Self-Diffusion and Tracer Diffusion in Styrene/2-Vinylpyridine Block Copolymer Melts

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ABSTRACT: Forced Rayleigh scattering (FRS) has been used to probe self-diffusion and tracer diffusion in unentangled, symmetric diblock copolymer melts. Two poly(styrene-*b*-2-vinylpyridine) (PS–PVP) diblocks, with $M_w = 1.1 \times 10^4$ and 2.2×10^4, were synthesized anionically and end-labeled with a photochromic *o*-nitrostilbene derivative, and two PS homopolymers, with $M_w = 1.4 \times 10^4$ and 2.5×10^4, were labeled with the same dye, randomly along the chain. Rheological measurements demonstrated that the lower M_w diblock was in the disordered state and the higher M_w diblock was in the ordered (lamellar) state, over the measurement temperature range (110–210 °C). The ordered samples were quenched, in the sense that no attempt was made to induce a preferred orientation to the lamellae. The self-diffusion coefficients of the two copolymers superpose, when scaled by the ratio of molecular weights, as expected for disordered Rouse chains, thus indicating that the lamellar order has little effect on the overall mobility. Similarly, the copolymer and homopolymer self-diffusion coefficients are nearly identical, for equal total M_w. This result is interpreted as reflecting unhindered motion of the copolymer chains in the lamellar planes. Tracer diffusion measurements for the homopolymers and the lower M_w copolymer in the ordered copolymer matrix also showed little difference from the corresponding self-diffusion coefficients but were qualitatively consistent with perturbation theory. In all cases, the FRS signals were well-described by single exponential decays, possibly suggesting that diffusion through the lamellae is not greatly retarded relative to diffusion in the lamellar planes and/or that the orientational correlation length of the lamellae is small.

Introduction

The dynamic properties of multicomponent polymer systems are often remarkable, although quite complicated to predict in detail. On the one hand, thermodynamic interactions between the different components can lead to self-assembly and macroscopic order or segregation. The resulting structures reflect a spatially-varying free energy density, which may affect chain dynamics in interesting ways. On the other hand, differences among the various components in factors such as local friction, local stiffness, and entanglement density can also perturb the observed dynamics substantially. Block copolymers are an important class of multicomponent systems and exhibit the general features just mentioned. Of the various dynamic properties that can be examined, the translational diffusion coefficient of the individual chains is particularly appealing, as it reflects the response of a single molecule to a complicated environment and may ultimately be accessible to quantitative interpretation. In this paper, we report measurements of the self-diffusion coefficient, D_s, for poly(styrene-*b*-2-vinylpyridine) (PS–PVP) block copolymer melts, in both the ordered and the disordered states. In addition, we examine the tracer diffusion coefficient, D_t, of PS–PVP block copolymers and PS homopolymers in the ordered copolymer matrix.

Several groups have recently described experimental studies of D_s and/or D_t in block copolymer melts and concentrated solutions, with forced Rayleigh scattering (FRS),[1-8] forward recoil spectrometry (FRES),[9] field gradient NMR,[10] and dynamic light scattering [11] the techniques of choice. Of these, those that examined block copolymer melts in, or near, the (lamellar) ordered state are of most relevance to the work described herein. Two nearly symmetric systems have been studied in some detail: poly(ethylenepropylene)–poly(ethylethylene) (PEP–PEE),[5-9] with $M_n = 8.1 \times 10^4$, 5.0×10^4, and 3.2×10^4, and PS–polyisoprene (PI),[3,4,10] with $M_w = 2.3 \times 10^4$, 1.6×10^4, and 1.1×10^4. On the basis of entanglement molecular weights (M_e) for the constituent homopolymers, the PEP–PEE chains are well entangled, whereas the PS–PI specimens are in the unentangled-to-entangled crossover regime. However, in both cases there is entanglement asymmetry, in that M_e values for the two blocks differ significantly. Measurements of $D_s(T)$ for PEP–PEE ($M_n = 5.0 \times 10^4$) via FRS and FRES were in quantitative agreement and showed no particular change in the temperature dependence on traversing the order–disorder transition (ODT).[6,8,9] In the FRS case, the experimental decays were almost all single exponentials, such that an unambiguous value of an isotropic average D_s could be obtained, in both the ordered and disordered states. By employing macroscopically shear-oriented samples, Dalvi was able to resolve the diffusivities parallel (D_{par}) and perpendicular (D_{perp}) to the lamellar planes.[5] Just below the ODT (*i.e.*, $\chi N/(\chi N)_{ODT} \approx 1.005$, where χ is the monomer–monomer interaction parameter and N is the degree of polymerization), there was no measurable anisotropy: $D_{par} \approx D_{perp}$. When the temperature was lowered, diffusion through the lamellar layers was progressively suppressed, such that $D_{perp}/D_{par} \approx 0.3$ when $\chi N/(\chi N)_{ODT} \approx 1.23$. The FRES measurements hinted at a much stronger anisotropy,[9] but this result is now felt to reflect a surface effect.[12]

The results for the PS–PI copolymers were qualitatively different. Primarily, in the FRS measurements,[3,4] a broad distribution of decay rates was seen, and a single value of D_s could not be extracted, while in the NMR study,[10] D_s appeared to be a strong function of diffusion distance, even in the disordered state. The interpretation of these results rests primarily on a strong diffusional anisotropy ($D_{par} \gg D_{perp}$), combined with a lamellar grain size comparable to the measurement length scale. Measurements on a partially-oriented sample implied that $D_{perp}/D_{par} \approx 0.3$, reminiscent of the PEP–PEE results, but nevertheless multi-exponential decays were still observed.[4]

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Thus, the origin of this difference between the two systems remains to be established. One possible contributing factor is the difference in local friction between the two blocks; PS and PI have widely differing glass transition temperatures, and the measurements were all made within approximately 100 deg of T_g (PS). In contrast, PEP and PEE have T_g's that differ by only about 40 deg, and the measurements were made at much larger values of reduced temperature, $T - T_g$. The PS–PVP system has the possible advantage of small asymmetry in local friction (and entanglement spacing) and may therefore shed some light on this issue. Note that for the molecular weights employed, PS–PVP is effectively unentangled, and in this regard resembles more the PS–PI than the PEP–PEE chains examined previously. Finally, attention should be drawn to recent theoretical treatments of aspects of block copolymer diffusion in lamellar phases,[13-16] which are directly applicable to some of the measurements described here.

Experimental Section

A. Synthesis and Labeling. Two poly(styrene-*b*-2-vinylpyridine) (PS–PVP) copolymers were prepared by sequential living anionic polymerization in THF. All solvents, monomers, and reagents were rigorously purified prior to use, following established procedures. Styrene monomer (Aldrich) was polymerized first, using *sec*-butyllithium as initiator; after an initial seeding at −78 °C, the remaining styrene monomer was allowed to react for approximately 12 h. A small portion of the reaction solution was removed and terminated with methanol. A small amount of 2-vinylpyridine monomer (Aldrich) was then added to the living polystyrene anions, to seed the growth of the second block. The remaining 2-vinylpyridine was added and allowed to react at −78 °C for about 6 h. The resulting polymer solution was divided into two portions. The larger portion was terminated with methanol, whereas the smaller portion was terminated with *p*-dichloroxylene (Aldrich), to provide a functional group for subsequent attachment of the photochromic dye label.

The dye, 4′-(*N,N*-dimethylamino)-2-nitrostilbene-4-carboxylic acid (ONS), was synthesized via a three-step procedure,[17] derived from one described by Ehlich.[18] In the first step, *p*-tolunitrile (Aldrich) was reacted with H_2SO_4 and HNO_3 to introduce the nitro functionality ortho to the methyl group. The second step involved condensation of the *o*-nitro-*p*-tolunitrile with *p*-(dimethylamino)benzaldehyde (Aldrich) in the presence of piperidine, to produce 4′-(*N,N*-dimethylamino)-4-cyano-2-nitrostilbene. The final step involved the hydrolysis of the cyano group to the corresponding carboxylic acid.

For the labeling reaction with the end-functionalized PS–PVP, the carboxylic acid was first converted to its cesium salt. The dye and 1 g of polymer were dissolved in anhydrous *N,N*-dimethylformamide (Aldrich), and the reaction mixture was stirred for 24 h at 60–70 °C. The dye was present in about a 5-fold molar excess over the chloromethyl functionality. The resulting labeled polymers were reprecipitated twice in methanol and then passed in chloroform solution through a silica gel column (EM Science silica gel 60) to remove the last traces of unattached dye. The polymers were then freeze-dried and stored under vacuum, in the dark.

Two polystyrene (PS) homopolymers were also labeled with ONS. They were obtained from the Pressure Chemical Co., with the following specifications: $M_w = 1.4 \times 10^4$, $M_w/M_n = 1.06$, Lot No. 30420, and $M_w = 2.5 \times 10^4$, $M_w/M_n = 1.06$, Lot No. 30811; they are henceforth designated PS-14 and PS-25. The labeling was achieved by first aminomethylating the phenyl rings in the 4-position, randomly along the chain, following the procedure described by Kim *et al.*[19] The carboxylic acid group on the ONS was reacted with the aminomethyl groups on the polymer, in benzene solution. The dye was present in 3–5 times molar excess, and an equivalent amount of *N,N*′-dicyclohexylcarbodiimide was added. Trace amounts of pyridine and (dimethylamino)pyridine were added as catalysts, and the solution was refluxed for 2 days. The resulting labeled polymers were reprecipitated twice, passed through a silica gel column, and freeze-dried; they were stored under vacuum and in the dark.

Table 1. Sample Characteristics

polymer	$10^{-4}M_w$	M_w/M_n	f_{PS}[a]	labeling[b]	T_g, °C
SVP-11	1.1	1.1	0.49	1.2	92.0
SVP-22	2.2	1.1	0.49	1.2	95.1
PS-14	1.4	1.06	1.0	0.13	92.6
PS-25	2.5	1.06	1.0	0.26	99.1

[a] Number fraction of styrene monomers. [b] Average number of labels per chain.

B. Characterization. The block copolymers were characterized by size exclusion chromatography (SEC), to determine the molecular weight and the molecular weight distribution, and by ^{1}H NMR, to determine the composition. The weight-average molecular weights were found to be 1.1×10^4 and 2.2×10^4, with polydispersities *ca.* 1.1; the samples are designated SVP-11 and SVP-22, respectively. The labeled polymers were characterized by UV–visible absorption spectrophotometry, to determine the extent of labeling, and by SEC, to establish that the labeling procedures had not perturbed the molecular weight distribution. Of the four labeled polymers, only in the case of SVP-22 did the labeling procedure affect the molecular weight distribution to any significant extent; apparently, some fraction of the sample was cross-linked. This high molecular weight portion was removed by filtration, and the resulting SEC trace compared favorably with the unlabeled polymer. The sample characteristics are given in Table 1. The nominal value of 1.2 labels per chain for the copolymers presumably reflects a labeling efficiency approaching 100%, combined with a systematic overestimate by the analysis protocol.

C. Forced Rayleigh Scattering. The FRS apparatus and experimental protocol have been described in detail elsewhere.[20,21] Briefly, each sample was exposed to crossed beams from an Ar$^+$ laser operating at $\lambda_0 = 488$ nm for a period of 100–250 ms, to create the transient grating. The subsequent state of the grating was probed by one of the same beams, after attenuation by a factor of 10^4. The diffracted signal was incident on a photomultiplier positioned at the first-order Bragg peak, and the resulting decay was recorded by a computer for subsequent analysis. Depending on the diffusivity of the labeled chains, signals were accumulated over a time scale ranging from seconds to hours. In almost all cases, a "single shot" experiment was sufficient to provide excellent signal-to-noise. The decays were fit to the following function:

$$I(t) = [A \exp(-t/\tau) + B]^2 + C^2 \qquad (1)$$

where I is the intensity, A, B, and C are the amplitudes of the signal, coherent baseline, and incoherent baseline, respectively, and τ is the decay time. This single exponential decay function, with only modest baseline contributions, was able to describe all of the measurements rather well. An example is shown in Figure 1, for the tracer diffusion of PS-25 in the ordered copolymer matrix, SVP-22. The signal-to-noise ratio displayed by these data is typical of all of the samples examined herein, except for the self-diffusion of SVP-22, for which the signals were somewhat smaller. By alteration of the crossing angle between the two beams, the grating spacing, d, could be systematically varied. For each sample, at at least one temperature it was established that τ increased linearly with d^2 (with no appreciable intercept), confirming the diffusive origin of the decay, according to the relation

$$\tau = d^2/4\pi D \qquad (2)$$

where D is the diffusivity of the labeled chain.

The FRS sample preparation required some care, in order to generate sufficiently bubble- and crack-free specimens. A mixture of approximately 5 mg of labeled and 95 mg of unlabeled polymer were co-dissolved in 8 mL of benzene, filtered through a 0.45 μm filter (Rainin), and freeze-dried. The mixture was then pressed into a 13 mm diameter, 0.5 mm thick circular disk by a hydraulic press (Beckman P-16M), under 12 tons of pressure. The disk was inserted into an aluminum ring spacer and sandwiched between two 25 mm diameter quartz disks (Heraeus-Amersil).

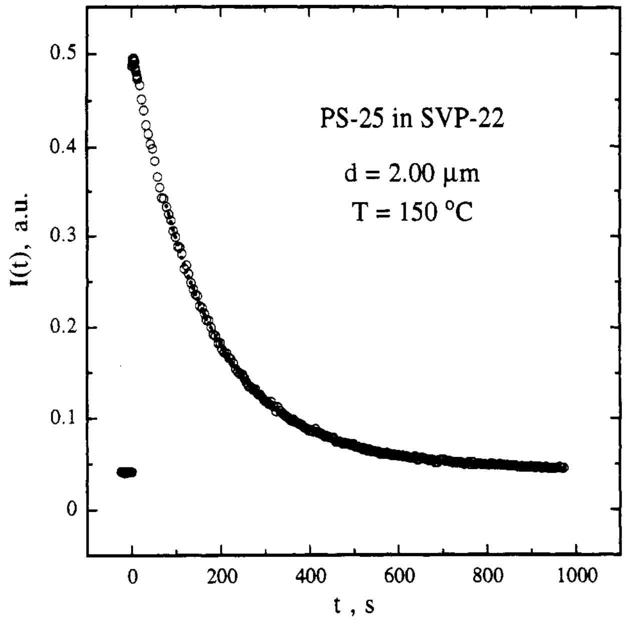

Figure 1. FRS decay for PS-25 diffusing in SVP-22. The large open circles correspond to the data, and the small filled circles to the fit.

The sandwich was clamped and placed in a vacuum oven. The temperature was raised at about 20 °C/h, until the polymer melted and uniformly filled the spacer; this usually occurred at about 110 °C. The sample was then allowed to cool to room temperature, at which point the sample cell was sealed with a silicone adhesive. Prior to use, each specimen was annealed overnight in a vacuum oven at 70 °C, and then the temperature was raised slowly to 140 °C. The sample was transferred to the FRS sample holder, which was also preheated to 140 °C; the temperature was then raised to about 160 °C, and the sample allowed to equilibrate overnight.

The diffusion measurements were made at 10 deg intervals, starting at 160 °C and first lowering the temperature to 110 or 120 °C and then raising it to 200 or 210 °C. The highest temperature measurement was thus the last one taken, as the dye rapidly became unusable near 200 °C. Care was taken to allow the samples to equilibrate prior to the measurement at each new temperature, with increasingly longer intervals allotted as temperature decreased. In all cases, the data acquired between 160 and 110 °C were independent of whether the temperature was previously increased or decreased. Temperatures were controlled to within ±0.2 deg throughout.

D. Rheology. Measurements were made on the unlabeled copolymers on a Rheometrics RMS-800 in the parallel plate configuration, with a 1 cm plate diameter and a 1 mm gap. Strains varied between 5 and 20% for SVP-11 and between 5 and 100% for SVP-22, depending on the temperature. Temperatures were controlled to within ±0.5 deg. The samples were prepared in a manner similar to that for the FRS specimens, by using a hydraulic press and subsequent annealing in a vacuum oven. Care was taken not to subject the samples to rapid changes in temperature, which could induce stress-cracking.

E. Differential Scanning Calorimetry. The glass transition temperatures of the polymers were determined by differential scanning calorimetry (DSC), using a Mettler TA3000. The samples were examined at two heating rates, 7 and 10 °C/min, over the range from 60 to 130 °C; each scan was repeated three times. The T_g was taken as the midpoint of the inflection in the curve, and the values reported in Table 1 correspond to averages over the two heating rates and the three scans.

Results and Discussion

A. Characterization of the State of Order. On the basis of rheological measurements, and by comparison with experimental and theoretical results from other laboratories, we conclude that SVP-11 is disordered and that SVP-22 is in the lamellar ordered state, across the diffusion measurement temperature range (110–210 °C). It has been well-established that the dynamic shear moduli, G' and G'', can be quite sensitive to the presence of microstructure in a block copolymer melt.[22-24] Furthermore, changes in the frequency dependence of the moduli have also been used as a diagnostic of the fluctuation regime, *i.e.*, in the nominally disordered state just above T_{ODT}.[23,24] Specifically, for lamellar block copolymers it has been observed that at sufficiently low frequencies, G' at any one frequency exhibits a sharp drop with increasing temperature, as the ODT is traversed. In this case, "low" means significantly below $\omega_c \approx 1/\tau_1$, where τ_1 is the longest relaxation time of the fully disordered sample. Furthermore, in the regime $\omega < \omega_c$ the moduli both scale approximately as $\omega^{0.5}$, in contrast to the $G' \sim \omega^2$ and $G'' \sim \omega$ characteristic of the terminal regime for liquids. Concurrently, time–temperature superposition fails for $\omega < \omega_c$, even though it may still appear to hold for $\omega > \omega_c$. The fluctuation regime is also marked by deviations from terminal scaling, particularly in G', but with a return to liquidlike response at still lower frequencies. Here, also, time–temperature superposition fails in the low frequency regime, due to the temperature dependence of the incipient structure in the liquid.

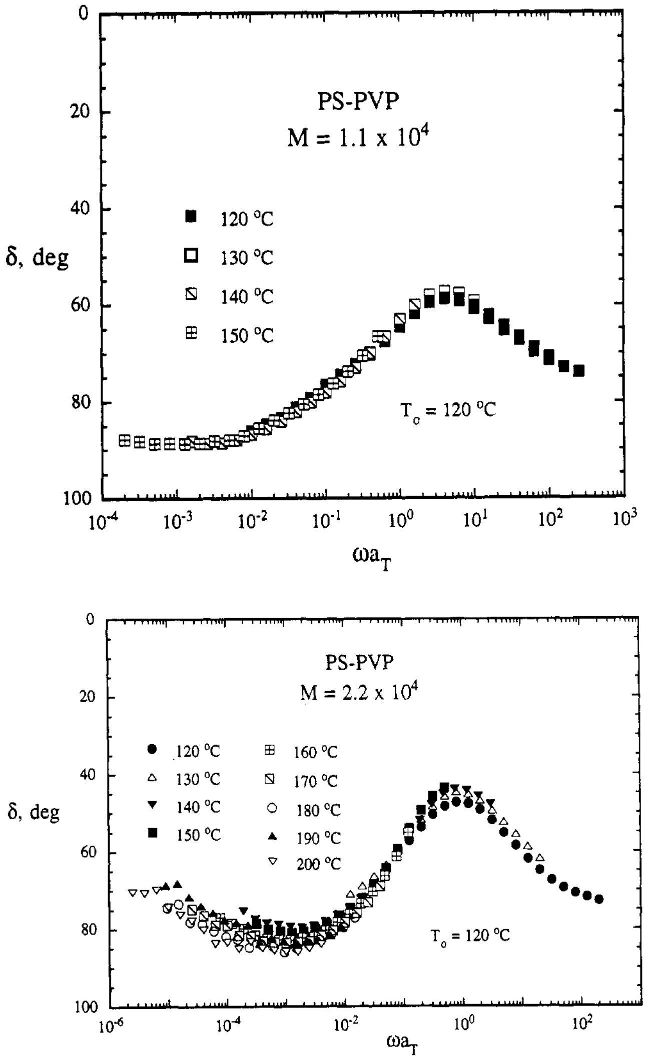

Figure 2. Rheological properties of PS–PVP copolymers, plotted as master curves of the phase angle, δ, versus reduced frequency, for (a) SVP-11 and (b) SVP-22.

The rheological results for the two PS–PVP block copolymers are shown in Figure 2a,b. We have chosen to present the results as the phase angle, δ, versus reduced frequency, ωa_T, where a_T is the time–temperature superposition shift factor. We believe that this plotting format is at least as sensitive to the onset of structure as the moduli themselves; $\delta \equiv \tan^{-1}(G''/G')$. Furthermore, superposition requires only a horizontal shift along the frequency axis; there is no opportunity to introduce small vertical shifts, to account for changes in density. For a monodisperse polymer melt in the terminal regime, the phase angle should increase smoothly to the low frequency limiting value of 90°. This is clearly seen in Figure 2a for SVP-11. Furthermore, the superposition is excellent over the accessible frequency range. From these results, therefore, we conclude that this sample is disordered over the measurement temperature range and that there is no obvious signature of a fluctuation regime. In contrast, the data for SVP-22 do not superpose well, and at lower frequencies there is clear evidence of the growth of structure. There is no evidence (in the accessible frequency range) of a return toward 90° at still lower frequencies, and the moduli individually are consistent with an $\omega^{0.5}$ scaling. We therefore conclude that this sample is in the ordered state over the temperature range of interest.

Strong support for these assignments comes from recent studies on PS–PVP diblocks by Bates and co-workers.[25] In particular, a symmetric sample with molecular weight 1.6×10^4 exhibited a clean lamellar-to-disordered transition upon heating above 180 °C. As this molecular weight falls almost exactly midway between SVP-11 and SVP-22, we may be confident that SVP-22 will undergo the ODT at a temperature significantly higher than 200 °C, whereas SVP-11 should have an ODT well below our measurement temperatures.

One can also utilize theory to estimate the location of the ordering transition for a block copolymer. The following expression for $\chi(T)$ for PS–PVP copolymers has been presented by Dai and Kramer,[26] based on self-consistent mean-field analysis of the segregation of PS–PVP copolymers to the interface between the constituent homopolymers:

$$\chi(T) = -0.033 + \frac{63}{T} \qquad (3)$$

From this expression, the temperature range examined corresponds to values of χN between 10 and 14 for SVP-11 and between 20 and 28 for SVP-22. Using Leibler's[27] mean-field prediction that $(\chi N)_{\mathrm{ODT}} = 10.495$ for symmetric diblocks, one might conclude that both samples should be ordered over the measurement range. However, as first calculated by Fredrickson and Helfand,[28] the disordered state should be stabilized by concentration fluctuations and by an amount that increases with decreasing N. Their development drew on the class of Hamiltonians described by Brazovskii[29] for systems near a phase transition, but in which the major fluctuations lie on, or near, a shell of non-zero wavevectors. The resulting Fredrickson–Helfand–Brazovskii–Leibler (FHBL) theory leads to the following expression for the ODT for a symmetric block copolymer:

$$(\chi N)_{\mathrm{ODT}} = 10.495 + 41.022\bar{N}^{-0.333} \qquad (4)$$

Here, $\bar{N} = Na^6/v^2$, where N is the degree of polymerization, a is the statistical segment length, and v is the monomer volume, as described in detail by Bates *et al.*[23] Taking 0.75 nm and 1.64×10^{-22} cm^3 as representative values for a and v for PS, respectively, and assuming that the same values apply for PVP, one arrives at estimates of T_{ODT} of 84 and 355 °C, for SVP-11 and SVP-22, respectively. These compare favorably with the conclusions based on the rheological measurements: the lower M sample is disordered, and the higher one ordered, throughout the measurement temperature range. For SVP-11, the theoretical estimate suggests that the lowest measurement temperature is very close to T_{ODT}. This appears to conflict with the lack of evidence of fluctuations in the rheological results. However, it is important to bear in mind that the FHBL theory is expected to be valid only for large $\bar{N}$ (*i.e.*, $> 10^4$), and thus the calculated T_{ODT}'s should be treated with caution. In addition, the inevitable uncertainty in copolymer molecular weight and composition leads to significant uncertainty in T_{ODT}, even if the theory were precisely correct. Thus, we conclude that the theoretical estimates are not inconsistent with the experimental evidence.

An additional possibility to consider is that SVP-11 is, in fact, in the fluctuation regime, but that the fluctuations are not apparent in the rheology. Previous rheological studies of the fluctuation regime have considered only entangled polymers,[22–24] whereas SVP-11 is unentangled. Measurements of diffusion on entangled and unentangled block copolymers have shown a qualitative difference, namely, that entangled polymers are unable to move freely parallel to an interface;[5–8] one consequence of this is a strong retardation of diffusion by fluctuations. Because unentangled copolymers are presumed to move freely parallel to an interface, it is therefore conceivable that fluctuations in such a system would not affect the long-time dynamics significantly.

B. Block Copolymer Self-Diffusion. The self-diffusion of the two diblocks was measured over the temperature range from 110 to 200 °C. In all cases, the FRS decays were well-represented by single exponentials, as noted in the Experimental Section. Furthermore, for each sample and at selected temperatures, measurements were repeated at various grating spacings, and the scaling of decay time with grating spacing squared, according to eq 2, was confirmed.

The observation of single exponential decays for SVP-22 is interesting. This sample is well into the ordered state, but quenched, so that the lamellar planes should have no preferred orientation. The single exponential character could indicate that the mobilities parallel and perpendicular to the lamellar planes are not vastly different. Consider the various length scales in the measurement: the lamellar period, L; the "grain" size or correlation length, ξ; the grating spacing, d; and the laser beam diameter. As d is typically 1–3 μm, each chain must diffuse a distance corresponding to 30–100 lamellar periods. The grain size is unknown, but must be at least several times L. Thus, during the measurement each diffusing chain samples a rather small number of grains. If D_{perp} were considerably smaller than D_{par}, *i.e.*, by 1 order of magnitude or more, one would expect a multiexponential decay, because in some fringes of the grating the lamellae would tend to be oriented parallel to the fringes, and in other regions, perpendicular. Only if $d/\xi \gg 1$ would this effect be averaged out. In measurements on the PEP–PEE system, single exponential decays were also routinely observed,[5–8] and it was also confirmed directly that D_{perp} was at most a factor of 3.3 less than D_{par}. The laser beams are approximately 1 mm in diameter at the sample, and thus the measurements confirm sample homogeneity over this length scale. Furthermore, due to the photobleaching of the dye, it was necessary to make measurements in different locations within any given sample, and there was only nominal spot-to-spot variation in D.

An additional possibility to consider is that the sample preparation protocol resulted in a substantial orientation of the lamellae parallel to the window surface. If this

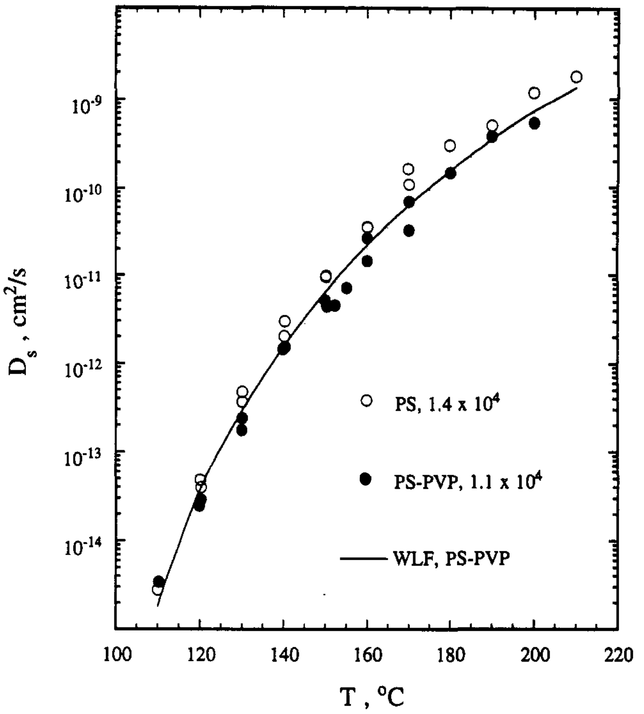

Figure 3. Self-diffusion of SVP-11 and PS-14, as functions of temperature, compared to the WLF curve for SVP-11.

were so, the measurement would essentially probe D_{par} and the single exponential decays would be a trivial result. However, we do not believe this to be the case. As a check, we measured the static birefringence, Δn, of the ordered block copolymer FRS samples; values in the neighborhood of 5×10^{-5} were obtained, with no preferred optical axis. For PS–PVP Δn reflects chain orientation,[30] and the observed magnitude is consistent with the depolarization resulting from passage through a series of randomly-oriented lamellar grains.[31] Conversely, a well-oriented sample with lamellar planes parallel to the cell windows would not be birefringent.

The measured self-diffusion coefficient of SVP-11 is shown in Figure 3, as a function of temperature. For comparison purposes, D_s for a PS homopolymer, PS-14, is included. Both the temperature dependence and the magnitude of D_s are very similar for the two polymers. A fit of the standard Williams–Landel–Ferry (WLF) equation to the SVP-11 data is also shown.[32] Consistently, the PS-14 mobility is slightly higher than that for the block copolymer, although the homopolymer has a higher molecular weight. This is not a simple glass transition effect, as the two samples have essentially equivalent T_g's (see Table 1). The difference is also greater than can be attributed to the uncertainty in M, because the M dependence of D_s is weak; $D_s \sim M^{-1}$ for these unentangled (Rouse) chains. Two possibilities remain: either the effective monomeric friction coefficient, ζ_0, for the copolymer is greater than that for the homopolymer or there are substantial composition fluctuations in the block copolymer that retard diffusion. We are not aware of independent measurements of ζ_0 for PVP, so we cannot assess this possibility quantitatively. However, we are inclined to attribute the difference in mobility primarily to this source. Although it has been shown clearly in the PEP–PEE case that concentration fluctuations do retard self-diffusion noticeably,[6,8] and although for lower M copolymers one expects fluctuations to be even more substantial,[28] the rheological measurements on SVP-11 show no evidence of fluctuations (Figure 2a). In addition, the effect of fluctuations on D would increase with decreasing temperature, whereas in Figure 3, the difference in mobilities is independent of, or possibly even decreasing with, decreasing temperature.

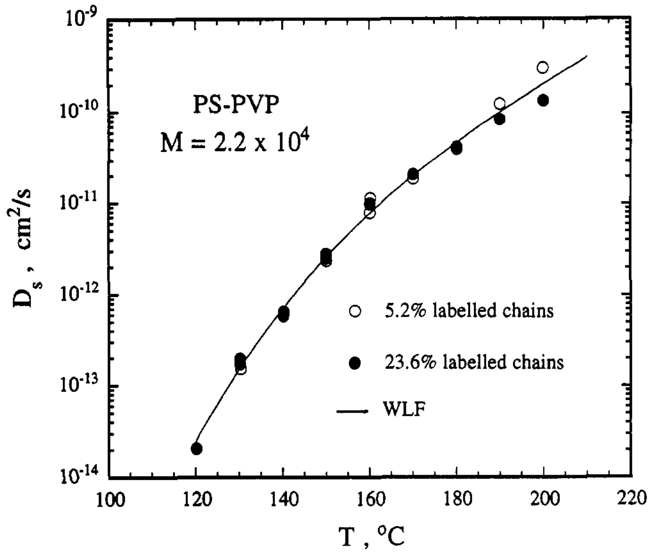

Figure 4. Self-diffusion of SVP-22 as a function of temperature, for two labeling levels, compared to the WLF curve for SVP-22.

The self-diffusion of the ordered copolymer, SVP-22, is shown in Figure 4. Two sets of data are shown; one was acquired with 5.2% of the chains labeled, and the other with 23.6%. Except for the highest temperature datum, the two sets agree quantitatively, implying that the presence of the dye has no measurable effect on the properties of the sample. A WLF fit to the combined data is also shown. Although not shown on the plot, D_s for PS-25, a PS homopolymer with $M = 2.5 \times 10^4$, is very close to D_s for this copolymer, just as in Figure 3. At first glance, therefore, the presence of lamellar order in this sample exerts no substantial influence on the measured mobility, which, it must be emphasized, represents a three-dimensionally averaged, isotropic quantity.

The diffusivities of the two copolymers are compared directly in Figure 5. Due to the 3 deg difference in T_g between the samples, the abscissa is taken as $T - T_g$. The data for the ordered copolymer have been scaled by a factor of 2, corresponding to the ratio of molecular weights, anticipating Rouse-like behavior. If both samples were completely disordered, this scaling should serve to superpose the two sets. To a reasonable approximation, in fact, superposition is observed. This indicates that the presence of lamellar order has no appreciable effect on the measured D_s for SVP-22. Close examination of Figure 5 reveals that the superposition is not perfect and that the temperature dependence of D_s is slightly weaker for the higher molecular weight sample. Consequently, at the lowest temperatures, the scaling brings the ordered copolymer diffusivity above that for the disordered sample. The possible significance of this observation is not clear. It could indicate that the ordered samples were not completely at equilibrium. For example, in PEP–PEE lamellar samples well into the ordered state, it was found that long annealing times were required at the lowest temperatures used (although still well above T_g), before the measured diffusivity became constant from day to day.[5,8] Prior to reaching this steady state, the measured diffusivities would be consistently higher, and the FRS decays noticeably non single exponential. For PS–PVP, however, we believe that the samples can be, at most, only slightly displaced from equilibrium. First, the FRS decays were still single exponential, and second, the results did not vary with position in the sample or during the several

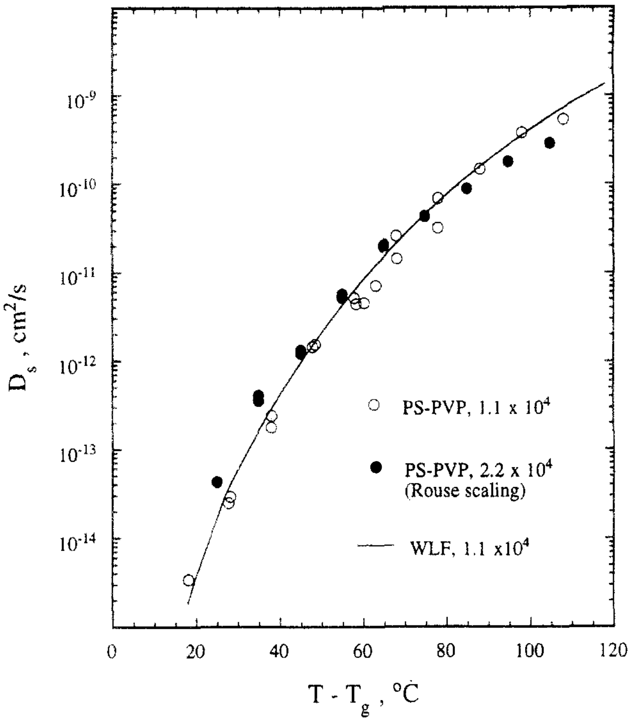

Figure 5. Self-diffusion of SVP-11 and SVP-22, compared after scaling the SVP-22 data by the molecular weight ratio (*i.e.*, Rouse scaling). The temperature axis is normalized by subtracting the respective values of T_g, and the WLF curve for SVP-11 is also shown.

days over which measurements were made. However, due to the thermal instability of the dye and the PVP block, it was not practical to anneal at elevated temperatures for more extended periods, so the possibility of incomplete equilibration cannot be completely discounted.

A tentative interpretation of the remarkable results in Figure 5 has been offered.[6] To a first approximation, one can estimate the measured D_s as follows:

$$D_s = \frac{2}{3}D_{par} + \frac{1}{3}D_{perp} \qquad (5)$$

This equation will certainly break down if $D_{par} \gg D_{perp}$, such that the chains can effectively move only along the lamellar planes, and if the sample topology is complex, *e.g.*, lamellae wound in spirals. Also, if defects and grain boundaries play a substantial role in transport, eq 5 will fail. On the other hand, as shown by Fredrickson,[14] if D_{par} and D_{perp} are not too different, and if the lamellar orientation varies smoothly in space, eq 5 should be an excellent approximation. For Rouse chains, D_{par} should be identical to the diffusivity in the absence of structure, D_{Rouse}; in other words, there is no thermodynamic penalty for a Rouse chain to move laterally. Thus, the measured D_s should fall between D_{Rouse} and $^2/_3D_{Rouse}$, depending on the value of D_{perp}. Given the scatter in Figure 5, the difference between 1 and $^2/_3$ is not significant. Thus, there are two important conclusions to be drawn. First, the lamellar order has no discernible effect on the three-dimensional, isotropic average mobility, because Rouse chains are free to move on two-dimensional surfaces. This is not true for entangled chains, as pointed out previously.[6] Second, it is not possible to say anything quantitative about D_{perp} relative to D_{par}, from these measurements.

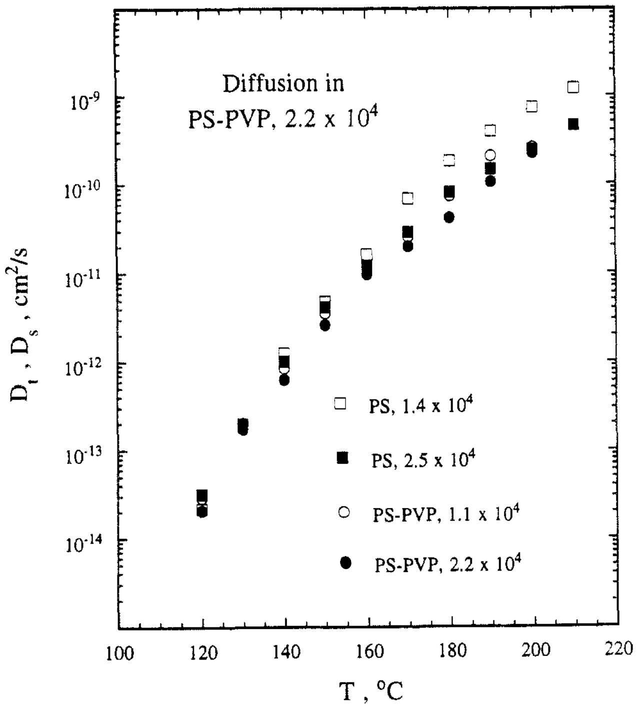

Figure 6. Self-diffusion of SVP-22, and tracer diffusion of SVP-11, PS-14, and PS-25 in the SVP-22 matrix, as functions of temperature.

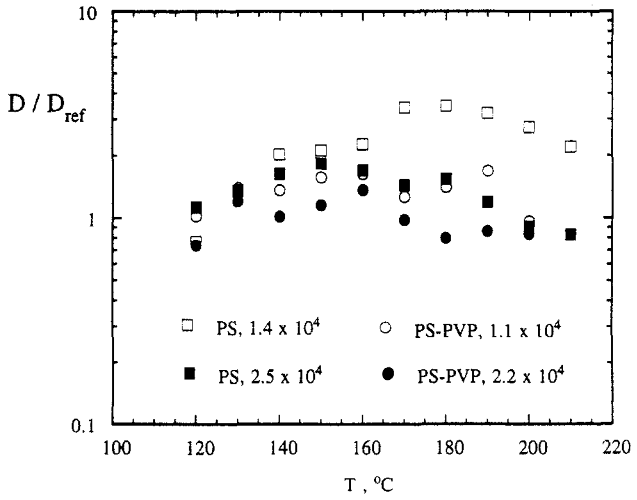

Figure 7. Data from Figure 6, normalized by the WLF curve for SVP-22.

C. Tracer Diffusion in an Ordered Block Copolymer. The tracer diffusion coefficient, D_t, of the two PS homopolymers and the SVP-11 copolymer were measured as a function of temperature, in the ordered copolymer matrix SVP-22. The results are shown in Figure 6, including the SVP-22 self-diffusion data (averaged from Figure 5) for comparison. The data appear to fall into two zones. Above approximately 160 °C, the different probes have measurably different mobilities, whereas at lower temperatures, the four data sets appear to converge. In order to see the similarities and differences more clearly, the data are replotted in Figure 7, as D normalized by D_{ref}, where D_{ref} is the WLF fit to $D_s(T)$ for the matrix polymer. Thus, if the $D_s(T)$ data for SVP-22 fit the WLF equation exactly, the filled circles in Figure 7 would all be unity. At first glance, the results in Figure 6 and 7 are rather surprising. As temperature decreases, the composition profiles of the PS and PVP microdomains sharpen, and one might expect increasing discrimination among the various probe mobilities; experimentally, the opposite is seen. However, this simple argument is not necessarily correct, as will be discussed below. A few other observations are pertinent. First, if the microstructure of the matrix had no effect on probe diffusion, and assuming the monomeric friction factors are all comparable, the various probe mobilities would only range over a factor of approximately 2, corresponding to the range of probe molecular weights. Experimentally, the mobilities vary by at most a factor of 4, so it is reasonable to conclude that, indeed, the structure has little effect. This is confirmed by comparing the various probe mobilities in SVP-22 with the corresponding self-diffusion coefficients: D_t(SVP-11) is slightly lower in SVP-22 than D_s(SVP-11); D_t(PS-25) in SVP-22 is essentially the same as D_s(PS-25), once the difference in T_g is taken into account; D_t(PS-14) is slightly lower than D_s(PS-14) ("slightly" in this context means "by less than a factor of 2"). The relative probe mobilities are also reasonable, *i.e.*, D_t(PS-14) $\geq D_t$(PS-25) and D_t(SVP-11) $\geq D_s$(SVP-22). Interestingly, however, at least in the higher temperature regime, the homopolymers are more mobile than the copolymers of similar molecular weight.

Fredrickson and Milner have considered the effect of lamellar concentration profiles on the tracer mobilities of Rouse homopolymers and copolymers, in the perturbation theory limit of a weakly sinusoidal concentration profile.[13] As all of these data correspond to a single matrix, we can utilize the Fredrickson–Milner results to estimate the relative effect of the microstructure on the four probes. As a cautionary note, this analysis is qualitative, at best. Firstly, it is almost certainly the case that the concentration profiles are stronger than the perturbation theory allows; using eq 4, χN for the matrix approaches 28 at the lowest temperature. Second, we make the assumption that the matrix is completely unaffected by the presence of the probe. Although we feel that these assumptions are reasonable, they have not been justified by direct experiment.

The Fredrickson–Milner analysis leads to the general expression[13]

$$D/D_0 = 1 - \epsilon K \ldots \qquad (6)$$

where D is the measured, three-dimensionally averaged diffusivity (D_s or D_t), D_0 is the corresponding diffusivity in the absence of microstructure (*i.e.*, D_{Rouse}), and ϵ is the perturbation variable, depending on χN and the height of the composition profile. The factor K depends on the ratio of the probe R_g to the lamellar period, and on the fractional composition, f; $f = 0$ or 1 for a homopolymer, and 0.5 for a symmetric diblock. On the basis of eq 6, and the particular calculations of K,[13] three predictions can be made, as temperature is decreased.

(i) For the two homopolymers, the matrix should act to bring the mobilities closer together than their unperturbed values; the matrix is more effective at retarding the smaller homopolymer.

(ii) For the two copolymers, the matrix should act to separate the mobilities; the matrix should retard self-diffusion more than tracer diffusion.

(iii) For a homopolymer and a copolymer of equal R_g, the homopolymer should be retarded more than the copolymer.

Examination of Figure 7 reveals that the first and third predictions are qualitatively consistent with the data. Specifically, the two homopolymer mobilities approach one another as the temperature decreases, and the homopolymer mobilities, initially higher at high temperature, converge to the copolymer results. The second prediction is not borne out; however, the magnitude of this effect (*i.e.*, from the relative values of K) is predicted to be much smaller in the copolymer–copolymer case than in either the homopolymer–homopolymer or homopolymer–copolymer comparisons. Thus, when factoring in experimental uncertainty and possible variations in ζ_0 among the various systems, the data are at least roughly consistent with the Fredrickson–Milner calculations.[13] The principal conclusion from Figures 6 and 7, however, remains that the microstructure has at most a minor influence on the mobilities of these probes. Presumably, this reflects freedom of motion within the lamellae, as in the copolymer self-diffusion case, probably coupled with non-negligible mobility perpendicular to the lamellae. This latter conclusion must be viewed as surprising, given that χN for the matrix is relatively large, albeit not completely in the strong segregation limit.

Summary

The self-diffusion of two PS–PVP copolymers and two PS homopolymers, and the tracer diffusion of the other three polymers in the higher molecular weight copolymer, has been measured over the temperature range from 110 to 210 °C by forced Rayleigh scattering. The principal observations and conclusions are as follows.

1. On the basis of rheological measurements, and consistent with other studies of PS–PVP copolymers, the higher molecular weight copolymer (SVP-22) is in the lamellar ordered state throughout the measurement temperature range, while the lower molecular weight sample (SVP-11) is disordered. These assignments are consistent with theory, utilizing an expression for $\chi(T)$ from the literature.

2. For all samples, ordered or disordered, the FRS signals were well-represented by single exponential decays. Furthermore, for each sample, at one or more temperatures, the distance-squared dependence of the decay time constant was established. In the case of the ordered matrix, these results suggest that diffusion through the lamellar planes may not be greatly retarded relative to diffusion in the lamellar planes.

3. The self-diffusion coefficients for the two block copolymers superposed reasonably well, when scaled according to the Rouse model, thereby indicating that the presence of lamellar order has little effect on the isotropic, three-dimensionally averaged chain mobility. This result is interpreted as reflecting the fact that ordered Rouse chains experience no thermodynamic penalty for motion in the lamellar planes and that therefore the chains can explore three-dimensional space relatively unhindered, essentially independent of the mobility perpendicular to the lamellae, provided that the lamellae are not macroscopically-oriented.

4. The self-diffusion coefficients of the two copolymers were slightly lower than those of the homopolymers of similar total molecular weight. As one copolymer was ordered and one disordered, this observation is attributed to a higher monomeric friction coefficient for the PVP block. The fact that the ordered copolymer has a mobility similar to that of the disordered homopolymer also supports the previous conclusion, *i.e.*, that lamellar order has little effect on the overall mobility.

5. The tracer diffusion coefficients of the various probes in the ordered copolymer matrix were comparable to one another and to the corresponding self-diffusion coefficients. This also indicates that the microstructure has, at most, a minor influence on the overall mobility. Subtle variations in the temperature dependence among the various probes were also qualitatively consistent with perturbation theory.

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