Macromolecules 1993, *26*, 2433–2438

Quasielastic Light Scattering from Poly(dimethylsiloxane)/Poly(methyl methacrylate)/Chloroform under the Optical Θ Condition[†]

L. Giebel,[‡] M. Benmouna,[§] R. Borsali,[*,⊥] and E. W. Fischer[‡]

Max-Planck-Institut für Polymerforschung, P.O. Box 3148, D-6500 Mainz, FRG, Physics Department, University of Tlemcen, P.O. Box 119, Tlemcen, Algeria, and CERMAV–CNRS and Université Joseph Fourier, P.O. Box 53X, F-38041 Grenoble Cedex, France

Received November 3, 1992; Revised Manuscript Received February 1, 1993

ABSTRACT: Quasielastic light scattering data are reported for a symmetrical mixture of PDMS/PMMA/chloroform satisfying the optical Θ condition. The measurements are made for several polymer concentrations ranging from approximately the overlap concentration to below the critical concentration for phase separation. The data are analyzed using a simple theory based on the random phase approximation. The Rouse model is sufficient to fit qualitatively the data, showing that hydrodynamic interaction is screened in the investigated range of concentration.

Introduction

In a recent paper[1] quasielastic light scattering (QELS) data obtained from a blend of PDMS/PMMA (poly(dimethylsiloxane)/poly(methyl methacrylate)) in various solvents were reported. The solvents were tetrahydrofuran (THF), which is isorefractive with PDMS since the increment of refractive index $(\partial n/\partial c)_{\mathrm{PDMS}} \approx 0$; toluene, which is isorefractive with PMMA, $(\partial n/\partial c)_{\mathrm{PMMA}} \approx 0$; and chloroform ($CHCl_3$), having a refractive index intermediate between those of PDMS and PMMA, namely, $(\partial n/\partial c)_{\mathrm{PDMS}} \approx -0.045$ and $(\partial n/\partial c)_{\mathrm{PMMA}} \approx +0.063$ mL/g measured at a wavelength of 546 nm.[2] One notes that these values of the increment of refractive indices depend on various experimental conditions such as temperature, and therefore the effects due to these uncertainties may have significant implications, especially on the static scattering experiments.[2d] To ease the notation, we refer to PDMS as polymer A and PMMA as polymer B, and the quantities referring to the solvent will be designated by a subscript s. The measurements reported in ref 1 were made by keeping the pressure, the temperature, and the total polymer concentration constant and changing the composition of polymer A, $x = c_A/(c_A + c_B)$. The latter was varied practically from 0 to 1. The purpose was to obtain complementary information by changing the optical conditions and to study the properties of the eigenmodes such as their amplitudes and relaxation rates. Two main observations were made: first, for nearly symmetrical mixtures, the dynamics is governed by two processes. One is an interdiffusive process which describes the relaxation of the local composition fluctuations. The second is a cooperative mode describing the relaxation of the total polymer concentration. These two modes are not coupled and can be identified unambiguously. The second observation is that the data can be analyzed quite well using a simple random phase approximation (RPA) model in the whole range of composition, keeping the concentration constant below the critical concentration for phase separation c_k.

The purpose of this paper is to explore the effect of concentration on the dynamic scattering properties of PDMS/PMMA/$CHCl_3$, the pressure being fixed at 1 atm, the temperature at 30 ± 0.1 °C, and the composition x at approximately 0.5; the molecular weight of the two polymers is around 7.3×10^5. The reason for selecting this mixture for the investigation of the effects of concentration is clear: since it is approximately symmetric (similar molecular dimensions, similar polymer–solvent interactions, and $x \approx 0.5$) and the increments of refractive indices are approximately equal and of opposite signs, the so-called *optical Θ condition* is satisfied. In this case, the theory predicts[3,4] that only the interdiffusive mode should be observed and the intermediate scattering function $S(q,t)$ should decay following a single exponential whose relaxation rate gives access to valuable information on the effect of polymer concentration. This is particularly interesting since the system can be treated as a pseudobinary mixture of two polymers swollen by a common good solvent. Extensive information is available for pure polymer blends and can serve here as a guide for the data interpretation and for a clear identification of the effects of the low molecular weight solvent. To some extent, this investigation is complementary to the study of temperature effects in the miscibility range of pure polymer blends. By lowering the temperature (if one deals with a mixture with an upper critical solution temperature (UCST)), one increases the χ-parameter, reducing the compatibility of the two polymers. Likewise, if one increases the polymer concentration keeping the temperature constant, the spinodal line shifts downward, decreasing the region of miscibility of the system. It is worth noting that within the mean field approximation the critical parameter χ_c is given by $2/(\Phi N)$, where N is the degree of polymerization and $\Phi = c/\rho_0$ is the volume fraction of the polymer, ρ_0 being its density. This expression is, of course, good for a symmetrical mixture where both polymers differ only by their scattering lengths or refractive indices and a finite interaction parameter χ. Obviously, the mixture under investigation here is not rigorously symmetric, and it will be characterized by averaged quantities such as a degree of polymerization $N = (N_A + N_B)/2$ and a monomer density $\rho_0 = (\rho_{0A} + \rho_{0B})/2$, where ρ_{0A} and ρ_{0B} are the densities of monomers A and B, respectively.

Theoretical Background

The generalization of the RPA technique[5,6] to binary polymer solutions[7] and to polymer blends in the presence of solvent[3] is straightforward and has been successful[8–11]

[†] In memory of the late Latifa Ould-Kaddour.

[*] To whom correspondence should be addressed.

[‡] Max-Planck-Institut für Polymerforschung.

[§] University of Tlemcen.

[⊥] Université Joseph Fourier.

0024-9297/93/2226-2433$04.00/0

in describing the data in the conditions where the fluctuations are not strong.[4] In a symmetric pseudobinary mixture, one finds that the intermediate scattering function decays in time following a single-exponential function if the increments of refractive indices satisfy the so-called *optical Θ condition*

$$\left(\frac{\partial n}{\partial c}\right)_A = -\left(\frac{\partial n}{\partial c}\right)_B; \qquad x = 0.5 \tag{1}$$

Quasielastic light scattering measurements[1] were reported for the same system at the total polymer concentration $c = 1.33 \times 10^{-2}$ g/cm^3 as a function of the composition x varying from 0 (i.e., PDMS/chloroform) to 1 (i.e., PMMA/chloroform). The results have shown that the relative amplitude of the cooperative mode was less than 5% in the range of composition $0.3 < x < 0.7$ (see Figure 2 in ref 1). Therefore at $x = 0.5$, where the present experiments are performed, the intermediate scattering function $S(q,t)$ is expected to be monoexponential:

$$S(q,t) = S_I(q,t) = S_I(q)e^{-\Gamma_I(q)t} \tag{2}$$

The subscript I stands for the interdiffusive process. The static structure factor $S_I(q)$ was derived in a previous paper[12] as

$$S_I^{-1}(q) = \frac{4}{\Phi N P(q)} - 2\chi \tag{3}$$

where $P(q)$ is the form factor of the polymer chain, q is the amplitude of the wavevector ($q = (4\pi/\lambda)n \sin(\theta/2)$, where λ is the wavelength of the incident radiation, n is the index of refraction of the medium, θ is the scattering angle), and χ is the Flory interaction parameter[13] between the two polymers. One notes in particular that $S_I(q)$ does not depend on the polymer–solvent interaction as already shown by Fukuda et al.[14] The relaxation frequency $\Gamma_I(q)$ is obtained as follows:

$$\Gamma_I(q) = q^2 D_s\left[\frac{1}{P(q)} - \frac{\chi \Phi N}{2}\right] + q^2\frac{k_B T}{6\pi\eta\xi}F(q\xi) \tag{4}$$

η is the viscosity of the medium and D_s is the self-diffusion coefficient which can be identified as the single-chain diffusion coefficient in the medium of all other chains and the solvent. In the Rouse description, D_s becomes

$$D_s = \frac{k_B T}{N\zeta} \tag{5}$$

where the monomer friction coefficient ζ is assumed to be the same for both monomer species and may be a function of the polymer concentration, k_B is the Boltzmann constant, and T is the absolute temperature. If the dynamics of the single chain is governed by other mechanisms such as reptation, eq 5 should be modified appropriately.[5,15] For Gaussian chains, the form factor $P(q)$ can be represented by the Debye function, allowing R_g to depend on the concentration. For simplicity, however, we adopt the form suggested by Edwards[15]

$$P(q) = \left[1 + \frac{q^2 R_g^{\ 2}}{3}\right]^{-1} \tag{6}$$

Substituting this expression into eq 4 yields

$$\Gamma_I(q) = q^2 D_s\left[1 - \frac{\chi}{\chi_c}\right][1 + q^2\xi^2] + q^2\frac{k_B T}{6\pi\eta\xi}F(q\xi) \tag{7}$$

The critical parameter for spinodal decomposition χ_c has been defined earlier in the mean field approximation, and ξ, the correlation length for composition fluctuations, is related to the radius of gyration R_g by

$$\xi^2 = \frac{R_g^{\ 2}}{3[1 - (\chi/\chi_c)]} \tag{8}$$

The second term on the right-hand side (rhs) of eqs 4 and 7 describes the hydrodynamic or mode coupling interactions, which, in the framework of the Oseen tensor, is given by the Kawasaki function[15]

$$F(u) = \frac{3}{4}\frac{1 + u^2}{u^3}[u + (u^2 - 1)\tan^{-1} u] \tag{9}$$

In dilute polymer solution, this term is present because of long-range hydrodynamic interaction mediated by a low molecular weight solvent and away from the conditions of critical fluctuations. In the case of polymer mixtures near the critical temperature, a similar term is introduced due to mode coupling effects. In the interpretation of the present data, this term is included to describe both effects simultaneously. The aim of this paper is to analyze QELS data for the mixture PDMS/PMMA/CHCl$_3$, keeping the pressure and temperature constant and changing the total polymer concentration from the overlap threshold c^* to a concentration which is slightly below the critical limit for phase separation c_k.

Experimental Section

Materials and Sample Preparation. PMMA was obtained from Polymer Standards Service, Mainz, FRG, and PDMS was prepared at the Max-Planck-Institut für Polymerforschung. The molecular weights and the polydispersities are $M_w = 7.3 \times 10^5$ and $M_w/M_n = 1.13$ for PMMA and $M_w = 7.17 \times 10^5$ and $M_w/M_n = 1.4$ for PDMS. Several PDMS/PMMA/CHCl$_3$ solutions were prepared at the same composition, roughly $x \approx 0.5$, and at total polymer concentrations ranging from $c = 2.7 \times 10^{-3}$ g/cm^3 to $c = 16.2 \times 10^{-3}$ g/cm^3. Using the average molecular weight of the two polymers ($M_w = 7.24 \times 10^5$), the average radius of gyration $[\langle R_g^2\rangle^{1/2} = \{[R_{gA}^2 + R_{gB}^2]/2\}^{1/2}$, where R_{gA} and R_{gB} are equal to 583 and 427 Å, respectively (see Table I of ref 9)], and the approximate definition of the overlap concentration ($c^* = M_w/[(4/3)\pi R_g^3 N_{av}]$), one finds $R_g = 510$ Å and $c^* = 2.17 \times 10^{-3}$ g/cm^3. This means that all the concentrations investigated are in the semidilute range and below the critical concentration for phase separation, which is reached at $c_k \approx 18 \times 10^{-3}$ g/cm^3. The solutions were allowed to mix during 2 weeks and they filtered with 0.45-μm Millipore filters. The solutions were allowed to equilibrate for 1 week following filtration and prior to measurements.

Equipment and Data Analysis. The full homodyne autocorrelation function of the scattered intensity was obtained by using the ALV-5000 autocorrelator from ALV, Langen, FRG. The scattered light of a vertically polarized 647-nm krypton laser (Spectra-Physics 2020) was measured at different angles in the range 30–140° at the temperature $T = 30$ ● 0.1 °C. The intermediate scattering function $S(q,t)$ is related to the measured homodyne intensity function by the Siegert relation[16]

$$G^2(q,t) = B[1 + \beta|S(q,t)|^2] \tag{10}$$

where B is the base line and β is the spatial coherence factor depending upon the geometry of the detection. A constrained regularization method (Contin) developed by Provencher[17] was used to obtain the distribution $A(\tau)$ of decay times. A statistical parameter "probability to reject" is calculated for each solution, and the suggested one is that closest to 0.5.

$$\left[\frac{G^2(q,t)}{B} - 1\right]^{1/2} \approx \int_0^\infty A(\tau)e^{-(t/\tau)}\,d\tau \tag{11}$$

The analysis of the autocorrelation functions was performed with a DEC 3100 workstation. This method is now routinely used to analyze QELS data for polymer systems and allows the determination of the relaxation modes which characterize the dynamics of these systems.

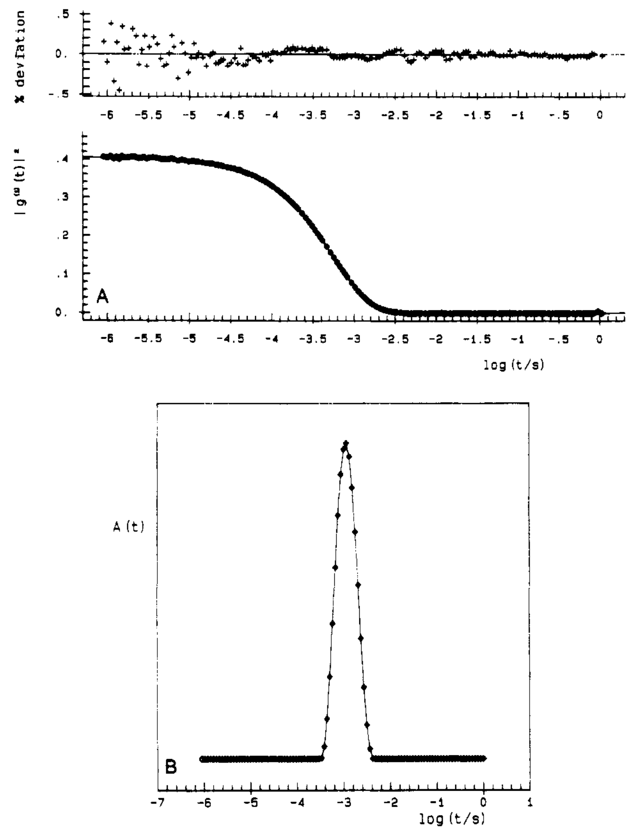

Figure 1. (A) Typical autocorrelation function as measured by QELS on the system PDMS/PMMA/CHCl$_3$ at T = 30 °C, θ = 50°, and $c = 5.6 \times 10^{-3}$ g/cm^3. The dots represent the experimental data, and the solid line is a monoexponential fit. (B) Relaxation time distribution obtained from Contin analysis for the same system as in (A).

Results and Discussion

A typical autocorrelation function obtained at the concentration $c = 5.6 \times 10^{-3}$ g/cm^3 and scattering angle $\theta = 50°$ is shown in Figure 1A. The dots represent the experimental data, and the solid line the monoexponential fit. This figure shows that $S(q,t)$ can be represented by a single exponential function as predicted by the theory in eq 2. In addition to the exponential fit, the Contin analysis was made for the same concentrations and angles. The result of this analysis, shown in Figure 1B, confirms the monoexponential decay. The same quality of fit (residuals < 0.5%) has been achieved for the corresponding binary systems, but the results are not reported here because it is not the aim of the paper. A similar treatment was repeated for all concentrations investigated and at each angle. In the range of high concentrations and scattering angles, there is a slight deviation from the monoexponential representation. A faster process with a relatively low amplitude appears indicating the emergence of a second mode which has not been analyzed in detail here. We only show an example of this behavior in Figure 2 for $c = 16.2 \times 10^{-3}$ g/cm^3 and $\theta = 110°$. In this case the attempt to describe the data with a single exponential results in systematic deviations which are illustrated in Figure 2A. A satisfactory description is achieved by using a two-exponential fit as shown in Figure 2B. The relaxation time distribution obtained from Contin analysis showed in Figure 2C and confirms the foregoing procedure by clearly resolving two modes. In all the cases where a second mode appears, its amplitude is smaller than about 5% of the total amplitude. Figure 3 represents the variation of the relaxation frequency $\Gamma_I(q)$ as a function of q^2 for the investigated concentrations. The continuous lines correspond to a theoretical fit with eq 7. In the fitting procedure D_s has been chosen in a way which will be described shortly, and χ/χ_c is considered as an adjustable parameter. The correlation length ξ has been deduced from fitting the full curves and in particular the upper q range where $\Gamma_I(q)$ deviates from a q^2 behavior.

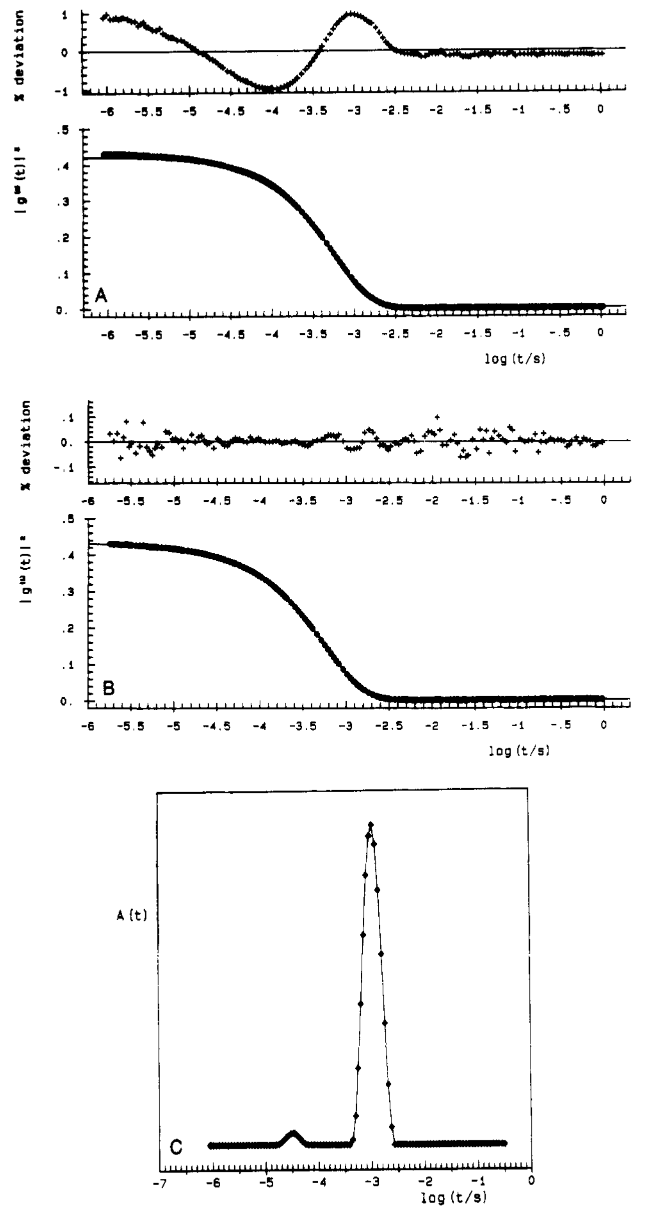

Figure 2. (A) Typical autocorrelation function as measured by QELS on the system PDMS/PMMA/CHCl$_3$ at T = 30 °C, θ = 110°, and $c = 16.2 \times 10^{-3}$ g/cm^3. The experimental data represented by the dots cannot be described by a single-exponential decay function. (B) Representation of the same data as in (A) with two exponentials. (C) The relaxation time distribution for the experimental data of (A) reveals an additional smaller contribution due to a faster mode.

The initial slopes of the curves $\Gamma_I(q)$ versus q^2 yield the diffusion coefficients $D_I(c)$. Its variation with concentration is displayed in Figure 4. The continuous line represents the theoretical prediction

$$\lim \frac{\Gamma_I(q)}{q^2}\bigg|_{q\to 0} = D_I(c) = D_s(c)\left[1 - \frac{\chi}{\chi_c}(c)\right] \tag{12}$$

where χ/χ_c is chosen as a fit parameter. It is found that the Rouse term is sufficient to account for the experimental behavior, and, therefore, the hydrodynamic term in eq 7 is disregarded. The data corresponding to PS/PDMS/

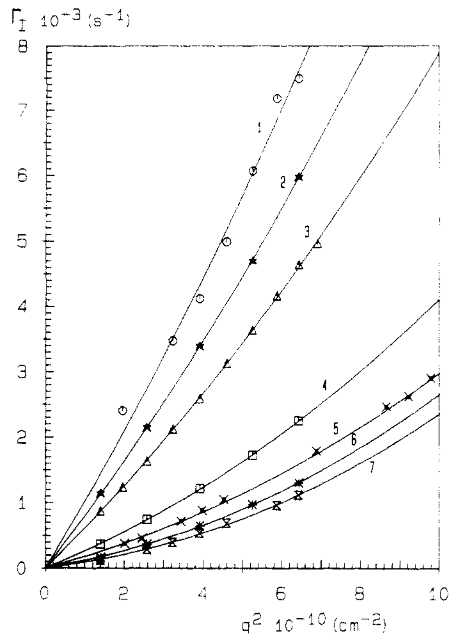

Figure 3. Variation of the relaxation frequency Γ_1 as a function of q^2 for different polymer concentrations. Curves 1–7 correspond to the following concentrations expressed in 10^{+3} g/cm^3: (1) 2.70; (2) 3.75; (3) 5.60; (4) 11.11; (5) 13.32; (6) 15.10; (7) 16.19. Curve 5 is included from ref 1 and was obtained at the wavelength λ = 488 nm.

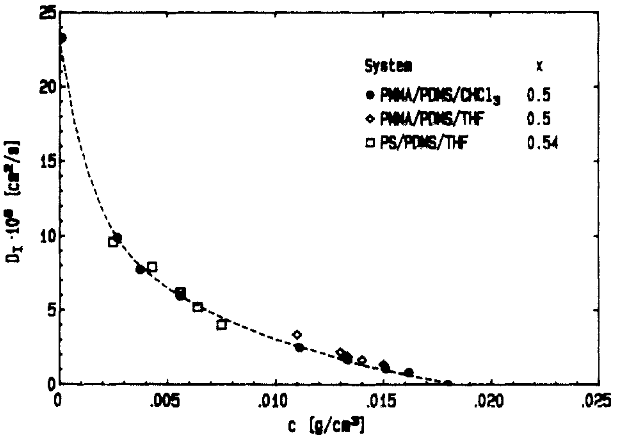

Figure 4. Variation of the interdiffusion coefficient D_I with the polymer concentration c for different systems: (●) PDMS/PMMA/CHCl$_3$; (◇) PDMS/PMMA/THF; (□) PS/PDMS/THF. The extrapolation to D_I = 0 gives c_k = 17.9 × 10^{-3} g/cm^3.

THF[19] and PDMS/PMMA/THF[9,20] are also included in this figure. All the data seem to lie on the same curve, showing that the type of solvents and the relative small differences in molecular weights of the samples are not sufficient to cause $D_I(c)$ to vary much in this range of concentration. For more compatible systems and other molecular weights, one may obtain a different variation of the interdiffusion coefficient.

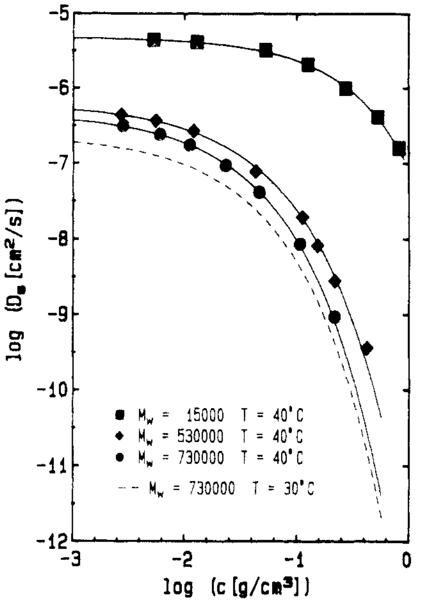

Figure 5. Concentration variation of D_s for the system PDMS/toluene[21] at T = 40 °C. The dotted line represents the system with M_w = 7.3 × 10^5 at T = 30 °C.

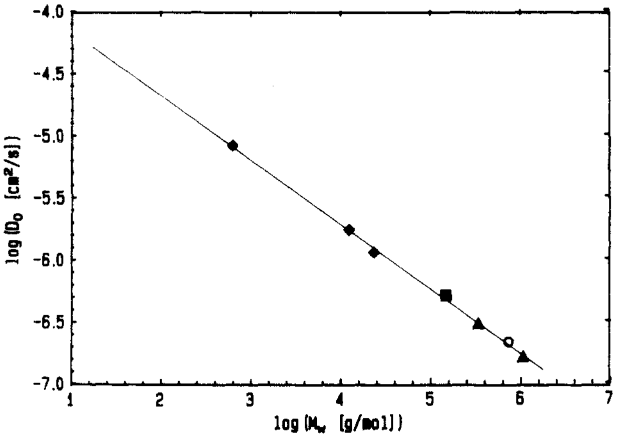

Figure 6. Variation of single-chain diffusion coefficient D_0 with the molecular weight for the system PDMS/toluene at T = 30 °C: (◆) ref 23a; (○) ref 23b; (▲) ref 23c. The open circle represents the system PMMA/toluene[20] at the same temperature.

With regard to the self-diffusion coefficient $D_s(c)$, there are extensive data describing its variation with the concentration.[21] These data are obtained by different techniques such as QELS, pulsed field gradient spin-echo NMR (PFG–NMR), forced Rayleigh scattering, etc. The main goal of these data is to derive the scaling behavior of D_s with the molecular weight and concentration and to determine the mechanism governing the diffusion of chains in dense media. Since there are no data in the literature concerning $D_s(c)$ for our system, our choice is guided by data available for a system which is sufficiently close to ours essentially in terms of molecular weight and concentration. In ref 21, one finds data obtained by PFG–NMR for several systems, and we selected in Figure 5 data corresponding to PDMS/toluene with three different molecular weights, the highest one being practically equal to the molecular weight of our samples. The concentration dependence $D_s(c)$ can be described quite well with the stretched exponential function as suggested by Phillies and co-workers[22]

$$D_s(c) = D_0 \exp[-uc^{\gamma}] \tag{13}$$

Since the continuous curves in Figure 5 are obtained at 40 °C, we deduce $D_s(c)$ for our system from the lower one assuming that γ and u are unchanged[22d] (i.e., u = 16.70, γ = 0.63 ± 0.06) and D_0 is slightly modified since the experiments are made at 30 °C. The resulting curve for $D_s(c)$ is represented by the dashed line in figure 5. The diffusion coefficient in the infinite dilute limit D_0 was also determined from data known in the literature.[23] In Figure 6 the variation of D_0 with the molecular weight M_w is plotted for the binary mixture PDMS/toluene[20] at 30 °C. D_0 for the binary solution PMMA/THF (open circle) with M_w = 7.3 × 10^5 is also included. One notes that the data

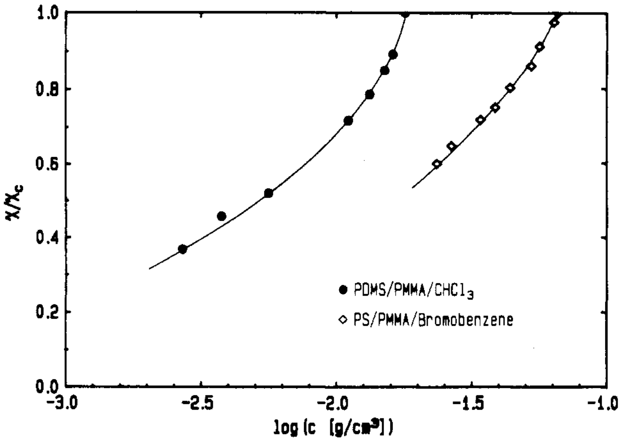

Figure 7. Variation of the ratio χ/χ_c with the total polymer concentration c. The filled circles represent the data for the system PDMS/PMMA/chloroform. The diamonds show the data of Fukuda et al.[14] for the system PS/PMMA/bromobenzene obtained from static light scattering.

lie on a single straight line represented by the following equation:

$$D_0 = 2.35 \times 10^{-4} M_w^{-0.52} \tag{14}$$

Assuming that the same data remain valid in chloroform and using the averaged molecular weight $M_w = 7.24 \times 10^5$, one obtains the following value of D_0 for the present mixture: 2.11×10^{-7} cm^2/s. Furthermore, the variation of D_s with concentration c can be used in eq 12 to obtain from the experimental values of $D_I(c)$ an estimate of the normalized interaction parameter χ/χ_c. The result is represented in Figure 7, showing that χ/χ_c is an increasing function of c and its extrapolation to 1 is reached at the critical concentration $c_k = 18 \times 10^{-3}$ g/cm^3, consistent with other data using static light scattering.[24] The critical concentration for phase separation c_k is found to depend on the molecular weight following the power law[24]

$$c_k = kM_w^{-0.58\pm0.03} \tag{15}$$

where k is a numerical factor which is slightly system dependent. For PS/PDMS/THF $k = 44.6$ and for our system $k = 45.3$.

In Figure 7, we have included data from Fukuda et al.[14] using static light scattering on the mixture PS/PMMA/bromobenzene. The critical parameter χ_c for these data is obtained from the extrapolation to the critical concentration c_k, i.e., $\chi_c = \chi(c = c_k)$. The comparison of the normalized interaction parameter with respect to its critical value is more reliable since it avoids using an expression for χ_c which may be too crude. One observes that the qualitative variation of χ/χ_c with c is approximately the same for both systems but the values corresponding to PS/PMMA are significantly smaller, which is expected since this mixture is much more compatible than PDMS/PMMA.

For high concentrations and angles $q\xi$ becomes larger than 1 and Γ_I deviates from the simple q^2 behavior. The fit of data with eq 7 enables us to determine the correlation length ξ, whose variation with concentration is displayed in Figure 8. As expected, one finds that ξ increases substantially with the polymer concentration and diverges at the critical value c_k. The extrapolation to $c = 0$ gives $\xi = 17.5$ nm, and using $\xi^2 = R_g^2/3$, one obtains a correlation length $\xi = 29.5$ nm with a radius of gyration of about 51 nm. One observes that the theoretical value overestimates the correlation length by a factor of 1.6. This numerical discrepancy is probably due to the fact that the extrapolation to $c \rightarrow 0$ can induce substantial errors because the investigated range of concentration is in the semidilute regime. Moreover, it should be kept in mind that the proportionality constant, 1/3, between ξ^2 and R_g^2 is only an approximation.

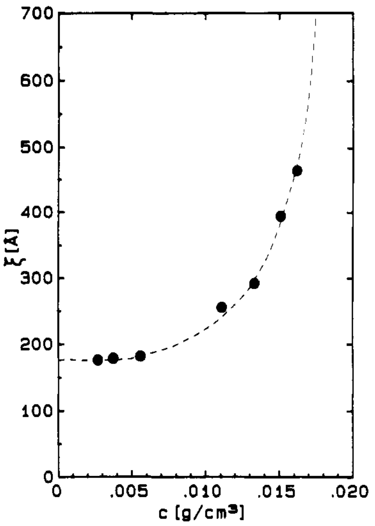

Figure 8. Variation of the correlation length ξ with the polymer concentration c. At $c = 17.9 \times 10^{-3}$ g/cm^3 the correlation length diverges.

Finally, it is interesting to note that recent dynamic light scattering measurements performed on dextran/poly(vinylpyrrolidone) (PVP) in water at different concentrations and compositions show that even when the optical Θ conditions (or the zero average contrast) are not satisfied, it is possible to have direct access to the concentration dependencies of the χ parameter and that of the self-diffusion coefficient D_s. The details of this investigation are reported in ref 25.

Conclusions

In this paper, we have investigated the dynamic scattering properties of the mixture PDMS/PMMA/CHCl$_3$ as a function of the polymer concentration covering the range from roughly c^* to slightly below c_k, the phase separation concentration. This mixture satisfies approximately the so-called *optical Θ condition* and represents a good candidate for exploring the dependence of the interdiffusive process upon the polymer concentration. Indeed, in this condition not only the interdiffusive process is completely decoupled from the cooperative process but the latter one disappears since its amplitude is vanishingly small.

Although this system satisfies only approximately the optical Θ condition, one finds that the theoretical prediction of a single-exponential decay for the intermediate scattering function is verified, except in the high range of concentrations and scattering angles where a second mode appears. The relaxation rate of the scattering function seems to be in good agreement with the theory, and the Rouse model is sufficient to describe the data. The fact that hydrodynamic interaction is screened and that the mean field approximation is good in the range of concentration explored was also observed elsewhere for other systems.[8–11,26] Nevertheless, a more detailed experimental investigation using different mixtures and a larger concentration range is necessary to draw a definite conclusion concerning both hydrodynamic interaction and deviations from the mean field approximation.

Acknowledgment. We thank the referees for very useful comments which helped to clarify many issues raised in this investigation. M.B. and R.B. would like to acknowledge the support of the Max-Planck-Gessellschaft and the hospitality of the Max-Planck-Institut für Polymerforschung, Mainz, where this work was performed.

References and Notes

(1) Giebel, L.; Borsali, R.; Fischer, E. W.; Benmouna, M. *Macromolecules* **1992**, *25*, 4378.

(2) (a) Ould-Kaddour, L. Ph.D. Thesis, University of Strasbourg Louis Pasteur, 1988. (b) Ould-Kaddour, L.; Strazielle, C. *Polymer* **1987**, *28*, 459. (c) Anasagasti, M.; Katime, I.; Strazielle, C. *Makromol. Chem.* **1987**, *188*, 201. (d) Kent, M. S.; Tirrell, M.; Lodge, T. P. *Polymer* **1991**, *32*, 314.

(3) Benmouna, M.; Benoît, H.; Duval, M.; Akcasu, A. Z. *Macromolecules* **1987**, *20*, 1107.

(4) (a) Roby, F.; Joanny, J. F. *Macromolecules*, in press. (b) Akcasu, A. Z.; Nägele, G.; Klein, R. *Macromolecules* **1991**, *24*, 4408.

(5) de Gennes, P.-G. *Scaling Concepts in Polymer Physics*; Cornell University Press: Ithaca, NY, 1979.

(6) Akcasu, A. Z. In *Dynamic Light Scattering*; Brown, W., Ed.; Oxford University Press: Oxford, 1993.

(7) Jannink, G.; de Gennes, P.-G. *J. Chem. Phys.* **1968**, *48*, 2260.

(8) Borsali, R.; Duval, M.; Benmouna, M. *Macromolecules* **1989**, *22*, 816.

(9) Giebel, L.; Borsali, R.; Fischer, E. W.; Meier, G. *Macromolecules* **1990**, *23*, 4054.

(10) Daivis, P. J.; Pinder, D. N.; Callaghan, P. T. *Macromolecules* **1992**, *25*, 170.

(11) Aven, M. R.; Cohen, C. *Macromolecules* **1990**, *23*, 476.

(12) (a) Benmouna, M.; Fischer, E. W.; Ewen, B.; Duval, M. *J. Polym. Sci., Polym. Phys. Ed.* **1992**, *30*, 1157. (b) Benmouna, M.; Borsali, R. *C. R. Acad. Sci. Paris* **1992**, *314*, Série II, 759.

(13) Flory, P. *Introduction to Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1965.

(14) Fukuda, T.; Nagata, M.; Inagaki, H. *Macromolecules* **1986**, *19*, 1411.

(15) Doi, M.; Edwards, S. F. *Dynamic Theory of Polymer Solutions*; Oxford University Press: Oxford, 1986.

(16) Siegert, A. J. F. *MIT Rad. Lab. Rep.* **1943**, *No. 465*.

(17) (a) Provencher, S. W.; Hendrix, J.; De Maeyer, L.; Paulussen, N. J. *J. Chem. Phys.* **1978**, *69*, 4273. (b) Provencher, S. W. *Makromol. Chem.* **1979**, *180*, 201. (c) Provencher, S. W. *Comput. Phys. Commun.* **1982**, *27*, 213. (d) Provencher, S. W. *Comput. Phys. Commun.* **1988**, *21*, 214.

(18) Borsali, R.; Duval, M.; Benmouna, M. *Polymer* **1989**, *30*, 610.

(19) Borsali, R.; Duval, M.; Benoît, H.; Benmouna, M. *Macromolecules* **1987**, *20*, 1112.

(20) Giebel, L. Ph.D. Thesis, Mainz, 1993.

(21) Skirda, V. D.; Sundukov, A. I.; Maklakov, A. I.; Zgadzai, O. E.; Gafrurov, I. R.; Vasiljev, G. I. *Polymer* **1988**, *29*, 1294.

(22) Phillies, G. D. J.; Ullmann, G. S.; Ullmann, K.; Lin, T.-H. *J. Chem. Phys.* **1985**, *82*, 5242. (b) Phillies, G. D. J.; *Macromolecules* **1986**, *19*, 2367. (c) Phillies, G. D. J. *Macromolecules* **1987**, *20*, 558. (d) Phillies, G. D. J.; Ahmed, S.; Li, L.; Xu, Y.; Rostcheck, D.; Cobb, M.; Tanaka, T. *Macromolecules* **1991**, *24*, 5299.

(23) Edwards, C. J. C.; Bantle, S.; Burchard, W.; Stepto, R. F. T.; Semlyen, J. A. *Polymer* **1982**, *23*, 873. (b) Aven, M. R. Ph.D. Thesis, Cornell University, 1989. (c) Haug, A.; Meyerhoff, M.; *Macromol. Chem.* **1962**, *53*, 91.

(24) Ould-Kaddour, L.; Strazielle, C. *New Trends in Physics and Physical Chemistry*; Lee, L.-H., Ed.; Plenum: New York, 1989.

(25) Desbrières, J.; Borsali, R.; Rinaudo, M.; Milas, M. *Macromolecules*, in press.

(26) Ferry, J. D. *Viscoelastic Properties of Polymers*, 3rd ed.; Wiley: New York, 1980.