependence could be detected within the accuracy of the results. If we maintain the proposition made earlier that q-independent correlations imply Rouse dynamics as far as light scattering is concerned, then we observe Zimm dynamics at short times and Rouse dynamics at long times. We have interpreted these results qualitatively in the text by saying that at short times the diffusion relaxation (which is fast) appears coupled with internal modes, whereas for longer times the diffusion decay is too fast to be monitored by the correlator, which sees only the slower internal modes (see also Figure 1 of paper 1). This result is however the reverse of the predictions for the single infinite chain.[9] It is probably due to the fact that the internal mode relaxations that we observe in our concentrated solutions are the cooperative internal modes of many entangled chains rather than the internal modes of the individual chains that are rather short in our samples (MW ~ 10^5 and $qR_G < 1$). The surprising appearance of what would be considered hydrodynamic interactions at polymer concentrations as high as 55% and 65% and the reverse wave vector behavior from that observed in dilute solutions has recently been corroborated by neutron spin-echo measurements on poly(dimethylsiloxane) solutions.[18]

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Theory of Intrachain Reaction Rates in Entangled Polymer Systems

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ABSTRACT: We give the exact solution of a model of diffusion-controlled reactions in entangled polymer melts, based on reptation theory. In particular we focus on the end-to-end intrachain cyclization rate of functionalized polymer chains, anticipating that the same fluorescence spectroscopy techniques which have proven valuable in studies of dilute solutions will also be applied to the entangled regime. We express the cyclization rate "constant", $k_{\text{cyc}}(t)$, and the reaction rate, $R(t)$, in terms of a two-point Greens function or memory function and solve for this correlation function analytically, in the continuum limit, from the earthworm equations of Doi and Edwards. The full time dependence of the cyclization rate is given; the slow power law decay for $t \ll \tau_{\text{rep}}$ (where τ_{rep} is the fundamental reptation or tube disengagement time) is identified with compact exploration, and the exponential decay for $t \gg \tau_{\text{rep}}$ for noncompact exploration. We propose that results of the cyclization experiments for entangled polymer melts will provide a uniquely unambiguous test of reptation theory. In order to distinguish reptation from Rouse-like behavior, however, the experiment will have to be performed on a time scale near the crossover of the compact to noncompact regimes, $t \lesssim \tau_{\text{rep}}$. This requirement necessitates choosing special chromophores, with particularly long-lived excited states, for attachment to the polymer chain ends. The theory also allows for corrections to the universal decay curve for the reaction rate, derived on the basis of the *discrete* earthworm equations. Our earlier solution of these equations for *finite* chains shows that the corrections due to nonuniversality are small.

1. Introduction

The study of diffusion-controlled reactions in polymer solutions has led to a great deal of new information about polymer dynamics at the molecular level.[1] In particular fluorescence spectroscopy techniques have been used to measure the end-to-end cyclization rates of functionalized polymer chains, and the molecular weight dependence of the rate constant has been accurately determined.[2,3] The results are in good agreement with the elegant Wilemski–Fixman theory for internal relaxation times of polymer chains in solution.[4]

Much less work along these lines has been done for concentrated polymer systems in the entangled regime, mainly because of the experimental difficulty of measuring the much smaller reaction rates associated with the slower diffusion processes. However, the choice of special organic chromophores, with exceptionally long-lived triplet excited states, covalently attached to the ends of the polymer chains may make cyclization reactions observable in these systems.

Theoretically, the development of models for diffusion-controlled reactions in polymer melts is attractive because one does not have to deal with the intricacies of the excluded volume effect. Thus, although the experiments will be more difficult to carry out than for the case of dilute solutions, the theoretical interpretation should be more straightforward. In this paper we propose that measurement of the cyclization rate constant, k_{cyc}, and in particular its molecular weight dependence, will allow a uniquely unambiguous test of the reptation theory of Edwards[5] and de Gennes.[6] Such a test would be welcome at this time, because recent experimental and theoretical

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