

# Effect of composition fluctuations on tracer diffusion in symmetric diblock copolymers

Rangaramanujam M. Kannan<sup>a)</sup>

*Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, Minnesota 55455-0431*

Jie Su<sup>b)</sup>

*Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455-0431*

Timothy P. Lodge<sup>c)</sup>

*Department of Chemistry and Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, Minnesota 55455-0431*

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We report forced Rayleigh scattering measurements of the tracer diffusion of poly(ethylenepropylene) (PEP) homopolymers in nearly symmetric poly(ethylenepropylene)-*b*-poly(ethylene) (PEP-PEE) block copolymer matrices, both above and below the order-disorder transition. Measurements of PEP-PEE copolymer diffusion in the same matrices have been reported previously. The results indicate that fluctuations suppress diffusion of both homopolymer and copolymer tracers, as predicted by recent theories. However, in the quenched ordered state, diffusion suppression is considerably stronger for block copolymer tracers than for homopolymer tracers, which appears to be counter to theoretical expectation. Varying the tracer molecular weight has little effect on the suppression of homopolymer diffusion, whereas it has a substantial effect on copolymer tracer diffusion. These differences are attributed to differential chain localization or confinement: an entangled copolymer tracer tends to be pinned near the interface between microdomains, and has to pay a significant enthalpic penalty for diffusion in any direction, as the reptating chain has to drag one block through the other microdomain. On the other hand, although a homopolymer tracer tends to be located within one microdomain, it can presumably diffuse across several grains without penalty, by reptating predominantly within a single lamella. © 1998 American Institute of Physics. [S0021-9606(98)51311-6]

## INTRODUCTION

Block copolymers are a fascinating class of materials capable of forming a wide range of controlled morphologies, and have thus been a subject of scientific and industrial curiosity. In the bulk, the phase behavior of these materials is governed by the enthalpic interaction between the two blocks, *A* and *B* (parameterized by  $\chi$ , the Flory-Huggins interaction parameter), the entropic contribution to the free energy (proportional to  $N^{-1}$ , where  $N$  is the degree of polymerization), and the relative fraction of the *A* component ( $f$ ). When the product  $\chi N$  reaches a critical value, copolymers undergo an order-disorder transition (ODT) into well-defined nanostructures. Via mean-field theory, Leibler showed that a symmetric diblock copolymer ( $f=0.5$ ) undergoes a second-order transition into a lamellar microstructure when  $\chi N \approx 10.5$ .<sup>1</sup> However, he also noted that the inclusion of composition fluctuations would affect the phase diagram. Fredrickson and Helfand<sup>2</sup> extended Leibler's theory by way of the Brasovskii Hamiltonian,<sup>3</sup> to consider the effect of large amplitude composition fluctuations on the ODT. The

resulting BLFH theory predicts a fluctuation-induced weakly first-order transition into the ordered state, with the ODT suppressed below the mean-field prediction (i.e., to higher  $\chi N$ ). Small angle scattering (SANS and SAXS) studies have confirmed the non-mean-field nature of the temperature dependence of the peak scattered intensity.<sup>4</sup> Recent liquid state theory (PRISM) also captures this effect.<sup>5,6</sup>

Fluctuations also affect the rheological properties, producing characteristic low-frequency features reflecting stresses arising from the distortion of the fluctuating concentration field.<sup>4,7</sup> In entangled systems, and with a relatively weak temperature dependence of  $\chi$ , the effect of fluctuations on rheology can extend to temperatures tens of degrees above the order-disorder transition. Similar phenomena have been recently reported in block copolymer solutions.<sup>8</sup> Under large amplitude oscillatory shear near the ODT, fluctuations have been suggested to induce macroscopic lamellar orientation "perpendicular" to the shear direction, such that the lamellar normals lie along the vorticity axis.<sup>9</sup> The effects of fluctuations on individual chain dynamics, such as tracer diffusion, are also not yet well understood. In a previous work, the retarding effect of fluctuations on entangled *block copolymer* tracer diffusion was demonstrated.<sup>10</sup> In this study, we explore the effect of composition fluctuations on the

<sup>a)</sup>Current address: Department of Chemical Engineering, Wayne State University, Detroit, MI 48202.

<sup>b)</sup>Current address: Department of Chemistry, SUNY Stonybrook, NY 11794.

<sup>c)</sup>Author to whom correspondence should be addressed.

translational diffusion of *homopolymer* tracers in nearly symmetric block copolymer melts.

## BACKGROUND

The effects of microstructure on chain diffusion can depend on a variety of factors, including morphology, the architecture of the tracer, the extent of phase segregation and the state of entanglement. It is helpful to define four diffusion coefficients:  $D$ ,  $D_0$ ,  $D_{\text{par}}$ , and  $D_{\text{perp}}$ , which correspond respectively to (i) the isotropic average diffusivity in a disordered, or ordered but unoriented, copolymer; (ii) the hypothetical “bare” diffusivity, equivalent to  $D$  with all variables the same except  $\chi \rightarrow 0$ ; the diffusivities (iii) parallel; and (iv) perpendicular to the microdomain interfaces. In nearly symmetric block copolymer melts,  $D(T)$  has been found to vary smoothly through the ODT, both for *unentangled* polystyrene-poly(2-vinylpyridine) (PS-PVP) and PS-polyisoprene (PS-PI) copolymers,<sup>11–13</sup> and for an *entangled* poly(ethylenepropylene-poly(ethylethylene)) (PEP-PEE) sample.<sup>10,14</sup> However, at the ODT  $D \approx D_0$  for unentangled PS-PVP<sup>11</sup> but  $D \approx (1/3)D_0$  for entangled PEP-PEE<sup>10</sup> (the situation for PS-PI is not yet clear, due to the strong friction factor contrast between the two blocks, which complicates determination of  $D_0$ <sup>13</sup>). This difference has been attributed to the ability of unentangled (Rouse) chains to move freely along the interfaces ( $D_{\text{par}} \approx D_0$ ) whereas entangled chains cannot ( $D_{\text{par}} < D_0$ ).<sup>15,16</sup> This conjecture is supported by direct measurements of  $D_{\text{par}}$  and  $D_{\text{perp}}$  in macroscopically oriented PEP-PEE samples, where it was found that  $D_{\text{par}}/D_0$  decreases exponentially with  $\chi N$ , indicating an activated process, and that near the ODT  $D_{\text{perp}}$  was not much less than  $D_{\text{par}}$ .<sup>15,17</sup> Furthermore, it has recently been reported that  $D_{\text{par}}/D_{\text{perp}} \approx 40$  in an unentangled PS-PI diblock at a similar degree of segregation,<sup>18</sup> which is also consistent with this picture. The smooth variation of  $D(T)$  through the ODT for PEP-PEE indicates suppression of diffusion even in the disordered state above the ODT; this slowing down can extend at least 100 °C above the ODT.<sup>10</sup> In effect, entanglements and segregation combine to pin the copolymer to the interface, an effect that extends into the fluctuation regime. The PEP-PEE results have been described quantitatively by polymer mode-coupling theory (PMC),<sup>6,19</sup> which, being a liquid-state theory, does not invoke specific resolution of  $D_{\text{par}}$  and  $D_{\text{perp}}$ .

Homopolymer tracer diffusion in copolymer matrices has been considered by several groups. For example, Baba *et al.* studied low molecular weight poly(dimethylsiloxane) (PDMS) homopolymer diffusion in a microphase-separated PS-PDMS diblock copolymer plasticized by benzene, using pulsed-field-gradient NMR.<sup>20</sup> Diffusion in the copolymer was significantly slower than self-diffusion, by a factor of 6 or more. Interestingly, this suppression increased with decreasing molecular weight. They attributed this to the spatial distribution of the tracer in the microdomains: short tracers may penetrate deeper into the brush, thereby “feeling” the effect of the interface more than larger tracers. Green and co-workers studied the diffusion of PS and poly(methyl methacrylate) (PMMA) homopolymers in lamellar PS-PMMA diblocks, via forward recoil spectrometry.<sup>21,22</sup> They

observed an order-of-magnitude decrease in the tracer diffusivity relative to self-diffusion, an effect attributed to a combination of lamellar domain orientation and tortuosity. In apparent contrast to Baba *et al.* this suppression did not depend greatly on tracer molecular weight.

Recent theories have addressed the effect of ordering and composition fluctuations on tracer diffusion in unentangled and entangled melts. Fredrickson and Milner considered the diffusion of an unentangled tracer molecule in weakly ordered lamellae, where a permanent (time-averaged) composition pattern exists.<sup>23</sup> They modeled the effect of the composition pattern using a Rouse–Langevin equation modified by the addition of a spatially periodic chemical potential field. This potential field can exert a net force on the tracer molecules, thereby reducing  $D_{\text{perp}}$ . Barrat and Fredrickson extended the above approach to symmetric copolymers diffusing in a macroscopically ordered lamellar microstructure, using perturbation theory and numerical simulation.<sup>24</sup> They predicted a modest (ca. 40%) reduction in mobility in the vicinity of the ODT. Recently, Leibig and Fredrickson took a perturbation approach to both homopolymer and copolymer tracers above the ODT.<sup>25</sup> In place of the static sinusoidal potential used previously, they employed a dynamic potential proportional to the local deviation from the average compositional field in the disordered state. For unentangled chains, with blocks of similar stiffness and monomeric mobility, the theoretical results for diffusion suppression in the fluctuation regime can be summarized as follows: (i) the diffusion suppression is stronger for homopolymer tracers than for symmetric copolymer tracers; (ii) for homopolymer tracers, the shorter the tracer relative to the matrix, the greater the diffusion suppression it would experience; (iii) for copolymer tracers, the diffusion suppression is maximum for tracers very close to the matrix size. These results can be qualitatively understood as follows. An *A* homopolymer pays a greater enthalpic penalty to traverse a *B*-rich region than a copolymer of equal molecular weight. The longer the homopolymer, the more it “samples” the macroscopic average composition, and thus the less it is affected by fluctuations. For a copolymer tracer, long chains are unaffected for the same reason as with homopolymers, whereas for very short copolymers the local composition does not vary sufficiently rapidly in space for the tracer to notice any potential gradient; consequently, there is a maximum suppression at intermediate lengths. For copolymer tracers, qualitative agreement was found<sup>25</sup> with the experimental studies in nearly symmetric PEP-PEE materials,<sup>10</sup> even though the latter are well-entangled.

Schweizer and co-workers have extended the PMC theory to tracer diffusion in entangled symmetric diblock copolymer matrices.<sup>6,19,26</sup> They describe concentration fluctuations through an effective friction arising from the time correlations between the forces exerted by the matrix on two different segments of a tracer chain. The predictions of this theory can be summarized as follows: (i) fluctuations retard the diffusion of both block copolymer and homopolymer tracers; (ii) the diffusion suppression is stronger for homopolymer tracers than for block copolymer tracers; (iii) the longer the tracer, the stronger the diffusion suppression.

TABLE I. Polymer characteristics.

Polymer	$M$ (g/mol)	wt % PEP	$T_{\text{ODT}}$ (°C)
PEP-23	23 000	100	
PEP-50	50 000	100	
PEP-PEE-1	31 500	53	ca. -41
PEP-PEE-2	50 100	56	96
PEP-PEE-3	81 200	53	291

Qualitatively, these effects are all attributable to the clustering of like monomers, which retards the long-time relaxation of each chain. These predictions agree very well with the diffusion of PEP-PEE tracers, both above and below the ODT, as noted by the authors.<sup>19</sup>

The theories of Leibig and Fredrickson<sup>25</sup> and Tang and Schweizer<sup>19</sup> predict that concentration fluctuations in a symmetric copolymer will retard diffusion of homopolymer tracers more than copolymers tracers, but differ in their predictions regarding the effect of molecular weight. For homopolymer tracers, the PMC theory predicts a stronger effect for longer tracers, whereas the perturbation theory predicts stronger effects for shorter tracers. For copolymer tracers, the PMC theory predicts stronger effects for longer tracers, whereas the perturbation theory predicts an optimum molecular weight relative to the matrix, near to the case of self-diffusion, where the diffusion suppression is maximized. These differences arise from a combination of factors, particularly the consideration or omission of entanglement effects. However, under certain assumptions the PMC approach can reproduce the perturbation calculation.<sup>26</sup>

In this paper, we address the effect of fluctuations and ordering on both homopolymer and block copolymer tracers in a symmetric diblock copolymer matrix, using forced Rayleigh scattering (FRS). The measurements have been performed in two matrix copolymers with nearly identical composition: one where composition fluctuations are present over a wide temperature range, and the other where fluctuations are virtually absent over the entire temperature range. Thus the effect of fluctuations can be isolated, and the results can be compared with the predictions of the two theories.

## EXPERIMENT

### Samples

The relevant characteristics of two PEP homopolymers (PEP-23 and PEP-50), and two PEP-PEE block copolymers (PEP-PEE-1 and PEP-PEE-2) used in this study are listed in Table I. These polymers were synthesized by Bates and co-workers via catalytic hydrogenation of 1,4-polyisoprene and 1,4-polyisoprene-*b*-1,2 polybutadiene precursors.<sup>27</sup> The hydrogenation proceeds to an extent greater than 99%. However, the small residual unsaturation is sufficient to functionalize the polymers and subsequently attach a photochromic dye, as previously described.<sup>10</sup> The photochromic dye used in this study was 4'-(*N,N*-dimethylamino)-2-nitrostilbene-4-carboxylic acid (ONS). The labeling procedure typically results in 1 to 4 dye labels per tracer chain, and it

has been demonstrated that the labeling reaction does not affect the molecular weight distribution of the polymer.

The sample cells for diffusion measurements were prepared as follows. Approximately 5% by weight of the labeled tracer and 95% by weight of the unlabeled matrix polymer were codissolved in *n*-pentane, filtered through an 0.45  $\mu\text{m}$  filter, and precipitated in methanol. The polymer was dried under vacuum for several days. The dried sample was then placed between two quartz discs separated by an aluminum spacer ring. The aluminum spacers were glued to the discs using a high temperature adhesive. The sample cells were 10 mm in diameter and 1 mm thick. The samples were annealed above the ODT of the sample, under vacuum. FRS measurements were conducted on quenched samples; no attempt was made to induce macroscopic orientation of the lamellae.

### Diffusion measurements

The tracer diffusion coefficients were measured using forced Rayleigh scattering, as previously described.<sup>10,28</sup> A transient grating was created in the sample by exposure to crossed beams from an Argon ion laser operating at 488 nm (Lexel). The dye molecules present in the bright regions of the interference pattern photoisomerize, thereby creating a volume grating. The erasure of the grating due to mass diffusion was monitored by following the diffracted intensity, using one of the incident beams attenuated by a factor of  $10^4$ . The grating period,  $d$ , was typically 1–5  $\mu\text{m}$ , and was varied by changing the crossing angle of the incident beams. The measurements were begun at the lowest temperature (usually 40 °C) and the sample was subsequently heated to higher temperatures. At the lowest temperature, the sample was equilibrated for at least 24 h. For higher temperatures, the equilibration times were at least one hour. When changing the grating spacing or the temperature, the sample was moved with respect to the beam, so that different regions of the sample cell were accessed.

In all cases described in this paper the diffracted intensity from the transient grating was reasonably well-described by a single exponential decay in time

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

where  $A$  denotes the amplitude,  $\tau$  the decay time,  $B$  the coherent background and  $C$  the incoherent background. The measurements were repeated at several grating spacings. The linearity of the inverse decay time ( $1/\tau$ ) versus inverse square of grating spacing ( $1/d^2$ ) confirms the diffusive origins of the signal decay. The diffusion coefficient was calculated from the slope, i.e.,

$$\frac{1}{\tau} = \frac{4\pi^2 D}{d^2} + \frac{1}{\tau_{\text{dye}}}, \quad (2)$$

where  $\tau_{\text{dye}}$  is the time constant for the thermal reversion of the dye; for ONS the photoreaction is essentially irreversible ( $1/\tau_{\text{dye}} = 0$ ). This is confirmed by the intercept of the  $1/\tau$  versus  $1/d^2$  plot, which is zero, within the uncertainty, in all our experiments. Previous reports have provided more details on the FRS protocol and signal analysis.<sup>10,28</sup>

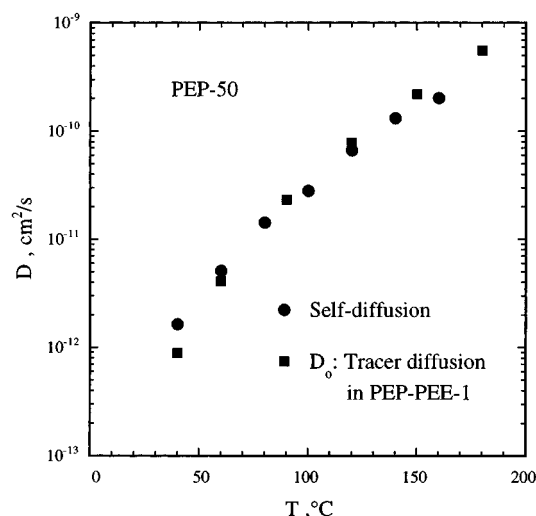


FIG. 1. Comparison of the self-diffusion of PEP-50 with its diffusion coefficient ( $D_0$ ) in the disordered PEP-PEE-1 matrix.

The FRS decays were consistently close to single-exponential functions even in the tracer diffusion case. It should be emphasized that diffusion on micron lengthscales in ordered block copolymers need not produce single exponential decays.<sup>12</sup> The results here imply either (i) a weak anisotropy of motion, such that  $D_{\text{perp}}$  is not greatly different from  $D_{\text{par}}$ , or (ii) a lamellar orientational correlation length, or “grain size”, significantly less than the grating spacing, such that each chain averages the two mobilities during a measurement. Our previous results<sup>10,11,13,15,16,29</sup> suggest that both factors could be operative simultaneously in the measurements reported here, but (ii) is sufficient to account for the results. It is difficult to assess grain size directly in PEP-PEE, as there is insufficient contrast for TEM, for example. However, the same sample preparation protocol has been shown in PS-PI to produce unoriented, quenched samples with grain sizes shorter than the grating period.<sup>13</sup>

## RESULTS AND DISCUSSION

The self-diffusion of PEP-50 was measured from 40 to 160 °C (Fig. 1). The entanglement molecular weight ( $M_e$ ) of PEP is approximately 1500 g/mol, and therefore PEP-50 is highly entangled and should be expected to follow reptation dynamics. Consequently, we can use the reptation scaling ( $D \sim M^{-2}$ ) to estimate the self-diffusion coefficient for the PEP-23 homopolymer from these data. The temperature dependence of  $D$  also provides information about the temperature dependence of the monomeric friction coefficient ( $\zeta_{\text{PEP}}$ ). We are unaware of previous measurements of PEP self-diffusion for comparison, except for a single measurement at 21 °C reported by Shull *et al.*<sup>14</sup> Using a WLF fit of our data with the parameters previously established for PEP,<sup>30</sup> we extrapolated these data to 21 °C. The result is roughly a factor of 2 higher than that of Shull *et al.*, which is probably within the combined uncertainties of the two techniques and the extrapolation.

In order to consider the effect of fluctuations, we first need to determine the “bare” diffusion coefficient  $D_0$ , i.e.,

the diffusion coefficient that one would observe in a hypothetical disordered matrix polymer with the same molecular weight, composition and temperature, but where fluctuations or microstructure would be absent. To this end, we examined  $D$  for the homopolymer tracers in the PEP-PEE-1 matrix, which has an ODT of  $-41$  °C, and is thus well into the disordered state for the temperatures of interest. (This also corresponds to  $D_0$  in the PEP-PEE-2 matrix, assuming negligible “constraint release” effects, which is reasonable considering the relative molecular weights of the tracers and the matrix used in this study.) To obtain  $D_0$  for copolymer tracers such as PEP-PEE-2 or PEP-PEE-3, Dalvi used the self-diffusion of the PEP-PEE-1 tracer and the reptation scaling, as described previously.<sup>10</sup> Over a wide range of temperature (50 to 160 °C),  $D$  of PEP-50 in PEP-PEE-1 is very similar to the self-diffusion coefficient (see Fig. 1). This suggests that, at least over this temperature range, the PEP-50 molecules do not experience a very different effective monomeric friction in the copolymer than in a PEP melt. This is consistent with the observations of Shull *et al.* for the same system.<sup>14</sup>

The diffusion of PEP-23 and PEP-50 in the PEP-PEE-2 matrix reveals the behavior in both the ordered state and the fluctuating, disordered state, as this matrix undergoes the ODT at 96 °C. Even at the lowest temperature used in this study, the matrix was relatively weakly segregated [ $\chi N/(\chi N)_{\text{ODT}} < 1.1$ ]. In the ordered state, the matrix was in a quenched lamellar morphology, and no attempt was made to induce macroscopic orientation. Coupled with the fact that the samples were 1 mm thick, this suggests that the measured  $D$  represents an isotropic average<sup>31</sup>

$$D = (D_{\text{perp}} + 2D_{\text{par}})/3. \quad (3)$$

The PEP-PEE-2 matrix does retard the diffusion of PEP-23 and PEP-50 compared to self-diffusion, as shown in Figs. 2(a) and 2(b). The slowing down is slightly more pronounced at lower temperatures (an average of approximately 40% for both tracers) than at high temperatures (an average of approximately 20% for both tracers). Interestingly, the retardation does not show an appreciable molecular weight dependence, as will be discussed subsequently.

The diffusion coefficients of PEP-23 and PEP-50 in PEP-PEE-2 are smaller both above and below the ODT, compared to  $D_0$ . The ratio  $D/D_0$ , shown in Fig. 3(a), represents the diffusion suppression due to composition fluctuations both above and below ODT. The diffusion suppression is thus about  $35\% \pm 15\%$  above the ODT, and is slightly smaller (about  $25\% \pm 15\%$ ) below the ODT; the diffusion suppression is not a strong function of either temperature or tracer molecular weight.

For the copolymer tracers (PEP-PEE-1, -2, and -3) in PEP-PEE-2 reported previously,<sup>10</sup> the diffusion suppression is stronger than that for the homopolymer tracers, and is also a much stronger function of temperature and molecular weight [Fig. 3(b)]. The ratio of the tracer molecular weight to the matrix molecular weight varies from 0.63 for PEP-PEE-1 to 1.62 for PEP-PEE-3. At the ODT, the tracer diffusion is reduced by approximately 35%, 65% and 85% for PEP-PEE-1, PEP-PEE-2, and PEP-PEE-3, respectively. In contrast with the homopolymer tracers, therefore, the diffu-

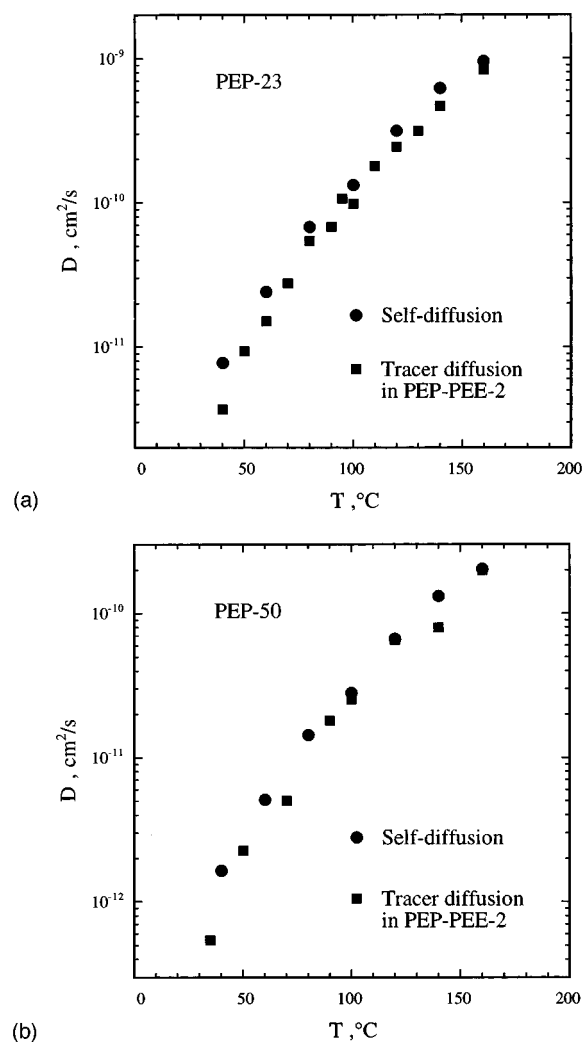


FIG. 2. Molecular weight dependence of homopolymer tracer diffusion in the nearly symmetric PEP-PEE-2 matrix. (a) Temperature dependence of  $D$  for PEP-23 (the self-diffusion coefficient is shown for comparison); (b) Temperature dependence of  $D$  for PEP-50 tracer (the self-diffusion coefficient is shown for comparison).

sion suppression increases appreciably, both with decreasing temperature and with increasing molecular weight.

The results can be compared qualitatively with the predictions of the theories of Leibig and Fredrickson<sup>25</sup> (perturbation theory) and Tang and Schweizer<sup>19</sup> (PMC theory). The experiments indicate that fluctuations suppress diffusion of both homopolymer and copolymer tracers, in agreement with both theoretical approaches. However, the suppression appears to be *stronger* for block copolymer tracers than for homopolymer tracers, which is in contrast with both theories. For the two homopolymer tracers used in this study, tracer molecular weight does not affect the diffusion suppression measurably. For the copolymer tracers, diffusion suppression appears to be stronger for longer tracers. This is consistent with the PMC theory, but not consistent with the perturbation theory.

One possible explanation for the different effects of composition fluctuations and ordering on the homopolymer and copolymer tracer diffusion relies on the different average tracer chain locations in the matrix. The measured  $D$  is a

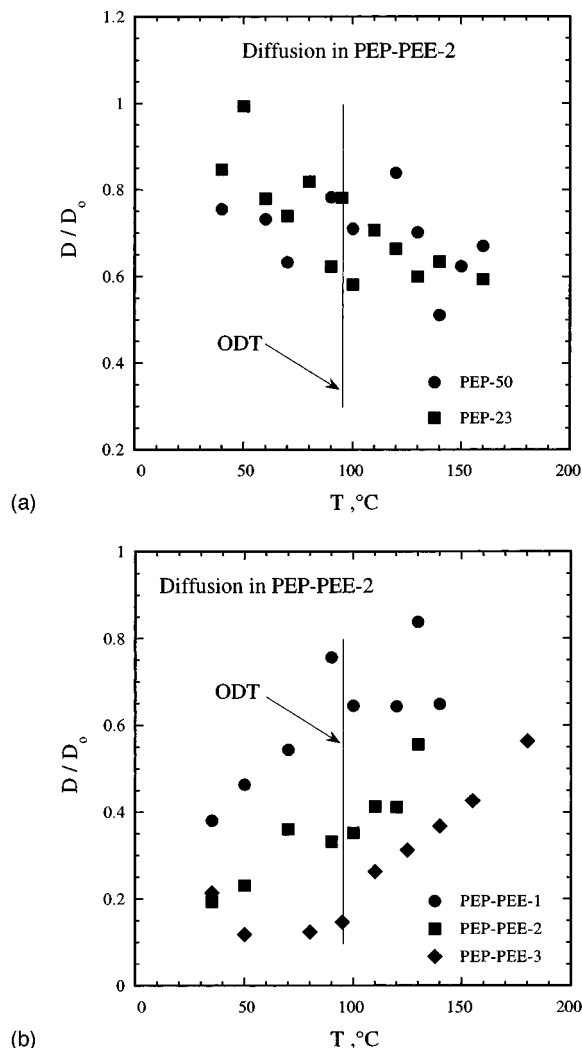


FIG. 3. Diffusion suppression for homopolymer and copolymer tracers due to composition fluctuations in the PEP-PEE-2 matrix: (a) Molecular weight and temperature dependence of  $D/D_0$  for homopolymer tracers. (b) Molecular weight and temperature dependence of  $D/D_0$  for PEP-PEE-1, PEP-PEE-2 and PEP-PEE-3 in PEP-PEE-2.

macroscopic average of diffusion in all directions, as in Eq. (3). Free energy constraints tend to place a copolymer tracer near the interface, with its average end-to-end vector oriented normal to the interface. In order to reptate a copolymer has to drag the  $A$  block into the  $B$ -rich microdomain, thereby incurring an enthalpic penalty even for diffusion along the lamellae. The resulting retardation in  $D_{\text{par}}$  has been quantified previously, and the postulated mechanism dubbed “activated reptation”; in particular,  $D_{\text{par}}/D_0$  decreases exponentially with  $\chi N$ .<sup>15</sup> Consequently, a copolymer tracer is retarded both by fluctuations and by microphase separation, in a manner that increases with increasing chain length ( $N$ ) and decreasing temperature ( $\chi$ ).

In contrast, an  $A$  homopolymer tracer tends to be confined in the  $A$ -rich lamellae, but is not pinned to the interface in the same manner as a copolymer. Consequently, it can move relatively unimpeded within its microdomain. In a quenched lamellar sample, the three-dimensional average diffusion coefficient need not be substantially lower than the

self-diffusion coefficient, so long as the lamellar domains percolate through the sample (over distances comparable to the grating spacing). Using Eq. (3), this would suggest that the measured  $D$  should be  $\approx (2/3)D_{\text{par}}$ , which is close to the experimental values [see Fig. 3(a)]. Preliminary FRS results on the diffusion of PEP-50 in a macroscopically oriented PEP-PEE-4 matrix support this picture: they indicate that  $D_{\text{par}}$  for the homopolymer is comparable to the self-diffusion coefficient, whereas diffusion perpendicular to the lamellae is significantly slower. Interestingly, above the ODT, the homopolymer diffusion appears to be more suppressed than in the ordered state. This effect is quantitatively small, and given the experimental uncertainty should be interpreted cautiously. One possible factor is a slight decrease in the monomeric friction factor in the ordered state, when the homopolymer experiences a more PEP-rich environment (PEP has a lower glass transition temperature than PEE).

Green and coworkers observed a larger suppression of homopolymer diffusion into quenched lamellar phases, by an order of magnitude or more.<sup>21</sup> Their samples were more strongly segregated, and consequently, the tracer mobility will be more sensitive to “defects” in the lamellar matrix, in that the barrier to traverse such defects could be substantial. Indeed, they found that the measured mobilities were sensitive to details of the sample preparation protocol, which is consistent with this interpretation.

In summary, we propose that the homopolymer chain is able to reptate across several grains, primarily by diffusing along the lamellae rich in the chemically similar block, without being significantly affected by the interface. In contrast, a copolymer tracer is pinned to the interface, and thus shows a strong dependence on the formation and growth of microphase segregation. Future experiments on homopolymer tracers located in the minor phase in cylindrical and spherical morphologies could provide more insight into this hypothesis.

## CONCLUSIONS

The effect of composition fluctuations and lamellar ordering of a block copolymer matrix on homopolymer and block copolymer tracer diffusion has been investigated using FRS. The results indicate that:

- (1) Composition fluctuations suppress homopolymer and copolymer tracer diffusion both above and below the ODT. This is consistent with recent theoretical predictions, based either on a mode-coupling approach or on perturbation theory.
- (2) Fluctuations suppress the diffusion of copolymer tracers much more than homopolymer tracers. This appears to be in contrast with the recent theoretical predictions, but may also reflect in part non-universal factors such as segmental friction and entanglement length asymmetry.
- (3) For homopolymer tracers, diffusion suppression due to fluctuations does not appear to be strong function of temperature or tracer molecular weight. For copolymer tracers, the diffusion suppression is a relatively strong function of temperature and tracer molecular weight.

- (4) We interpret the qualitative differences between the homopolymer and copolymer tracers as reflecting the pinning of the copolymer to the interface. A copolymer tracer tends to be located near the interface, thereby paying a strong enthalpic penalty for reptating in any direction, whereas a homopolymer tracer tends to be located in the lamellar domain rich in the chemically similar block, and is able to diffuse relatively freely along the lamellae.

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