Dynamic Light Scattering from PDMS/PMMA/Solvent: Effect of Optical Properties

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ABSTRACT: Quasi elastic light scattering (QELS) experiments have been performed on PDMS/PMMA mixtures in three different solvents: (i) THF, isorefractive with PDMS; (ii) toluene, isorefractive with PMMA; (iii) chloroform, having a refractive index intermediate between those of PDMS and PMMA. The experiments were made at one total polymer concentration c_T, in the semidilute range ($c_T > c^*$). Two relaxation modes have been found in THF and in toluene, in the whole investigated range of compositions $x = c_{PMMA}/c_T$, $0 < x < 1$. In chloroform, however, the effect of composition shows two different behaviors depending on the value of x. For x about 0.5, a single relaxation is observed whereas, for the values of x different from 0.5, two exponential relaxations are recovered. All these results are in good agreement with the theoretical predictions based on the random phase approximation (RPA).

Introduction

In an earlier paper,[1] experimental results were reported describing the dynamic behavior of the PDMS/PMMA/THF system using the QELS technique. THF is a good solvent for both polymers and is isorefractive with PDMS. Two relaxation modes characterized the autocorrelation function in the whole range of composition x ($0 < x < 1$). These two dynamic processes are interpreted as follows: The first one represents the total polymer concentration fluctuations and is referred to as the cooperative mode. It has an amplitude A_C and a diffusion coefficient D_C such that the corresponding frequency is $\Gamma_C = q^2 D_C$. The second one describes the relaxation of the composition fluctuations and is known as the interdiffusive mode. It is characterized by the amplitude A_I and the coefficient diffusion D_I. The variations of the amplitudes (A_C, A_I) and the diffusion coefficients (D_C, D_I) of these two processes were found in good agreement with theoretical predictions.[2] Indeed, it has been shown that in any ternary mixtures of two polymers in solvent, the dynamic scattering function $S(q,t)$ is a sum of two exponentials:

$$S(q,t) = A_C e^{-q^2 D_c t} + A_I e^{-q^2 D_I t} \tag{1}$$

where t is the time and $q = (4\pi n/\lambda) \sin (\theta/2)$ (λ is the wavelength of the incident radiation, θ is the scattering angle, and n is the refractive index of the medium.

Using the RPA, this model has explained several experimental results: two homopolymers in solution[3-7] and diblock copolymer-solvent[8-11] systems.

Since we are essentially interested in the study of optical conditions on the measured scattering intensity $I(q,t)$, it is useful to recall that the latter is in general expressed as follows:

$$I(q,t) = \left[\frac{\partial n}{\partial c}\right]_1^2 S_{11}(q,t) + \left[\frac{\partial n}{\partial c}\right]_2^2 S_{22}(q,t) + \left[\frac{\partial n}{\partial c}\right]_1 \left[\frac{\partial n}{\partial c}\right]_2 [S_{12}(q,t) + S_{21}(q,t)] \tag{2}$$

where $S_{ij}(q,t)$ are the partial dynamic structure factors and $(\partial n/\partial c)_i$ is the increment of refractive index of polymer i.

It is common in dynamic light scattering (DLS) experiments on ternary mixtures to choose a solvent which is isorefractive with one of the polymers, i.e. $(\partial n/\partial c)_i = 0$ (i = 1 or 2). This choice allows for an easier interpretation of the relaxation processes than it does in the case of an arbitrary solvent. Besides this case, there is another interesting situation where the average scattering length (in neutron scattering) or refractive index (in light scattering) of the two polymers matches exactly the scattering length or the refractive index of the solvent. This is the so-called "zero average contrast" condition (ZAC) expressed by the equation

$$x\left[\frac{\partial n}{\partial c}\right]_1 + (1-x)\left[\frac{\partial n}{\partial c}\right]_2 = 0 \tag{3}$$

where x is the composition of polymer 1. Under these conditions, and at $x = {}^1/_2$, only one relaxation mode should be observed. The second mode disappears because its amplitude is zero ($A_C = 0$). Recent experiments have been carried out using the neutron spin echo (NSE) technique by Jannink et al.[5] on a mixture of ordinary and deuterated PDMS chains in a mixture of deuterated and ordinary toluene and by Borsali et al.[3] using QELS on the PS/PDMS/toluene system,[3] where the ZAC is fulfilled and the dynamic structure factor $S(q,t)$ is governed by only one relaxation process: the interdiffusion mode.

In this paper we are mainly concerned with the effect of optical conditions on the dynamic behavior of the PDMS/PMMA/solvent system. We report new data obtained using QELS for the same polymer blend in two different solvents. In toluene, which is isoreractive with PMMA, we obtained results similar to those in THF. The other solvent is chloroform, for which the increments of refractive indices of both polymers are approximately equal and of opposite signs. In this case it is possible to satisfy the condition of ZAC (eq 3). Following our earlier work, we have investigated the effect of composition $x = C_{PMMA}/C_T$ on the amplitude and the frequencies (diffusion coefficients) for the same total polymer concentration C_T which was used in the PDMS/PMMA/THF system,[1] where C_T was roughly $5C^*$. If M_w denotes the molecular weight of the polymer and R_g its radius of gyration, C^* is defined as $C^* = 3M_w/4\pi R_g{}^3$.

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Table I
Properties of Polymer Samples

sample	$10^{-3}M$	$I = M_w/M_n$	R_g, Å	$10^{-4}A_2$, mol cm^3 g^{-2}
PMMA	730	1.13	371[a]	2.40[a]
PDMS	717	1.40	427[b]	2.75[c]

[a] From static light scattering measurements (PMMA/THF). [b] $R_g = (0.15 \pm 0.01)M_w^{0.59\pm0.01}$.[16] [c] $A_2 = (80 ● 3) \times 10^{-4}M_w^{-0.25\pm0.01}$.[16]

Experimental Section

Materials and Sample Preparation. PMMA was obtained from Polymer Standards Service, Mainz, FRG, and PDMS was prepared in our laboratory. The characteristics of these polymers are given in Table I. The weight-average molecular weight M_w, the radius of gyration R_g, and the second virial coefficient A_2 of PMMA were determined by static light scattering measurements on THF. Those values for PDMS were calculated from the literature. Several PMMA/PDMS/THF solvents solutions were prepared at the same total polymer concentration $C_T = 1.33 \times 10^{-2}$ g cm^{-3} in the range of composition $x = C_{PMMA}/C_T$ ($0.1 < x \leq 1$). The solutions were allowed to mix during 3 weeks. They were filtered with 0.45-μm, Millipore filters. Solutions were allowed to equilibrate for a few days following filtration and prior to measurements. The homogeneity of the solutions was tested by classical light scattering.

Equipment and Data Analysis. The full homodyne correlation function of the scattered intensity defined on 1023 channels was obtained by using the ALV-3000 autocorrelator from ALV, Langen, FRG. The scattered light of a vertically polarized 4880-Å argon laser (Spectra-Physics 2020) was measured at several angles in the range 30–140° at the temperature $t = 30.0 \pm 0.1$ °C. The total intermediate scattering function $S_T(q,t)$ is related to the measured homodyne intensity autocorrelation function $G^{(2)}(q,t)$ by the Siegert relation.[12]

$$G^{(2)}(q,t) = B(1 + \alpha|S_T(q,t)|^2) \tag{4}$$

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

$$\left[\frac{G^{(2)}(q,t)}{B} - 1\right]^{1/2} = \int_0^\infty A(\tau)e^{-(t/\tau)}\,d\tau = S(q,t) \tag{5}$$

The analysis of the autocorrelation functions was made with a DEC 3100 workstation.

Results

The experiments were performed at several angles between 30 and 140° at one total polymer concentration, namely $C_T = 1.33 \times 10^{-2}$g cm^{-3} and a temperature $t = 30$ °C for $0 \leq x \leq 1$.

(a) PMMA/PDMS/Toluene. In these experiments we have a direct access to the signal due to PDMS, namely $S_{22}(q,t)$ which is found to be a superposition of two exponential functions. The diffusion coefficients for this system show similar behavior with the composition as it does in the case of THF. This is illustrated in Figure 1 where the data are represented by open circles for the PDMS/PMMA/THF system, diamonds for the PDMS/PMMA/toluene system, and filled squares for the PDMS/PMMA/CHCl$_3$ system. We observe that D_C is independent of x whereas D_I shows the predicted behavior as illustrated by the solid line which represents the theoretical curve.

As for the amplitudes of these two relaxation processes, we have plotted in Figure 2 the variations of the relative amplitude of the cooperative mode. The data are represented by the same symbols as in Figure 1, and the solid line corresponds to the best fit according to relation 13 of ref 1 where x should be replaced by $(1 - x)$ and vice versa. From this figure, it is clear that the two curves for THF and toluene are approximately symmetric with respect to $x = 0.5$.

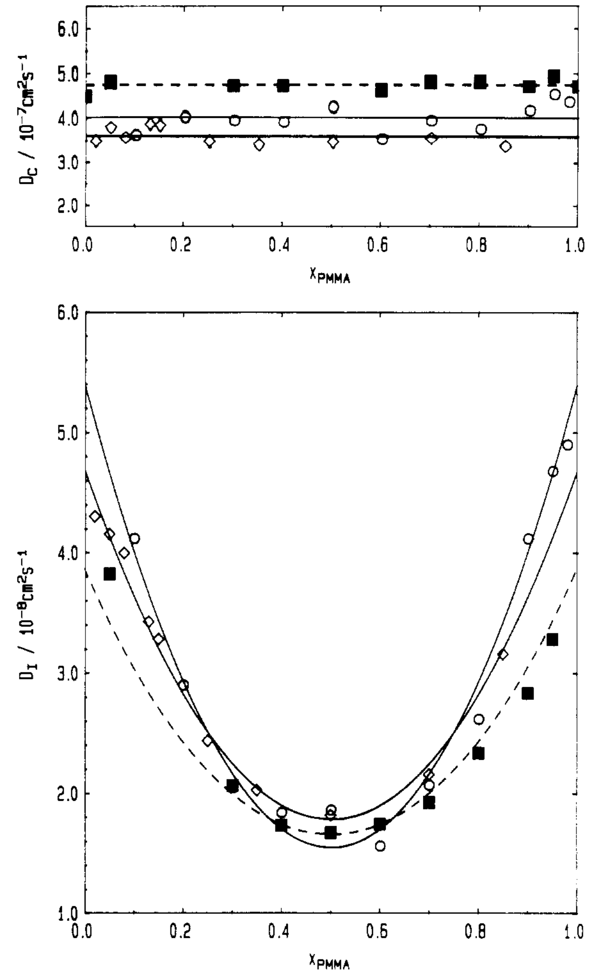

Figure 1. Diffusion coefficients as a function of the polymer composition: (○) PDMS/PMMA/THF; (◇) PDMS/PMMA/Toluene; (■) PDMS/PMMA/chloroform. The continuous lines represent theoretical curves. This figure shows that the cooperative diffusion coefficients D_C (horizontal lines) are independent of x and the diffusion coefficient of the interdiffusion process D_I follows the predicted parabolic behavior $x(1 - x)$.

(b) PDMS/PMMA/Chloroform. Since the increments of refractive indices in this system are such that

$$(\partial n/\partial c)_1 \approx -(\partial n/\partial c)_2 \tag{6a}$$

eq 2 shows that the dynamic scattering intensity becomes

$$I(q,t) = (\partial n/\partial c)_1^2 S_I(q,t) \tag{6b}$$

where $S_I(q,t)$ is defined as

$$S_I(q,t) = S_{11}(q,t) + S_{22}(q,t) - S_{12}(q,t) - S_{21}(q,t) \tag{6c}$$

For an arbitrary composition x, one shows that $S_I(q,t)$ is a superposition of two exponential decay modes. For $x = 1/2$, eq 3 corresponds to the zero average contrast (ZAC) condition (see eq 2) and $S_I(q,t)$ is given by a single exponential function corresponding to the interdiffusive mode which means that the amplitude of the cooperative mode is zero. In fact, one obtains a single exponential mode for $0.4 < x < 0.6$ as it will be discussed shortly after.

A typical intensity autocorrelation function obtained from the ternary mixture PDMS/PMMA/chloroform at $x = 0.05$ and $\theta = 50°$ is displayed in Figure 3a. The dots represent the experimental data, and the solid line represents a monoexponential fit. This figure clearly shows

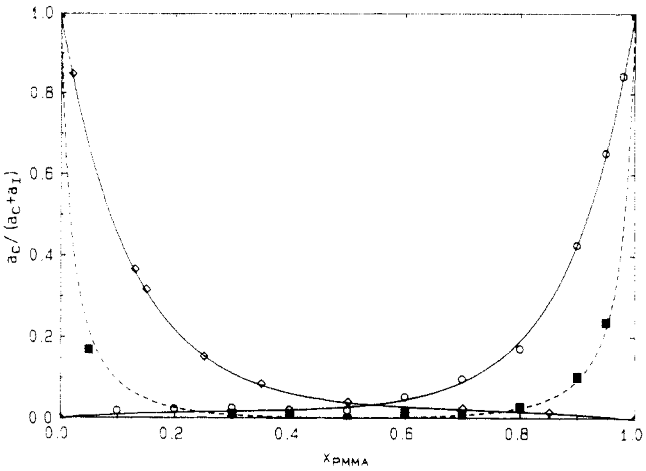

Figure 2. Relative amplitude of the cooperative mode $a_C/(a_C + a_I)$ for the three mixtures indicated in Figure 1 and using the same symbols. The continuous lines are the theoretical curves.

an unsatisfactory monexponential fit. Therefore we analyzed the data with two exponential functions and indeed a good agreement was found, as shown in Figure 3b. Moreover, CONTIN analysis was also made and confirmed clearly the existence of two relaxation processes. This behavior is illustrated in Figure 3c. Exploring the range of composition $0 < x < 1$ shows that the autocorrelation function is characterized by a single exponential in the range $0.4 < x < 0.6$. In Figure 4a,b, we have represented the autocorrelation function and the CONTIN analysis for $x = 0.5$ and $\theta = 50°$. The solid line in Figure 4a represents a satisfactory monoexponential fit which is confirmed by the existence of one peak in the CONTIN analysis (Figure 4b).

Discussion and Conclusions

The main results of this paper are summarized in Figures 1 and 2. The first one collects all the data for the diffusion coefficients D_C and D_I as a function of composition x for the three different solvents. The second describes the variations of the relative amplitude of the fast cooperative mode also for the three solvents. In both figures the following symbols are used: THF (○), toluene (◇), and chloroform (□). The general observation from these results is that the agreement with the theory is quite satisfactory for arbitrary compositions. The results for the solvent THF were already discussed in detail in ref 1. The results for toluene were not reported before, but they can be analyzed using the same procedures as for THF essentially replacing x by $(1 - x)$. A detailed investigation of these three ternary mixtures was performed in ref 13. Here we would like to focus more on the case of chloroform corresponding to ZAC conditions. For $0.4 < x < 0.6$, the amplitude of the cooperative mode is vanishingly small and therefore the dynamics are described by the interdiffusion mode. For x outside of this range, two relaxation modes characterize the autocorrelation functions of the mixture. The dashed line represents the best fit using eqs 2, 3, 13, and 17 of ref 1 where the parameters $\chi\phi N$ and $v\phi N$ are adjusted to the following values:

$$(v\phi N)_{\text{chlo}} = 11.24$$

$$(\chi\phi N)_{\text{chlo}} = 1.14$$

The quantities v, χ, ϕ, and N represent the excluded volume parameter, the Flory–Huggins interaction parameter, the polymer number concentration, and the degree of polymerization, respectively.

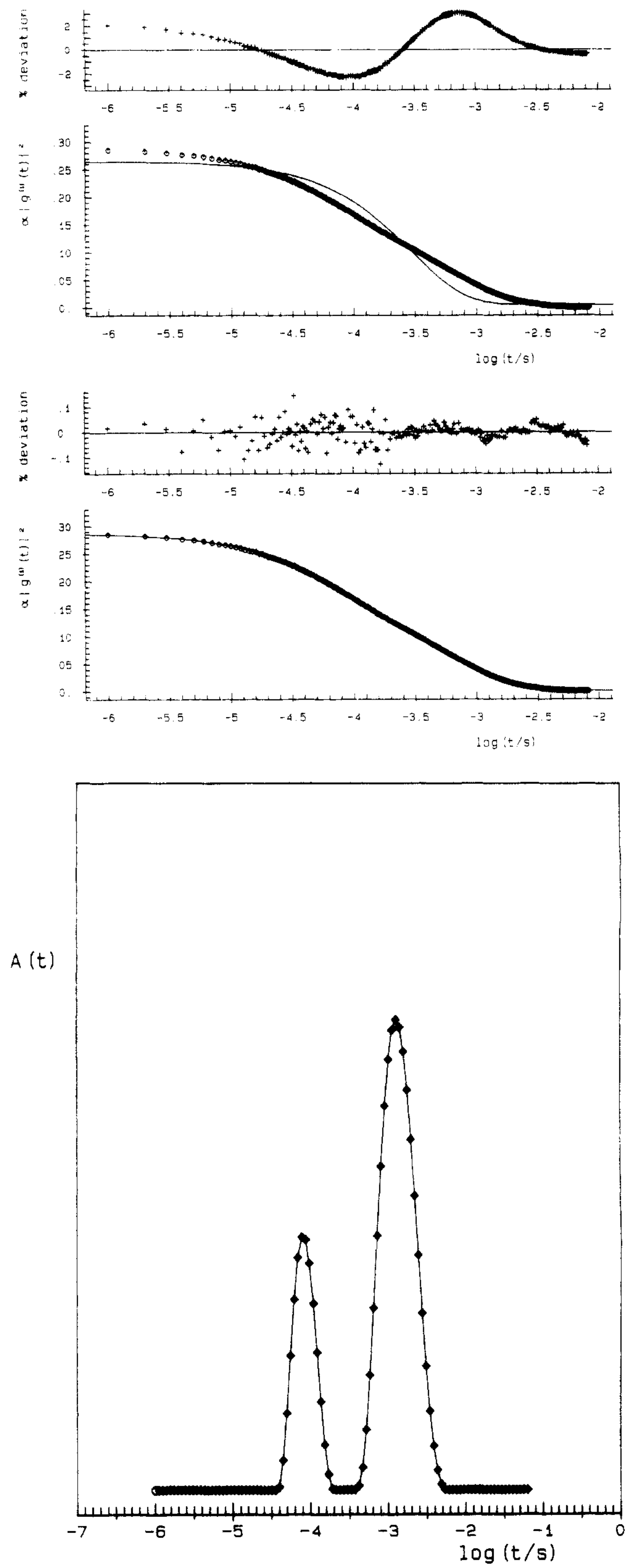

Figure 3. Typical autocorrelation function as measured by QELS on PDMS/PMMA/chloroform at $T = 30$ °C, $c_T = 1.33 \times 10^{-2}$ g cm^{-3}, $x = 0.05$, and $\theta = 50°$. The dots represent the experimental data and the solid line (a) a single exponential fit and (b) a double exponential fit. (c) Relaxation–time distribution obtained from CONTIN for PDMS/PMMA/chloroform under the same conditions as in (a) and (b).

A similar procedure has been used to evaluate the interaction parameters v and χ for the mixture PDMS/

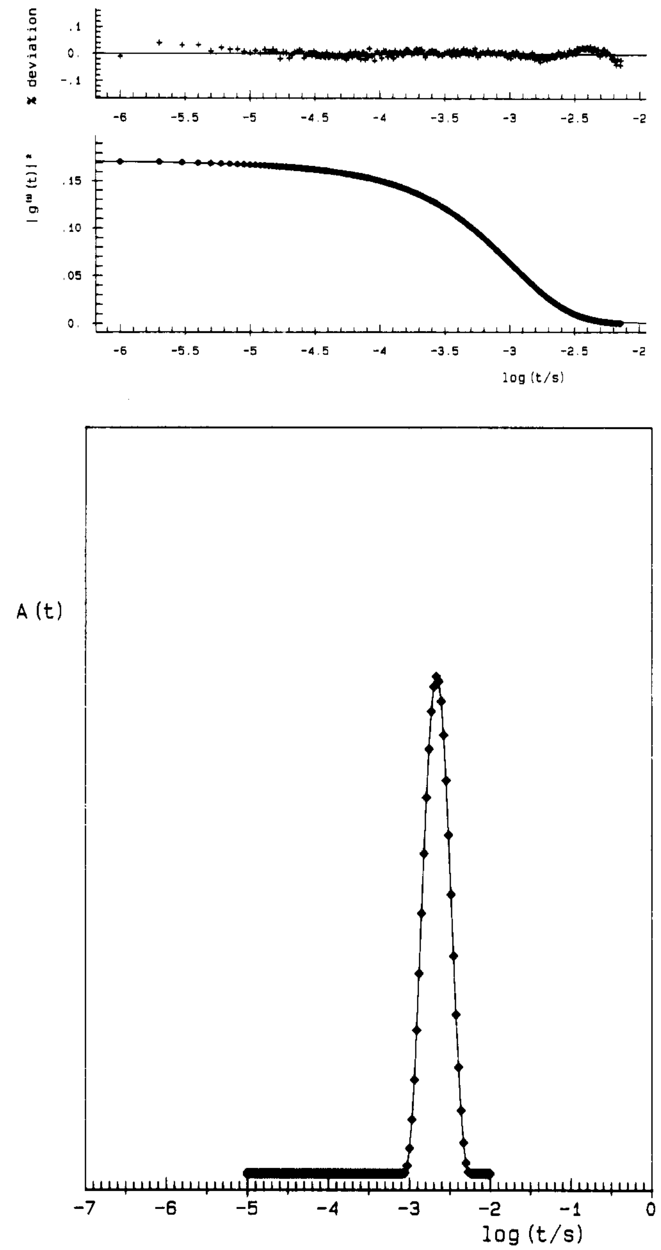

Figure 4. Typical autocorrelation function as measured by QELS on PDMS/PMMA/chloroform at $T = 30$ °C, $c_T = 1.33 \times 10^{-2}$ g cm^{-3}, $x = 0.5$, and $\theta = 50°$. (a) The dots represent the experimental data and the solid line a single exponential fit. (b) Relaxation-time distribution obtained from CONTIN for PDMS/PMMA/chloroform under the same conditions.

PMMA in toluene and THF, and the results are

$$(v\phi N)_{\text{tol}} = 7.21 \qquad (v\phi N)_{\text{THF}} = 7.85$$

$$(\chi\phi N)_{\text{tol}} = 1.32 \qquad (\chi\phi N)_{\text{THF}} = 1.50$$

One notes that Anasagasti and Strazielle[14] performed static light scattering experiments on the same polymer blend in chloroform and obtained approximately the same values as the ones reported here for chloroform within experimental error.

As far as the diffusion coefficients of the two processes are concerned, they are reported in Figure 1 as a function of composition for the three solvents. The D_C values are x-independent for all solvents

$$D_C = D_S(1 + v\phi N) \qquad (7)$$

The fit of the data with the theory yields values of $v\phi N$ which are slightly higher for chloroform. This is consistent with the values of the second virial coefficients reported in the literature.[14-16] One notes that this difference is also due to the fact that the thermodynamic quality of the three solvents is not exactly the same. The data for the interdiffusion coefficients represented in Figure 1b are also in agreement with the theoretical prediction:

$$D_I = D_S[1 - 2x(1 - x)\chi\phi N] \qquad (8)$$

where D_S and $\chi\phi N$ were adjusted to the following values in order to get the best fit: $D_S = 5.4 \times 10^{-8}$ cm^2 s^{-1} and $\chi\phi N = 1.46$, 4.7×10^{-8} cm^2 s^{-1} and $\chi\phi N = 1.41$, and 3.9×10^{-8} cm^2 s^{-1} and $\chi\phi N = 1.23$ in THF, toluene, and chloroform, respectively. It is interesting to note that D_S is comparable to the slow mode diffusion coefficient observed in certain cases of binary polymer/solvent mixtures.[17-20] Furthermore, the investigation of this ternary system (i.e. PMMA/PDMS/chloroform) was limited here to one polymer concentration which was chosen in the semidilute range. It has been shown that it is possible to have direct access to the interaction parameter χ and, consequently, it can be used to measure accurately this parameter χ as a function of concentration and temperature using QELS. Such measurements are currently under progress, and the results will be reported later.

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Registry No. PMMA, 9011-14-7; THF, 109-99-9; TOL, 108-88-3; chloroform, 67-66-3.