easy to obtain. This could perhaps explain the experimental data of Hadgraft et al.[17]

Relations with Experiments. The former discussion shows that if we have only one relaxation mode for monodisperse systems there are two relaxation modes in the case of a bimodal distribution. Evidently these two modes are not always distinguishable depending on the experimental conditions. Since there are experimental results available (Nemoto et al.[18]), it is interesting to see if this theory can explain them. These authors have studied mixtures of polystyrene fractions in benzene in the semidilute regime. In one case, $M_{w1} = 775000$, $c_1 = 4.18 \times 10^{-2}$ g/g, $M_{w2} = 42800$, $c_2 = 2.58 \times 10^{-2}$ g/g, they obtain two relaxation times with a ratio 12.4 and a relative amplitude of the slow mode of 0.125. Knowing the second virial coefficient, one is able to evaluate these values with our model obtaining 11.4 and 0.06, respectively. Considering the precision, specially in the evaluation of the amplitude, the agreement is quite satisfactory. We did not try to show why in some other cases they report only one relaxation times since our purpose was just to show that this theory is able to explain the existence of two modes without being obliged to introduce sophisticated models.

IV. Conclusions

In this paper, we have investigated the dynamics of mixtures of homopolymers in a solvent using the RPA. We have given a general formalism that can be applied to mixtures having arbitrary properties of structure, concentration, thermodynamics, etc. The main point of this formalism is that it predicts two decay modes, which we have identified as cooperative and interdiffusion processes.

It seems that in some cases this theory can explain the results but much work remains to be done in order to see to what extent and with what precision this "mean-field" theory can describe the experimental data.

The same formalism can be readily applied to copolymer solutions, and this problem will be the subject of a forthcoming paper.

Acknowledgment. M.B. thanks Professor G. Weill, Director of the Institut Charles Sadron (CRM), for his invitation to spend 1 month at the ICS, during which this work was completed.

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Diffusion of Polymers in Semidilute Ternary Solutions. Investigation by Dynamic Light Scattering

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Received September 29, 1986

ABSTRACT: The dynamical behavior of a polystyrene/poly(methyl methacrylate)/toluene ternary mixture has been investigated by quasi-elastic light scattering in the semidilute range of concentration. According to theoretical calculations, two relaxation modes have been found. The slow motion is related to the relative motion of the two polymers (interdiffusion process). The fast motion is the classical cooperative motion of the physical network formed by the two polymers. The relative amplitude and the ratio of the frequencies of the two modes are in agreement with the theoretical predictions (Benmouna, M.; Benoit, H.; Duval, M.; Akcasu, Z. *Macromolecules*, preceding paper in this issue).

Introduction

The dynamical behavior of ternary systems containing two polymers and one solvent has been extensively studied by quasi-elastic light scattering (QELS). Two main groups of problems have been explored experimentally.

a. Two polymers, P1 and P2, differing in nature, are dissolved in a solvent that has the same index of refraction as P2. This implies that, from a scattering point of view, the system behaves like a quasi-binary mixture. Information on the motion of P1 entangled in P2 is obtained, and the concentration of P2 can be varied to see how the diffusion motion of P1 is affected.[1-8]

b. The second type of problem is a simple model of polydispersity. In the ternary mixture P1/P2/solvent, P1 and P2 have the same chemical nature but different molecular weights and relative concentrations.[9-11]

From these studies, it is seen that the correlation function of the scattered intensity $C(q,t)$ is usually not monoexponential; it has been sometimes analyzed as the sum of two exponentials. In both types of experiments when it is impossible to detect two relaxation phenomena, the experimentalists have analyzed $C(q,t)$ as if it was

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monoexponential, but they often obtain a wave-vector-dependent diffusion coefficient, which has no physical meaning.

Recently Benmouna et al.[12,13] published theoretical papers where they showed that, using the random phase approximation (RPA), the intermediate scattering function $S(q,t)$ is, when one deals with a binary polymer blend or a ternary system (two polymers and one solvent), the sum of two exponential functions. It can be written as

$$S(q,t) = A_I \exp(\Gamma_I t) + A_c \exp(\Gamma_c t) \tag{1}$$

This relation shows that there are two relaxation modes characterized by Γ_c and Γ_I, called cooperative and interdiffusion modes, respectively.

In the present work the dynamical behavior of a polystyrene (PS)/poly(methyl methacrylate) (PMMA)/toluene ternary mixture, where PMMA and toluene are isorefractive, has been studied by QELS in order to compare experimental results and theoretical calculations.

The experimental parameters such as the molecular weight of the polymers (M), the total polymer concentration (C_T), and the weighted fraction of PS (x) were chosen in order to get, according to the theory, a large difference between Γ_I and Γ_c and similar amplitudes A_I and A_c.

In this preliminary study of ternary mixtures the experimental results are compared with those that were obtained on a PS/toluene binary system where the PS concentration is equal to the total polymer concentration used in the ternary mixture.

Theoretical Section

In eq 1 $S(q,t)$ represents the dynamical intermediate scattering function, where t is the delay time and q is the scattering vector ($q = (4\pi/\lambda) \sin \theta/2$, where λ is the wavelength of the incident light and θ is the scattering angle). It is assumed that the solvent has the same quality for both polymers or, using the notation of ref 12, the same excluded volume $v_{11} = v_{22} = v$. Moreover the interaction parameter $\chi_{12} = \chi$ between P1 and P2 is defined following Flory. For the sake of simplicity it is also assumed that both polymers have the same dimensions, the same structure factor $P(q)$, and the same number of monomer units N. The volume fractions of P1 and P2 are respectively ϕx and $\phi(1-x)$. The theoretical expressions of the amplitudes and frequencies of the two relaxation modes that characterize the dynamical behavior of a ternary mixture P1/P2/solvent, where P2 and the solvent are isorefractive, are given by

$$A_I = x(1-x)\phi NP(q) \frac{1 + v\phi NP(q)}{1 + v\phi NP(q)(1 - \chi/\chi_c(q))} \tag{2}$$

$$A_c = x^2\phi NP(q) \frac{1 - 2\chi(1-x)\phi NP(q)}{1 + v\phi NP(q)(1 - \chi/\chi_c(q))} \tag{3}$$

$$\Gamma_I = \Omega_0(q)(1 - \chi/\chi_c(q)) \tag{4}$$

$$\Gamma_c = \Omega_0(q)(1 + v\phi NP(q)) \tag{5}$$

where ϕ is the total segmental concentration and

$$\chi_c(q) = [2x(1-x)\phi NP(q)]^{-1} \tag{6}$$

In these relations $\Omega_0(q)$ is the single-chain relaxation frequency. If it is assumed that the concentration is high enough to be able to neglect hydrodynamic interactions and use the Rouse model, the expression of $\Omega_0(q)$ is

$$\Omega_0(q) = q^2kT/N\zeta P(q) \tag{7}$$

where k is the Boltzman constant, T the absolute temperature, and ζ the friction coefficient of a monomer unit.

Table I
Properties of Polymer Samples

sample	M_w,[a] kg mol^{-1}	M_w/M_n[b]
PS-S52	646	1.17
PS-473	970	1.40
PMMA-A460 F1	950	1.32

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

It is more convenient for the experimentalist to use concentration c in g/cm^3, molecular weight M, and generalized second virial coefficient $A_2(c)$. $A_2(c)$ is assumed to be concentration dependent and expresses the excess of osmotic pressure.

One verifies easily that $\phi N \sim cM$ and $v\phi N = 2A_2Mc$. One should be reminded that, strictly speaking, this theory, being a mean-field theory, is only valid above c^*, the overlap concentration.

Experimental Section

A. Materials and Sample Preparation. Polystyrene samples were prepared by anionic polymerization under inert atmosphere according to a process described elsewhere.[14] The poly(methyl methacrylate) sample was purchased from Aldrich and fractionated in benzene/methanol mixtures. The characteristics of these polymers are given in Table I.

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 over 2 h at 15 000 rpm and then directly pipeted into the scattering cells. The concentration range investigated in the binary solution covers both the dilute and semidilute regime. The total polymer concentration in the ternary mixture PS-473/PMMA-A460F1/toluene was $c_T = 3.84 \times 10^{-2}$ g/cm^3 and the weight fraction of PS-473 was $x = 0.92$.

B. Equipment. The full homodyne correlation function of the scattered intensity, defined on 100 channels, is obtained on a spectrometer that has already been described.[15a] A Spectra Physics 2-W argon ion laser operated at 488 nm was used as the light source. The cylindrical cells were mounted in a bath that was thermostated at 25.0 ± 0.1 °C. Scattered intensities, recorded at several angles between 20° and 140°, were sent to a minicomputer (DEC-PDP 11/34) that calculated the correlation functions $C(q,t)$. Normalized intensity autocorrelation functions are 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 depending upon experimental conditions. In the case of a simple diffusive process defined by a diffusion constant D, $S(q,t)$ is given by

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

It comes out that $C(q,t)$ is monoexponential with a relaxation time given by

$$t_c = 1/(2\Gamma) = 1/(2Dq^2) \tag{10}$$

All the experimental correlation functions $C(q,t)$ were analyzed by fitting with a monoexponential curve that included an optional base line.[15b]

Data sets for the ternary mixture were built from the correlation functions measured at two sampling times differing usually by a factor 20 or more.

Results and Discussion

A. Dilute and Semidilute Solutions of Binary Mixtures. The experimental correlation functions $C(q,t)$ of the scattered intensity were measured on sample PS-S52 ($M_w = 646\,000$) dissolved in toluene at small and large sampling times. No slow modes could be detected for the solutions under test. At small sampling time, $C(q,t)$ was monoexponential and the quantity t_cq^2 (cf eq 10) was independent of q in the range (6.7–19.3) × 10^4 cm^{-1}. The

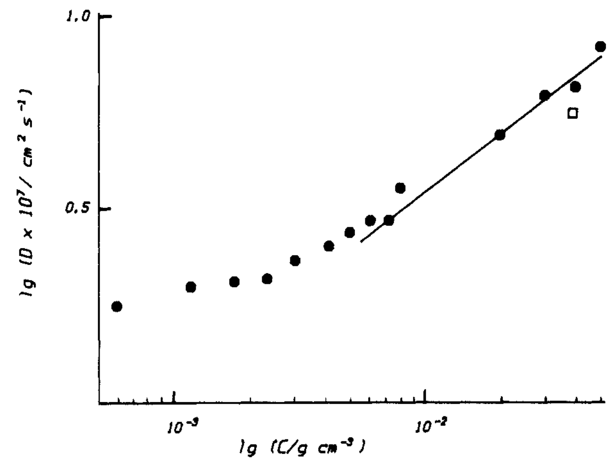

Figure 1. log-log plot of concentration dependence of the cooperative diffusion coefficient D_c for samples PS-S52 (●) and PS-473 (□). The straight line illustrates the power-law dependence of D on the concentration in the semidilute range.

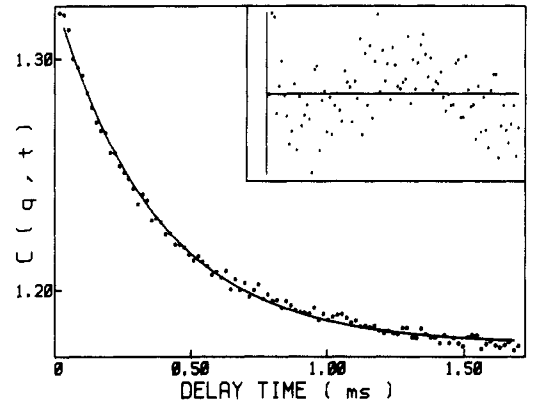

Figure 2. Correlation function of the scattered intensity by the ternary solution: PS-473 at 3.53 × 10^{-2} g/cm^3; PMMA-A460F1 at 0.31 × 10^{-2} g/cm^3; toluene at 25 °C; scattering angle, 20°; time window, 17 μs. The insert shows the distribution of the residuals.

concentration dependence of D is shown in Figure 1. In the semidilute range of concentration ($c > c^*$, c^* being of the order of 1.0 × 10^{-2} g/cm^3), least-squares fitting of the data gives the solid line expressed by

$$D = 3.64 \times 10^{-6} c^{0.51} \text{ (cm}^2\text{/s)} \quad (11)$$

It is well-known that, in this concentration range where chains overlap, the motion of each chain is governed by the entanglements.

Following present theories this curve is classical, though the value of the exponent in eq 11 is lower than what has been observed by other authors on equivalent binary mixtures.[16]

The square that appears in Figure 1 represents the experimental result obtained on the PS-473 sample dissolved in toluene at a concentration (c = 3.87 × 10^{-2} g/cm^3), which corresponds to the total polymer concentration used in the study of the ternary mixture.

B. Semidilute Solution of Ternary Mixture. Two very different correlation functions are observed at small and large sampling times in the ternary mixture under study (PS-473/PMMA-A460F1/toluene). Both can be precisely fitted with an exponential function. Typical curves, measured at a scattering angle of 20° and at two sampling times (t = 17 and 450 μs), are represented in Figures 2 and 3.

In the ternary mixtures where two relaxation modes are present, the correlation function of the scattered field is given by eq 1. The correlation function of the scattered intensity $C(q,t)$, which is measured experimentally, should therefore be written as (cf. eq 1 and 8)

$$C(q,t) = 1 + \beta(A_c \exp(-\Gamma_c t) + A_I \exp(-\Gamma_I t))^2 \quad (12)$$

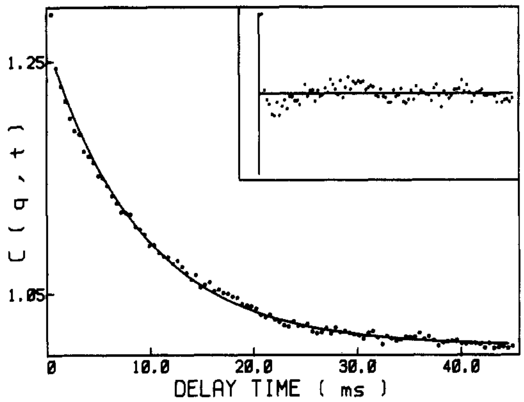

Figure 3. Correlation function of the scattered intensity by the ternary solution (same as in Figure 2): time window, 450 μs.

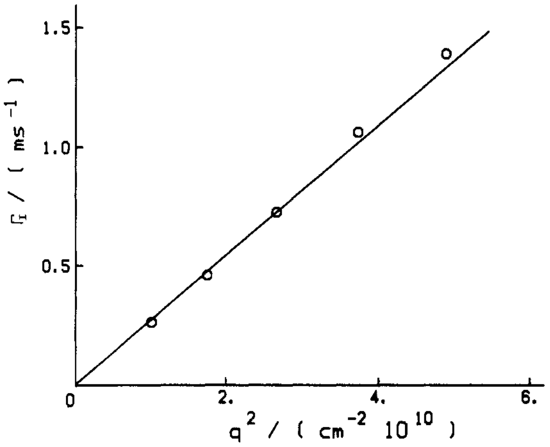

Figure 4. Angular dependence of the slow exponential decay rate for the ternary solution.

At slow sampling time, since $\Gamma_I < \Gamma_c$, $C(q,t)$ can be approximated as

$$C_s(q,t) = 1 + \beta A_I^2 \exp(-2\Gamma_I t) \quad (13)$$

while, at fast sampling time, eq 12 becomes

$$C_f(q,t) = 1 + \beta\{2A_c A_I \exp(-\Gamma_c t) + A_I^2\} \quad (14)$$

In this last equation it is supposed that the amplitude A_c is small compared to A_I as will be justified later on by the theoretical curve of Figure 5.

Equations 13 and 14 show that the scattered intensity correlation function, sampled at two different time windows, must be monoexponential. This is what was observed experimentally.

The relaxation frequencies Γ of the two modes are proportional to q^2 according to eq 10. Such a variation is shown in Figure 4 for the slow mode. Two averaged diffusion coefficient values D_I and D_c are calculated from the variation $\Gamma = f(q^2)$

$$D_I = 1.36 \times 10^{-8} \text{ cm}^2\text{/s} \quad (15a)$$

$$D_c = 5.94 \times 10^{-7} \text{ cm}^2\text{/s} \quad (15b)$$

Meanwhile the experimental value of the relative amplitude of the fast motion is 28%.

Using eq 2–6, it is possible to evaluate the theoretical ratios Γ_c/Γ_I and $A_c/(A_c + A_I)$ as a function of the composition x of the mixture and as a function of the values of the thermodynamic parameters. In order to evaluate

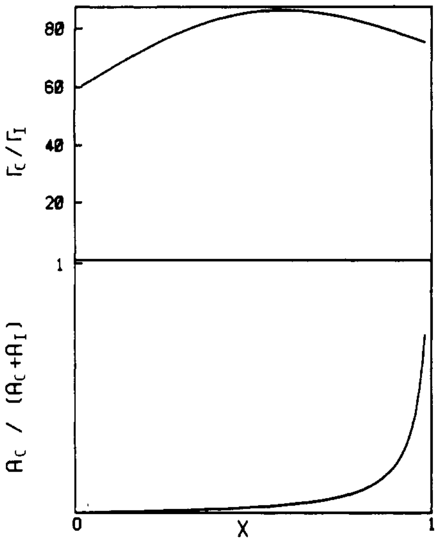

Figure 5. Theoretical variation of Γ_c/Γ_I and $A_c/(A_c + A_I)$ as a function of the weighted fraction x of the visible polymer (cf. eq 2–6). Molecular weight of the two polymers, 950000; total polymer concentration, 3.84×10^{-2} g/cm^3.

these parameters it is assumed that this mixture obeys the Flory–Huggins theory and that, in a first approximation, one can use the χ values determined in the low concentration range. The numerical values given by Fukuda et al.[17] were used in this study.

Figure 5 shows the theoretical variations of Γ_c/Γ_I and $A_c/(A_c + A_I)$ as a function of x. From these curves it appears that, for $x = 0.92$ which corresponds to the experimental case, the theoretical values are $\Gamma_c/\Gamma_I = 78$ and $A_c/(A_c + A_I) = 0.15$. It comes out that the experimental ratios $D_c/D_I = 43.7$ and $A_c/(A_c + A_I) = 0.28$ are in satisfactory agreement with the theoretical values, taking account of the fact that only a rough estimation of the thermodynamic parameters has been made.

Figure 5 shows that it is better to work at rather high x values in order to observe both slow and fast motions. Most of the works dealing with the study of the motion of one chain in the invisible entanglement formed by the second polymer were done at low x values.[1-7] In this x range the amplitude of the cooperative mode is very low, and this makes its detection practically impossible. Following the theory the frequency of the interdiffusion mode decreases when the total polymer concentration increases (cf. eq 4 and 6); this has been observed experimentally.[1-7]

C. Comparison between Binary and Ternary Systems. From the theoretical eq 5 it appears that the cooperative mode is independent of the interaction parameter χ and should be the same for a ternary PS/PMMA/toluene solution and for a binary PS/toluene solution at the same total polymer concentration c_T. The cooperative diffusion coefficient of PS-473 in toluene at the concentration $c_T = 3.87 \times 10^{-2}$ g/cm^3 is 5.62×10^{-7} cm^2/s. This point has been reported in Figure 1. It does not fit exactly the curve already established using the PS-S52 sample, but the difference is too small to be significant. This value compares well with the value of the cooperative diffusion coefficient (5.94×10^{-7} cm^2/s) that has been measured in the ternary mixture at the total polymer concentration $c_T = 3.84 \times 10^{-2}$ g/cm^3. This is another confirmation of the validity of eq 5.

Conclusion

These preliminary results show that, at least semiquantitatively, there is a good agreement between the theory of Benmouna et al.[12] and the experiments. At this point it is difficult to know if the small differences observed are due to the lack of precision of the experiments or to the approximations involved in the theory. Nevertheless it seems that this theory is a very good tool to find the conditions that have to be satisfied in order to have two observable decay modes.

As soon as one deals with a ternary system there are two relaxation modes, which do exist even if they cannot always be well separated experimentally.

Two relaxation modes have sometimes been observed in binary mixtures and have been the object of controversy.[18-20] One question that can be raised is the following: could these two relaxation modes not be interpreted by the presence of aggregates similar to those observed by static light and neutron scattering?[21,22] More precise experiments are needed to answer this quesion.

Acknowledgment. We thank Professor A. Z. Akcasu for his helpful discussions and Dr. Cl. Picot and Dr. Cl. Strazielle for their interest and valuable comments on this work.

Registry No. PS, 9003-53-6; PMMA, 9011-14-7; $C_6H_5CH_3$, 108-88-3.

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