Dynamic Light Scattering from Semidilute Solutions of Styrene–Isoprene Diblock Copolymer

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ABSTRACT: The dynamic properties of semidilute solutions of a styrene–isoprene diblock copolymer in 1,1-diphenylethylene, a solvent isorefractive with the polystyrene block, have been studied by quasielastic light scattering spectroscopy. Decay time distributions having a complex structure with three separate bands have been observed at higher copolymer concentrations. The slowest mode has been attributed to diffusion of copolymer aggregates or associates. The two faster dynamic modes have been interpreted on the basis of the mean-field theory developed by Benmouna et al.

Introduction

Recently, Benmouna and co-workers have published a series of papers in which they develop a theory of quasielastic light scattering (QELS) from ternary mixtures of two homopolymers and a solvent[1] and binary semidilute solutions of diblock copolymers[2,3] based on the random-phase approximation. The main result of the theory is a prediction of the existence of two dynamic modes in QELS spectra of these systems. The physical meaning attributed to the relaxation modes that characterize the dynamic behavior of ternary polymer systems has been discussed by Akcasu and co-workers.[4-6] These two modes were experimentally observed in ternary mixtures of two different homopolymers in a solvent isorefractive with one of the polymers[7-11] and in solutions of two chemically identical polymers having different molar masses.[12,13] Just after the original version of this paper had been submitted to the editors, Borsali et al.[14] published the first experimental evidence of the existence of two relaxation modes in polystyrene–poly(methyl methacrylate) diblock copolymer solutions using dynamic light scattering.

In this paper, the experimental evidence of these two modes is revealed by QELS for semidilute solutions of a styrene–isoprene diblock copolymer in 1,1-diphenylethylene, isorefractive with the polystyrene blocks, and provides a sufficient optical contrast for the polyisoprene ones. The experimental data have been interpreted in terms of the mean-field theory developed by Benmouna and co-workers.[2]

Experimental Section

Material: A styrene–isoprene diblock copolymer sample, used as a model substance in the present study, was synthesized by anionic polymerization, employing a previously described[15] initiator system, reaction conditions, and stabilizer. Its characterization, given in ref 16 under a code symbol SI-*n*, can be summarized as follows: Mass- and number-average molar mass values of the whole copolymer are, respectively, 183 000 and 170 000 g/mol; mass- to number-average molar mass ratios, characterizing the polydispersity, are 1.10 and 1.24 for the polystyrene block and the polyisoprene block, respectively, the chemical composition, expressed by the mass fraction of the styrene units, is 0.58 (all other important molecular parameters can be calculated from these data, using well-known relations); mole fractions of 1,2-, 3,4-, and 1,4-addition structures of the polyisoprene block are 0.05, 0.62, and 0.33, respectively.

The copolymer samples were dissolved in 1,1-diphenylethylene at room temperature, and the solutions were filtered through a glass G-5 bacterial filter into dust-free measuring cells. 1,1-Diphenylethylene is isorefractive with the polystyrene block, provides a sufficient optical contrast for the polyisoprene block, and is a thermodynamically good solvent for both blocks.[16] Moreover, the high viscosity of this solvent slows down the dynamic processes under study, a circumstance advantageous for the dynamic light scattering experiment.

Apparatus and data treatment: Quasielastic light scattering measurements were carried out with a photon correlation spectrometer described elsewhere.[17] The homodyne spectrometer equipped with a 96-channel digital correlator enabled us to measure the multi-time-correlation function (MTCF) covering 3.5 decades of delay time. The correlator operated with three simultaneous sampling times.

The autocorrelation functions were treated by inverse Laplace transform, where a constrained regularization calculation (REPES[18]), similar to that of CONTIN[19] was used to obtain the distribution, $A(\tau)$, of decay times τ. This method uses an equidistant logarithmic grid of fixed components (here, a grid of 12 components/decade) and determines their normalized scattering amplitudes.

Results and Discussion

The decay time distributions $A(\tau)$, obtained by the inverse Laplace transform of the multi-time-correlation functions (the scattering angle $\theta = 45°$), are shown in Figure 1 for several polymer concentrations c. For $c = 8 \times 10^{-3}$ g/mL, which is close to the overlap concentration c^* ($\simeq 7 \times 10^{-3}$ g/mL), only two dynamic modes are present. With increasing concentration the decay time distribution becomes broader and displays a complex structure with three separate bands peaked at τ_f, τ_m, and τ_s ($c = 4$ and 6×10^{-2} g/mL). The concentration dependences of decay times τ_f and τ_m and the ratios of the corresponding scattering amplitudes, A_f/A_m, are summarized in Table I.

Since τ_s and A_s of the very slow mode (s-mode) are strongly dependent on the sample history (e.g., the long time peak is very weak in freshly prepared samples with $c = 4 \times 10^{-2}$ g/mL and increases with time), we suggest that this contribution to the scattered light could come from traces of aggregates/associates of the copolymer molecules. The present hypothesis has been supported by measurements of the angular dependences of the integral scattering intensity where a pronounced downward curvature of radiation envelopes, typical of such a contingence, was observed at low scattering angles.

The contribution to the dynamic light scattering of the remaining two faster modes (τ_f, τ_m) has been found to be independent of the procedure of sample preparation and the storing conditions. We therefore suppose that these modes result from the macromolecular dynamics. According to a recently developed theory of quasielastic light scattering from semidilute copolymer solutions, based on

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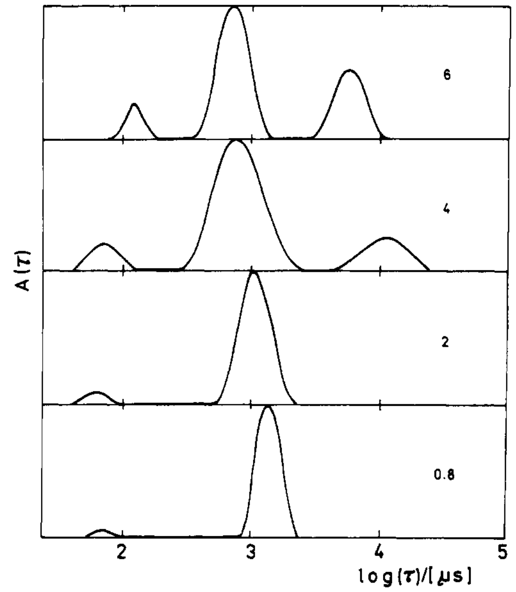

Figure 1. Distribution function $A(\tau)$ of decay time τ of block copolymer solutions (Ar ion laser, scattering angle $\theta = 45°$). Numbers on the right side of the figure represent the respective concentrations (10^{-2} g·cm^{-3}).

Table I
Values of $\tau_{f(I)}$, $\tau_{m(C)}$, and τ_s Decay Times Pertaining to f-, m-, and s-Process Ratios of τ_f/τ_m and the Corresponding Scattering Amplitudes, A_f/A_m[a]

$c \times 10^2$, g·cm^{-3}	$\tau_{f(I)}$, μs	$\tau_{m(C)}$, μs	τ_s, μs	τ_f/τ_m	A_f/A_m
0.8	70	1370		0.05	0.03
2.0	62	1070		0.06	0.06
4.0	71	790	11 000	0.09	0.13
6.0	130	720	5 800	0.18	0.18

[a] Concentration dependence, Ar ion laser (514.5 nm), $\theta = 45°$.

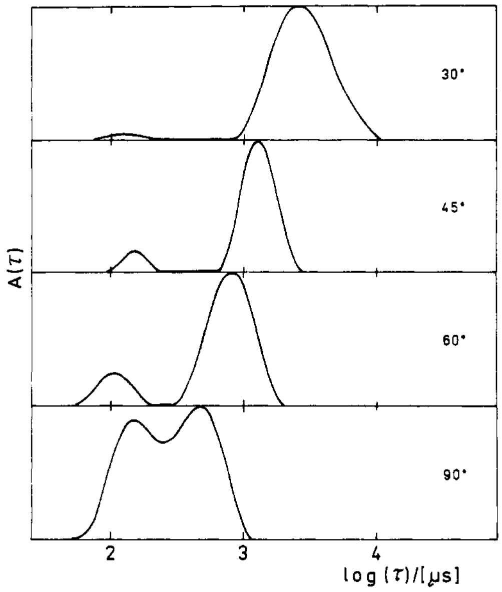

Figure 2. Distribution function $A(\tau)$ of decay time τ of block copolymer solutions (He–Ne laser, $c = 4 \times 10^{-2}$ g·cm^{-3}). Numbers on the right side of the figure represent the respective scattering angles.

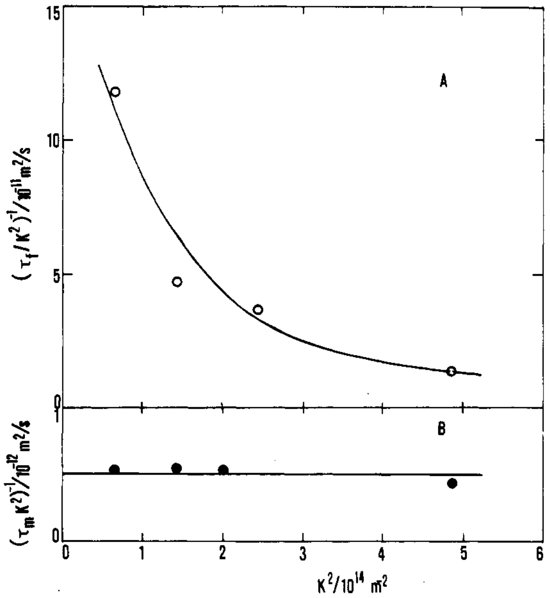

Figure 3. (a) Plot of the quantities $(\tau_f/K^2)^{-1}$ for the f-mode and (b) $(\tau_m K^2)^{-1}$ for the m-mode as a function of K^2 (where K is the scattering vector).

Table II
Values of $\tau_{f(I)}$ and $\tau_{m(C)}$ Decay Times and Ratios of τ_f/τ_m and the Corresponding Scattering Amplitudes, A_f/A_m[a]

θ, deg	$\tau_{f(I)}$, μs	$\tau_{m(C)}$, μs	τ_f/τ_m	A_f/A_m
30	130	2900	0.05	0.03
45	150	1290	0.12	0.12
60	110	780	0.14	0.18
90	150	490	0.3	0.9

[a] Angular dependence, He–Ne laser (632.8 nm), $c = 4 \times 10^{-2}$ g·cm^{-3}.

the random-phase approximation,[2] the fast (f-) and medium (m-) modes should correspond to the I- and C-relaxation modes, respectively.[2] The former is characteristic of the motion of one block of the copolymer with respect to the other. It is an internal mode in solution. The latter (C) corresponds to the cooperative diffusion mode. The above interpretation ensues from the following considerations:

(i) Apparently, the m-mode links up with the cooperative diffusion mode at low concentrations.

(ii) The m-mode depends on the copolymer concentration in solution in that τ_m decreases with increasing c in accordance with predictions for the C-mode.[2]

(iii) According to the theoretical implication,[2] the I-mode should be faster than the C-mode for $R_{gT}{}^2K^2 < 1$, where R_{gT} is the radius of gyration of the total chain and K is the scattering vector; this condition is met in our case and, therefore, the f-mode has been attributed to the I-mode.

In order to support the above interpretation, the MTCF's have been measured as a function of the scattering angle θ for a freshly prepared sample ($c = 4 \times 10^{-2}$ g/mL). Results of the REPES calculations are given in Figure 2 (the weak s-bands are omitted). It is seen from Figure 3 that the m-mode has a plausibly diffusive character ($1/\tau_m \sim K^2$), while the f-mode seems to be relaxational; τ_f is independent of the scattering angle within the limits of experimental error (Table II). The relative contribution of the fast (internal) mode increases with increasing K in accordance with predictions for the I-mode. Unfortunately, the accuracy of the determination of τ_f and A_f is rather poor due to a generally low level of the excess scattering intensity of the copolymer solution in 1,1-diphenylethylene and weakness of the fast dynamic process, which leads to a considerable scatter of the results (about ±20% of the mean value of τ_f). The angular dependences of τ_f and τ_m decay times and of the ratios of the corresponding amplitudes A_f/A_m are given in Table II.

To check quantitatively the results of the theory of Benmouna et al.,[2] we used their relations for semidilute solutions of a hypothetical 50/50 diblock copolymer in a solvent, isorefractive with one of the blocks and providing a sufficient optical contrast for the other block. Assuming that the copolymer chains are made of two blocks having the same radius of gyration and also the same number of monomeric units N of identical volume (the assumption being comparatively well fulfilled for the binary system under study), from relations (21) and (22) in ref 2 we have

$$\frac{\tau_C}{\tau_I} = \frac{P_T(K)}{P_{1/2}(K) - P_T(K)} \frac{1 - \chi/\chi_c(K)}{1 + 2v\varphi N P_T(K)} \tag{1}$$

where $\chi_c(K) = N\varphi(P_{1/2}(K) - P_T(K))$, N and $P_{1/2}$ are, respectively, the number of monomeric units per the "visible" part of the chain and the form factor of a block, P_T is the form factor of a chain of $2N$ monomeric units, χ is the Flory–Huggins interaction parameter, φ is the number of monomeric units per unit volume, v is the excluded volume parameter of monomeric units, and τ_I and τ_C are characteristic relaxation times corresponding to the I- and C-modes, respectively.

From (24) and (25) in ref 2 we obtain A_C/A_I

$$\frac{A_C}{A_I} = \frac{P_T(K)}{P_{1/2}(K) - P_T(K)} \frac{1 - \chi/\chi_c(K)}{1 + 2v\varphi N P_T(K)} \tag{2}$$

As the right-hand sides of (1) and (2) are identical, we may write

$$A_C/A_I = \tau_C/\tau_I \tag{3}$$

regardless of the scattering angle and copolymer concentration. The validity of relation (3) is shown in Tables I and II. The differences between τ_f/τ_m and A_f/A_m values are smaller than the experimental error ($\approx\pm 20\%$). For $\theta = 90°$, the agreement could not be checked because the characteristic relaxation times of the f- and m-modes are too close to each other and cannot be distinguished adequately by the inverse Laplace transform.

The experimental finding that the f-mode is relaxational ($\tau_{f(I)}$ is independent of K^2) is in accordance with predictions for the I-mode in the small-K region. Indeed, $(KR_{gT})^2 \ll 1$ for the copolymer sample used ($R_{gT} \simeq 23$ nm as estimated from static light scattering experiments). The limiting value of $\tau_f(K \rightarrow 0)$ can be employed for the estimation of R_{gT} using the simply modified relation (27) in ref 2

$$\tau_I(K \rightarrow 0) = R_{gT}^2/6D_0 \tag{4}$$

where D_0 is the diffusion coefficient of a single total chain. $R_{gT} = 47 \pm 5$ nm was obtained using the mean value of $\tau_{f(I)}$ for $c = 4 \times 10^{-2}$ g/mL in Table II, and D_0 was calculated from the zero concentration limit of τ_m. This R_{gT} value is twice as high as that estimated from the static light scattering measurements (23 nm) and is comparable with R_g of an analogical polystyrene homopolymer in a thermodynamically good solvent.[20]

Conclusion

The existence of a bimodal distribution of relaxation times predicted by the theory of Benmouna et al.[2] for semidilute solutions of diblock copolymers was corroborated experimentally, and some physical implications of the theory were checked.

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Registry No. Styrene–isoprene (copolymer), 105729-79-1; 1,1-diphenylethylene, 530-48-3.