

## Diffusion in Microstructured Block Copolymers: Chain Localization and Entanglements

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The diffusion ( $D_s$ ) of entangled and unentangled symmetric block copolymers is compared, above and below the ordering transition. The lamellar samples were not macroscopically oriented, and thus  $D_s$  reflects a combination of mobilities parallel and perpendicular to the lamellar planes. For unentangled (Rouse) chains,  $D_s$  is unaffected by the microstructure, whereas entangled (reptating) chains are retarded significantly; this difference reflects an interesting combination of thermodynamic and entanglement constraints. Furthermore, this retardation persists into the nominally disordered state.

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Block copolymers constitute an important class of self-assembling materials, with remarkably rich structural and dynamic behavior [1]. The thermodynamic repulsion between monomers of the constituent blocks induces a disorder-to-order transition (ODT) into one of several microstructures, depending on the chain length  $N$ , the monomer-monomer interaction parameter  $\chi$ , and the chain composition. The resulting free energy density varies spatially, which can lead to *localization* of individual chains in preferred regions of the microstructure. Furthermore, the lamellar and cylindrical (hexagonal) morphologies are inherently *anisotropic*, which can also exert an influence on properties such as the chain mobility. Whereas certain features of block copolymer morphologies resemble the liquid crystalline or microemulsion phases of small molecules, the polymeric nature of the constituents can also be expected to lead to unique properties, particularly in terms of dynamics. For example, homopolymers in concentrated solutions and melts exhibit the phenomenon of interchain *entanglement* when a critical chain length  $N_e$  is significantly exceeded; dynamic properties such as the shear viscosity and the diffusivity are qualitatively very different for  $N \gg N_e$  and  $N \leq N_e$ . In a block copolymer microstructure, therefore, it is interesting to explore the interplay between structural (i.e., thermodynamic) and entanglement effects on chain dynamics.

In this paper we compare the self-diffusion coefficients  $D_s$  of nearly symmetric diblock copolymers in both the ordered (lamellar) and the disordered states, and for both unentangled and entangled chains. The ordered samples are quenched, or "polycrystalline," in the sense that no effort is made to induce a preferred direction to the local lamellar normal; this morphology is analogous to that in conventional smectics. Thus, we are primarily concerned here with chain localization and its effect on diffusion in three dimensions, rather than with any anisotropy in mobility that may exist at the local level. A remarkable qualitative difference is seen between the behavior of unentangled and entangled block copolymers, even though the thermodynamic conditions (i.e., values of  $\chi N$ ) are comparable. Specifically, the presence of lamellar order leads to a substantial reduction in  $D_s$  only in the en-

tangled case. Furthermore, this retardation persists through the ODT and into the nominally disordered state.

Investigation of chain diffusion in block copolymer microstructures has only recently begun. Shull *et al.* used forward recoil spectrometry and deuterium labeling to follow  $D_s$  of a poly(ethylenepropylene)-poly(ethylethylene) (PEP-PEE) diblock copolymer, both above and below the ODT, and found that there was little or no evidence of the ODT in the temperature ( $T$ ) dependence of  $D_s$  [2]. Hashimoto and co-workers attempted to determine  $D_s$  for a polystyrene-polyisoprene diblock via forced Rayleigh scattering (FRS), but found very complicated experimental signals [3]. Nevertheless, they were also able to conclude that  $D_s$  showed little sensitivity to the ODT. We examined the same PEP-PEE sample as Shull *et al.* with FRS, and obtained results substantially equivalent to theirs [4]; this sample is also employed herein. In addition, we were able to resolve the diffusivities parallel and perpendicular to the lamellar grains,  $D_{\text{par}}$  and  $D_{\text{perp}}$ , by use of specimens which had shear-induced macroscopic order [4];  $2^\circ$  below  $T_{\text{ODT}}$  ( $96^\circ\text{C}$ ),  $D_{\text{par}} \approx D_{\text{perp}}$ , but as  $T$  decreased to  $25^\circ\text{C}$ ,  $D_{\text{perp}}/D_{\text{par}}$  decreased smoothly to about 0.3.

Block copolymer self-diffusion coefficients were determined by FRS, a well-established transient optical grating technique. Gratings were created in the sample by exposure to crossed beams from an  $\text{Ar}^+$  laser, with the grating "recorded" by photobleaching of an *o*-nitrostilbene dye [4'-(*N,N*-dimethylamino)-2-nitrostilbene-4-carboxylic acid]. The decay of the grating by mass diffusion was monitored by diffraction of a probe beam from the same laser (attenuated by a factor of  $10^4$ ). In all cases the signal was very well described by a single exponential decay, and the expected linear dependence of the decay time on the square of the grating spacing was confirmed at several temperatures for each sample. Decay time ranged from seconds to hours, grating spacings from ca. 0.6 to 3  $\mu\text{m}$ , and  $D_s$  varied between  $10^{-9}$  and  $10^{-15}$   $\text{cm}^2/\text{s}$ . Further details on the apparatus and the experimental protocol may be found elsewhere [4-6].

Two polymer systems and a total of four samples were examined. Two polystyrene (PS)-poly(2-vinylpyridine) (PVP) block copolymers were prepared by living anionic

polymerization, terminated with *p*-dichloroxylylene, and the dye attached to the pendant function group [5]. The weight-average molecular weights  $M$  were  $1.2 \times 10^4$  and  $2.5 \times 10^4$ , the polydispersities less than 1.1, and the compositions 50% PS by weight.  $M_e$  for PS is approximately  $1.7 \times 10^4$  [7], and is presumably similar for PVP. Thus, these systems are essentially unentangled; the onset of entanglement effects typically is not apparent until  $M \geq 2-3M_e$  [7]. Two PEP-PEE samples were randomly labeled through trace amounts ( $< 1\%$ ) of residual double bonds that survived the hydrogenation of the polyisoprene-polybutadiene precursors [4,6]. The weight-average molecular weights of the samples were  $3.15 \times 10^4$  and  $5.0 \times 10^4$ , the polydispersities less than 1.05, and the compositions 55% PEP by weight [8].  $M_e$  for PEP and PEE is  $1.5 \times 10^3$  and  $1.1 \times 10^4$ , respectively [9], and so both of these samples are well entangled. It should be noted that quantitative application to block copolymers of entanglement molecular weights determined for homopolymers is probably not appropriate. For example, one does not know the effect of having different degrees of entanglement for the two blocks, nor the entanglement spacing for an *A* block in a *B*-rich domain, nor whether the segregation and stretching of chains in the ordered state perturbs the entanglement density. However, for the purposes of this paper, the important distinction is qualitative: The PEP-PEE chains have many entanglements, and the PS-PVP chains at most one [10]. Similarly, any effects of temperature on the entanglement density are beyond the scope of this paper.

For the FRS measurements, labeled and unlabeled chains were mixed in the approximate proportion 1:20, with the labeled chains having, on average, less than 1 label per chain. Measurements on the PS-PVP samples were made from  $110^\circ\text{C}$  to  $200^\circ\text{C}$ , the lower limit being set by proximity to the glass transition (near  $95^\circ\text{C}$ ) and the upper limit by the stability of the dye. Measurements for PEP-PEE were extended down to room temperature. Temperatures were controlled to within  $\pm 0.2^\circ\text{C}$  throughout. Further details on the synthesis of the polymers and the dye and the characterization procedures may be found elsewhere [4-6].

On the basis of rheological [5] and electron microscopic [11] characterization, the  $1.2 \times 10^4$  PS-PVP sample is disordered throughout the range of measurement temperatures [11]. For example, the dynamic shear elastic modulus  $G'$  displayed the low frequency scaling,  $G' \sim \omega^2$ , characteristic of disordered liquids, and also obeyed time-temperature superposition. In contrast, the  $2.5 \times 10^4$  sample is in the ordered state throughout the measurement range: The elastic modulus showed the distinctive low frequency  $G' \sim \omega^{0.5}$  regime observed for several other lamellar block copolymer samples [8,12], time-temperature superposition failed, and the electron micrographs indicated a well-defined lamellar pattern. The order-disorder transition temperatures,  $T_{\text{ODT}}$ , can also be estimated via the Fredrickson-Helfand-Brazovskii-Leibler

expression for  $(\chi N)_{\text{ODT}}$  [13], using the expression for  $\chi(T)$  recently given by Dai and Kramer [14]. The resulting values are approximately  $100^\circ\text{C}$  and  $400^\circ\text{C}$ , respectively [15], which are consistent with the experimental observations. These estimates should not be taken too literally, however, as the theoretical expression is expected to be strictly valid only for larger values of  $N$  [13].

The  $T$  dependence of  $D_s$  for these two samples is shown in Fig. 1. The horizontal axis is  $T - T_g$ , to account for the slight ( $\approx 3^\circ\text{C}$ ) difference between the glass transition temperatures of the two samples; due to the proximity of the  $T_g$ 's of PS and PVP, only a single  $T_g$  was observed for the block copolymers [5]. The values of  $D_s$  for the lower  $M$  sample have been divided by 2.1, the ratio of the two molecular weights. As unentangled chains, the diffusivities would be expected to follow the Rouse scaling,  $D_s \sim M^{-1}$ , in the disordered state. The fact that these two sets reduce to a reasonable master curve is a clear indication that the lamellar order has no discernible effect on the measured chain diffusivity. Furthermore,  $D_s$  for each copolymer is numerically comparable to  $D_s$  for PS homopolymers of the same total  $M$  [5,16]. It is important to note that the higher  $M$  block copolymer is not macroscopically ordered, and that therefore the observed  $D_s$  represents some combination of the diffusivities parallel and perpendicular to the lamellar planes, as will be discussed subsequently. The smooth curve through the data represents a fit of the standard Williams-Landel-Ferry (WLF) temperature dependence [7] to the data for the lower  $M$  sample. The WLF function, which may be correlated empirically with the amount of available "free volume," generally describes the temperature dependence of any dynamic property in a homogeneous polymer melt, at least over the interval  $T_g \leq T \leq T_g + 100^\circ\text{C}$ , and provided the process of interest occurs over the length scale of a segment, or longer. It might be expected to fail in a

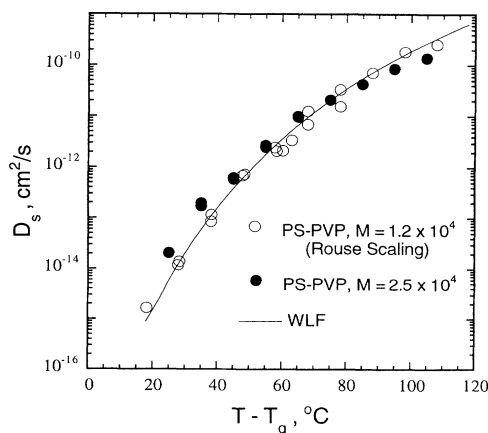


FIG. 1. Self-diffusion of symmetric PS-PVP diblock copolymers;  $D_s$  for the lower molecular weight sample, which is disordered at these temperatures, has been scaled down by a factor of 0.48, assuming Rouse dynamics.

block copolymer melt, however, if significant structural changes occur over narrow ranges of temperature, or in the strongly segregated state when the  $T_g$ 's for the two blocks are very different. However, as the  $T_g$ 's for the PS-PVP copolymers are only slightly different from those of the homopolymers, the success of the WLF fit in Fig. 1 does not imply that there is no segregation of PS and PVP. Finally, we note that at the lowest temperatures, the data for the higher  $M$  sample lie slightly above those for the lower  $M$  chain; no explanation for this observation, other than experimental uncertainty, is apparent.

The  $5.0 \times 10^4$  PEP-PEE sample exhibits an ODT at  $96 \pm 1^\circ\text{C}$  [8], and thus the measurements of  $D_s$  extend into both ordered and disordered states. The  $3.15 \times 10^4$  sample, on the other hand, is estimated to undergo an ODT at  $-72^\circ\text{C}$  [8]. The  $T$  dependence of  $D_s$  for these two samples is compared in Fig. 2. Here,  $D_s$  for the disordered sample has been scaled down by the square of the  $M$  ratio, assuming that these polymers would follow the reptation scaling,  $D_s \sim M^{-2}$ , characteristic of well-entangled chains in the disordered state. It is immediately clear that the ordered block copolymer has a much lower mobility than its disordered equivalent. The difference between the two data sets increases as  $T$  decreases, i.e., as the strength of the segregation between the two blocks in the microstructure increases. The smooth curves through the data represent the WLF functions determined from the  $T$  dependence of the rheological properties of the two samples. Remarkably, even above  $96^\circ\text{C}$ , where the larger  $M$  sample is disordered, the reduced data from the two samples do not superpose. Extrapolation of the WLF dependence suggests that the two curves might not converge until above  $200^\circ\text{C}$ , or more than  $100^\circ\text{C}$  above the ODT, although such an extrapolation should be viewed with some skepticism, owing to the fact that  $T \gg T_g$ .

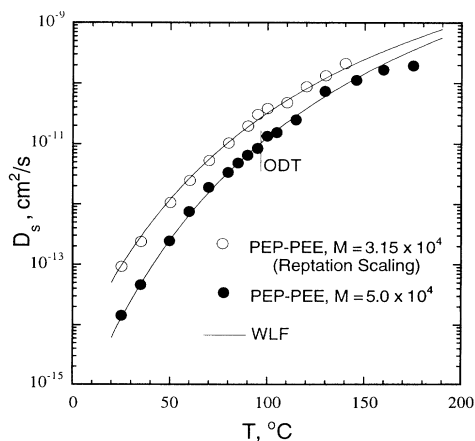


FIG. 2. Self-diffusion of symmetric PEP-PEE diblock copolymers;  $D_s$  for the lower molecular weight sample, which is disordered at these temperatures, has been scaled down by a factor of 0.40, assuming reptation dynamics.

To a first approximation, we can estimate

$$D_s \approx \frac{1}{3} D_{\text{perp}} + \frac{2}{3} D_{\text{par}}. \quad (1)$$

This equation certainly need not hold in a complicated heterogeneous structure, particularly if  $D_{\text{par}}$  and  $D_{\text{perp}}$  differ greatly, and/or the local lamellar orientation is not random over the measurement distance. Fredrickson has analyzed the problem of diffusion in quenched lamellar phases [17], and shown that Eq. (1) should be a good approximation (i.e., to within a few percent) for lamellar block copolymers near the ODT, where  $D_{\text{par}}$  and  $D_{\text{perp}}$  are within an order of magnitude of one another (as noted above,  $D_{\text{perp}}/D_{\text{par}}$  varies from 1 to about 0.3 over this  $T$  range for the higher  $M$  PEP-PEE sample [4]). For Rouse chain, the mobilities in the different directions are uncoupled, and the lamellar microstructure presents no thermodynamic barrier to  $D_{\text{par}}$ ; thus,  $D_{\text{par}} \approx D_0$  [18], where  $D_0$  is the self-diffusion coefficient of a hypothetical disordered but otherwise equivalent block copolymer (i.e., a block copolymer in which  $\chi$  is artificially set to 0). The measured  $D_s$  will thus lie between  $D_0$  and  $\frac{2}{3} D_0$ , depending on the value of  $D_{\text{perp}}$ . This explains the PS-PVP results in Fig. 1:  $D_s$  for the ordered sample should be essentially identical to  $D_0$  (estimated on the basis of the disordered sample), independent of the magnitude of  $D_{\text{perp}}$  (assuming  $0 \leq D_{\text{perp}} \leq D_{\text{par}}$ ). Given the experimental uncertainty, it is not possible to conclude anything quantitative about  $D_{\text{perp}}$ , but the single exponential nature of the FRS decays suggests that  $D_{\text{perp}}$  and  $D_{\text{par}}$  are not greatly different, as also found for PEP-PEE [4]. It is also not possible to quantify any localization of the chain junctions to the interfaces between the microdomains; this experiment does not discriminate sensitively between Rouse chains confined to two dimensions or free to move in all directions.

The situation for PEP-PEE is different. Here,  $D_s$  is significantly less than  $D_0$ , an effect directly attributable to entanglements. The physical picture is illustrated in Fig. 3. On average, the end-to-end vector for each copolymer lies normal to the lamellar planes, and the junction between the two blocks resides near the interface between microdomains. In order to diffuse by reptation, the copolymer must drag one block into the microdomain rich in the other component; indeed, to escape the "tube" defined by the entanglements at time  $t=0$ , one chain end must reach the interface at the point originally occupied by the junction between the two blocks. There is thus a thermodynamic penalty for motion in any direction; both  $D_{\text{perp}}$  and  $D_{\text{par}}$  are suppressed by the microstructure, and the chain experiences substantial localization. Consequently,  $D_s < D_0$ , and by a factor that increases as  $T$  is decreased. Note that this mechanism does not require that  $D_{\text{perp}}$  and  $D_{\text{par}}$  be reduced by the same amount. For example, a chain could reptate and still remain primarily close to the interface [19]. Near the ODT, where the composition profiles are assumed to be sinusoidal, the interfacial zone occupies a substantial part of the material,

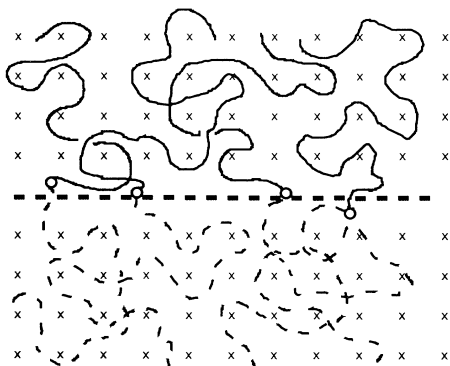


FIG. 3. Schematic illustration of an entangled block copolymer at the interface between microdomains. The dashed line represents the interface, which in reality is nanometers wide; the field of  $\times$ 's represent the entanglement constraints, and the circles the junction points between the two blocks. In order to reptate through the entanglements, an individual chain must drag one block across the interface, and thus into a thermodynamically less favorable location.

and even far into the ordered state, the interfacial breadth ( $\sim 1/\chi^{0.5}$ ) is typically of order 3–4 nm [1]. Alternatively, far into the ordered state, diffusion in the lamellar plane could proceed by an arm retraction process, analogous to that seen in entangled star-branched polymers, while  $D_{\text{perp}}$  would effectively vanish.

An additional interesting feature of the results in Fig. 2 is that the relation  $D_s < D_0$  persists well above the ODT, i.e., in the disordered state. Rheological measurements on these, and similar, samples have revealed substantial concentration fluctuations above the ODT [8,12]. Such fluctuations can be viewed as regions of transient local lamellar order, which could act to suppress diffusion in much the same manner as below the ODT. The extrapolation of the WLF temperature dependence indicates that the fluctuation regime may be even wider than that evident in the rheological properties. This observation also explains the previously reported apparent insensitivity of diffusion measurement to the ODT [2–4].

In summary, we have determined the  $T$  dependence of  $D_s$  for symmetric block copolymers in the regimes just above and just below the ordering transition. In terms of the quantity  $(\chi N)/(\chi N)_{\text{ODT}}$ , the ranges covered are estimated to be 0.77 to 0.98 and 1.7 to 2.2 for PS-PVP, and 0.82 to 1.2 and 0.50 to 0.68 for PEP-PEE. For those samples in the ordered state, no attempt was made to orient the lamellae, and the measured diffusivity corresponds to a macroscopic, isotropic average. For unentangled chains, the lamellar order has no appreciable effect on  $D_s$ . This reflects the ability of Rouse chains to move freely in the lamellar planes, and is not particularly sensitive to any suppression of the mobility perpendicular to the lamellae. Conversely, for entangled chains,  $D_s$  is sup-

pressed in the ordered state, relative to a disordered but otherwise equivalent chain. This suppression increases monotonically as temperature is decreased. This phenomenon is directly attributable to chain localization, resulting from a combination of thermodynamic and entanglement constraints. The microstructure favors chain conformations in which the junction point resides in the interfacial regime, while the entanglements inhibit lateral motion. Thus, a reptating block copolymer experiences a thermodynamic barrier to motion in any direction in a lamellar structure. Finally, localization was apparent even in the disordered state, just above the ODT. Thus, the composition fluctuations evident in rheological measurements are also sufficient to retard the overall mobility of the individual chains.

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- [1] See, for example, F. S. Bates and G. H. Fredrickson, *Annu. Rev. Phys. Chem.* **41**, 525 (1990).
- [2] K. R. Shull, E. J. Kramer, F. S. Bates, and J. H. Rosedale, *Macromolecules* **24**, 1383 (1991).
- [3] D. Ehlich, M. Takenaka, and T. Hashimoto, *Macromolecules* **26**, 492 (1993).
- [4] M. C. Dalvi and T. P. Lodge, *Macromolecules* **26**, 859 (1993).
- [5] C. E. Eastman, Ph.D. thesis, University of Minnesota, 1993; C. E. Eastman and T. P. Lodge (to be published).
- [6] M. C. Dalvi and T. P. Lodge (to be published).
- [7] J. D. Ferry, *Viscoelastic Properties of Polymers* (Wiley, New York, 1980), 3rd ed.
- [8] J. H. Rosedale and F. S. Bates, *Macromolecules* **23**, 2329 (1990).
- [9] L. J. Fetters (private communication).
- [10] If one computes the number of entanglements per chain by dividing each block  $M$  by the corresponding  $M_e$ , and summing, one arrives at an estimate of 8–12 entanglements per PEE-PEE chain; however, this procedure would be *ad hoc*, for the reasons identified in the text.
- [11] G. H. Kim and E. L. Thomas (unpublished).
- [12] F. S. Bates, J. H. Rosedale, and G. H. Fredrickson, *J. Chem. Phys.* **92**, 6255 (1990).
- [13] G. H. Fredrickson and E. Helfand, *J. Chem. Phys.* **87**, 697 (1987).
- [14] K. H. Dai and E. J. Kramer (to be published).
- [15] In order to apply the fluctuation theory in Ref. [13], it is necessary to take into account the monomer and segment volumes, as discussed in detail in Ref. [12].
- [16] M. Tirrell, *Rubber Chem. Tech., Rubber Rev.* **57**, 523 (1984).
- [17] G. H. Fredrickson, *Acta Polym.* **44**, 78 (1993).
- [18] J.-L. Barrat and G. H. Fredrickson, *Macromolecules* **24**, 6378 (1991); G. H. Fredrickson and S. T. Milner, *Mater. Res. Soc. Symp. Proc.* **177**, 169 (1990).
- [19] S. T. Milner and G. H. Fredrickson (unpublished).