Dynamic Light Scattering from Microstructured Block Copolymer Solutions

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ABSTRACT: Solutions of a nearly symmetric polystyrene–polyisoprene diblock copolymer in toluene, a neutral solvent, have been examined by dynamic light scattering, at compositions both above and below the order–disorder transition. In all cases the scattered intensity autocorrelation function exhibits two distinct modes. The faster mode is diffusive and decreases in rate approximately exponentially with increasing concentration. The magnitude of the diffusivity suggests that it reflects the translational diffusion of the block copolymers. The slower mode scales with approximately the third power of the scattering vector and is tentatively attributed to cooperative rearrangements of microdomains. Furthermore, the slower mode undergoes a sharp decrease in rate over a narrow range of composition; this range of composition also corresponds to the best estimate for the location of the order–disorder transition.

Introduction

Concentrated block copolymer (BC) solutions and melts exhibit a rich variety of structural and dynamic behavior. The dominant feature of BC liquids is the order–disorder transition (ODT), where the thermodynamic repulsion between blocks induces a spontaneous assembly of the individual chains into an ordered array.[1] In general, the ordered state may be accessed by increasing the BC chain length, N, increasing the BC concentration (in solution), or increasing the segment–segment interaction parameter, χ (usually by decreasing the temperature). A great deal of experimental attention has been devoted to identifying and classifying the resulting microscopic morphologies; X-ray and neutron scattering, and electron microscopy, have been the methods of choice. More recently, the dynamics of BC liquids have received increasing attention, for example, as a means to diagnose the ODT or related, order–order transitions. Particularly in the neighborhood of the ODT, i.e., in the so-called "weak segregation limit", fundamental questions remain about the disposition of the individual blocks, such as their conformation and spatial profile in concentration.[2-4] One may anticipate that dynamic properties, such as chain mobility and conformational relaxation, will provide important insight into this region of the phase diagram.

In this paper we investigate the dynamic light scattering (DLS) from toluene solutions of a nearly symmetric polystyrene–polyisoprene BC, at concentrations both above and below the ODT. This work was undertaken with two primary goals: to see whether DLS was sensitive to the ODT and to explore the effect of solution microstructure on the dynamics of the composition fluctuations sensed by DLS. The results are interpreted in conjunction with X-ray scattering and rheological measurements on, and tracer diffusion measurements of polystyrene homopolymer in, some of the same solutions.

Experimental Section

Materials. The polystyrene (PS)–polyisoprene (PI) diblock was synthesized by anionic polymerization under high vacuum, using *sec*-butyllithium as the initiator and methanol as the terminator. The PI block was polymerized first, in *n*-heptane, followed by the PS block, in toluene. The molecular weights were determined to be 1.2×10^4 and 1.9×10^4 for the PS and PI blocks, respectively, with polydispersities less than 1.05, using size-exclusion chromatography. The PI block molecular weight was determined from the homopolymer precursor, using THF as the solvent and PI standards for calibration. The chemical composition of the copolymer was obtained by ^{1}H NMR spectroscopy. The sample is thus designated SI(12–19). A small amount (<0.5%) of 2,6-di-*tert*-butyl-4-methylphenol was added to the sample to inhibit degradation of the PI block. The purification of reagents and solvents, the reaction conditions, and the characterization procedures have been described elsewhere.[5] The toluene solvent (HPLC grade) was distilled over CaH_2 before use.

Dynamic Light Scattering. Measurements were made on a homebuilt apparatus described previously.[6] The time autocorrelation function of the scattered intensity was accumulated in the homodyne mode in three stages, using a multiple sample-time hardware correlator (Brookhaven BI2030) in parallel with a homebuilt software correlator. Two correlation functions were measured consecutively with the BI2030, typically using base sample times of 1 and 300 μs. Concurrently, the photomultiplier signals were fed to a personal computer via a data acquisition board (Scientific Solutions). The computer summed the incoming pulses for a selected sample time (either 0.3 or 1.0 s) in 32-bit registers. The correlation functions were then computed offline. The three correlation functions thus obtained were spliced together to give one composite correlation function extending over 9 decades in time. The three correlation functions were spliced pairwise by a linear routine which yields a multiplicative and an additive constant such that the difference between the functions is minimized in the overlapping regions. The additive constant is needed because the three experimental correlation functions never have an absolutely identical base line, although in principle they should. The splicing procedure has been tested previously, and a comparison of spliced curves versus those obtained in a single run on a 23-τ ALV correlator demonstrates that it is reliable.[7] Total acquisition times varied between 12 and 60 h for each solution and angle. The correlation functions were analyzed via a nonlinear regularized inverse Laplace transformation technique.[8] Measurements were made at 25 ± 0.5 °C.

Results and Discussion

DLS measurements were made on five different solutions, with BC weight fractions, w, of 0.083, 0.294, 0.417, 0.485, and 0.600. A typical autocorrelation function, $c(t)$, and its Laplace inversion, $A(\Gamma)$, are shown in parts a and

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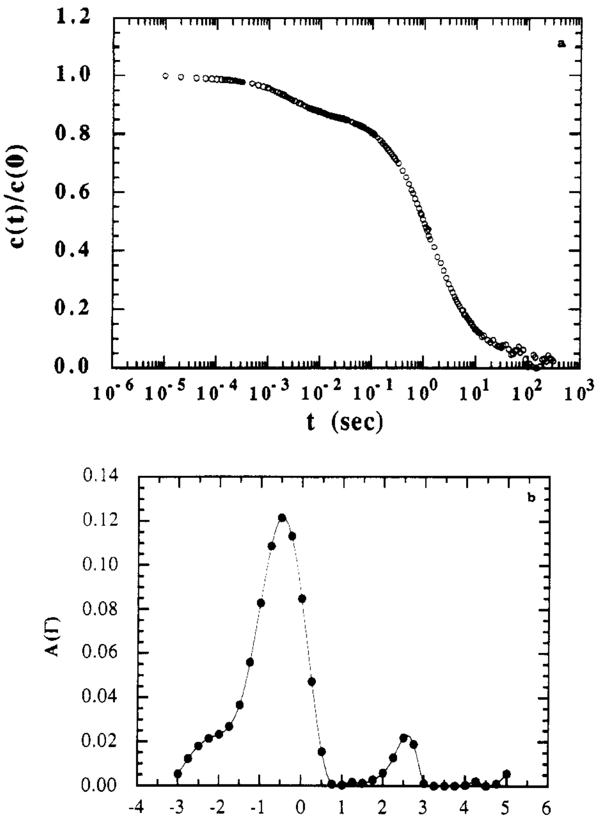

Figure 1. (a) Normalized correlation function $c(t)/c(0)$ (baseline subtracted) vs t and (b) corresponding distribution of decay rates, for w = 0.417 and a scattering angle of 90°.

b of Figure 1, respectively, for the solution with $w = 0.417$ and a scattering angle of 90°. The correlation function is dominated by two clearly separated modes. Both $c(t)$ and $A(\Gamma)$, which are related by

$$c(t) = B\{1 + \alpha[\int_0^\infty A(\Gamma)\exp(-\Gamma t)\,d\Gamma]^2\} \qquad (1)$$

where $A(\Gamma)$ is the distribution of decay rates, display some noise at times longer than about 10 s, due to the small number of samples acquired. Nevertheless, $c(t)$ typically decayed to within 5% of the estimated base line. For solutions in which $c(t)$ decayed to the base line on a millisecond time scale, the measured and theoretical base lines agreed to within 0.1%. For $w \geq 0.294$, two modes were always cleanly resolved. For $w = 0.083$, $c(t)$ was dominated by the faster mode, and the spectrum at long times indicated several small peaks. These peaks combined contributed only about 10% of the overall signal and were thus averaged to give one approximate value of Γ_{slow}. This solution is below the estimated coil overlap concentration of $w^* \approx 0.2$ and is consequently of less interest here.

The concentration dependence of Γ_{fast} and Γ_{slow} at a scattering angle of 90° is shown in Figure 2. Both decay rates decrease with increasing w, with Γ_{fast} exhibiting an approximately exponential dependence on w. In contrast, the slow process undergoes a relatively sharp drop, falling by about 2 orders of magnitude between $w = 0.417$ and $w = 0.485$. The q dependence of the two modes is also quite distinct. The fast mode is diffusive, with $\Gamma_{fast} \sim q^2$ at all w; an example is shown in Figure 3, for $w = 0.417$. Typical uncertainties for the fast mode were ±5–10%. The slow mode, on the other hand, scales approximately as q^3, as shown in Figure 4 for $w = 0.417$ and $w = 0.485$. Typical uncertainties for the slow mode were estimated to be ±20%. The relative amplitudes of the two modes are shown in Figure 5; for all but the most dilute solution, the slow dominates the scattered intensity.

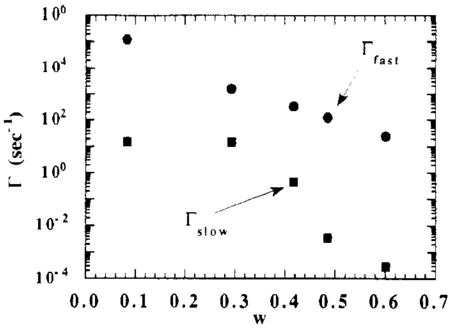

Figure 2. Decay rate for the fast and slow modes vs w, for a scattering angle of 90°.

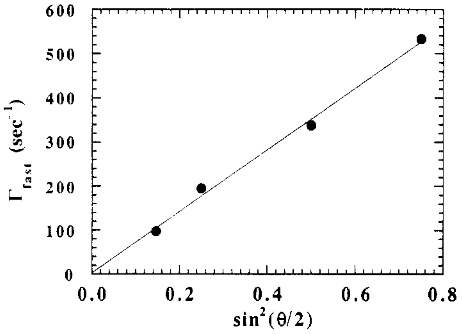

Figure 3. Dependence of the fast-mode decay rate on the scattering angle, for w = 0.417.

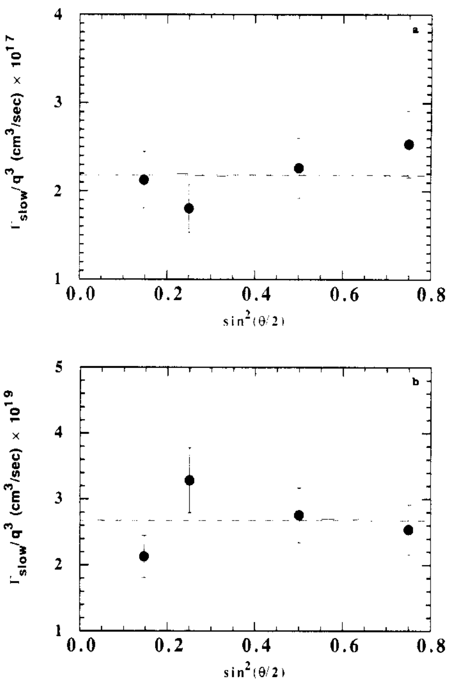

Figure 4. Dependence of the slow-mode decay rate (normalized by q^3) on the scattering angle, for (a) w = 0.417 and (b) w = 0.485.

The magnitude, q^2 dependence, and w dependence of Γ_{fast} all suggest that it corresponds closely to the translational diffusion of the individual BC chains. Two additional pieces of evidence support this interpretation. Recently, the tracer diffusion, D_t, of PS homopolymers has been determined in the same BC solutions, by forced Rayleigh scattering.[5] For a PS tracer with $M = 3.2 \times 10^4$, which is very close to the total molecular weight of the SI(12–19) BC, D_t is virtually identical with D_{fast} (=Γ_{fast}/

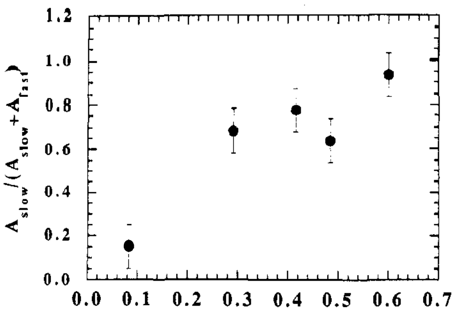

Figure 5. Relative amplitudes of fast and slow modes vs w, at a scattering angle of 90°.

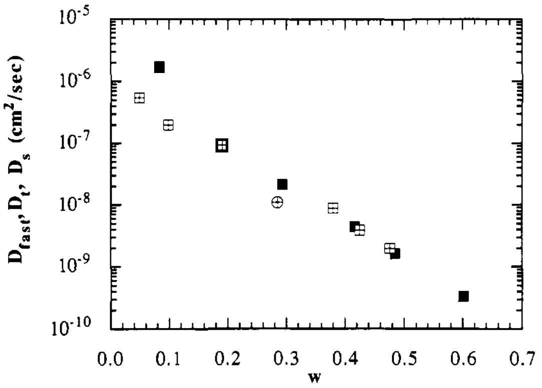

Figure 6. Filled squares: Diffusion coefficient for SI(12–19) extracted from the DLS fast mode. Hatched squares: Tracer diffusion coefficient for polystyrene ($M_W = 3.2 \times 10^4$) in SI(12–19) solutions, obtained by forced Rayleigh scattering.[5] Hatched circle: Self-diffusion of SI(12–19) from pulsed-field-gradient NMR.[8]

q^2) for $w > 0.2$, as shown in Figure 6. This indicates that D_{fast} has both the appropriate magnitude and concentration dependence for translational diffusion. Also indicated in Figure 6 is the actual self-diffusion coefficient, D_s of the BC for $w = 0.28$, as determined by pulsed-field-gradient NMR.[9] The value lies below D_{fast} by a factor of 1.8, confirming that D_{fast} is at least very close to the translational diffusion coefficient. Further measurements will be required to assess the possible significance of the factor of 1.8.

The interpretation of D_{fast} as corresponding to D_t for the BC is remarkable for at least two reasons. First, it would represent the first time to our knowledge that translational diffusion has been determined by DLS from concentrated solutions of a *single* polymer species. (Note that this is distinct from the ternary (polymer 1/polymer 2/solvent) solution case, where DLS has been used extensively to examine translational diffusion.[10,11]) In many cases of DLS from semidilute and concentrated binary solutions, two (or more) modes have been seen.[12] The fast (or fastest) mode increases in rate with increasing concentration and has been associated with cooperative diffusion, whereas the slow modes have been assigned to some kind of cluster diffusion, and/or viscoelastic relaxation of the entangled polymer structure. Second, D_t for the BC exhibits no particular evidence of the ODT, which is estimated to lie in the range $0.4 < w < 0.5$ (vide infra) for this sample. In other words, the spontaneous self-assembly of the BC chains into lamellar microdomains is not reflected by a change in slope of $D_t(w)$ for either the PS homopolymer tracer or the BCs themselves. Furthermore, as noted elsewhere,[5] D_t for the homopolymer was very similar in solutions of symmetric BCs as in solutions of PS homopolymer matrices with the same concentration and overall molecular weight. Thus, the initial formation of microdomains appears to have little effect on chain diffusion. This is, perhaps, not too surprising. Near the ODT the system is expected to be in the weak segregation limit, and microdomains rich in one component are by no means impenetrable to the other component; furthermore, the junction points of individual BC chains only tend to be localized in the interfacial regions, rather than strictly confined as in the limit of strong segregation.

The assignment of the slower mode is equally interesting, although less easily checked against other experiments. A q^6 dependence for Γ has been well-established in polymer systems under at least two circumstances, namely, the internal modes of a flexible chain in dilute solution[13] and the relaxation of composition fluctuations within the correlation length in a polymer blend near the spinodal[14] (in the mode-coupling regime[15]). In both of these examples in common features are that the experimental length scale (q^{-1}) is shorter than the correlation length and the composition fluctuations are coupled hydrodynamically. One possible interpretation, therefore, is to assign the slower mode to composition fluctuations in the incipient microdomains, or grains, in the BC solution. Certainly the fact that the Γ_{slow} is 2 or more orders of magnitude slower than translational diffusion suggests that it must involve the cooperative motions of many chains. If this picture is correct, the correlation length associated with these structures must be in excess of 1000 Å, which may be compared with the individual BC chain radius of gyration, R_g, estimated as 65 Å, and the characteristic period of the microstructure, d, of approximately 360 Å (from X-ray scattering[5]).

Another possible origin for the q^3 dependence could be the "free film fluctuation mode", which has been observed and described for lamellar bilayer membranes.[16,17] In this case, the proportionality constant between Γ_{slow} and q^3 is anticipated to be (K/η), the ratio of the membrane bending modulus to the solvent viscosity. However, rough estimates for these quantities give values of Γ that are considerably larger than those observed.

It is tempting to interpret the abrupt slowing down of these "internal modes" near $w = 0.45$ as reflecting the ODT. Although the location of the ODT as a function of w has not been determined unambiguously, we estimate that it falls in the range given above ($0.4 < w < 0.5$) on the basis of several pieces of evidence. First, X-ray scattering on these solutions indicates the onset of a distinct peak at $w = 0.35$ and a second peak at $w = 0.6$. The concentration dependence of the small-angle X-ray scattering from SI-(12–19) solutions is shown in Figure 7 (additional details are available in ref 5). The appearance of a single peak does not identify the ODT, of course, but it is certainly a necessary condition. The appearance of a second peak, with the q spacing associated with lamellar symmetry, is strong evidence that these solutions are in the ordered state. These results, therefore, can be viewed as providing upper and lower bounds for the ODT on the concentration axis. Second, Hashimoto et al., in their pioneering study of microdomain formation in BC solutions,[18] estimated the ODT to occur at $w = 0.38$ for an SI diblock of identical molecular weight and composition, also in toluene. This assignment was based on a change in slope of d vs w and is therefore neither unambiguous nor particularly precise but is completely consistent with the X-ray scattering results on the solutions examined here. Third, following the extensive results of Bates and co-workers on BC melts,[19] where the temperature dependence of the shear elastic modulus, G', has been shown to be a very sensitive indicator of the ODT, some preliminary rheological measurements

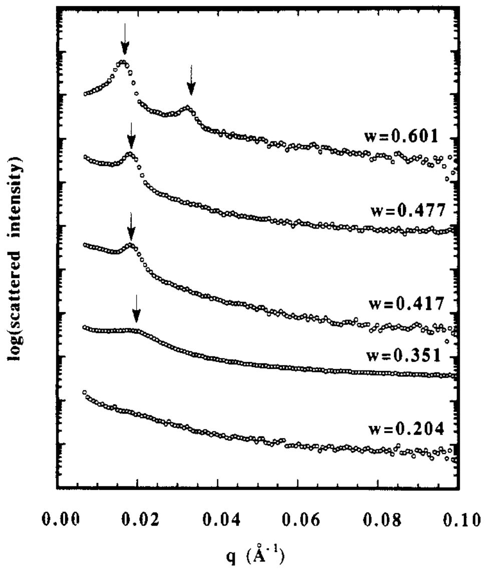

Figure 7. X-ray scattering intensity vs q for various SI(12-19) solutions, as indicated. The intensities have been shifted vertically by arbitrary amounts.

on an SI solution with $w = 0.48$ were attempted.[20] Upon gradual heating, both G' and G'' exhibited a sharp drop around 55 °C, suggesting that this is the ODT for this composition. If we make the simplest assumptions, i.e., that the ODT scales with $w\chi N$ and that $\chi \sim T^{-1}$, then this would correspond to $w = 0.44$ at 25 °C, the temperature where the DLS measurements were made. The volatility of the toluene solvent makes the quantitative interpretation of such rheological measurements uncertain, but these results are certainly consistent with the assignment of the ODT given above.

A model for the dynamic light scattering from BC solutions, based on the random-phase approximation, has been presented by Benmouna et al.[21] The principal result of this treatment is the prediction of two q^2-dependent modes, one termed the "cooperative mode", and the other the "interdiffusion mode". However, this model applies to disordered solutions, so that it is not directly applicable to the results presented here. Nevertheless, it is conceivable that the fast mode observed in SI(12-19) solutions corresponds to the predicted interdiffusion mode and that the cooperative mode was simply not observed.

Summary

Dynamic light scattering measurements on concentrated toluene solutions of a polystyrene-polyisoprene diblock copolymer reveal the presence of two distinct modes. The fast mode is q^2-dependent and decreases in rate approximately exponentially with increasing polymer concentration. It is numerically indistinguishable from the translational diffusion of a tracer polystyrene homopolymer in the same copolymer solutions, measured by forced Rayleigh scattering, and within a factor of 1.8 of the self-diffusion of the BC determined by NMR, and is thus attributed to the translational diffusion of the individual chains. The slow mode is q^3-dependent and is tentatively interpreted as reflecting the internal dynamics of the block copolymer microdomains. The slow mode exhibits a sharp decrease in rate near a copolymer concentration of 45%, which is interpreted as the order-disorder transition (ODT). This estimate of the ODT is consistent with X-ray scattering and rheological results on the same system.

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Registry No. (PS)(PI) (block copolymer), 105729-79-1.