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Quasi-Elastic Light Scattering from Ternary Mixtures of Polystyrene/Poly(dimethylsiloxane)/Solvents

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ABSTRACT: Ternary mixtures of polystyrene/poly(dimethylsiloxane)/tetrahydrofuran (PS/PDMS/THF) and PS/PDMS/toluene were investigated by quasi-elastic light scattering experiments. In THF, the increment of refractive index of PDMS is practically zero, and one "sees" only the PS. One obtains two relaxation modes which are characterized unambiguously for concentration around c^*. In toluene, which is a solvent with "zero average contrast", only one relaxation mode has been observed. This is in perfect agreement with theoretical predictions published earlier. It shows that in many cases the presence of two modes is normal, and artifacts or special dynamical features do not have to be invoked.

I. Introduction

In recent years, there has been a growing interest on the dynamic properties of polymer mixtures in bulk and in solution.[1-7] Most of the works published in the literature dealt with compatible (such as polystyrene/poly(vinyl methyl ether) (PS/PVME))[8-11] or slightly incompatible (such as polystyrene/poly(methyl methacrylate) (PS/PMMA))[12-15] mixtures in solvents presenting no contrast with one of the polymers. The idea is that, when one polymer is not "visible", the dynamics of the only visible polymer is observed and the interpretation is easier. At infinite dilution of the visible polymer, one observes its self-diffusion coefficient at a finite concentration of the other polymer, i.e., in a matrix which is a solution of the invisible polymer. These studies were limited to the determination of the scaling laws of the self-diffusion coefficient as a function of the molecular weight of the visible polymer and the concentration of the matrix. All the reported experiments dealt with a system far from the "cloud point" or the phase separation concentration.

In this work, since we have at our disposal a theory[4] which allows us to envisage all the experimentally possible cases, we have focused our attention on the following points:

(i) In ternary systems, two modes characterize the time evolution of the intermediate scattering function, $S(q,t)$, given by

$$S(q,t) = A_c e^{-\Gamma_c t} + A_I e^{-\Gamma_I t} \qquad (1)$$

q is the scattering wavevector ($q = (4\pi/\lambda_0)n_0 \sin(\theta/2)$), λ_0 is the wavelength of the incident radiation, θ is the

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scattering angle, n_0 is the index of refraction of the medium, and t is the time. The theory gives expressions for the amplitudes (A_c and A_I) and the frequencies (Γ_c and Γ_I) as a function of various parameters characterizing the system. Even in the case where only component 1 is visible, $S(q,t)$ is given by

$$S(q,t) = S_{11}(q,t) = (\partial n/\partial\varphi)_1^{\,2}(a_c e^{-\Gamma_c t} + a_I e^{-\Gamma_I t}) \qquad (2)$$

where $(\partial n/\partial\varphi)_1$ is the increment of refractive index of polymer 1 and φ is its total volume fraction; Γ_c and Γ_I are independent of the optical conditions. This means that the case $(\partial n/\partial\varphi)_2 = 0$ is not as advantageous as claimed, because the response depends also on the dynamics of the second polymer.

(ii) There are two main relaxation mechanisms among which one disappears when a solvent with "zero average contrast" is used. Therefore, it is of particular interest to work in these conditions for a precise determination of the other relaxation time. In this paper we do not want to use the terminology introduced by Tanaka and Inagaki,[16] calling the solvent of "zero average contrast" the "optical Θ solvent". The reason is that this denomination is not clear and implies that it has something to do with thermodynamical properties.

(iii) The theory predicts a slowing down of one of the relaxation mechanisms when the spinodal concentration is approached. Even if it is experimentally difficult to reach the spinodal, it is possible to explore the trend of this relaxation time by increasing the concentration toward the "cloud point". In order to achieve our goal, we have chosen the system PS/PDMS because it is easy to find a solvent which satisfies the condition of zero average contrast. This system has not been used by other experimentalists because of the limited concentration domain where the solution is stable. Since this polymer couple is more incompatible than PS/PMMA, for example, a large range of concentration cannot be explored. This is a major drawback when one is interested in the scaling relations between diffusion coefficients and molecular weight or concentration. To our knowledge, this is the first time that such a system is investigated by quasi-elastic light scattering. Recently, a detailed experimental analysis has been performed by static light scattering on this system in our laboratory.[17] These results will be useful for the interpretation of the dynamical experimental data. In order to explain why and how we made the experiments, we present first a brief account of the theory in the first section. Among the equations given in ref 4, we recall those that are useful here. We adjust the parameters to match our experimental conditions. This makes possible a clear and hopefully convincing comparison between theory and experiments. In the second part, we present the Experimental Section with the sample preparation, equipment, and the procedure for data analysis. In the last section, we present the results and discuss their interpretation.

II. Theoretical Section

In ref 4, the general expressions of A_c, A_I, Γ_c, and Γ_I are developed. In this part, two cases corresponding to our experimental conditions are considered.

(1) Polymer 2 Having No Contrast with the Solvent. This first case corresponds to the solvent tetrahydrofuran (THF) where only one polymer is "visible" [i.e., $(\partial n/\partial\varphi)_2 = 0$]. The intermediate scattering function is given by eq 2. In the theory, it was assumed that the length and the volume of the statistical elements of both polymers were identical. Since the results depend only on the dimensions through the form factor $P(q)$, the choice of the length of the statistical element is irrelevent. Therefore, one can release the first hypothesis and define N as the volume of the chain divided by the volume, v_s, of a solvent molecule as it is usually done. Furthermore, we assume that the excluded volume parameters satisfy the relations $v_{11} = v_{22} = v_{12} - \chi = v$, where χ is the Flory interaction parameter between segments of different species having the same volume, v_s. Assuming that N is the same for both polymers, and χ is relatively small as compared to v, we obtain the following expressions for the amplitudes

$$a_c = x^2\varphi NP(q)\frac{1 - \chi/\chi_c(q)}{1 + v\varphi NP(q)[1 - \chi/\chi_c(q)]} \qquad (3)$$

$$a_I = x(1 - x)\varphi NP(q)\frac{1 + v\varphi NP(q)}{1 + v\varphi NP(q)[1 - \chi/\chi_c(q)]} \qquad (4)$$

and the frequencies

$$\Gamma_c = \Gamma_s[1 + v\varphi NP(q)] \qquad (5)$$

$$\Gamma_I = \Gamma_s[1 - \chi/\chi_c(q)] \qquad (6)$$

where

$$\Gamma_s = q^2\frac{kT}{N\zeta}\frac{1}{P(q)} = q^2\frac{D_s}{P(q)} \qquad (7)$$

and

$$\chi_c(q) = [2\varphi Nx(1 - x)P(q)]^{-1} \qquad (8)$$

x is the relative composition of the visible polymer (PS) ($x = \varphi_1/\varphi$). $D_s = kT/N\zeta$ is the self-diffusion coefficient, ζ the friction coefficient per "segment", k the Boltzmann constant, and T the absolute temperature. In the framework of this theory, Γ_s characterizes the time evolution of the self or bare intermediate scattering function, $S_s(q,t)$. The latter is related to the bare or self-response function $\chi_s(q,t)$[2,18] by

$$kT\chi_s(q,t) = -\frac{\partial}{\partial t}S_s(q,t) \qquad (9)$$

As in every random phase approximation (RPA) approach, bare response functions are introduced. These functions represent the responses obtained by measurements on a single molecule in a matrix made of both polymers at the concentration of the system. This means that the dynamical time response of a single molecule, Γ_s^{-1}, has no reason to be equal to the time response at infinite dilution, Γ_0^{-1}. Therefore, Γ_I is a function of the concentration, the molecular weight, and the thermodynamical and hydrodynamical interactions between polymers of the same species as well as of different species.

The relative amplitude, $a_c/(a_c + a_I)$, and the ratio of frequencies, Γ_c/Γ_I, as predicted by the theory, were a guide for choosing the optimal conditions in this study. To illustrate this point, we have represented in Figure 1 the variation of these quantities with the composition, x, at different total volume fractions, φ. The figure shows that even if $x \simeq {}^1/_2$ the two modes should be easily detectable in the range of intermediate concentrations (i.e., $2.0 \times 10^{-3} < c$ (g cm^{-3}) $< 6.5 \times 10^{-3}$).

(2) Zero Average Contrast Condition. The second case corresponds to zero average contrast conditions with $x = {}^1/_2$. It reads

$$(\partial n/\partial\varphi)_1 = -(\partial n/\partial\varphi)_2 \qquad (10)$$

To see how the amplitude, A_c, vanishes, we recall the result

$$A_c = \frac{\varphi NP(q)(1 - \chi/\chi_c(q))}{1 + v\varphi NP(q)(1 - \chi/\chi_c(q))}\left\{x^2\left(\frac{\partial n}{\partial\varphi}\right)_1^2 + (1 - x)^2\left(\frac{\partial n}{\partial\varphi}\right)_2^2 + 2x(1 - x)\left(\frac{\partial n}{\partial\varphi}\right)_1\left(\frac{\partial n}{\partial\varphi}\right)_2\right\} \qquad (11)$$

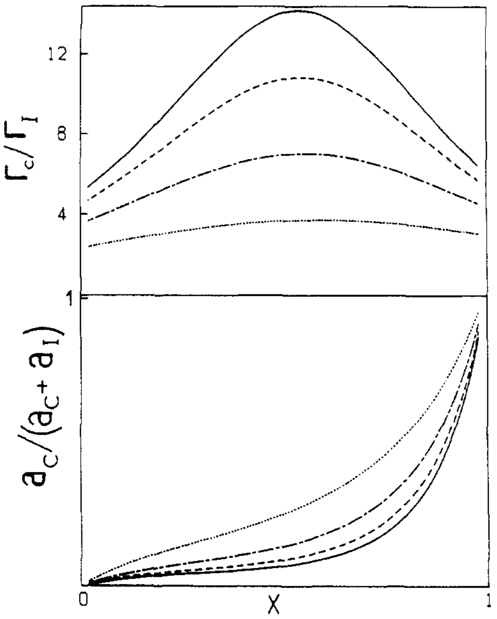

Figure 1. Theoretical variation of Γ_c/Γ_I and $a_c/(a_c + a_I)$ as a function of the weight fraction (x) of the visible polymer (see eq 3–8). Molecular weight of the two polymers: $M = 1.4 \times 10^6$, 1.2×10^6. Total polymer concentration (g cm^{-3}): (···) 2.5×10^{-3}, (–·–) 4.3×10^{-3}, (- - -) 5.6×10^{-3}, (—) 6.4×10^{-3}.

Table I
Molecular Weight (M_w), Radius of Gyration (R_g), and Second Virial Coefficient (A_2) Measured by Time-Averaged Light Scattering in THF (PS) and Toluene (PDMS)[17]

sample	M_w, kg mol^{-1}	R_g, Å	$10^4 A_2$, mol mL g^{-2}
PS	1400	660	2.8
PDMS	1220	540	2.6

This equation shows that if $(\partial n/\partial\varphi)_2 = 0$ the result in eq 3 is recovered and if $(\partial n/\partial\varphi)_1 = -(\partial n/\partial\varphi)_2$ then $A_c = 0$ for $x = 1/2$. Therefore, the cooperative mode disappears and the interdiffusion mode alone survives. Its amplitude, A_I, is given by

$$A_I = \left(\frac{\partial n}{\partial\varphi}\right)_1^2 \varphi N P(q) \frac{1 + v\varphi N P(q)}{1 + v\varphi N P(q)[1 - \chi/\chi_c(q)]} \qquad (12)$$

III. Experimental Section

(1) Materials and Sample Preparation. Polystyrene sample was prepared by anionic polymerization following a classical procedure that has already been described.[19] The poly(dimethylsiloxane) sample is a commercial sample which was fractionated using toluene as the solvent and methanol as the precipitant. The characteristics of these samples are listed elsewhere[17] and are summarized in Table I.

Reagent-grade solvents were used throughout. Several solutions of PS/PDMS/solvents were prepared with the same weight fraction in PS ($x = c_{PS}/c_T = 0.54$). The total polymer concentrations ranged from $c_T = 0.25 \times 10^{-2}$ to 1×10^{-2} g cm^{-3}. We recall that the overlap concentration, the cloud point concentration, and the concentration at the spinodal for this PS/PDMS/solvent system are respectively $c^* \simeq 3 \times 10^{-3}$ g cm^{-3}, $c_k \simeq 1.06 \times 10^{-2}$ g cm^{-3}, and $c_{SP} \simeq 1.1 \times 10^{-2}$ g cm^{-3}. The solutions were allowed to mix during 3 days. They were centrifuged at an acceleration of 15000g for 3 h and then pipeted into the scattering cells.

(2) Equipment and Data Analysis Procedure. Classical light scattering technique was used in order to test the homogeneity of the solutions and to be sure that the intensity correlation measurements were made in the monophasic domain at 25 °C. The full homodyne correlation function of the scattered intensity defined on 200 channels was obtained on a spectrometer that has already been described.[20a] The scattered light of a vertically polarized 488-nm Ar-ion laser was measured at several angles in the range 20–140°. The normalized intensity autocorrelation functions, $C(q,t)$, where q is the scattering vector, are calculated by a minicomputer (DEC-PDP 11/34). They are related to the field autocorrelation function, $S(q,t)$, by the Siegert relation

$$C(q,t) = 1 + \beta|S(q,t)|^2 \qquad (13)$$

where β is a spatial coherence factor depending upon experimental conditions. In the case of a simple diffusive process, $C(q,t)$ is monoexponential with a relaxation time given by

$$t_c = 1/(2Dq^2) \qquad (14)$$

where D is the diffusion coefficient of the process.

All the experimental correlation functions, $C(q,t)$, were analyzed by fitting with a monoexponential curve that included an optional base line.[20b] The sampling time was chosen so that the accumulated autocorrelation function displayed a reasonable portion of an apparent exponential decay (3–4.5 decay times). It was also verified that at large sampling time the measured base line and the calculated base line were identical with an accuracy of 0.5%. In a second step, all the experimental correlation functions were analyzed by histogram approximation.[21] From the comparison between different methods of analysis,[22] it appears that the histogram method is well adapted to the study of a bimodal distribution of the relaxation time. Following this procedure, the computed net signal autocorrelation function, $C_n(t) = A\beta|S(q,t)|^2$, has the form

$$C_n(t) = A\beta\{\sum_{j=1}^{M}(-a_j/t)[\exp(-(\Gamma_j + \Delta\Gamma/2)t) - \exp(-(\Gamma_j - \Delta\Gamma/2)t)]\}^2 \qquad (15)$$

where A is related to the base line, M is the number of steps in the histogram, $\Delta\Gamma = (\Gamma_{max} - \Gamma_{min})/M$ is the width of each step, and Γ_{min} and Γ_{max} are the start and the stop of the range of the histogram where $\Gamma = t_c^{-1}$. The parameters a_j are the relative contribution of the jth step to the total histogram. A typical value of $M = 10$ was used in the fitting process.

IV. Results and Discussions

Two series of experiments were performed. In the first one, the PS/PDMS/THF system was investigated, and in the second one, the PS/PDMS/toluene system was considered. The concentration as well as the angular variations of the relaxation time was analyzed.

(1) Solvent Where PDMS Has No Contrast. Experiments were made in a range of concentrations going approximately from c^* to $3c^*$ (i.e., $2.5 \times 10^{-3} \le c$ (g cm^{-3}) $\le 10^{-2}$). It was impossible to use higher concentrations since the cloud point is reached at $c \simeq 1.06 \times 10^{-2}$ g cm^{-3}. A typical correlation function is given in Figure 2. It has been obtained at $c = 4.26 \times 10^{-3}$ g cm^{-3}. The dots represent the experimental data and the line a monoexponential fit; the insert gives the distribution of residuals. Taking into account the accuracy of the measurements, it is clear that the monoexponential fit is not satisfactory. Similar observations were made at the other concentrations. The histogram method was used to analyze the experimental correlation functions. Two relaxation modes were identified in the intermediate range of concentration (i.e., $2.5 \times 10^{-3} \le c$ (g cm^{-3}) $\le 6.3 \times 10^{-3}$). At higher concentrations, only the slow mode was observed. This is expected since the amplitude, a_c, tends to zero with the concentration, as shown in Figure 1. Figure 3 represents the variation of the diffusion coefficients $D_c = \Gamma_c/q^2$ and $D_I = \Gamma_I/q^2$ as a function of the concentration. Several comments can be made on these results:

(i) D_c increases and D_I decreases with the concentration. A similar behavior has been observed on PS/PMMA/toluene.[13] Essentially a decreasing relaxation frequency with the concentration has been reported in the literature.[7-12,14,15] It has been attributed to reptation[18] or to other

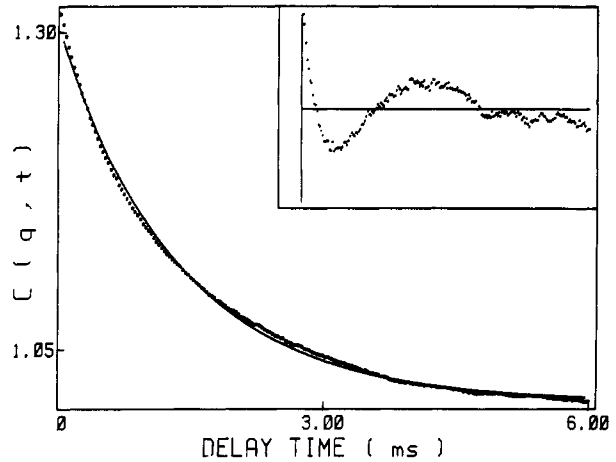

Figure 2. Correlation function of the scattered intensity by the system PS/PDMS/THF at $c = 4.26 \times 10^{-3}$ g cm^{-3} and $x = 0.54$; scattering angle, 20°; time window, 30 μs. The solid line is for single-exponential fit. The insert shows the distribution of the residuals.

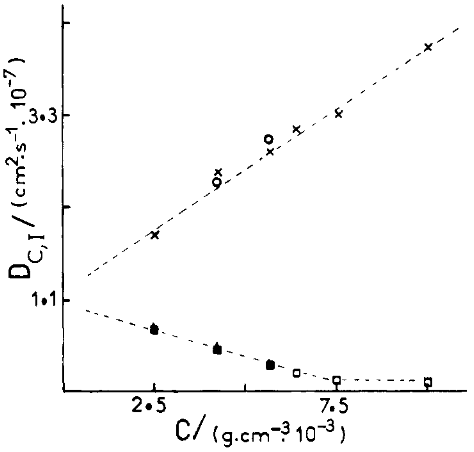

Figure 3. Total polymer concentration dependence of cooperative diffusion coefficient (D_c) and interdiffusion coefficient (D_I). (×) D_c of PS in binary system PS/THF; (○) D_c and (□) D_I in ternary system PS/PDMS/THF ($x_{PS} = 0.54$); (▲) D_I in ternary system PS/PDMS/toluene ($x_{PS} = 0.54$).

Table II
Ternary System PS/PDMS/THF. Theoretical and Experimental Values of the Amplitudes and Relaxation Frequencies at a PS Composition of $x = 0.54$ at Several Total Polymer Concentrations

10^3c, g cm^{-3}	$a_c/(a_c + a_c)$	$(\Gamma_c/\Gamma_I)_{theo}$	$(\Gamma_c/\Gamma_I)_{exp}$
2.5	0.27	3.8	2.4[a]
4.3	0.15	7.1	5[b]
5.6	0.09	11.0	9.4[b]
6.4	0.08	14.5	13.6[a]

[a] Γ_I is measured on ternary PS/PDMS/THF solution, Γ_c is measured on binary system PS/THF. [b] Γ_I and Γ_c are measured on ternary PS/PDMS/THF solution.

Table III
Calculated Self-Diffusion Coefficients D_s^c (Cf. Equations 5 and 7) and D_s^I (Cf. Equations 6 and 7) in the Ternary PS/PDMS/THF Solutions

10^3c, g cm^{-3}	2.5	4.3	5.6	6.4	7.5	10
$10^8D_s^c$, cm^2 s^{-1}	6.8[a]	6.4	5.9	5.7[a]	5.2[a]	5.0[a]
$10^8D_s^I$, cm^2 s^{-1}	9.6	7.9	6.2	5.2	4.0	8.8

[a] Obtained from Binary PS/THF solutions.

complicated mechanisms.[23] It seems that the hypothesis we propose is simpler since it does not require any special effect.

(ii) The values of D_c measured in the corresponding binary system PS/THF are also reported in this figure (crosses ×). One observes the similarity between binary and ternary systems. This is the reason why the fast mode is identified as a cooperative mode describing the relaxation of the concentration fluctuations. The same conclusion has been reached for PS/PMMA/toluene[6,13] and PS/toluene systems. Figure 3 shows a linear decrease of D_I in two steps. The change of slope in the upper range of c cannot be explained by the theory that is probably inadequate in this range. The mean field theory is less and less valid when the concentration fluctuations become important.

(iii) The ratio $\Gamma_c/\Gamma_I = D_c/D_I$ increases with the concentration. This behavior is consistent with the theoretical result[4] as shown in Figure 1. There is a good agreement between the theoretical and experimental values of Γ_c/Γ_I which are reported in Table II. In this table, we have also given the theoretical $a_c/(a_c + a_I)$ values. At high concentrations ($c > 6.3 \times 10^{-3}$ g cm^{-3}), the cooperative relaxation mode cannot be detected by histogram analysis because its amplitude is low (<8%).

(iv) The region of concentrations below 2.5×10^{-3} g cm^{-3} was not explored because it was difficult to separate the two modes; Γ_c and Γ_I are approximately equal, and the correlation function tends to a single exponential.

(v) We have listed in Table III the D_s^c values calculated from the experimental D_c values at small angle, following

$$D_s^c = \frac{D_c}{1 + v\varphi N} = \frac{D_c}{1 + 2A_2Mc} \tag{16}$$

It is supposed for the lower and higher concentrations that the cooperative motions are equivalent in ternary and in binary solutions. A mean value of $D_s^c = 5.8 \times 10^{-8}$ cm^2 s^{-1} is deduced from these results. In Table III we have also listed the D_s^I values calculated from the experimental D_I values as

$$D_s^I = \frac{D_I}{1 - \chi/\chi_c} \tag{17}$$

with

$$\chi/\chi_c = 4A_2Mcx(1 - x)\chi/v \tag{18}$$

and where χ/v has been replaced by[17]

$$\frac{\chi}{v} = \frac{2m_am_bA_{2,ab}}{m_a^2A_{2,a} + m_b^2A_{2,b}} - 1 \tag{19}$$

In this last relation, m_a and m_b are the molecular weights of the monomer units and $A_{2,a}$, $A_{2,b}$, and $A_{2,ab}$ characterize the interactions between PS and the solvent, PDMS and the solvent, and PS and PDMS, respectively. $A_{2,a}$ and $A_{2,b}$ are listed in Table I, and $A_{2,ab} \simeq 3.43 \times 10^{-4}$ mol mL g^{-2}.[17] The D_s^I values of Table III appear to be more scattered than D_s^c around a mean value of $D_s^I = 6.9 \times 10^{-8}$ cm^2 s^{-1}. The D_s^I and D_s^c values are close together but different from the self-diffusion coefficient of PS in THF[24] ($D_0 \simeq 12.3 \times 10^{-8}$ cm^2 s^{-1} at $M = 1.3 \times 10^6$). At a finite value of the polymer concentration, the hydrodynamic interactions are not screened. However, the linear extrapolation of D_c and D_I to zero concentration on Figure 3 leads to $D_{c,I}^0 = 11 \times 10^{-8}$ cm^2 s^{-1}, which is not very different from D_0.

(2) Solvent with Zero Average Contrast. Considering the characteristics of the polymers (see Table I), this condition is approximately satisfied at $x = 0.54$. We have seen in the Theoretical Section that only the slow interdiffusion relaxation mode should be observed. The experiments were performed at three different concentra-

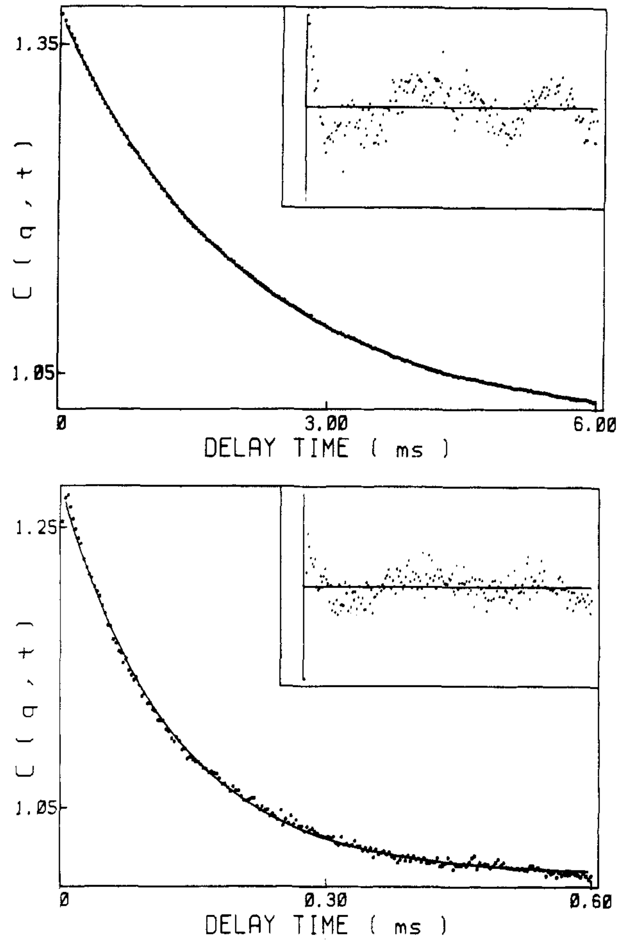

Figure 4. Correlation function of the scattered intensity by (a, top) PS/PDMS/toluene at $c = 4.26 \times 10^{-3}$ g cm^{-3} and $x = 0.54$ (scattering angle, 20°; time window, 30 μs); and (b, bottom) PS/THF at $c = 4.26 \times 10^{-3}$ g cm^{-3} (scattering angle, 40°; time window, 3 μs). The solid line is for single-exponential fit. The insert shows the distribution of the residuals.

tions, $c = 0.25 \times 10^{-2}$, 0.426×10^{-2}, and 0.568×10^{-2} g cm^{-3}. A correlation function obtained at $c = 0.426 \times 10^{-2}$ g cm^{-3} is given in Figure 4a. This correlation function and the insert showing the distribution of the residuals can be directly compared to the correlation function shown in Figure 2 for PS/PDMS/THF or to the correlation function of Figure 4b obtained on a binary PS/THF solution at the same total polymer concentration. It appears that in PS/PDMS/toluene only one mode subsits and this is confirmed by the histogram analysis which is efficient to separate the modes especially in the concentration range investigated. The value of D_{I} deduced from this analysis was found to be equal to the value obtained in the system PS/PDMS/THF. This is consistent with the theoretical predictions.

(3) **Angular Dependence.** The angular variations of Γ_{I} and Γ_{c} have also been investigated for scattering angles ranging from 20° to 140°. The experimental values of $\Gamma_{\mathrm{c,I}}$ are given in Figure 5 as a function of q^2. The variation of Γ_{c} versus q^2 is linear for all the concentrations investigated. For comparison on this figure, we have also plotted the variations of Γ_{I} versus q^2 for PS/PDMS/toluene and PS/PDMS/THF at two concentrations. There is a significant deviation from the q^2 behavior as depicted by the initial slopes.

By use of eq 6–8, the best fit between experimental and theoretical results is obtained by adjusting the values of the radius of gyration, R_{g}, in the Debye function

$$P(q) = 2(e^{-u} + u - 1)/u^2 \qquad u = q^2R_{\mathrm{g}}^2 \qquad (20)$$

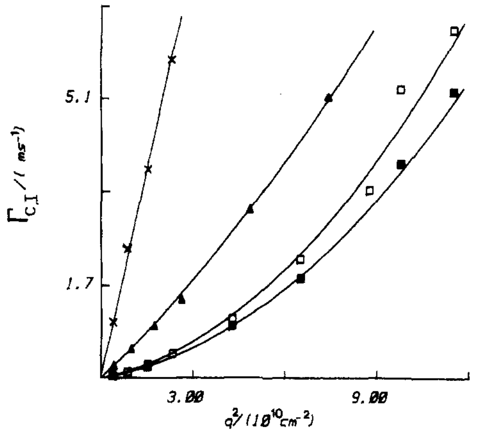

Figure 5. Angular dependence of cooperative and interdiffusion relaxation mode. (×) Γ_{c} in PS/THF solution and (▲) Γ_{I} in PS/PDMS/toluene solution for $c = 4.3 \times 10^{-3}$ g cm^{-3}. (□) (■) Γ_{I} in PS/PDMS/THF solution for $c = 7.5 \times 10^{-3}$ and 1×10^{-2} g cm^{-3}, respectively. Solid line: theoretical variation (see eq 16–18).

Values of $R_{\mathrm{g}} = 300$ Å at $c = 10^{-2}$ g cm^{-3} and $R_{\mathrm{g}} = 480$ Å at $c = 7.5 \times 10^{-3}$ g cm^{-3} have been obtained. The increase of the radius of gyration when the concentration decreases has already been observed.[25]

V. Conclusion

In this paper, we have investigated the dynamic light scattering from ternary mixtures of PS/PDMS in two solvents. The first one THF is a good solvent for both polymers and has no contrast with PDMS. This means that only the PS scatters light. After careful analysis of the data, it is possible to ascertain the existence of two relaxation modes. When the concentration is decreased, the largest diffusion coefficient corresponding to the fast mode decreases, the smaller one increases, and both seem to merge together at low concentration. These results are in good agreement with a recent theory using the RPA to describe the dynamics of polymer mixtures. The fast mode was interpreted as a cooperative relaxation of the concentration fluctuations in the mixture. The slow mode corresponds to the fluctuations of relative concentration of the two polymers and is called interdiffusion relaxation mode.

In the second series of experiments, toluene was used. In this solvent, the average contrast for the polymer mixture composition is zero. The theory shows that the amplitude of the fast mode vanishes, and therefore, only the slow mode should be observed. The experimental results indeed confirm this prediction. The measured diffusion coefficient, D_{I}, decreases with concentration as predicted by the theory. However, experimental values of D_{I} tend to be constant for concentration values approaching the cloud point. We have chosen a composition $x = 0.54$ of PS *in the mixture to satisfy the zero average* contrast. This value of x does not correspond to the optimal conditions for observing the two modes, as shown in the theoretical curves of Figure 1. It is worth noting that in the case of PS/PMMA/toluene[6,13] the experimental parameters (for example, $x > 0.80$) were chosen to correspond to the optimal conditions for separating the two modes. The analysis was done just by selecting different sampling times. In the present work, all the experimental correlations functions were analyzed by the histogram method which is known to be efficient in analyzing multimodal distributions. For all concentrations, it was easy to identify the slow mode with relaxation time Γ_{I}^{-1} because its relative amplitude is high, as expected by the theory (see Figure 1). The identification of the fast mode with relaxation time Γ_c^{-1} depended on the range of concentration.

(i) In the higher concentration range $c \geq 0.6 \times 10^{-2}$ g cm^{-3}, the amplitude, a_c, was very low.

(ii) In the lower concentration range $c \leq 0.25 \times 10^{-2}$ g cm^{-3}, the ratio Γ_c/Γ_I was less than 2.

In these two ranges, the histogram analysis gave only one mode.

(iii) In the intermediate concentration range, two modes were identified.

Most of the experimental data obtained from the ternary system PS/PDMS/solvent were consistent with the simple theory based on RPA. This conclusion was also drawn for other more compatible system (e.g., PS/PMMA/solvent).[6,13] The RPA was found to be a good model for explaining the static scattering experiments for polymer mixtures.[26] Our results show that its generalization to dynamic properties is well justified.

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Registry No. PS, 9003-53-6; THF, 109-99-9; toluene, 108-88-3.

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