Communications to the Editor

Quasi-Elastic Light Scattering by a Polystyrene–Poly(methyl methacrylate) Diblock Copolymer Solution in Toluene near the Overlap Concentration of the Copolymer Chains

Introduction. A few years ago theoretical investigations[1,2] had been made on the dynamic behavior of the ternary A/B/solvent systems formed by two polymer species in a good solvent, i.e., in the homogeneous phase. At the macromolecular scale this dynamic behavior is characterized by two normal modes and the dynamic scattering function $S(q,t)$ is a weighted sum of two exponentials with decay rates Γ_1 and Γ_2

$$S(q,t) = A_1e^{-\Gamma_1 t} + A_2e^{-\Gamma_2 t} \qquad (1)$$

where q is the usual scattering vector and t is the time. Quasi-elastic light scattering experiments (QELS) on different ternary polymer solutions[3] have confirmed the bimodal nature of $S(q,t)$.

Recently[4] we have studied by QELS new "quasi-ternary" systems formed by an A–B diblock copolymer in a nonselective solvent, i.e., a good solvent for both the A and B blocks. Two relaxation modes have been simultaneously observed in the system under investigation [polystyrene–poly(methyl methacrylate) (PS–PMMA)/toluene] above the overlap concentration of the copolymer chains (C^*). The slow relaxation mode (Γ_s) was attributed to the diffusive motion of the aggregates formed by the copolymer molecules in the solution. The frequency of the fast mode (Γ_1) was equal to the frequency (Γ_c) of the cooperative mode observed in the binary equivalent polystyrene (PS)/toluene system in the whole range of concentration investigated ($C^* \leq C \leq 8C^*$). The binary equivalent PS/toluene system is formed by a homopolystyrene that has the same molecular weight as the molecular weight of the copolymer at the same concentration as the copolymer concentration. This fast relaxation mode (Γ_1) was related to one of the normal modes predicted by the theory. At that time the other relaxation mode (Γ_2) was not observed. It was argued that, due to its small amplitude, this mode could be hidden by the presence of the two other modes (Γ_s and Γ_1).

Recently Borsali et al.[5] have studied the dynamic behavior of a PS–PMMA diblock copolymer in toluene. In this study the authors have found two relaxation modes. The fastest mode was interpreted as the structural mode (Γ_2) predicted by the theory. In the q vector range investigated the values of the frequency of this mode were of the same order of magnitude as the values of the frequency (Γ_c) of the cooperative mode of the equivalent PS/toluene solution. The frequency of the slow mode was much lower than Γ_c. Nevertheless, the authors have interpreted this mode as the Γ_1 mode predicted by the theory. This interpretation is questionable knowing that, even in good solvent for the PS and the PMMA blocks aggregate or micelle formation can occur.[4,6]

In the present study we show some results that were obtained in toluene on a PS–PMMA diblock copolymer of higher molecular weight and at a lower concentration than in the previous studies[4,5] in order to avoid the formation of aggregates.

Experimental Section. The poly(styrene-*b*-(methyl methacrylate)) diblock copolymer (1g4) was synthesized by anionic polymerization under inert atmosphere.[4] The copolymer sample was fractionated from benzene/chlorobenzene [1:1 (v/v)] solution by progressive addition of petroleum ether. The fraction which was used in this study (1g4f2) was characterized by a high molecular weight (M_w = 640 000) and a low polydispersity (PI = 1.06). The weight fraction of PS in the copolymer was $x = 0.38$.

The dynamic behavior of this copolymer has been studied in toluene (Aldrich, 99%) by quasi-elastic light scattering. The polymer concentration was $C = 0.669 \times 10^{-2}$ g·cm^{-3} which is equivalent to $C \simeq 1.6C^*$ where C^* is calculated according to the relation

$$C^* = 3M_w/(4\pi R_{gT}{}^3N_a) \qquad (2)$$

where N_a is Avogadro's number. The radius of gyration R_{gT} of the copolymer has been estimated to 390 Å by interpolation of experimental data[7] obtained on the polystyrene/toluene system.

The solution was centrifuged for 3 h at 15 000 rpm in order to remove dust particles. The dynamic light scattering measurements were performed at 25 °C on a home-built spectrometer. The experimental setup is described elsewhere.[8] The light of a vertically polarized 488-nm Ar ion laser (Spectra Physics 2020) was measured at several scattering angles in the range 20–80° ($0.26 \leq qR_{gT} \leq 0.96$). At each angle the autocorrelation function of the scattered light $G^{(2)}(\tau)$ was defined on 200 points and accumulated for 30 min in a ALV-3000 (ALV-Langen Co. FRG) digital autocorrelator. The measurements were repeated three to seven times, and the correlation functions were sampled at several delay times ranging from 1 to 60 μs. In a first step the normalized electric field correlation functions $C(\tau)$ were analyzed by the method of cumulants[9]

$$\log\,[C(\tau)] = \log[G^{(2)}(\tau)/C_0 - 1]^{1/2} = C_1 - \Gamma_0\tau + \mu_2/2!(\Gamma_0\tau)^2 - \mu_3/3!(\Gamma_0\tau)^3 ... \qquad (3)$$

where C_0 is the calculated far point of the autocorrelation function of the scattered intensity, C_1 is a constant, and Γ_0, μ_2, and μ_3 are the first, second, and third cumulants, respectively. Furthermore, the CONTIN method[10] has been systematically used for correlation function profile analysis of $G(\Gamma)$ or $G(D)$ distributions where Γ and D are related by

$$\Gamma = 2Dq^2 \qquad (4)$$

The experimental curves were carefully analyzed with floating and fixed base lines in the fitting procedure and with IQUAD = 1 in the CONTIN program taking account of the fact that for the standard IQUAD = 3 CONTIN undersmoothed in the region of short decay times.[11]

Results and Discussion. The experimental correlation functions of the intensity of the light scattered by the 1g4f2 copolymer solution were systematically compared to those obtained on a solution of polystyrene PSS52 (M_W = 630 000; PI = 1.17) in toluene at the same concentration. Furthermore, a solution of poly(methyl methacrylate)

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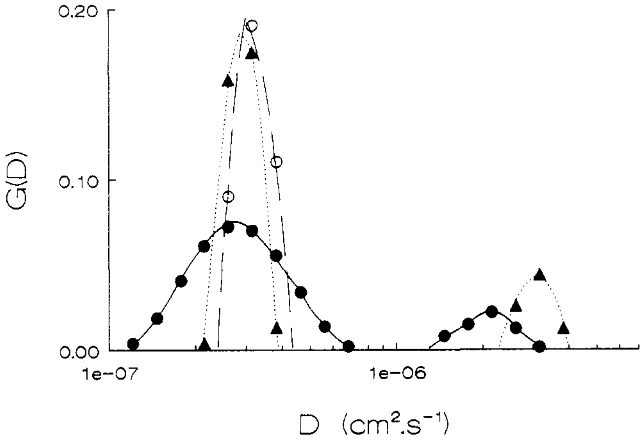

Figure 1. Diffusion coefficient distribution $G(D)$ vs D obtained from the CONTIN analysis: (-O-) polystyrene PSS52, $\theta = 30°$, $\tau = 4\ \mu s$; (···▲···) copolymer 1g4f2, $\theta = 30°$, $\tau = 4\ \mu s$; (—●—) copolymer 1g4f2, $\theta = 60°$, $\tau = 1\ \mu s$.

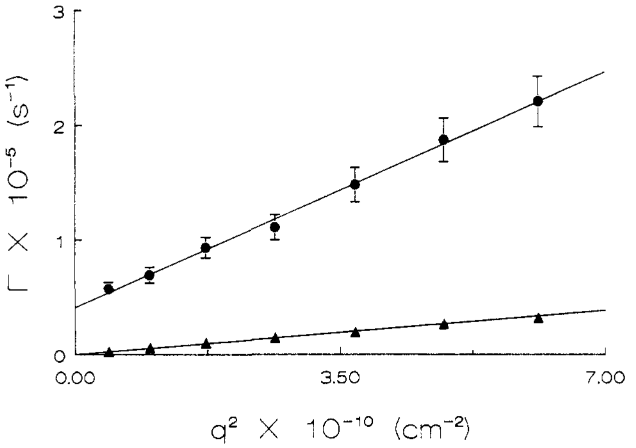

Figure 2. Variation of the relaxation frequencies Γ of the slow (▲) and fast (●) modes as a function of q^2. The solid lines represent the best linear fits to the experimental data.

PMMA459f2 (M_W = 710 000; PI = 1.58) in toluene has given flat correlation functions of the scattered intensity in the same conditions of observation as those for the copolymer solution at an equivalent concentration in PMMA. The experimental correlation functions obtained on the copolymer solution are characterized by a large value ($0.080 \leq \mu_2 \leq 0.120$) of the second cumulant μ_2 as compared to the value given by the PSS52 solution (μ_2 = 0.025). In Figure 1 we have represented the distribution function of the diffusion coefficient $G(D)$ obtained from the CONTIN analysis of the experimental correlation functions given by the PSS52 and by the 1g4f2 solutions. This distribution function is sharp for the homopolymer solution ($D_c = 3.0 \times 10^{-7}$ cm²·s⁻¹) while it is bimodal for the copolymer solution. The position of the slow mode in the distribution does not move with the scattering angle θ. Furthermore, it coincides with the mode observed in the equivalent binary solution, whatever the θ value. The position of the fast mode depends on the scattering angle and is shifted toward the low D values as θ increases. Only one mode has been detected in the PS/toluene solution; the bimodal distribution is specific to the copolymer solution.

The variation of the relaxation frequencies of the slow (Γ_1) and fast (Γ_2) modes is represented as a function of q^2 in Figure 2. This variation is linear for the two modes, but the curve corresponding to the fast mode extrapolates to a constant value very different from zero at zero scattering angle. Each experimental value reported in this figure is the mean value obtained after several measurements at several delay times. From these repeated measurements the experimental accuracy on each point has been estimated to 2% for the slow mode with a large amplitude and to 10% for the fast mode with a smaller amplitude.

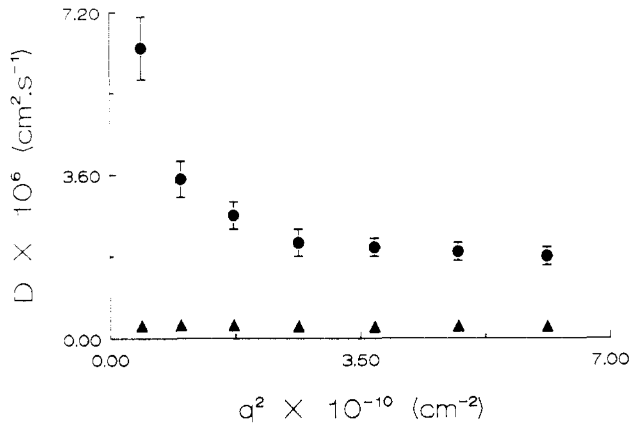

Figure 3. Variation of the slow (▲) and fast (●) diffusion coefficients as a function of q^2.

The average D_1 value calculated from the slope of the straight line represented in Figure 2 is $D_1 = 2.74 \times 10^{-7}$ cm²·s⁻¹. This value is comparable to the value of the cooperative diffusion coefficient measured on the equivalent binary PS/toluene solution ($D_c = 3.0 \times 10^{-7}$ cm²·s⁻¹). Recently Akcasu et al.[12] have shown that the two normal modes observed in a ternary A/B/solvent system can be assimilated to the cooperative and the interdiffusive modes in some special case where the two polymer species differ only by their contrast factor and are thermodynamically and hydrodynamically equivalent. Nevertheless, our experimental results show that, even when these conditions are not fulfilled, there is only a small difference between the value of the cooperative diffusion coefficient of the equivalent binary A/solvent solution and the value of the diffusion coefficient of the slow normal mode that characterizes the ternary A/B/solvent system.

The variation of the diffusion coefficients D_1 and D_2 that characterize the dynamics of the copolymer solution is drawn as a function of the square of the wavevector in Figure 3. While the D_1 value calculated from the CONTIN analysis is independent of the scattering angle, the D_2 value increases as q decreases. The value of the ratio $D_2^{\theta=20°}/D_2^{\theta=80°} \simeq 3$ is much higher than the value of $\simeq 1.2$ found by Borsali et al.[5] Taking account of the accuracy in the measurement, it is clear that D_2 varies with the scattering angle. This is typical of a structural mode.

In this work, if we discard a slow mode probably due to aggregation since it disappears at low concentration,[4] it has been shown experimentally that two modes of relaxation characterize the dynamical behavior of diblock copolymer solutions in nonselective solvent. The fast mode (Γ_2) is a structural mode that was already observed by neutron spin echo on PSH-PSD/benzene solutions.[13,14] In peculiar cases[12] this mode reflects the relative motion of one species with respect to the other. The slow mode (Γ_1) is a diffusive mode which, in the same peculiar cases, is the cooperative mode of the physical network formed by the copolymer chains in the solvent.

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