Macromolecules **1994,** *27,* 3487-3492 **3487**

Diffusion in Block Copolymer Melts: The Disordered Region and the Vicinity of the Order-Disorder Transition

M. C. Dalvi and T. P. Lodge*

Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455

Received December 30, 1993; Revised Manuscript Received April 14, 1994[⊛]

ABSTRACT: Forced Rayleigh scattering (FRS) has been used to measure the self-diffusion and tracer diffusion of nearly symmetric, well-entangled, poly(ethylenepropylene)-poly(ethylethylene) (PEP-PEE) block copolymers. A procedure has been developed for the labeling of these polymers with a photochromic molecule (4′-(*N,N*-dimethylamino)-2-nitrostilbene-4-carboxylic acid), an essential requirement of the FRS technique. The temperature and molecular weight dependence of diffusion in PEP-PEE 1, a completely disordered block copolymer, was studied using three tracers: PEP-PEE 1, PEP-PEE 2, and PEP-PEE 3 ($M_n = 3.1_5 \times 10^4$, $5.0_1 \times 10^4$, and $8.1_2 \times 10^4$, respectively). The data clearly indicate that, in this region of the phase diagram, block copolymers behave no differently than linear homopolymers, *i.e.*, they appear to obey reptation dynamics. These three tracers were also studied in a matrix, PEP-PEE 2, which exhibits an order-disorder transition (ODT) at 96 °C. In the ordered matrix, the mobility of all three tracers was suppressed relative to the disordered state. The temperature dependence of the diffusivity was smooth through the ODT. For the two higher molecular weight tracers, fluctuations retard chain mobility at temperatures well above the ODT, which explains the observed insensitivity of diffusion measurements to the ODT itself.

Introduction

Block copolymers, an important class of self-assembling materials, exhibit a rich variety of structural and dynamic behavior.[1] The thermodynamic repulsion between dissimilar monomers causes the system to adopt a microphase-separated morphology. This order-disorder transition (ODT) occurs when the product χN achieves some critical value, where χ is the temperature-dependent monomer-monomer interaction parameter and N is the degree of polymerization. A variation in the temperature or molecular weight enables the ODT to be accessed, while the composition, $f = N_A/N$, determines the specific morphology adopted by an A-B diblock in the ordered state. Relatively little is known, however, about the effect of thermodynamic interactions on the dynamics of these molecules in terms of the single chain and/or cooperative motions.

A fundamental quantity reflecting the dynamics of individual polymer chains is the translational diffusivity, D. The influence of the spatially-varying free energy density on D makes microstructured block copolymer systems potentially very different from homopolymer systems. A possible consequence of this local spatial structure is the confinement of individual molecules in preferred regions of the morphology. Furthermore, the lamellar and cylindrical morphologies are inherently anisotropic and this can also exert an influence on D. In order to thoroughly understand chain mobility in block copolymers, four regions of the phase diagram need to be explored for both unentangled and entangled systems: the completely disordered region, the fluctuation region, and, in the ordered regime, the weak and strong segregation limits.

An aspect of the transition region peculiar to systems such as block copolymers is the presence of substantial composition fluctuations in the disordered state well above the ODT.[2-4] In his initial theoretical treatment of the weak segregation regime, Leibler[2] acknowledged that the presence of such fluctuations would influence phase behavior. Fredrickson and Helfand[3] outlined the changes in the phase diagram that resulted from these fluctuations. Initial experimental evidence of composition fluctuations in the disordered state has been provided by Bates and co-workers.[4,5] They have shown that the low frequency rheological response changes significantly as the ODT is approached from the disordered state. A new relaxation mode is seen, at frequencies below a certain critical frequency, at temperatures about 45-50 deg above the ODT. The terminal liquidlike behavior progressively shifts to lower frequencies as the ODT is approached. This response has been assigned to transient concentration fluctuations. The presence of fluctuations has been confirmed by a small angle neutron scattering (SANS) study[4] of the temperature dependence of the peak scattering intensity, the nonlinear dependence being consistent with the fluctuation theory.[3] Bates and co-workers have also used the SANS results to demonstrate that an instantaneous real-space image of the composition pattern in the disordered state is similar to that seen in the spinodal decomposition of binary fluid mixtures. The amplitude of this fluctuating pattern is expected to be large near the ODT and to gradually decrease with increasing temperature. It may be expected that fluctuations will also influence the mobility of individual chains.

It is only recently that some progress has been made toward investigating block copolymer diffusion in bulk systems. Shull *et al.*[6] studied the self-diffusion coefficient, D_s, in a well-entangled poly(ethylenepropylene)-poly(ethylethylene) (PEP-PEE) diblock copolymer ($M_n = 5.0_1 \times 10^4$), using forward recoil spectrometry, and found that there was little or no evidence of the ODT in the temperature dependence of D. Ehlich *et al.*[7,8] used forced Rayleigh scattering (FRS) to measure the D_s of a low molecular weight polystyrene-polyisoprene diblock copolymer. The authors were also able to conclude, despite very complicated experimental signals, that D_s showed little sensitivity to the ODT. They report that the signal complexity is less pronounced, or absent, at temperatures above the ODT and have assigned the multiple exponential signals obtained at lower temperatures to anisotropic diffusion in the lamellar domains. Fleischer *et al.*[9] have measured D_s for polystyrene-polyisoprene diblocks using field gradient NMR. They report that heating the sample through the ODT does not lead to an abrupt crossover to unrestricted diffusion.

[⊛] Abstract published in *Advance ACS Abstracts,* May 15, 1994.

0024-9297/94/2227-3487$04.50/0

Table 1. Polymer Characteristics

sample	M_n	M_w/M_n	wt % PEP	$c_1{}^a$	$c_2{}^a$	T_{ODT}, °C
PEP-PEE 1	31 500	1.05	53	6.68	146.8	−41
PEP-PEE 2	50 100	1.07	56	7.98	148.6	96
PEP-PEE 3	81 200	1.05	53	8.13	151.5	291

[a] T_{ref} = 35 °C.

The PEP-PEE system examined by Shull *et al.*[6] was studied previously by us, with FRS. We have used the capability of the FRS technique to measure uniaxial diffusion, to resolve D_s parallel and perpendicular to the lamellar domains (D_{par} and D_{perp}, respectively) by the use of specimens which had shear-induced macroscopic order.[10] We found that for the self-diffusion of the $5.0_1 \times 10^4$ PEP-PEE, $D_{par} \approx D_{perp}$ just 2 deg below the ODT (96 °C) but, when the temperature was further reduced to 25 °C, D_{perp}/D_{par} decreased steadily to about 0.3. Similar results have also been presented for this tracer diffusing in a more strongly segregated PEP-PEE matrix.[11] The influence of entanglements on block copolymer diffusion, above and below the ODT, has also been presented recently.[12] We observed that in a quenched lamellar sample, the isotropic, average D_s of unentangled (Rouse) chains is unaffected by the microstructure, whereas entangled (reptating) chains are significantly retarded. The combined influence of thermodynamic and entanglement constraints on D has thus been established. Eastman *et al.*[13] have recently demonstrated that Rouse scaling ($D_s \sim M^{-1}$) holds for unentangled symmetric copolymers, irrespective of the state of order of the system. They have interpreted this result as reflecting unhindered motion of the copolymer chains in the lamellar planes. In this paper, we present results of both self-diffusion and tracer diffusion in two PEP-PEE matrices; one is in the completely disordered state across the measurement temperature range (25-190 °C), whereas the other undergoes the order-disorder transition in the middle of the accessible range. The latter matrix enables us to study the fluctuation region as well as the weak segregation regime.

Experimental Section

Materials and Sample Preparation. The poly(ethylenepropylene)-poly(ethylethylene) (PEP-PEE) block copolymers used in this study are listed in Table 1. These polymers were generously supplied by Professor F. S. Bates and co-workers. The PEP-PEE polymers were prepared by the catalytic hydrogenation of 1,4-polyisoprene-1,2-polybutadiene precursors.[14] The hydrogenation of these precursors proceeds to an extent of about 99.5% or greater. We have made use of the small residual unsaturation to functionalize the polymers and to subsequently label them with a photochromic molecule.

A 0.4% (w/v) solution of the polymer in chloroform was treated with a slight excess, relative to the expected residual unsaturation, of a 19.4 mM solution of bromine in chloroform, at room temperature, for 100 min. Bromine and chloroform of ACS reagent grade were purchased from Fisher Scientific and used as received. Bromine reacts with any vinyl groups present on the polymer, forming a dibromo derivative. The reaction was carried out in the absence of light. The brominated polymer was recovered by precipitation with methanol. Size exclusion chromatography (SEC) traces confirmed that there was no change in the molecular weight distribution after the functionalization reaction. The polymer chain was then labeled by eliminating the bromine on the polymer with the cesium salt of the photochromic moiety, 4′-(*N*,*N*-dimethylamino)-2-nitrostilbene-4-carboxylic acid (ONS). ONS was synthesized in our laboratory via a procedure[15] derived from the protocol previously described by Ehlich.[16] The absence of a solvent capable of dissolving both the brominated polymer and the cesium salt of ONS necessitated a two-phase reaction for labeling the polymer. The polymer was dissolved in benzene (1% w/v), and an approximately 5-fold molar excess of the dye, along with a trace of the phase transfer catalyst, tetra-*n*-butylammonium bromide (Eastman Chemicals), was dissolved in water. This nucleophilic substitution reaction was carried out in the absence of light. The progress of the reaction was monitored by following the UV-vis absorbance of the polymer at 440 nm; the increase in the absorbance was due to the dye on the polymer. It usually took between 4 and 12 weeks to attain an adequate number of dye labels per chain. The labeled polymer was recovered by precipitation with methanol, and any unattached dye was removed by passing a solution of the polymer in chloroform through a silica gel column.[15] The molecular weight distribution of the polymer was confirmed by SEC to be unaffected by the labeling reaction. Table 2 details the number of labels per tracer chain and the amount of tracer polymer mixed with each matrix.

Table 2. Sample Characteristics

matrix	tracer	no. of labels/ tracer chain	wt % tracer
PEP-PEE 1	PEP-PEE 1	3.5	2.7
PEP-PEE 1	PEP-PEE 2	1.7	3.3
PEP-PEE 1	PEP-PEE 3	4.5	3.0
PEP-PEE 2	PEP-PEE 1	3.5	2.1
PEP-PEE 2	PEP-PEE 2	0.9	4.9
PEP-PEE 2	PEP-PEE 3	4.5	3.0

The sample cells were prepared as follows. After appropriate amounts of tracer and matrix polymer were codissolved in pentane (4-5% w/v), the solution was filtered through a 0.45-μm filter and the polymer precipitated with methanol. The polymer was then placed on a 25-mm-diameter glass disk (Heraeus-Amersil) which had a 0.5-1.0-mm thick aluminum spacer glued to it. The polymer was made to flow and occupy the volume of the spacer by annealing it at a high temperature under vacuum. The annealing temperature was 115-120 °C for the samples involving PEP-PEE 2 as the matrix polymer. Since this temperature is above the ODT of PEP-PEE 2 (96 °C), it ensured that a quenched lamellar phase would be formed on cooling the polymer. The samples using PEP-PEE 1 as the matrix polymer were annealed at 70-80 °C. Another glass disk was then used as a cover plate and the cells were sealed under an inert atmosphere.

Diffusion Measurements. The diffusion coefficients of the block copolymers were determined by FRS. The experimental protocol and data analysis schemes have been presented elsewhere.[10,17] A transient grating was created in the sample by exposure to crossed beams from an Ar$^+$ laser operating at λ_o = 488 nm. The duration of this pulse was between 10 and 100 ms. The erasure of the grating, due to mass diffusion, was monitored by following the decay of the diffracted intensity from one of the same incident beams, attenuated by a factor of 10^4. The grating period was varied between 1 and 5 μm, by changing the crossing angle of the writing beams. The temperature was controlled to within ±0.2 deg throughout each measurement. The measurements were initiated at the lowest temperature studied and continued upon progressive heating of the samples.

Figure 1 shows the normalized experimental signals observed over a wide range of temperature, for the tracer diffusion, D_t, of PEP-PEE 3, in the PEP-PEE 2 matrix. The fringe spacing is 1.6 μm. A thousand data points were acquired for each decay, although only a subset has been shown in the figure, for clarity. These decays are representative of all the systems presented in this study. The data are plotted on a semilogarithmic scale to facilitate comparison. It is clear that in all cases the signals decay to the baseline, irrespective of whether the system is in the ordered or disordered state. Furthermore, the expression for the diffracted intensity

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

where A denotes the amplitude, τ the decay time, B the coherent background, and C the incoherent background, describes the decays very well. It should be noted that the initial portion of the FRS decays usually contain contributions from thermal relaxation processes and non-center-of-mass diffusion and are therefore not included in the fitting. Also, the values of B and

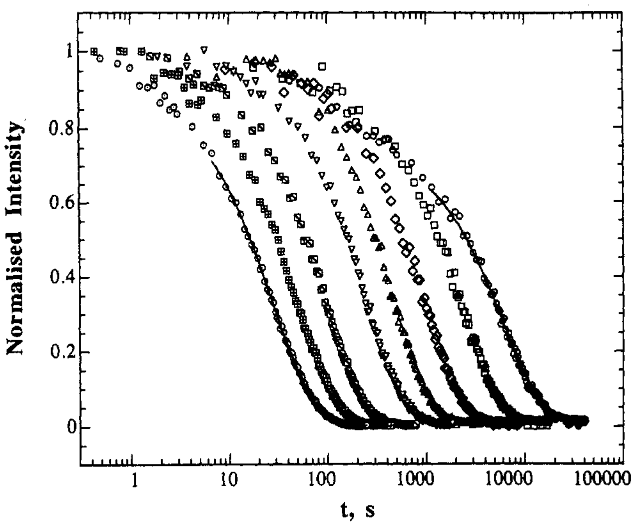

Figure 1. Normalized forced Rayleigh scattering signals for PEP-PEE 3 diffusing in PEP-PEE 2, at a fringe spacing of 1.6 μm. The temperatures from right to left are 50, 60, 70, 80, 90, 100, 110, and 120 °C. The solid lines represent the fits to the signals obtained at 50 and 120 °C, using eqs 2 and 1, respectively.

C obtained from the fitting were small relative to the amplitude of the exponential decay ($B/A < 0.05$ and $C/A < 0.15$). Such signal-to-noise was typical of all the samples studied. However, at the lowest temperature shown, *i.e.* 50 °C, the following second-order cumulant expression was used to better describe the data

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

where β is related to the width of the distribution of the decay rate. The solid lines in Figure 1 are the fits to the experimental signals obtained at 120 and 50 °C, using eqs 1 and 2, respectively. We have observed that eq 2 is usually necessary to fit the experimental signals obtained at temperatures below 50 °C. This is perhaps due to an increased sensitivity to the finite polydispersity of the samples at low temperatures, as a consequence of the strong χN dependence of diffusion in these systems.

Another important aspect of the low temperature measurements is the annealing time at each temperature. Diffusion coefficients were seen to progressively decrease, by more than 1 order of magnitude in some cases, as the sample was annealed at a given temperature. The experimental signals during this period were complicated and non single exponential. In fact, we have used such behavior as an indicator of inadequate annealing. Annealing times at 25 and 35 °C for the PEP-PEE 1 matrix were on the order of a few days or less, whereas the PEP-PEE 2 matrix required annealing for at least 3 weeks at 25 °C and several days at 35 °C. Ehlich *et al.*[8] report similar reductions in D with annealing, which they attribute to the healing of grain defects. However, they still need an additional exponential term in eq 1 to appropriately describe their data at temperatures below the ODT, and apparently even at some temperatures above the ODT.

The diffusive origins of the measurements are confirmed by the linearity of the decay time versus grating distance squared, with no appreciable intercept. An example is shown in Figure 2 for PEP-PEE 3 diffusing in PEP-PEE 2, for a variety of temperatures. Regression on such data yields error bars on D; such an analysis has been performed at almost all temperatures below 135 °C. The error bars (*i.e.*, ±1 standard deviation) on these measurements are typically between 5 and 15%.

Results and Discussion

There is an important issue, relevant to block copolymer diffusion in general, that needs to be addressed at this point. The individual blocks of a copolymer are very likely to have different entanglement molecular weights, M_e. This can give rise to several different scenarios, a particularly interesting one having block A well-entangled while block B is unentangled. It is not clear how the dynamics of such a chain should be described. The definition of the number of effective entanglements experienced by an individual chain in the completely disordered region, where the two blocks are well-mixed and the system homogeneous, is unclear. Furthermore, it is possible that the number of entanglements will change in the ordered state, where the chain is stretched relative to its disordered dimensions and where the concentrations are nonuniform. Also, in the ordered region, the constraints seen by block A as it diffuses through the unentangled block B have not been defined, and the value of $M_e(\mathrm{A})$ in another block B, or vice versa, is not known. Therefore, a quantitative application to block copolymers of entanglement molecular weights determined for homopolymers is probably not appropriate. However, the use of these numbers to achieve at least a qualitative understanding of block copolymer dynamics is not unreasonable. This is particularly true for the FRS experiment, where grating erasure involves the motion of chains over length scales at least 15–20 times the radius of gyration of the chain, and entanglements, if present, would undoubtedly dominate the behavior. M_e for the PEP and PEE blocks is 1.5×10^3 and 1.1×10^4, respectively.[18] Thus the PEP-PEE samples used in this study are well entangled and it is clear that entanglement dynamics should influence their behavior, even though the majority of entanglements are felt by the PEP block.

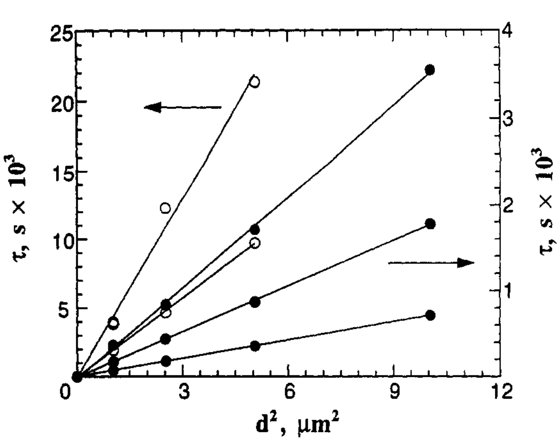

Figure 2. Decay time versus grating distance squared, for PEP-PEE 3 diffusing in PEP-PEE 2. The open circles (left axis) correspond to 50 and 60 °C while the filled circles (right axis) correspond to 80, 90, and 100 °C.

The results are presented in two parts, the first describing diffusion in the completely disordered PEP-PEE 1 matrix, and the second diffusion in the PEP-PEE 2 matrix, both above and below T_{ODT}.

Disordered State. Figure 3 shows the temperature dependence of the self-diffusion of PEP-PEE 1. The smooth curve through the data represents the WLF function as determined from the temperature dependence of the rheological properties;[5] the values of the WLF parameters are given in Table 1. It should be noted that the WLF function has been shifted arbitrarily along the ordinate to match the diffusion data. The excellent agreement of the temperature dependence implies that these experiments reflect identical segmental dynamics, as is expected. This set of measurements has been located on the phase diagram by computing χN using the experimentally determined expression for χ[4]. In terms of the quantity $(\chi N)/(\chi N)_{\mathrm{ODT}}$, the range covered is estimated to be from 0.57 to 0.78 and the system is expected to be completely disordered, without substantial fluctuations, even at the lowest measurement temperature.

The data obtained for the tracer diffusion of PEP-PEE 2 and PEP-PEE 3 in the disordered PEP-PEE 1 matrix are shown in Figure 4. The dashed lines represent the

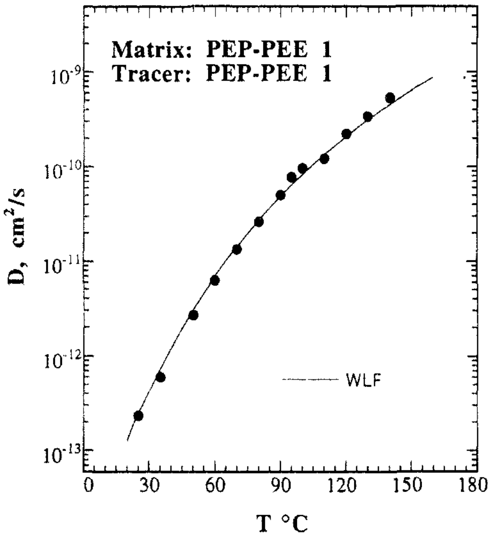

Figure 3. Self-diffusion of PEP-PEE 1 (filled circles) as a function of temperature. The smooth curve corresponds to the WLF function determined from the rheological properties of PEP-PEE 1.

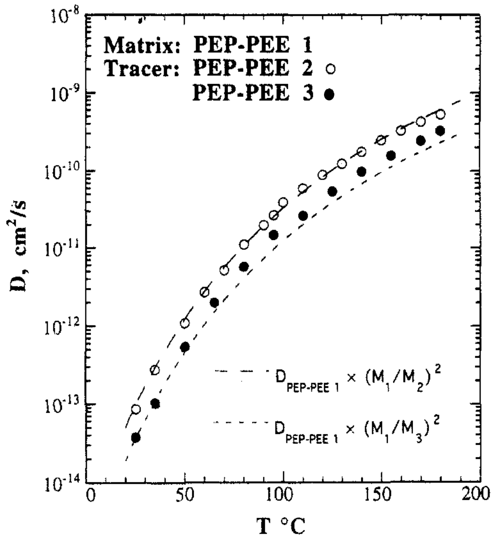

Figure 4. Diffusion of PEP-PEE 2 (open circles) and PEP-PEE 3 (filled circles) in the disordered PEP-PEE 1 matrix. The dashed lines represent the PEP-PEE 1 WLF function multiplied by the appropriate molecular weight ratio, assuming reptation scaling.

WLF function for PEP-PEE 1 scaled down by the square of the molecular weight ratios, assuming that these tracer chains would obey the reptation scaling ($D_t \sim M^{-2}$) characteristic of well-entangled chains in the disordered state. It is clear, from the figure, that the measured D_t of PEP-PEE 2 agrees very well with the reptation prediction. However, the PEP-PEE 3 tracer diffuses slightly more rapidly than the strict reptation prediction. This, too, is not entirely surprising because the PEP-PEE 3 tracer is about 2.5 times larger in molecular weight than the PEP-PEE 1 matrix, and it is reasonable to expect "constraint release" contributions to enhance D_t. At the lowest temperatures, the PEP-PEE 3 data move closer to the dashed line. This might reflect the first onset of composition fluctuations in the matrix (*vide infra*), but this possibility is clearly speculative.

The data very clearly indicate that entanglements are influencing the dynamics of diffusion in the completely disordered state. This leads us to conclude that these block copolymers behave in the completely disordered region of the phase diagram no differently than do linear homopolymers.

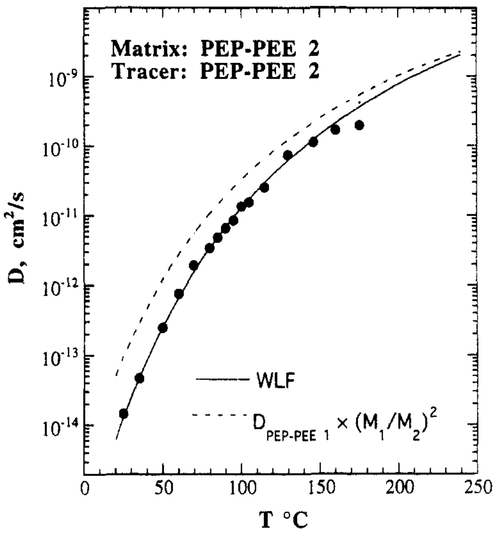

Figure 5. Self-diffusion of PEP-PEE 2 (filled circles) as a function of temperature. The smooth curve corresponds to the WLF function determined from the rheological properties of PEP-PEE 2. The dashed line represents the self-diffusion of PEP-PEE 2 in a hypothetically disordered state and is obtained from the PEP-PEE 1 WLF function, assuming reptation scaling.

Fluctuation Region and Weak Segregation Region. As has been stated earlier, PEP-PEE 2 has an ODT at 96 °C. Our measurement window being 25-190 °C, it was possible to study the influence of fluctuations on D using PEP-PEE 2 as a matrix. In terms of the quantity $(\chi N)/(\chi N)_{ODT}$, the range covered is estimated to be from 0.82 to 1.2. The matrix should be in the weak segregation limit even at the lowest temperatures studied. It should also be noted that the matrix, in these cases, had a quenched lamellar morphology in the ordered state and that no attempt was made to induce macroscopic order. The measured D therefore corresponds to a macroscopic, isotropic average.

The temperature dependence of the self-diffusion of PEP-PEE 2 is shown in Figure 5. The data agree well with the measurements of Shull *et al.*[6] for the same system. The WLF function has been determined from the temperature dependence of the rheological properties[5] and is shown in the figure as the smooth curve through the data. It should be noted that this curve has been shifted arbitrarily along the ordinate to match the diffusion data. The dashed line is the WLF function of PEP-PEE 1 scaled down by the square of the molecular weight ratio. This reptation scaling has been shown, in the earlier section, to be valid for disordered block copolymers. The dashed line, therefore, represents D_s of PEP-PEE 2 in a hypothetically disordered state. It is immediately apparent that the ordered block copolymer is diffusing more slowly than its disordered equivalent, the difference increasing with decreasing temperature. Interestingly, this difference persists even at temperatures above the ODT, there being no discontinuity in the temperature dependence of D at the transition. It is possible that this suppression in D would vanish at temperatures greater than 200 °C, as is suggested by an extrapolation of the WLF curves. These temperatures, however, are well above the glass transition temperatures of both the blocks of the copolymer, and the WLF dependence may not be followed at these temperatures.

Figure 6 shows the measured D_t of PEP-PEE 3 in the PEP-PEE 2 matrix. The dashed line is the WLF function of PEP-PEE 1 scaled down by the square of the molecular weight ratio of PEP-PEE 1 and PEP-PEE 3, and represents D for the hypothetical disordered state of PEP-

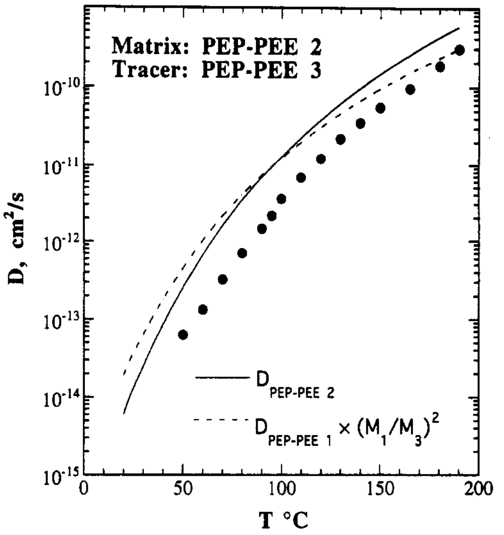

Figure 6. Diffusion of PEP–PEE 3 in PEP–PEE 2 (filled circles) as a function of temperature. The solid line is the PEP–PEE 2 WLF function. The dashed line represents the self-diffusion of PEP–PEE 3 in a hypothetically disordered state and is obtained from the PEP–PEE 1 WLF function, assuming reptation scaling.

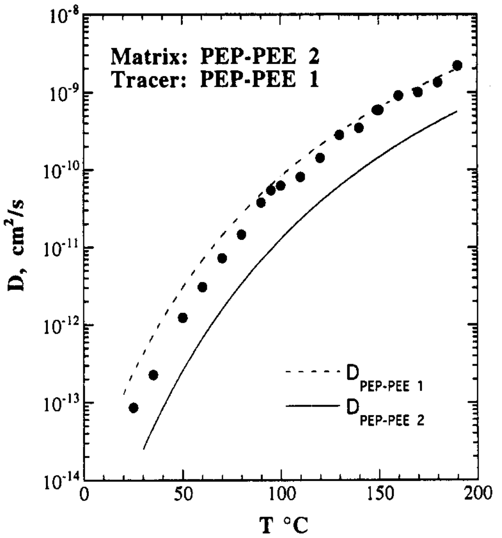

Figure 7. Diffusion of PEP–PEE 1 in PEP–PEE 2 (filled circles) as a function of temperature. The solid line is the PEP–PEE 2 WLF function. The dashed line represents the self-diffusion of PEP–PEE 1.

PEE 3. The measured D_s of PEP–PEE 2 is also shown as the solid line, and it is not surprising that the data fall below this curve. What is remarkable, however, is that there is evidence of suppression in the mobility of the tracer, relative to the disordered equivalent, almost 100 °C above the ODT of the matrix (96 °C). The extent of retardation increases with decreasing temperature and, as seen in Figure 5, there is no discontinuity in D_t as the matrix passes through the ODT.

The temperature dependence of D_t of PEP–PEE 1 in the PEP–PEE 2 matrix is shown in Figure 7. The solid line shows the measured D_s of PEP–PEE 2, and as expected, the data for this lower molecular weight tracer fall above this line. The dashed line is the measured D_s for PEP–PEE 1. Retardation of the PEP–PEE 1 tracer, relative to the disordered state, sets in only below the ODT of the matrix, though the extent of this retardation increases as the temperature is lowered in the ordered region. There is some scatter in the data just above the ODT, but at higher temperatures the tracer behaves as if it were diffusing in a completely disordered matrix.

In order to understand the results presented in Figures 5–7 one must recall that all these chains are well-entangled and, as has been shown in the earlier section, appear to diffuse by the reptation mechanism. Well into the ordered state, the junction between the two blocks will reside near the interface between microdomains, with the end-to-end vector of the chain lying, on average, normal to the lamellar plane. Consequently, a reptating chain trying to escape the confines of its "tube" would have to drag one block through a domain rich in the other component. This results in the chain experiencing a thermodynamic penalty for motion either parallel or perpendicular to the domains.[12] Thus, there is a substantial localization of the chain due to the microstructure, leading to a suppression of D relative to the completely disordered state. As the temperature is decreased, the composition profile evolves from weakly sinusoidal at the ODT toward a step function well into the ordered state, *i.e.*, in the strong segregation limit. The interfacial zone becomes progressively narrower with decreasing temperature, further suppressing the chain mobility. Such a mechanism does not preclude diffusion perpendicular to the domains from being slowed down at a rate which is different from parallel diffusion. It is probable that in the well ordered state, diffusion parallel to the lamellar domains would still proceed but by an arm retraction mechanism, analogous to that seen in star polymers. The thermodynamic barriers to diffusion perpendicular to the domains would, probably, be too severe to overcome.

The suppression in mobility immediately above the ODT can be rationalized using similar arguments. Rheological and SANS measurements[4] have indicated the presence of concentration fluctuations above the transition. These fluctuations, or regions of transient local lamellar order, have a real-space profile similar to that seen in the spinodal decomposition of binary fluid mixtures. Under these circumstances, temporary localization of the junction points would persist even above the ODT, causing a retardation in the mobility. This could explain the insensitivity of the diffusion measurements[8,9] to the ODT. The amplitude of this fluctuating pattern should decrease with increasing temperature and eventually vanish at some distance from the ODT. Rheological evidence suggests that this occurs approximately 50 deg above the transition. However, Figures 5 and 6 show evidence of suppression of D for the PEP–PEE 2 and PEP–PEE 3 tracers at least 100 deg above the matrix ODT. This leads us to believe that the fluctuation window may be even broader than that suggested by the rheological properties. The PEP–PEE 1 tracer, shown in Figure 7, is apparently unaffected by these fluctuations. It is reasonable to expect the thermodynamic barriers faced by these tracers to depend on their molecular weight, the effect decreasing with decreasing N. The low molecular weight PEP–PEE 1 tracer could therefore experience the least suppression in mobility, and the high molecular weight PEP–PEE 3 tracer the most, at any given temperature. This is exactly the trend seen in the data, in both the fluctuation regime and the ordered state.

Conclusions

We have used PEP–PEE 1 ($T_{ODT} \approx -41$ °C) as a matrix, to explore the molecular weight dependence of D in the fully disordered state. The results show that entangled block copolymers obey reptation dynamics and behave no differently than linear homopolymer melts. The influence of microstructure, in the ordered state, and composition fluctuations, in the nominally disordered state, was studied using PEP–PEE 2 (ODT ≈ 96 °C) as a matrix. A suppression in D, relative to a disordered state, was seen for all tracers at temperatures below the matrix order–disorder transition temperature, *i.e.*, in the weak segregation region. This retardation is due to the localization of the junction between the blocks to the interfacial region. Since the interfacial region becomes narrower with decreasing temperature, it causes an increase in the extent of retardation. The presence of composition fluctuations, however, causes the suppression in mobility to persist even in the disordered region for the two higher molecular weight tracers. The diffusion measurements apparently detect these fluctuations, as suggested by the onset of retardation, at temperatures as much as 100 deg above the matrix ODT. This implies that the fluctuation regime is broader than that previously suggested by the rheological properties.

Acknowledgment. This work was supported by the Center for Interfacial Engineering, an NSF-supported Engineering Research Center at the University of Minnesota. The PEP–PEE samples were generously provided by J. H. Rosedale and F. S. Bates.

References and Notes

(1) Bates, F. S.; Fredrickson, G. H. *Annu. Rev. Phys. Chem.* **1990**, *41*, 525.

(2) Leibler, L. *Macromolecules* **1980**, *13*, 1602.

(3) Fredrickson, G. H.; Helfand, E. *J. Chem. Phys.* **1987**, *87*, 697.

(4) Bates, F. S.; Rosedale, J. H.; Fredrickson, G. H. *J. Chem. Phys.* **1990**, *92*, 6255.

(5) Rosedale, J. H.; Bates, F. S. *Macromolecules* **1990**, *23*, 2329.

(6) Shull, K. R.; Kramer, E. J.; Bates, F. S.; Rosedale, J. H. *Macromolecules* **1991**, *24*, 1383.

(7) Ehlich, D.; Takenaka, M.; Okamoto, S.; Hashimoto, T. *Macromolecules* **1993**, *26*, 189.

(8) Ehlich, D.; Takenaka, M.; Hashimoto, T. *Macromolecules* **1993**, *26*, 492.

(9) Fleischer, G.; Fujara, F.; Stühn, B. *Macromolecules* **1993**, *26*, 2340.

(10) Dalvi, M. C.; Lodge, T. P. *Macromolecules* **1993**, *26*, 859.

(11) Lodge, T. P.; Xu, X.; Jin, X.; Dalvi, M. C. *Makromol. Chem. Macromol. Symp.* **1994**, *79*, 87.

(12) Dalvi, M. C.; Eastman, C. E.; Lodge, T. P. *Phys. Rev. Lett.* **1993**, *71*, 2591.

(13) Eastman, C. E.; Lodge, T. P. *Macromolecules*, submitted for publication.

(14) Bates, F. S.; Rosedale, J. H.; Bair, H. E.; Russell, T. P. *Macromolecules* **1989**, *22*, 2557.

(15) Eastman, C. E. Ph.D Thesis, University of Minnesota, 1993.

(16) Ehlich, D. Diplomarbeit, Universität Mainz, 1984.

(17) Huang, W. J.; Frick, T. S.; Landry, M. R.; Lee, J. A.; Lodge, T. P.; Tirrell, M. *AIChE J.* **1987**, *33*, 573.

(18) Fetters, L. J. Personal communication.