Quasi-elastic light scattering from ternary mixtures of polystyrene/poly(methyl methacrylate)/toluene

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The dynamical behaviour of ternary solutions of polystyrene/poly(methyl methacrylate)/toluene has been investigated by quasi-elastic light scattering. Two distinct relaxation modes have been observed in the autocorrelation function of the scattered light. The variation of these modes has been examined as a function of the total polymer concentration C, the relative composition of polystyrene ($x = C_{PS}/C$) and the wavevector q. The experimental results are in good agreement with recent theoretical calculations based on the random-phase approximation. The first mode or the fast one is independent of the composition and characterizes the total concentration fluctuations; it is a cooperative diffusion mode. The second one is sensitive to the composition. It describes the diffusion of one species with respect to the other and is called the interdiffusion mode.

(Keywords: polymer; dynamical behaviour; ternary mixtures; semi-dilute solutions; quasi-elastic light scattering; polystyrene; poly(methyl methacrylate))

INTRODUCTION

In the last few years, the dynamic properties of polymer mixtures in solution have been the subject of intensive studies from both experimental and theoretical points of view. Several types of mixture were considered. Polystyrene (PS)/(poly(vinyl methyl ether) (PVME)/solvent[1–4] was the most frequently studied system owing to the high degree of compatibility between these two polymers. The solvents were chosen to mask one of the polymers and the concentration of the visible polymer was taken to be small. Interest was focused on the single motion of the visible polymer in the matrix of arbitrary concentration of the invisible polymer. Scaling laws describing the variation of the self-diffusion coefficient with the molecular weight of the visible polymer and the concentration of the invisible one were derived. The aim of these studies was to verify if the slow motion observed in these ternary mixtures could be interpreted in terms of a reptation motion[5] or if other sophisticated dynamical processes[6] must be considered. With such compatible systems, a wide range of molecular weights and concentrations could be explored. Other polymer mixtures such as PS/poly(methyl methacrylate) (PMMA)/solvent were considered in the framework of similar studies[7–11]. However, because of the interaction between these two polymers, a limited range of molecular weights and concentrations could be explored to reach precise conclusions about scaling laws. Except for a few cases where two modes were reported[8,9], most of the literature on this subject reported measurements and discussions on the self-diffusion coefficient. In the present work, we propose to investigate in more detail the dynamical coupling between two polymers, PS and PMMA, in solution. This investigation has been stimulated by the simple theory developed recently to describe the dynamics of polymer mixtures in solution[12]. The main finding of this theory based on the random-phase approximation (r.p.a.) was the emergence of two relaxation modes. The fast one characterizes the total concentration fluctuations and was called the cooperative diffusion mode. The other mode describes the motion of one species with respect to the other and was called the interdiffusion mode. In these theoretical calculations, general expressions have been derived for the amplitudes and frequencies of the two modes under various conditions of the thermodynamical parameters (i.e. excluded volume), contrast factor, molecular weight, concentration, etc. The relations that were obtained are very useful for estimating the optimal experimental conditions (i.e. approximately equal amplitudes and widely different frequencies) to observe the two modes simultaneously. We recall some of these expressions, especially in the case where the increment of refractive index of polymer 2, $(\mathrm{d}n/\mathrm{d}\varphi)_2$, is equal to zero. In this case the dynamic scattering function $S(q, t)$ is given by:

$$S(q,t) = (\mathrm{d}n/\mathrm{d}\varphi)_1^2 S_{11}(q,t) \qquad (1)$$

with

$$S_{11}(q,t) = a_C \exp(-\Gamma_C t) + a_I \exp(-\Gamma_I t) \qquad (2)$$

where $q = (4\pi/\lambda)n \sin(\theta/2)$ and λ is the wavelength of the incident radiation, θ the scattering angle, n the index of refraction of the medium, and t the time. Furthermore we shall assume that the polymers have the same degree of polymerization N and the same form factor $P(q)$. We assume also that $v_{11} = v_{22} = v$, where v_{ii} is the excluded-volume parameter between monomers of species i. The expression for the excluded-volume parameter $v_{12} = v + \chi$ between monomer species 1 and 2 allows one to

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take into account the degree of compatibility between PS and PMMA. In this simplified case the amplitudes a_C and a_I (C and I representing cooperative diffusion and interdiffusion, respectively) of the dynamic scattering function are given by:

$$a_C = x^2 \varphi N P(q) \frac{[1-\chi/\chi_C(q)]}{1+v\varphi N P(q)[1-\chi/\chi_C(q)]} \tag{3}$$

$$a_I = x(1-x)\varphi N P(q) \frac{[1+v\varphi N P(q)]}{1+v\varphi N P(q)[1-\chi/\chi_C(q)]} \tag{4}$$

and the frequencies by:

$$\Gamma_C = q^2[D_S/P(q)][1+v\varphi N P(q)] \tag{5}$$

$$\Gamma_I = q^2[D_S/P(q)][1-\chi/\chi_C(q)] \tag{6}$$

Here $D_S = kT/\zeta N$ is the classical self-diffusion coefficient and φ is the total volume fraction of polymer; $\chi_C(q)$ is defined as:

$$\chi_C(q) = [2x(1-x)\varphi N P(q)]^{-1} \tag{7}$$

The other parameters have their standard definitions (see ref. 12). In these theoretical results, we have assumed that χ/v is small compared to unity.

The present study is the continuation of preliminary work[8] on a PS/PMMA/toluene mixture, which was done at a total polymer concentration of $C = 3.84 \times 10^{-2}$ g cm^{-3}. In this preliminary study, unlike other authors, the composition of the visible polymer PS was chosen to be high (i.e. $x = C_{PS}/C = 0.92$) in order to be able to observe simultaneously the two relaxation processes predicted by the theory. Two modes were indeed found. The value of the cooperative diffusion coefficient measured in the semi-dilute regime on this ternary PS/PMMA/toluene mixture was equal to the value obtained on the corresponding binary PS/toluene mixture at the same total polymer concentration. This result is expected by the theory. In the present work, different series of experiments were performed, as follows.

(i) In the ternary mixtures of PS/PMMA/toluene, the experiments were performed at two different compositions of the visible polymer, namely $x = 0.92$ and $x = 0.80$. These values of x were chosen to be able to identify the two modes easily.

(ii) At each composition, we have investigated the variation of the relaxation times with concentration above C^* and, of course, below the cloud-point concentration.

(iii) We have also investigated the binary PS/toluene system using the same PS in the same range of concentration in order to compare the cooperative diffusion coefficients in binary and ternary mixtures.

(iv) Finally, the angular dependence of the relaxation times was also studied.

EXPERIMENTAL

Materials and sample preparation

The polystyrene sample was prepared by anionic polymerization under an inert atmosphere according to a process described elsewhere[13]. The poly(methyl methacrylate) sample was purchased from Aldrich and fractionated in benzene/methanol mixtures. The characteristics of these polymers are given in *Table 1*. The weight-average molecular weight M_w, the radius of gyration R_g and the second virial coefficient A_2 of each sample were determined by light scattering in toluene and/or acetone. The polydispersities of the polymer samples, measured by gel permeation chromatography in tetrahydrofuran (THF), appear to be higher than 1.3. Nevertheless, in the semi-dilute regime of concentration, where all the measurements were done, the effect of polydispersity is negligible.

Table 1 Properties of polymer samples

Sample	M_w[a] (kg mol^{-1})	M_w/M_n[b]	R_g[a] (Å)	$A_2 \times 10^4$[a] (mol cm^3 g^{-2})
PS473	970	1.40	440	3.0
PMMA-A460F1	950	1.32	420	2.0

[a] From time-averaged light scattering
[b] From gel permeation chromatography

Reagent-grade solvents were used throughout. The solutions were allowed to mix thoroughly over the course of 3 days, assisted by gentle agitation. Prior to use they were centrifuged for 2 h at 15000 rpm and then directly pipetted into the scattering cells. The total polymer concentration range investigated in ternary and binary systems was $1.4 \times 10^{-2} < C$ (g cm^{-3}) $< 3.9 \times 10^{-2}$. The homogeneity of the solutions in this concentration range was tested by classical light scattering.

Equipment and data analysis

The dynamic light scattering instrument used in this study has been described elsewhere[14]. The correlation functions of the light scattered ($\lambda = 488$ nm) by polymer mixtures were measured at 25.0 ± 0.1°C and at several angles between 20° to 140°C. The normalized intensity autocorrelation function $C(q, t)$ is related to the field autocorrelation function $S(q, t)$ by the Siegert relation:

$$C(q,t) = 1 + \beta|S(q,t)|^2 \tag{8}$$

where β is a spatial coherence factor, which depends upon the geometry of the detection. In the case of a simple diffusive process, characterized by a diffusion constant D, $S(q, t)$ is given by:

$$S(q,t) = S(q,0)\exp(-Dq^2 t) \tag{9}$$

and $C(q, t)$ is monoexponential with a relaxation time:

$$t^C = 1/2\Gamma = 1/2Dq^2 \tag{10}$$

When two modes arise in the diffusion process, the experimental intensity correlation function becomes:

$$C(q,t) = 1 + \beta[a_C \exp(-\Gamma_C t) + a_I \exp(-\Gamma_I t)]^2 \tag{11}$$

At large sampling time, since $\Gamma_I \ll \Gamma_C$, $C(q, t)$ can be approximated as:

$$C(q,t) = 1 + \beta a_I^2 \exp(-2\Gamma_I t) \tag{12}$$

whereas, at short sampling time, equation (11) becomes:

$$C(q,t) = 1 + \beta[a_C \exp(-\Gamma_C t) + a_I]^2 \tag{13}$$

If the amplitude a_C of the fast mode is small compared to a_I, equation (13) can be written as:

$$C(q,t) = 1 + \beta a_I^2 + 2\beta a_C a_I \exp(-\Gamma_C t) \tag{14}$$

Typical experimental data, obtained on ternary PS/PMMA/toluene mixtures, are presented in *Figure 1a* for intermediate sampling time ($\Delta t = 50$ μs). Clearly these data show a multimodal time decay. At short sampling time (*Figure 1b*; $\Delta t = 11$ μs), the data are analysed

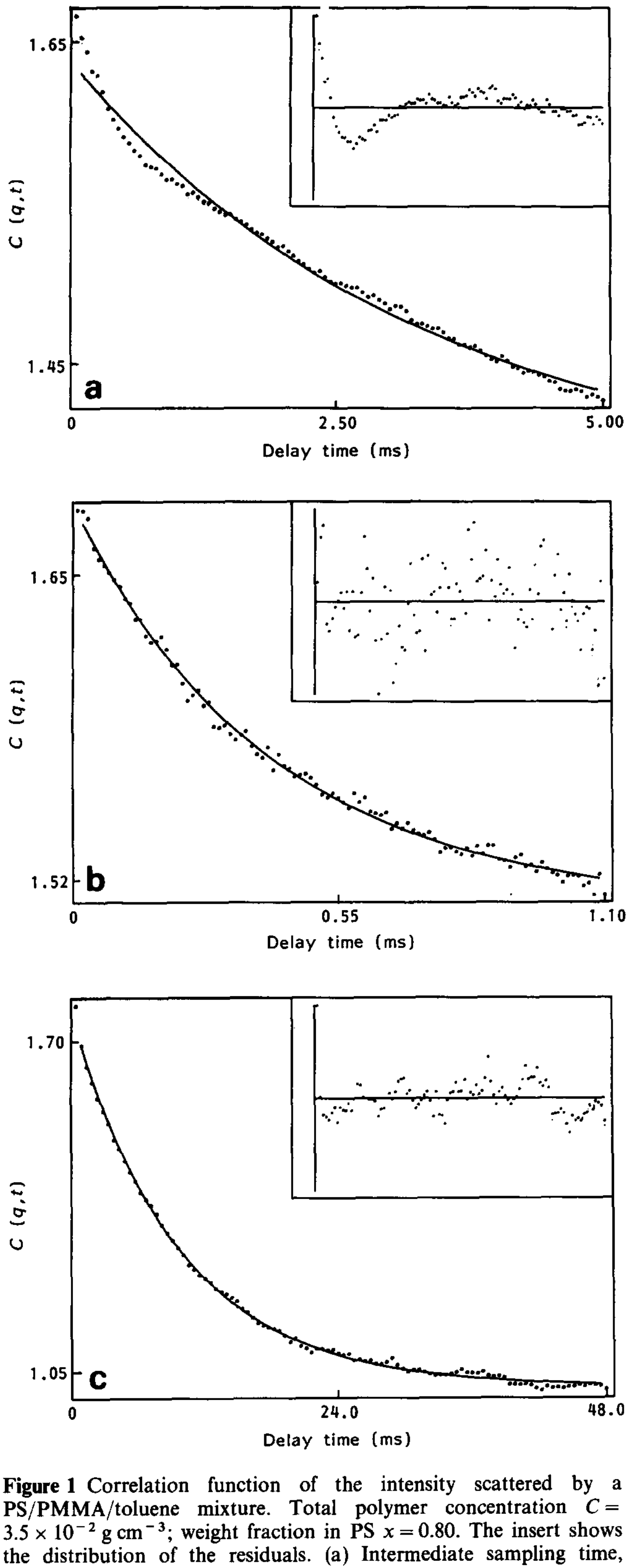

Figure 1 Correlation function of the intensity scattered by a PS/PMMA/toluene mixture. Total polymer concentration $C = 3.5 \times 10^{-2}\,\mathrm{g\,cm^{-3}}$; weight fraction in PS $x = 0.80$. The insert shows the distribution of the residuals. (a) Intermediate sampling time, $\Delta t = 50\,\mu s$; (b) short sampling time, $\Delta t = 11\,\mu s$; (c) large sampling time, $\Delta t = 480\,\mu s$

according to equation (14), where the baseline is allowed to float. At large sampling time (*Figure 1c*; $\Delta t = 480\,\mu s$), the experimental correlation functions decrease to the square of the mean value of the scattered intensity. In this case the data are analysed according to equation (12). For all the experimental data, the values of the standard parameters calculated at the end of the fitting process were of the same order of magnitude as those deduced in the analysis of standard monoexponential correlation functions (e.g. correlation functions given by latex spheres or monodisperse binary polymer solutions).

RESULTS AND DISCUSSION

Effect of concentration and composition

The experiments were performed at two different compositions of PS, namely $x = 0.92$ and $x = 0.80$. Two relaxation modes were observed at all total polymer concentrations from $C = 1.4 \times 10^{-2}\,\mathrm{g\,cm^{-3}}$ to $C = 3.9 \times 10^{-2}\,\mathrm{g\,cm^{-3}}$. The overlap concentration C^* is approximately $0.5 \times 10^{-2}\,\mathrm{g\,cm^{-3}}$. Typical correlation functions are displayed in *Figure 1* at $x = 0.80$, $C = 3.5 \times 10^{-2}\,\mathrm{g\,cm^{-3}}$, $\theta = 20°$ and for different sampling times. Two relaxation times t_C and t_I were deduced from these experimental data. The first one corresponds to the cooperative relaxation of the total concentration fluctuations (fast mode) and the second one to the interdiffusion relaxation of one polymer species with respect to the other (slow mode). The associated diffusion coefficients ($D_C = 1/q^2t_C$ and $D_I = 1/q^2t_I$) are plotted in *Figure 2* as a function of the total polymer concentration.

Cooperative diffusion coefficient D_C

Figure 2 shows the variations of D_C as a function of C for various compositions x of the visible polymer (PS). One notes that D_C increases with concentration. Within experimental errors, D_C appears not to be affected by composition. It is interesting to note that the values of D_C obtained from the binary PS/toluene system and the ternary PS/PMMA/toluene system are approximately equal. This justifies our earlier interpretation of D_C as a cooperative diffusion coefficient. It is not simply related to the dynamics of the invisible polymer, as is sometimes claimed. The same observation was made for the system PS/poly(dimethylsiloxane) (PDMS)/tetrahydrofuran (THF)[15] at a composition around 50/50. This is consistent with the theoretical result given in equation (5).

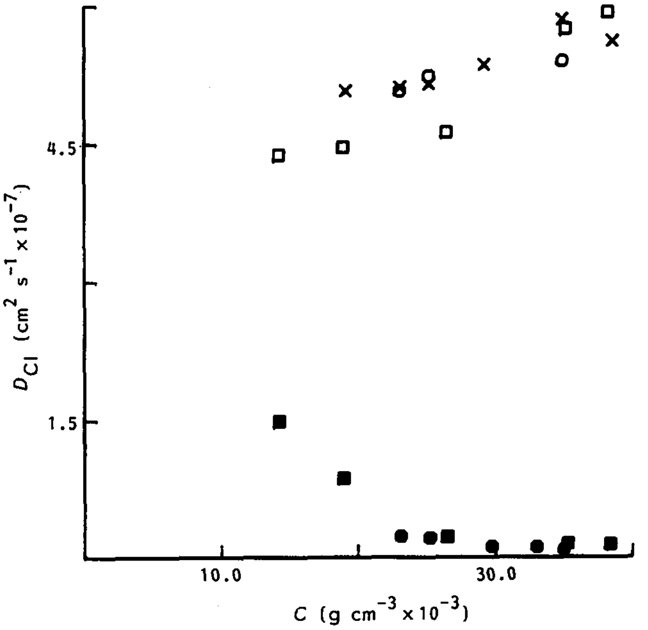

Figure 2 Variation of the interdiffusion D_I (●, ■) and cooperative diffusion D_C (□, ○, ×) coefficients with total polymer concentration C: ×, binary PS/toluene mixtures; ●, ○, ternary PS/PMMA/toluene mixtures, $x = 0.80$; ■, □, ternary PS/PMMA/toluene mixtures, $x = 0.92$

Interdiffusion coefficient D_I

Figure 2 shows that D_I decreases when the concentration increases, and its values are approximately independent of composition for $x = 0.80$ and $x = 0.92$. However, as expected, the interdiffusion mode disappears for $x = 1$. A slowing down of the interdiffusion mechanism is observed when one approaches the cloud point ($C = 4 \times 10^{-2}$ g cm^{-3}). This behaviour cannot be explained by the linear theory based on the r.p.a., which is not valid when the concentration fluctuations become important. Similar observations were made in the case of PS/PDMS/toluene[15]. One also notes that the ratio $\Gamma_\mathrm{C}/\Gamma_\mathrm{I} = D_\mathrm{C}/D_\mathrm{I}$ increases with concentration, as predicted from the theory. We have not explored the range of concentration below $C = 1.4 \times 10^{-2}$ g cm^{-3} because it was difficult to separate the two modes. Obviously, one cannot use a concentration much higher than 3.90×10^{-2} g cm^{-3} because phase separation occurs at about 4×10^{-2} g cm^{-3}.

Table 2 gives the D_S^C and D_S^I values calculated from the relations:

$$D_\mathrm{S}^\mathrm{C} = \frac{D_\mathrm{C}}{1 + v\varphi N} = \frac{D_\mathrm{C}}{1 + 2A_2MC} \tag{15}$$

$$D_\mathrm{S}^\mathrm{I} = \frac{D_\mathrm{I}}{1 - \chi/\chi_\mathrm{C}} = \frac{D_\mathrm{I}}{1 - 4A_2MCx(1-x)\chi/v} \tag{16}$$

where D_C and D_I are the experimental values measured at small angle (20°). In the calculation of D_S^I the quantity χ/v has been replaced by[16]:

$$\frac{\chi}{v} = \frac{2A_{2\mathrm{ab}}m_\mathrm{a}m_\mathrm{b}}{A_{2\mathrm{a}}m_\mathrm{a}^2 + A_{2\mathrm{b}}m_\mathrm{b}^2} - 1 \tag{17}$$

In this expression A_{2i} characterizes the thermodynamical interaction between the monomer species i (molecular weight m_i) and the solvent. Their values are listed in *Table 1*. The parameter $A_{2\mathrm{ab}}$ (2.8×10^{-4} mol cm^3 g^{-2}, ref. 17) represents the thermodynamical interaction between styrene and methyl methacrylate. From *Table 2* it appears that, whatever the composition, D_S^C and D_S^I decrease when the concentration increases (i.e. when the local viscosity increases).

Table 2 Calculated self-diffusion coefficient D_S^C (see equation (15)) and D_S^I (see equation (16)) as functions of composition x and concentration

$C \times 10^2$ (g cm^{-3})	$D_\mathrm{S}^\mathrm{C} \times 10^8$ (cm^2 s^{-1})			$D_\mathrm{S}^\mathrm{I} \times 10^8$ (cm^2 s^{-1})	
	$x = 1$	$x = 0.92$	$x = 0.80$	$x = 0.92$	$x = 0.80$
1.425	–	5.60	–	–	–
1.900	4.98	4.42	–	–	–
2.310	4.23	–	4.20	–	3.98
2.520	3.93	–	4.00	–	3.89
2.650	–	3.38	–	2.89	–
2.900	3.57	–	3.08	–	2.46
3.300	–	–	2.79	–	2.69
3.500	3.28	3.20	3.03	2.11	2.34
3.800	2.87	3.05	–	2.01	–

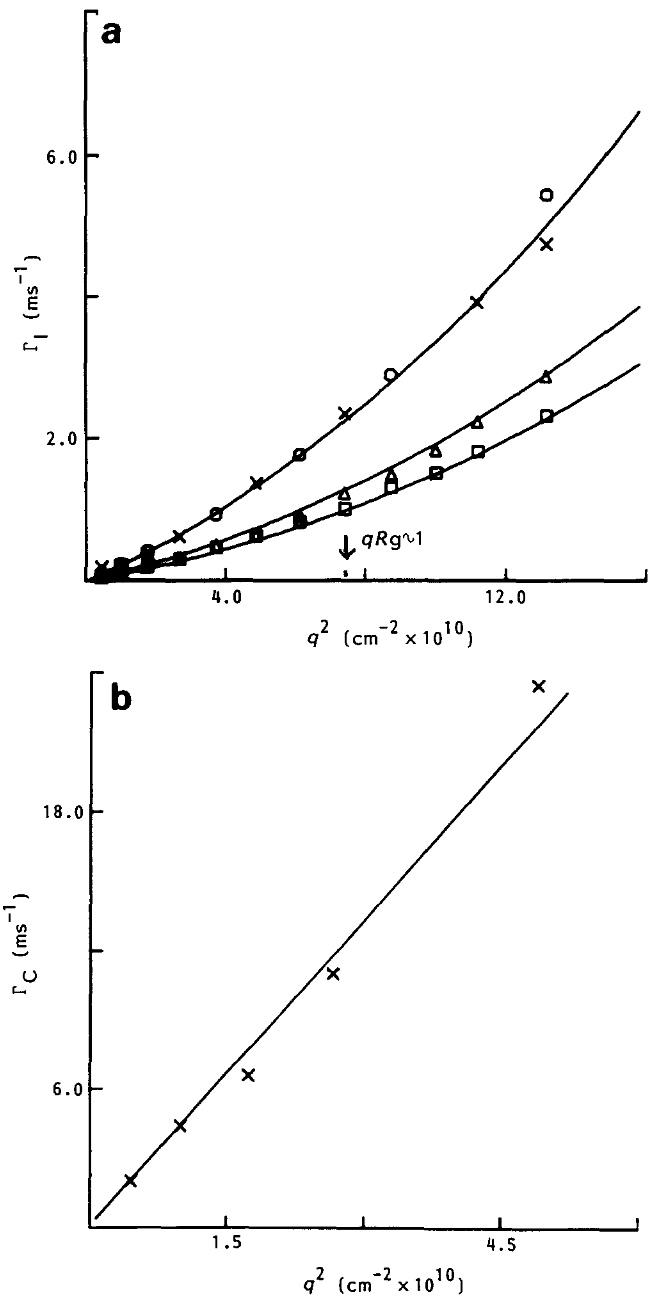

Figure 3 Variation of the relaxation frequencies of PS/PMMA/toluene mixtures as a function of the square of the wavevector. (a) Low relaxation frequency; $x = 0.80$ at various total polymer concentrations $C = 2.31 \times 10^{-2}$ (○), 2.52×10^{-2} (×), 2.97×10^{-2} (△) and 3.3×10^{-2} g cm^{-3} (□). (——) Best fit according to equations (18) and (19). (b) High relaxation frequency; $x = 0.92$ and $C = 1.9 \times 10^{-2}$ g cm^{-3}. (——) Linear fit

Angular dependence

The angular dependence of Γ_C and Γ_I was also investigated. We have reported in *Figure 3a* the experimental Γ_I values as a function of q^2 at fixed composition ($x = 0.80$) and various concentrations. The deviation from the q^2 behaviour (initial slope) increases with concentration. The experimental data have been fitted following the relation:

$$\Gamma_\mathrm{I} = q^2 D_\mathrm{I}(\theta = 20°)/P(q) \tag{18}$$

which is an approximation of equation (6) and where the form factor $P(q)$ has been represented by the Debye function:

$$P(q) = (2/u^2)[\exp(-u) + u - 1] \qquad u = (qR_\mathrm{g})^2 \tag{19}$$

From this analysis we have deduced the variation of the radius of gyration R_g with concentration (see *Table 3*). At low polymer concentration the value of R_g is equal to the value at infinite dilution. This value decreases when the polymer concentration increases, as has been observed in other systems[18].

Table 3 Calculated radius of gyration R_g at fixed composition ($x = 0.80$) and various concentrations

$C \times 10^2$ (g cm^{-3})	3.30	2.97	2.52	2.31
R_g (Å)	390	400	440	440

In the whole concentration and angular range investigated $v\varphi NP(q) \gg 1$. For such conditions, equation (5) gives:

$$\Gamma_C = q^2 D_S v\varphi N \qquad (20)$$

The experimental variation of Γ_C as a function of q^2 is shown in *Figure 3b*. No q^2 deviation is observed according to the theoretical variation.

CONCLUSIONS

In this paper, we have investigated the dynamics of ternary PS/PMMA/toluene mixtures by the quasi-elastic light scattering technique. The effects of concentration, composition and wavevector q were considered. The data were analysed in terms of a linear theory based on the r.p.a. Both experiments and theory show that the dynamics of this system is characterized by two relaxation modes. We have observed a good qualitative agreement with this theory. The cooperative diffusion coefficient D_C is found to increase with concentration; it is not sensitive to composition and is approximately equal to the value D_C measured in the corresponding binary PS/toluene system. This confirms its interpretation given in the theory[12]. The interdiffusion coefficient D_I is found to decrease when the concentration increases, as predicted by the theory. However, when the cloud point is approached, the variation of D_I with concentration is less significant. It must be pointed out that a mean-field theory cannot be applied successfully to a system where the concentration fluctuations become important (i.e. in the vicinity of a critical point).

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