

Spin-Echo Neutron Scattering from Copolymers in Intermediate Solvents

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ABSTRACT: Dynamics of a diblock copolymer of deuterated styrene-ordinary styrene in semidilute solutions have been investigated by the spin-echo neutron-scattering technique. In the zero-average contrast conditions, the short-time interdiffusion mode has been analyzed as a function of the concentration. The results are discussed in the framework of the random phase approximation (RPA).

1. Introduction

In a recent paper¹ we have discussed some preliminary results of spin-echo neutron-scattering experiments² from symmetric diblock PSH-PSD copolymers in an intermediate solvent. This solvent was approximately a 50/50 mixture of deuterated and ordinary benzene, chosen to satisfy the zero-average contrast condition

$$(a_H - a_0)x + (a_D - a_0)(1 - x) = 0 \quad (1a)$$

or

$$a_H x + a_D (1 - x) = a_0 \quad (1b)$$

and for a 50/50 diblock copolymer $x = 1/2$

$$(a_H + a_D)/2 = a_0 \quad (1c)$$

In these equations a_H , a_D , and a_0 are the coherent scattering lengths per unit volume of the ordinary polymer, the deuterated polymer, and the solvent, respectively, and x is the volume fraction of the nondeuterated block within the copolymer. As will be explained later, this condition is particularly favorable for measuring the interdiffusion mode of the copolymer. In ref 1, only one polymer concentration was considered and the discussion was limited to angular variation of the amplitude and frequency of this mode; the purpose of this paper is to extend this work to other concentrations in the semidilute regime. Before presenting the experimental data, we briefly recall the main formulas needed for their analysis.

The intermediate scattering function, $S(q, t)$, which is directly accessible by the spin-echo neutron-scattering technique, has been calculated with the random phase approximation (RPA) for any arbitrary copolymer-solvent system.³ In the particular case of a symmetric diblock PSH-PSD copolymer, the result has the simple form

$$\frac{S(q, t)}{\varphi N} = \left(\frac{a_D - a_H}{2} \right)^2 (P_{1/2} - P_T) e^{-\Gamma_1 t} + \left(\frac{a_D + a_H}{2} - a_0 \right)^2 \frac{P_T}{1 + \nu \varphi N P_T} e^{-\Gamma_C t} \quad (2)$$

The symbols have their usual definitions: t is the time, $q = (4\pi/\lambda) \sin(\theta/2)$, λ is the wavelength of the incident beam and θ the scattering angle, φ is the volume fraction of polymer and N the total degree of polymerization, $P_{1/2}$

and P_T are the form factors for the block H or D and the total copolymer chain in the system, respectively, which are normalized to unity at $q = 0$. Equation 2 is obtained assuming that the Flory interaction parameter between H and D monomers is zero (i.e., $\chi_{HD} = 0$); this is a reasonable assumption for the low molecular weight considered here.⁴ It was also assumed that the excluded-volume parameters are equal ($\nu_H = \nu_D = \nu$); this implies that the interaction parameters between the solvent and the ordinary or the deuterated monomers are the same.

If one uses the concentration as a variable and the generalized second virial coefficient (A_2) as a characteristic of the interaction, these quantities are related to ν and φ by the classical relation⁵

$$2A_2 M c = \nu \varphi N$$

where M is the molecular weight of the copolymer.

Γ_1 and Γ_C are the relaxation frequencies characterizing the system; they depend on the dynamic model used to describe the motion of the copolymer molecules in solution. Their general expressions have been already discussed,³ we give their dependence as a function of q and c in connection with analysis of the experimental data.

Equation 2 shows that, in general, two modes must be observed, but, if one chooses a solvent satisfying the zero-average contrast conditions given in eq 1, the amplitude of the second mode vanishes and only the short time interdiffusion mode is observed:

$$\frac{S(q, t)}{\varphi N} = \left(\frac{a_D - a_H}{2} \right)^2 (P_{1/2} - P_T) e^{-\Gamma_1 t} \quad (3)$$

The total scattering intensity, $S(q)$, has also been measured. Its theoretical value obtained either directly⁶ or by letting $t = 0$ in eq 2 is

$$\frac{S(q)}{\varphi N} = \left(\frac{a_D - a_H}{2} \right)^2 (P_{1/2} - P_T) + \left(\frac{a_D + a_H}{2} - a_0 \right)^2 \frac{P_T}{1 + \nu \varphi N P_T} \quad (4)$$

In the zero-average contrast condition, we have evidently

$$\frac{S(q)}{\varphi N} = \left(\frac{a_D - a_H}{2} \right)^2 (P_{1/2} - P_T) \quad (5)$$

Table I
Polymer Characterization

sample	M_n^a	M_w^a	M_z^a	polydispersity	% PSD ^b
PSD-PSH561	9100	10 800	13 500	1.12	0.46

^a Measured by GPC. ^b Measured by NMR.

This result shows that the ratio of the static scattering intensity to the concentration is independent of the concentration. It is obtained only if the three following conditions are fulfilled:

- (i) The diblock copolymer has to be geometrically symmetrical; namely, the two blocks must have the same radius of gyration and the same volume per monomer.
- (ii) The zero-average contrast condition in eq 1c must be satisfied.
- (iii) The χ -parameter between the two monomeric species must be zero.

2. Experimental Section

The copolymer used in this study is a diblock copolymer of deuterated styrene-ordinary styrene. This situation allows us to disregard all the problems connected with the partial compatibility of the two blocks. The same sample PSD-PSH561 was used in previous experiments.^{1,6} The methods of preparation and characterization are given in these references, and the useful characteristics of the sample are recalled in Table I.

Four copolymer solutions were prepared in the range $0.154 < c$ ($\text{g}\cdot\text{cm}^{-3}$) < 0.484 . The solvent used was a mixture of deuterated and hydrogenated benzene (48.7/51.3), which corresponds precisely to the zero-average contrast conditions.¹ The overlap concentration c^* is, for this system, on the order of $0.14 \text{ g}\cdot\text{cm}^{-3}$. All the measurements were carried out at room temperature.

Neutron-scattering experiments were performed at the Institute von Laue Langevin (Grenoble, France), with the NSE spectrometer IN11.² The wavelength of the incident neutrons was $\lambda = 8.5 \text{ \AA}$, and the domain of the angular variation was $2^\circ < \theta < 13^\circ$. The intermediate scattering functions $S(q, t)$ were recorded in the observed time range $0.3 < t$ (ns) < 17 . The experimental data were analyzed following a classical treatment.²

Depending on the experimental configuration, the spin-echo spectrometer gives, as final output, the normalized intermediate dynamic scattering function $S(q, t)/S(q, 0)$ and the static structure factor $S(q)$.

3. Experimental Results and Discussion

As an illustration of the results, Figure 1 shows the values of the intermediate scattering function $S(q, t)/S(q, 0)$ (in log scale) versus time as directly obtained by the spin-echo spectrometer (IN11).

The data are given for three different angles (small, intermediate, and high angles) to illustrate the behavior of $S(q, t)$ as function of q . One observes that, in the low q -range, all the data fall on a straight line, indicating a single-exponential behavior at all times. In the high q -range, one notes a tendency of deviation from the initial slope when t increases. This deviation, which has been found in homopolymer systems,⁷ can be attributed to the effect of internal modes, since in this domain of q , qR_g is much larger than 1 ($qR_g \approx 5$).

(a) Behavior in the Low q -Range. From Figure 1 one obtains the relaxation frequencies Γ_1 's, which are plotted as function of q^2 in Figure 2 for the four concentrations investigated. (All of these concentrations are larger than c^* .) For the sake of simplicity these data are analyzed first by neglecting hydrodynamic interactions (Rouse model).

In this case, Γ_1 in eq 3 is given by

$$\Gamma_1 = q^2 \frac{D_0}{N} (P_{1/2} - P_T)^{-1} \quad (6)$$

where D_0 denotes the diffusion coefficient of a monomer

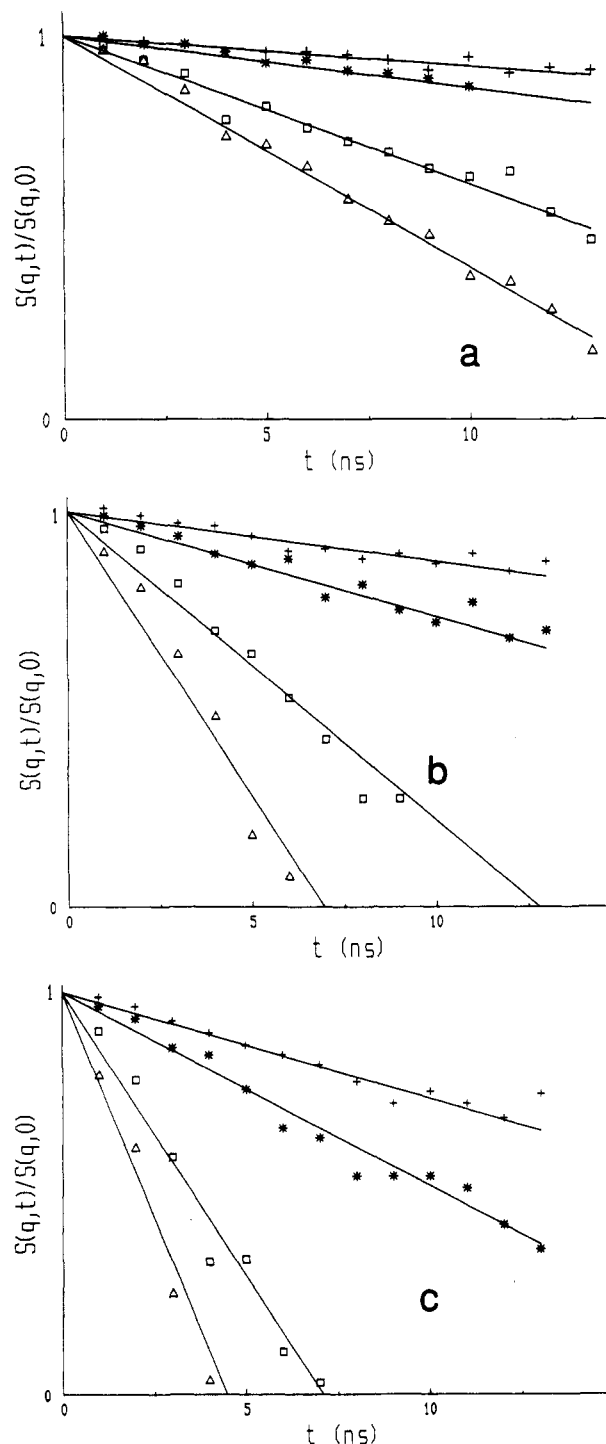


Figure 1. Dynamic structure factor of PSD-PSH copolymer in benzene solutions: (a) $\theta = 6^\circ$; $q = 7.8 \times 10^{-2} \text{ \AA}^{-1}$; (b) $\theta = 10^\circ$; $q = 13 \times 10^{-2} \text{ \AA}^{-1}$; (c) $\theta = 13^\circ$; $q = 17 \times 10^{-2} \text{ \AA}^{-1}$. (+), (*), (\square), and (Δ) correspond, respectively, to $c = 48.4 \times 10^{-2}$, 41.1×10^{-2} , 24.6×10^{-2} , and $15.4 \times 10^{-2} \text{ g/cm}^3$.

unit or $D_0 \approx kT/\xi$, ξ being the monomeric friction coefficient. Expanding this equation in the low q -range gives

$$\Gamma_1 = \frac{6D_0}{NR_g^2} + q^2 \frac{9D_0}{4N} \quad (7)$$

R_g is the radius of gyration of the whole copolymer.

One sees that the intercept at $q = 0$ gives D_0/NR_g^2 and the slope D_0/N directly. Both quantities decrease when the concentration increases. This decrease can be attributed mainly to D_0 since the variation of R_g with concen-

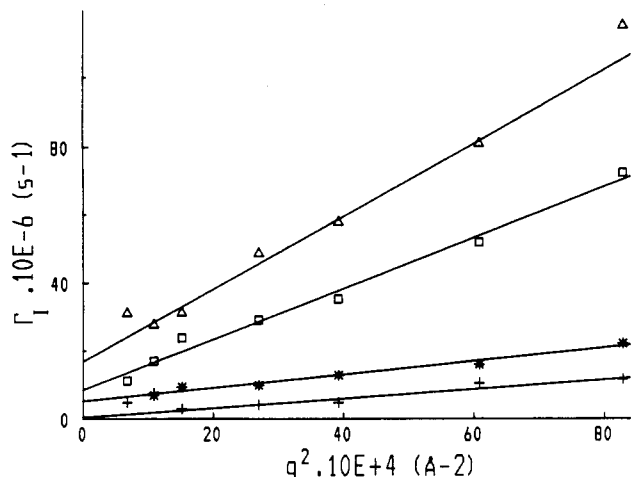


Figure 2. Variation of the relaxation frequency as a function of q^2 . The symbols are the same as in Figure 1.

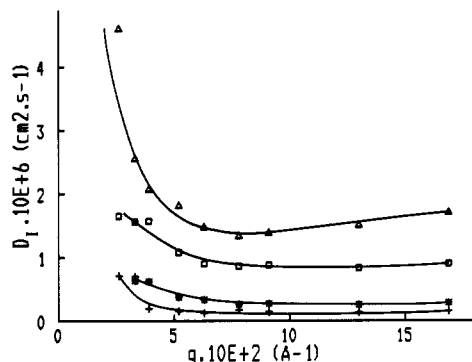


Figure 3. Generalized diffusion coefficient $D_I(q, c)$ as a function of q . Same symbols as in Figure 1.

tration can be neglected for this range of low molecular weight polymer ($M_w = 10\,800$). It is also known that in this range excluded-volume effects are practically negligible. The z -average radius of gyration R_{gz} is on the order of 30 Å as calculated by the relation⁶

$$R_{gz} (\text{Å}) = 0.283 M_w^{0.5} \quad (8)$$

(b) Behavior in the Whole q -Range. Figure 3 shows the generalized diffusion coefficient

$$D_I(q, c) = \Gamma_I(q, c) / q^2 \quad (9a)$$

as a function of q for the concentrations indicated before. Following eq 6, $D_I(q, c)$ should be equal to

$$D_I(q, c) = \frac{D_0}{N} (P_{1/2} - P_T)^{-1} \quad (9b)$$

One notes that D_I increases in the small q -range, confirming our earlier preliminary experiment.¹ This increase is more pronounced for the lower concentrations. In order to discuss more precisely these data, one can introduce the generalized mobility $\mu(g, c)$ defined as

$$kT\mu(q, c) = D_I(q, c) [P_{1/2}(q) - P_T(q)] \quad (10)$$

Following the Rouse model $kT\mu(q, r) = D_0/N$ is independent of q . In order to plot the curves μ versus q , one needs the experimental values of $[P_{1/2}(q) - P_T(q)]$. These values have been evaluated from the experimental results using eq 5 and are plotted in Figure 4 for the four concentrations investigated. The theory⁶ predicts that this quantity should be independent of c . This is approximately the case, taking into account the lack of precision on the measurement of the static structure factor

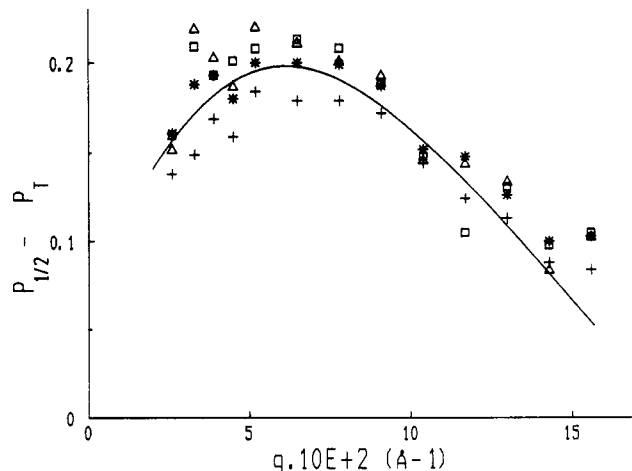


Figure 4. Variation of $S(q)$ as a function of q . Same symbols as in Figure 1. Full line: theoretical curve, taking into account polydispersity (see ref 6).

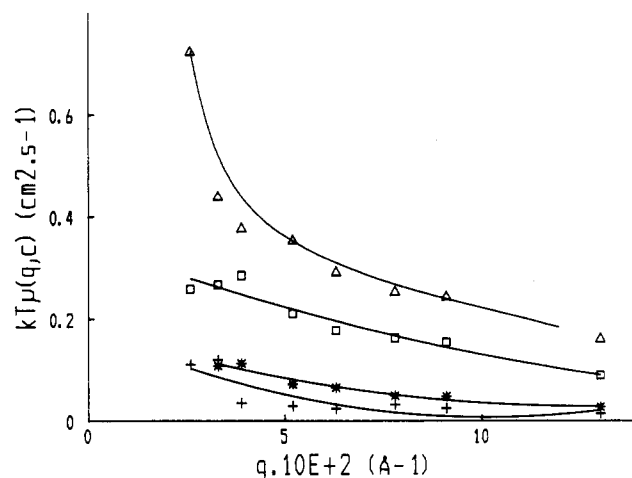


Figure 5. Mobility $\mu(q, c)$ as a function of q . Same symbols as in Figure 1.

by the spin-echo technique. The full line represents the theoretical values corrected for the effect of polydispersity.⁶ We have used these last values to calculate the generalized mobility $\mu(q, c)$, and the results are plotted in Figure 5.

(i) Influence of q . For the highest two concentrations, the mobility is practically constant in the whole q -range, confirming that the hydrodynamic interactions are completely screened. One observes that, for the lowest concentrations, the mobility increases in the low q -range, indicating that the hydrodynamic effect should be taken into consideration. A more detailed discussion of this effect will be reported elsewhere.

(ii) Effect of Concentration. One sees that for any value of q the mobility decreases when the concentration increases. This means that the effective frictional coefficient ξ increases with the concentration⁸ as one would expect.

4. Conclusion

These measurements, made with the spin-echo neutron-scattering technique under the condition of zero-average contrast, allow the direct determination of one of the two relaxation mechanisms of the system, called the short-time interdiffusion. This experimental approach is the only known possibility for a direct measurement of this quantity. It has been shown that (1) this diffusion coefficient decreases when the polymer concentration

increases, which is the expected behavior, (2) the variation of the normalized static structure factor as a function of q is given by $(P_{1/2} - P_T)$ for any concentration, and (3) the generalized mobility is independent of q only for the highest concentrations, indicating that at low concentrations the hydrodynamic interactions should be taken into account.

All these results were interpreted with the RPA, and the agreement is found to be good.

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