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Self-Diffusion of Symmetric Diblock Copolymer Melts near the Ordering Transition

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ABSTRACT: Self-diffusion in thin solution-cast films of nearly symmetric block copolymer was probed by forward recoil spectrometry, both above and below the bulk order–disorder temperature. Diffusion in the as-prepared films is characteristic of diffusion in an isotropic medium. The diffusion coefficient is lower than the diffusion coefficient for a homogeneous melt but shows no discontinuity at the ordering temperature. The mobility of a certain fraction of the copolymer chains is reduced dramatically by annealing the as-prepared films before allowing the diffusion to take place. This slowing down of the diffusion process is assumed to be associated with the preferential orientation of lamellar domains parallel to the film surface. Diffusion in the direction perpendicular to the lamellae is much slower than diffusion parallel to the lamellae, and the diffusion process in the preannealed samples can only be modeled by using two very different values for the diffusion coefficient.

Introduction

Polymer blends are characterized by a low entropy of mixing and undergo phase separation when the enthalpic interactions between the components are even mildly unfavorable. When the polymeric components are covalently linked to each other, as they are in block copolymers, macroscopic phase separation can no longer occur. In such systems microphase-separated (ordered) states are obtained, with the detailed phase structure dependent on the strength of the interaction between the different polymer repeat units and on the molecular weight of each block. Increasing temperature, or decreasing molecular weight, increases the entropic contributions to the overall block copolymer free energy, ultimately leading to a spatially homogeneous, disordered state. These two regimes are separated by a weak, first-order phase transition known as the order–disorder transition (ODT).

A mean-field treatment that neglects concentration fluctuations has traditionally been used to calculate the equilibrium properties of block copolymer melts.[1] However, recent theoretical[2,3] and experimental[4–6] work has shown that concentration fluctuations are an important factor in determining the thermodynamic and dynamic properties of block copolymers in the vicinity of the ODT. Above the ODT, such concentration fluctuations spatially average to zero over long times. Dynamic mechanical measurements, conducted in the appropriate frequency regime, are sensitive to these concentration fluctuations and indicate that the fluctuations persist to temperatures as much as 50 °C above the transition temperature.[4] Dynamic mechanical measurements at very low frequencies are sensitive primarily to concentration fluctuations that are frozen into a given configuration at the ODT, and these measurements can be used to very accurately determine the order–disorder transition.[4]

Information concerning the dynamic properties of polymer melts can also be obtained from measurements of the self-diffusion coefficient. Analysis of the results is straightforward for well-entangled homogeneous systems where concentration fluctuations are not important.[7] Nonuniformities in the local composition are expected to significantly affect the self-diffusion coefficient for diblock copolymer systems, especially in the ordered phase. The situation is further complicated when the variations in the local composition are not isotropic, in which case the diffusion coefficient itself will no longer be isotropic. We have measured the self-diffusion of a nearly symmetric diblock copolymer of poly(ethylenepropylene)–poly(ethylethylene) (PEP–PEE) both above and below the ODT in an effort to analyze the effects of a nonuniform composition on the mobility of individual block copolymer chains.

Experimental Section

The synthesis and characterization of PEP–PEE block copolymers have been described elsewhere.[8] The PEP block contains 95% alternating ethylene and propylene units with 5% randomly distributed polyisobutylene units. The PEE block is >98% poly(ethylethylene). The overall number-average molecular weights, M_n, of PEP–PEE-1 and PEP–PEE-2 are 31 500 and 50 100 with $M_w/M_n = 1.05$ and 1.07, respectively. Partially deuterated samples were prepared by substituting deuterium for hydrogen in the catalytic saturation of the polydiene precursors. The ODT for PEP–PEE-2 was determined[4] to be 96 °C. The WLF parameters that characterize the temperature dependence of the dynamic shear moduli have also been measured for these polymers.[4]

Diffusion couples consisting of 1000-Å layers of a partially deuterated PEP–PEE copolymer on thick (>2-μm) layers of the corresponding hydrogenated PEP–PEE copolymer were prepared by first spin casting the hydrogenated layers directly onto polished silicon substrates from toluene solutions. The deuterated layers were spun cast from toluene solution onto freshly cleaved NaCl crystals, floated onto a water bath, and then picked up on top of the hydrogenated layers. Some of the H/D pairs were annealed at 70 °C prior to their combination to form diffusion couples, in order to analyze the effects of this preannealing treatment on the diffusion. Deuterium volume fraction vs depth profiles in annealed diffusion couples were determined by forward recoil spectrometry (FRES) as described elsewhere.[9]

Annealing times for samples where the diffusion coefficient was less than 10^{-12} cm/s were at least 10 min. These anneals

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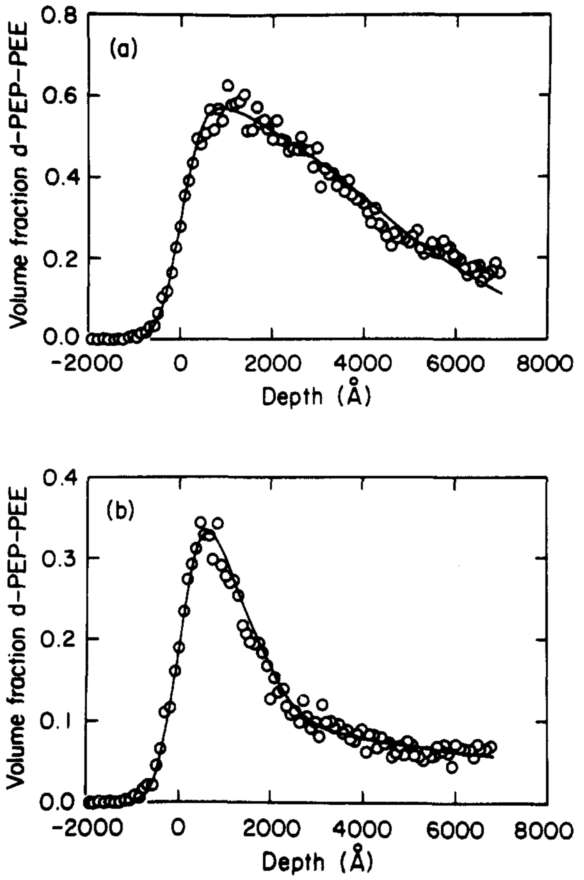

Figure 1. Volume fraction deuterated PEP–PEE-2 as a function of depth in thin film diffusion couples after two different annealing treatments: (a) 14 min at 68 °C with no preannealing treatment. The solid line is a fit to eq 1 with $D = 7 \times 10^{-13}$ cm²/s. (b) 44 min at 71 °C after a 4-day preannealing treatment at 70 °C. The solid line is a fit to eq 2 with $\phi_1 = 0.64$, $\phi_2 = 0.36$, $D_1 = 9 \times 10^{-13}$ cm²/s, and $D_2 = 1.5 \times 10^{-14}$ cm²/s.

were carried out in air for temperatures of 35 °C or less and in a vacuum oven for temperatures greater than 35 °C. In order to avoid errors associated with the attainment of an equilibrium temperature, shorter anneals were carried out in a water bath for temperatures to 100 °C and in a bath of silicone oil for temperatures greater than 100 °C. Silicone oil was removed from the sample surfaces by rinsing in ethyl acetate. Different annealing methods for the same sample and annealing temperature give the same result, indicating that these results are not affected by the method of anneal.

Results

A concentration vs depth profile for the deuterated species from a PEP–PEE-2 sample after a 14-min anneal at 68 °C is shown in Figure 1a. The hydrogenated and deuterated layers were not preannealed prior to the diffusion. The solid line in Figure 1a represents the profile obtained from the solution to the diffusion equation for diffusion from a deuterated film of thickness h, into a semiinfinite hydrogenated matrix:

$$\phi(x) = 0.5\left\{\mathrm{erf}\left[\frac{h-x}{(4Dt)^{0.5}}\right] + \mathrm{erf}\left[\frac{h+x}{(4Dt)^{0.5}}\right]\right\} \qquad (1)$$

Here t is the annealing time and D is the diffusion coefficient, equal to 7×10^{-13} cm²/s in this case. The profile calculated from eq 1 has been convolved with a Gaussian with a full-width at half-maximum of 800 Å in order to simulate the instrumental broadening associated with FRES. The good agreement between the measured concentration profile and the prediction of eq 1 indicates that the diffusion process occurring in this particular sample can be appropriately described by a single diffusion coefficient. This situation holds for the PEP–PEE-2 copolymer at all temperatures for which the self-diffusion coefficient was measured, i.e., 22–115 °C, provided that the hydrogenated and deuterated layers were not preannealed prior to the diffusion step. The temperature dependence of the self-diffusion coefficient for nonpreannealed PEP–PEE-2 is shown in Figure 2. The bulk ODT for PEP–PEE-2 is 96 °C. In contrast to the behavior of the low-frequency dynamic shear moduli,[4] there is no dramatic change in the self-diffusion coefficient at this temperature.

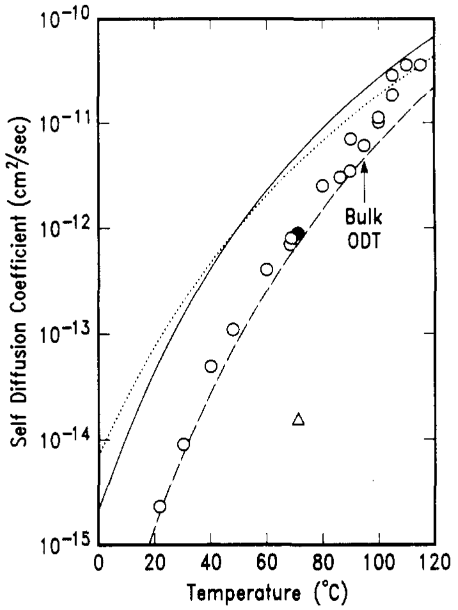

Figure 2. Values of the diffusion coefficient of PEP–PEE-2 obtained when no annealing treatment was done (○) and the values of D_1 (●) and D_2 (△) obtained after a 4-day preannealing treatment at 70 °C. The curves correspond to the self-diffusion coefficients for homogeneous phases of PEP–PEE (—), PEP (· · ·), and PEE (– –), all with molecular weights equal to that of PEP–PEE-2 (50 100).

The behavior of diffusion couples made from hydrogenated and deuterated layers that have been preannealed is dramatically different from the behavior exhibited by the samples that were not preannealed. Figure 1b shows the deuterium volume fraction vs depth profile from a PEP–PEE-2 diffusion couple after a 4-day preanneal of the individual layers at 70 °C followed by diffusion at 71 °C for 44 min. The profile is clearly non-Fickian and cannot be fitted by eq 1 for any given value of D. In order to obtain an estimate of the effect of the preanneal, we assume that a volume fraction, ϕ_1, of the deuterated layer diffuses at a rate characterized by D_1, whereas the remaining volume fraction, ϕ_2, diffuses at a rate characterized by D_2. The concentration profile after an annealing time of t is therefore given by

$$\phi(m) = \frac{\phi_1}{2}\left\{\mathrm{erf}\left[\frac{h-x}{(4D_1t)^{0.5}}\right] + \mathrm{erf}\left[\frac{h+x}{(4D_1t)^{0.5}}\right]\right\} + \frac{\phi_2}{2}\left\{\mathrm{erf}\left[\frac{h-x}{(4D_2t)^{0.5}}\right] + \mathrm{erf}\left[\frac{h+x}{(4D_2t)^{0.5}}\right]\right\} \qquad (2)$$

The solid line in Figure 1b is the concentration profile given by eq 2 for $\phi_1 = 0.64$, $\phi_2 = 0.36$, $D_1 = 9 \times 10^{-13}$ cm²/s, and $D_2 = 1.5 \times 10^{-14}$ cm²/s. These values of D_1 and D_2 are included in Figure 2 as the filled circle and the open triangle, respectively. The value of D_1 is similar to the value obtained from a sample that was not preannealed, whereas D_2 is decreased from this value by nearly 2 orders

Table I
Diffusion Coefficients for Various Homogeneous Polymer Melts

			D	
polymer	mol wt	temp, °C	measd, cm^2/s	scaled to M = 50 100, cm^2/s
PEP–PEE-1	31 500	52.5	3.2×10^{-12}	1.3×10^{-12}
PEE homopolymer	160 000	40	3.0×10^{-15}	3.1×10^{-14}
PEE homopolymer	160 000	69.5	5.0×10^{-14}	5.1×10^{-13}
PEP homopolymer	160 000	21	8.0×10^{-15}	8.2×10^{-14}

of magnitude. The effect of the preanneal is therefore to significantly reduce the mobility of a certain fraction of the copolymer chains.

We have also measured the self-diffusion coefficient of PEP–PEE-1 and of PEP and PEE homopolymers. These values are included in Table I, along with values scaled to the molecular weight of PEP–PEP-2 (51 000), by assuming the M^{-2} dependence characteristic of reptation. The ODT of PEP–PEE-1 is much too low to be measured but is estimated to be −72 °C.[4] Fluctuation effects are therefore expected to be unimportant for PEP–PEE-1 at 52.5 °C, and all the diffusion coefficients shown in Table I are characteristic of homogeneous polymer melts in the absence of fluctuation effects.

Discussion

We begin with a discussion of diffusion in simple, homogeneous polymer melts. In well-entangled systems the self-diffusion coefficient is given by[10]

$$D_{\mathrm{rep}} = \frac{4M_0M_{\mathrm{e}}k_{\mathrm{B}}T}{15\zeta_0M^2} \qquad (3)$$

where D_{rep} signifies the reptation diffusion coefficient, M_0 is the monomer molecular weight, M_{e} is the entanglement molecular weight, and ζ_0 is the monomeric friction coefficient. Corrections to the reptation diffusion coefficient are small for $M/M_{\mathrm{e}} > 3$.[11] For PEP $M_{\mathrm{e}} \approx 1500$ while for PEE $M_{\mathrm{e}} \approx 11\,000$.[12] Thus PEP–PEE-1 and PEP–PEE-2 are reasonably well-entangled in the sense that reptation is expected to accurately describe the self-diffusion in a homogeneous phase.

The temperature dependence of D_{rep} is determined by the temperature dependence of ζ_0. The temperature dependence of the homogeneous polymer melt dynamic shear moduli is also governed by ζ_0, so that the temperature-dependent rheological data can be used to extract the temperature dependence of D_{rep}. Frequency-dependent dynamic shear moduli obtained at different temperatures superpose when plotted against ωa_{T}, where ω is the frequency corresponding to a given measurement and a_{T} is a temperature-dependent shift factor. This shift factor is proportional to ζ_0/T,[13] so D_{rep} is proportional to $1/a_{\mathrm{T}}$.

This simple relationship between D and a_{T} is not expected to be valid for block copolymers when fluctuation effects are important. As mentioned previously, fluctuation effects are expected to be insignificant for PEP–PEE-1 over the temperature range studied here, and we may assume that D for this polymer does in fact scale as $1/a_{\mathrm{T}}$. Measurement of the diffusion coefficient at a single temperature, along with a rheological determination of a_{T} and the known M^{-2} dependence, can be used to estimate the self-diffusion coefficient of a hypothetical homogeneous PEP–PEE melt over a broad regime of temperature and molecular weight. The predicted temperature dependence for a homogeneous melt with a molecular weight equal to that of PEP–PEE-2 is shown by the solid curve in Figure 2. The dotted and dashed curves represent the respective diffusion coefficients of PEP and PEE homopolymers of this same molecular weight. The shapes of the three curves are determined by the temperature dependence of a_{T} as reported in ref 4, while the vertical positions are fixed by the scaled values shown in Table I. The self-diffusion coefficient of a homogeneous PEP–PEE copolymer is similar to the self-diffusion coefficient of a PEP homopolymer of the same molecular weight, indicating that $M_0M_{\mathrm{e}}/\zeta_0$ is similar for these two polymers.

The difference between the solid line in Figure 2 and the actual measured values for the self-diffusion coefficient of PEP–PEE-2 represents the estimated decrease in mobility associated with a transition from a completely disordered melt to an ordered lamellar structure. The "fast" component of diffusion in this ordered structure, represented by the circles in Figure 2, is similar to the diffusion of PEE, which has the lower diffusion coefficient of the two homopolymers. The significance of this result is not obvious, since the ordered block copolymer phase is in the weak segregation regime, and does not consist of pure PEE and PEP domains. The periodicity of the composition within the lamellar phase is still important in that it imposes a periodicity in the potential field in which the block copolymer diffuses. As discussed by Fredrickson and Milner in a recent theoretical treatment,[14] the presence of even a small periodic potential can have a profound impact on the mobility of the block copolymer chains. The self-diffusion coefficient in a lamellar structure is a tensor, which can be written such that $D_{11} = D_{22} = D_{\parallel}$, $D_{33} = D_{\perp}$, with all off-diagonal components equal to zero. Here, $D_{\parallel}$ is the diffusion coefficient in the direction parallel to the lamellae and $D_{\perp}$ is the diffusion coefficient in the direction perpendicular to the lamellae.

Ordering of initially homogeneous films takes place very rapidly below a narrow temperature range near T_{ODT}.[4] For PEP–PEE-2, this narrow temperature window lies between 89 °C and the ODT; here the ordering process takes longer than approximately 4 min.[4] At lower temperatures the ordering process is much faster and is expected to be essentially instantaneous at room temperature. There is no reason to expect that the ordering process in the thin block copolymer films studied here should be substantially slower. Our explanation for the qualitative behavior of the data shown in Figure 2 is therefore as follows. The hydrogenated and deuterated PEP–PEE-2 films cast from solution have very small microdomains with random orientation, as illustrated schematically in Figure 3a. The average diffusion coefficient is given by $1/3\{D_{11} + D_{22} + D_{33}\} = 2/3D_{\parallel} + 1/3D_{\perp}$, and this is the diffusion coefficient that is measured in the samples that were not preannealed. Domains become preferentially aligned in a direction parallel to the surface during the preanneal, as shown schematically in Figure 3b. Such a surface effect on the orientation of lamellar microdomains has been observed in other block copolymer systems.[15,16] We measure diffusion in the direction perpendicular to the film surface, so our measurement is highly sensitive to polymer chains in the surface region that are diffusing perpendicular to the lamellar domains. Diffusion in this direction is greatly restricted by the periodic potential associated with the lamellar order,[14] and we obtain a value for D_2 that approaches $D_{\perp}$ and that is much less than $D_{\parallel}$. A similar effect, involving the diffusion of homopolymers in lamellar microdomain structures, has been observed by Green et al.[17]

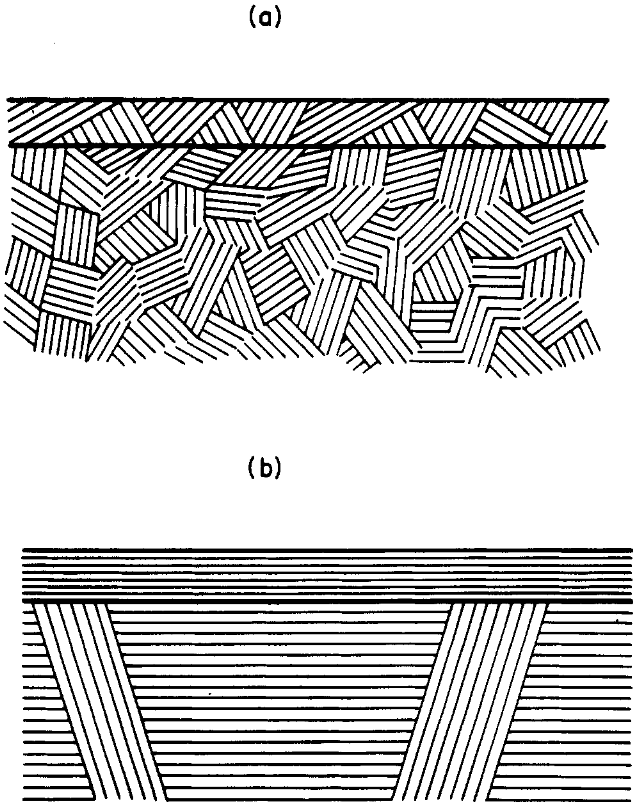

Figure 3. (a) Schematic representation of the block copolymer bilayer film before preannealing. The substrate has an ordered lamellar structure, but these lamellae are arranged in domains that have roughly random orientation relative to the surface. (b) Bilayer film after preannealing. The ordered lamellar domains near the surface have become oriented so that the lamellae in most of them are parallel to the surface.

A more detailed analysis of the data is difficult because of a lack of understanding of the domain structure. Nevertheless, a great deal can be learned from the simple picture presented above. Clearly, diffusion and rheology for block copolymer melts are not related in a simple way as they are for homopolymer melts. The overall diffusion coefficient characterizing an ordered structure is dominated by the fastest diffusion path. In the case of the polymers studied here, this fastest path is for diffusion parallel to the lamellae. Diffusion in this parallel direction is slowed down by the ordering, but there is not noticeable discontinuity in this diffusion coefficient at the ODT. The diffusion coefficient is lower than the value corresponding to a hypothetical homogeneous phase for temperatures up to 20 °C greater than the ODT. This reduction in the diffusion coefficient can be attributed to the presence of composition fluctuations in this temperature regime.

This result is in contrast to the temperature dependence of the low-frequency dynamic shear moduli, which do show a very sharp discontinuity at the ODT. These shear moduli must be dominated not by the fastest relaxation mechanism but by a slower relaxation mechanism such as the motion of copolymer chains perpendicular to the lamellar structure. The mobility of chains in this direction is much lower than the mobility of polymer chains in the parallel direction, so the ordering has a much greater effect on the low-frequency shear moduli than it does on the diffusion. In effect the self-diffusion and the rheological properties can be modeled as if a series of stiff elements with low diffusion coefficients were connected in parallel to a series of flexible elements with high diffusion coefficients. The overall stiffness of the collection of elements is dominated by the stiffer components, whereas the overall diffusion coefficient for the collection is dominated by the more flexible elements.

Conclusions

Self-diffusion in the lamellar block copolymer melts studied here is complicated by the anisotropic nature of the diffusion process. Diffusion in a direction perpendicular to the ordered lamellae is orders of magnitude slower than diffusion in the direction parallel to the lamellae, so diffusion in a randomly oriented ordered lamellar material is dominated by diffusion along the parallel directions. This diffusion coefficient is lower than the homogeneous phase diffusion coefficient but does not show a discontinuity at the order–disorder transition temperature. Diffusion in the surface regions of block copolymer melts is dominated by the tendency of the lamellar domains to orient themselves in a direction parallel to the film surface, so that diffusion into the bulk of the film is governed largely by the perpendicular diffusion coefficient.

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