Translational Dynamics of Diblock Copolymers

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Received August 22, 1994; Revised Manuscript Received December 27, 1994[⊗]

ABSTRACT: A study of the translational diffusion of a symmetric A–B diblock copolymer into homopolymer, A and B, host is reported. The segmental mobilities of homopolymer A into homopolymer B, A into A, B into A, and B into homopolymer B hosts were independently determined. These segmental mobilities were observed to differ by orders of magnitude. Using a straightforward formalism based entirely on reptation, reliable predictions of the magnitude of the diffusivity of the diblock were made using these independently determined mobilities. Current theories which address the diffusion of diblock copolymer chains all assume, in the absence of any experiments in this area, that a single, constant, friction factor characterizes the diffusion of diblock chains. It is anticipated that the incorporation of such differences in the relative magnitudes of the segmental mobilities might alter quantitative conclusions of such theories.

Introduction

The complex phase behavior that diblock copolymers exhibit is a natural consequence of the thermodynamic incompatibility between the covalently bonded dissimilar blocks, A and B, that comprise the chains.[1] Their equilibrium phase behavior is reasonably well understood theoretically[2,3] and is described in terms of N_c, the overall degree of polymerization of the copolymer chain, f, the volume fraction of the A-phase, and χ, the Flory interaction parameter. The value of f determines whether the system will exhibit one of a series of ordered microstrucures of varying geometries which include body-centered-cubic arrangement of spheres, hexagonal arrangement of cylinders, and lamellar structures. A weak first-order transition from an ordered phase to a disordered phase occurs at the order–disorder transition (ODT). The location of the ODT is dictated by the condition $\chi N \approx \Phi(f)$, where for a lamellar phase $\Phi(0.5) \approx 10.5$; note that $\chi \sim 1/T$, where T is the temperature. In the vicinity of the ODT fluctuations in composition, characterized by a wave vector q^* whose magnitude is on the order of the inverse of the radius gyration of the chain, $R_g \sim N^{1/2}$ are present. This is described as the weak segregation regime (WSR),[2] whereas below the ODT, where $\chi N \gg 10.5$, the system approaches the strong segregation regime (SSR)[3] where the structural dimensions vary as $N^{2/3}$. Considering the complexity of these structures, the dynamics of these systems promise to be complicated. A complete understanding of the dynamical properties of block copolymer systems is still lacking.[4] Of the experiments conducted on these systems[5–7] there is no consensus on the general behavior of their translational dynamics. Some interesting findings were recently presented by Lodge and co-workers. Their forced Rayleigh scattering studies of the temperature dependence of the self-diffusion in poly(ethylene propylene)–poly(ethyleneethylene) (PEP–PEE) showed that the temperature dependence of the self-diffusion coefficient, D_s, was insensitive to the system passing through the ODT, a result also shown by Shull et al.[6] This appears to be the result of significant fluctuations in composition which persist even at temperatures above the ODT, a point mentioned by Lodge and co-workers and also addressed by Anastasiadis et al.[8] An observation regarding unentangled chains in the ordered phase is that the lamellae had no influence on D_s. In particular, in the poly(styrene-*b*-vinylpyridine) (PS–PVP) system D_s was comparable to the self-diffusivity of PS. They also determined that in the PEP–PEE system, close to the ODT, the diffusion coefficients parallel, D_{par}, and perpendicular, D_{perp}, to the lamellae orientation were comparable and considerably below the ODT $D_{perp}/D_{par} \approx 0.3$. Their rationalization of these findings in terms of the thermodynamics and entanglements offers some insight into why these results might be reasonable. However, a more critical evaluation is required to determine general characteristics of the dynamics of copolymers.

Complementary information about the dynamics of copolymer melts was earlier provided by photon correlation spectroscopy studies of Anastasiadis et al.[8] on the dynamics of poly(dimethylsiloxane-*b*-methylethylsiloxane) (PDMS–PMES) above the ODT. These measurements revealed evidence of wave vector, q, independent internal relaxation modes and long-range q^2-dependent diffusive modes. An unsuccessful attempt was made to predict the self-diffusion coefficients by assuming that a single segmental mobility characterized the dynamics of the entire copolymer chain.

Some time ago, we studied the diffusion of PS and PMMA homopolymers into the symmetric diblock copolymer structures of PS and PMMA.[9,10] It was revealed that the homopolymer chains diffused into domains with which its interactions were thermodynamically most compatible, i.e., d-PS into PS domains and d-PMMA into PMMA domains. Furthermore, the ratio of the diffusivity of PS into PS, D_{PS}(PS), to that of PS into PS–PMMA, D_{PS}(PS–PMMA), could be as low as 0.1. Comparable, though less dramatic, results were observed for the diffusion of the PMMA homopolymers. This difference in the magnitudes of the diffusivities was shown to result from the tortuosity of the domains.

Here we provide further important insight into what might generally be anticipated about the translational diffusion of diblock copolymers in ordered copolymers below the ODT. Using information about the segmental mobilities of the A and B components of the diblock in the pure homopolymer phases and of the relevant homopolymer chain mobilities, reasonable predictions of the chain diffusivities can be made. It will become clear that measurement of self-diffusion coefficients in diblock copolymers whose structures are far from equilibrium might not yield great insight into the true

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[⊗] Abstract published in *Advance ACS Abstracts,* February 15, 1995.

translational dynamics unless the relevant diffusivities in the homopolymer phases are known. The results of this paper also provide a simple mean-field framework with which one might understand the translational dynamics of such systems. These results should emphasize the importance of the development of a new theory that addresses the underlying physics that determines the segmental mobilities, or equivalently the friction factors, in melts.

Experimental Section

The systems investigated in this study are polystyrene (PS) and poly(methyl methacrylate) (PMMA) diblocks and homopolymers of PS and PMMA. Each of these polymers is characterized by dispersions of less than 1.1. The glass transition temperatures of the polymers are comparable, T_g(PS) = 100 °C and T_g(PMMA) = 115 °C. Both polymers have comparable entanglement molecular weights, N_e(PS) = 170 and N_e(PMMA) = 150. The diblock copolymers used in this study were SMI (d-PMMA(M=130)-*b*-d-PS(M=132)), SMII (PS(M=404)-*b*-PMMA(M=420)), and SMIII (PS(M=1510)-*b*-PMMA(M=1600)). One of the difficulties associated with tracer measurements using diblocks is that they show a strong tendency to aggregate and form micelles. We have chosen concentrations of the labeled diblock (SMI) which are such that they are below the concentration where they can form micelles.

Measurements of diffusion were performed using an ion beam analysis technique, elastic recoil detection (ERD), which has been discussed in detail in a number of earlier publications.[10] The samples were composed of bilayers of films. A thick (microns) underlying layer of a host polymer and a thin outer layer which was usually a blend of the host polymer and small quantities of the deuterated diffusant. The diffusion coefficient was extracted from the profile, determined using ERD, of the tracer using a solution of the diffusion equation. Briefly, the ERD process involves measuring the energy and number of scattered ions (helium nuclei) from the sample. Knowledge of the energy of ions incident on the sample, of their energy loss rates in the materials, and of the scattering cross sections enabled the determination of the concentration profile of the deuterated species in the host layer.

Results and Discussion

Ultimately, for any dynamic process, the primary aim is to gain insight into the mechanism of transport and to make predictions about the general behavior. There is general agreement that reptation[11] provides useful and accurate insight into the mechansim of diffusion of chains into entangled homopolymer melts. In systems of unentangled chains, the Rouse model provides a reasonable description. What ultimately determines the time scales of the translational dynamics of a chain are two parameters, a quantity that describes the resistance that a segment experiences as it diffuses, ζ, and N, the degree of polymerization of the diffusant. ζ also determines the temperature dependence of diffusion. In special cases the length of the chains that compose the host environment will influence the diffusivity.[12]

In reptation, there are effectively two relevant time scales. At short times there are rapid segmental motions involving the propagation of "kinks" (stored length) which facilitate the longer time scale motion described by τ_d. τ_d characterizes the translational motion of the chain along the "tube" in which it diffuses. Reptation predicts that

$$D = \frac{4}{15}\frac{N_e k_B T}{\zeta}N^{-2} \tag{1}$$

where N_e is the number of segments between entanglements and k_B is the Boltzmann constant. For unentangled Rouse chains

$$D_{\mathrm{Ro}} = \frac{M_0 k_{\mathrm{BT}}}{\zeta}N^{-1} \tag{2}$$

Because of the ordered phases in copolymer melts the motion of an A–B diblock into a lamellar microstructure, say, involves the motion one segment, A, through an unlike phase, B. For each A-block in a B-phase there is an increase in free energy, proportional to χN_A, associated with the presence of N_A segments. This free energy change is the source of the large resistance associated with the mobility of a diblock chain through the homopolymer phase. Under these conditions, the A-block might assume conformations that it would not otherwise possess in an A-phase. At short times, conformational transitions that should facilitate the motion of the chain would be different compared to that which it would have in an A environment.

In this context, the translational diffusion of a single A–B diblock copolymer necessarily involves different friction factors, or indeed segmental mobilities. The factors associated wtih diffusion of the diblock through an ordered diblock phase involve the friction factor for the translation of the diblock through the B-phase, $\zeta_{A-B}(B)$, and through the A-phase, $\zeta_{A-B}(A)$. In general, the friction factor for the A–B diblock, ζ_{A-B}, should be related to some combination of $\zeta_B(B)$, $\zeta_B(A)$, $\zeta_A(B)$, and $\zeta_B(A)$. Considering that a diblock chain experiences a minimum in free energy when its junction is located at the interface of the unlike phases, translational diffusion might be expected to occur perpendicular to the interfaces, where the interfaces are the equilibrium "sites". Except in very unusual cases, the friction factors that govern the tracer diffusion of A into B differ considerably from that for A into A or B into B. This is true even in miscible blends.[13] In some cases this difference can be orders of magnitude. The ratio $R = \tau_i/\tau_p$ of the time that the chain spends at the interface τ_i to that which it spends in the A or B phase, τ_p, is important. τ_p will be determined by the magnitude of the larger of the two friction factors that govern the diffusion of the diblock in each phase. On the other hand, τ_i will be determined by the degree of segregation of the diblock probe chain at the interface. This will be a function of χN for the host and the length of the probe chain. In cases where $R \sim 1$, the trapping of the diblock tracer at the interface is important and the periodicity of the domain structure will affect the diffusion time scales considerably. Particularly in a highly segregated system, the diffusivity will depend on the relative dimensions of the phase, L_D, to that of the copolymer block, L_B. When L_D is comparable to L_B, translational diffusion can occur if one block of the probe chain can span one entire layer of the structure and "drag" its attached segment through the unlike phase.[14] On the other hand, if $R \ll 1$, the effect of interface becomes considerably less important and the diffusion mechanism is expected to be a straightforward reptation mechanism, where the time scale of diffusion is controlled by the block with the larger friction factor through each phase. This should be the case where $\chi N \sim 10$ (WSR) and the friction factors differ considerably in magnitude ($\zeta_A(B) \gg \zeta_A(A)$, $\zeta_B(A) \gg \zeta_B(B)$, and $\zeta_A(A)$ and $\zeta_B(B)$ differ considerably). This might also be the case in the SSL and where the friction factors differ considerably but the probe diblock chain is relatively short. It should be emphasized, however, at equilibri-

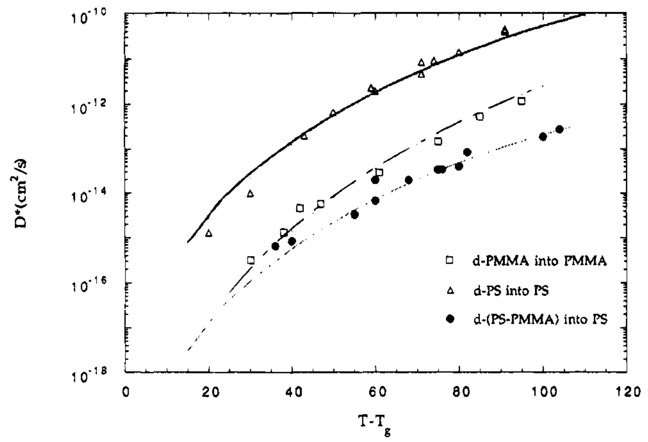

Figure 1. Temperature dependence of the tracer diffusion d-PS of $N = 269$ into PS (filled circles), of d-PMMA of $N = 262$ segments into PMMA (the actual measurements were scaled from d-PMMA of $N = 2100$ into PMMA in order to make the comparison), and of a symmetric diblock of $N_c = 262$ into PS of degree of polymerization of $N = 2240$.

um, that the diblock probe chains should all reside at the interfaces.

A particularly important situation concerns thin film diblock copolymers. Under equilibrium conditions, the lamellae of diblock copolymers are aligned parallel to the interfaces.[15] However, under nonequilibrium conditions, the diffusion of the diblock is complicated since the structure attempts to reorient in order for the lamellae ($f \approx 1/2$) to align parallel to the interfaces. The rate at which it does so depends on the strength of the interactions between the chains and the interfaces and on the film thickness. Therefore, the self-diffusion coefficient of a diblock chain will be complicated by the collective motions of the host chains. It follows that the ratio D_{par}/D_{perp} will depend not only on temperature but also on the degree to which the system departs from equilibrium. The mechanism of diffusion parallel to the lamellae must occur by some cooperative process involving some "defect" mechanism.

Let us now examine the results for the diffusion of a symmetric diblock of PS and PMMA of $N_c = 262$ ($f_{PS} = 0.51$) into PS of degree of polymerization $P = 2240$. Figure 1 shows the temperature dependence of the $D_{PS-PMMA}$(PS) of this chain. The line drawn through the data was calculated with the Vogel–Fulcher equation using the same constants used to fit the data of the diffusion d-PS into PS. As an obvious comparison we show the temperature dependence of the diffusion of a d-PS chain, characterized by the same degree of polymerization as the diblock, into PS. It is clear that $D_{PS-PMMA}(PS) \approx 10^{-2}D_{PS}(PS)$. The temperature dependence is also described by the same Vogel–Fulcher constants. This difference is evidently associated with the very large activation processes associated with the motion of the attached PMMA block on the overall translational dynamics of the copolymer chain. As a further comparison, we also show the temperature dependence of the diffusion of d-PMMA ($N = N_c$) into PMMA, D_{PMMA}(PMMA). The line drawn through this data is also a Vogel–Fulcher fit for PMMA, which is different from PS. Interestingly, while D_{PMMA}(PMMA) is comparable to $D_{PS-PMMA}$(PS), it is somewhat larger in magnitude, which should not be surprising. Considering that both polymers have the same N_e, eq 1 suggests that variations in ζ are primarily responsible for differences in magnitude of the diffusivities.

Table 1. Friction Factors, ζ (Ns/m), Obtained from Tracer Diffusion of d-PS and of d-PMMA into PS and PMMA Homopolymers at $T - T_g = 70$ °C

	PS host	PMMA host
PS tracer	4×10^{-9}	4.3×10^{-6}
PMMA tracer	2.8×10^{-6}	4×10^{-7}

In order to gain some insight into these observations, it would be importnat to examine the relevant friction factors associated with the diffusivity d-PS into PMMA, ζ_{PS}(PMMA), and of d-PMMA into PS, ζ_{PMMA}(PS). Equation 1 is used to calculate the friction factors from the tracer diffusivities of d-PS into PMMA ($P = 1000$) and of d-PMMA ($N = 210$) into PS ($P = 2140$). These factors are tabulated in Table 1. It is noteworthy that, if we compare the value of the friction factor calculated from the diffusion of the d-(PS–PMMA) diblock into the PS phase, we find that $\zeta_{PS-PMMA}(PS) \approx \zeta_{PMMA}(PS)$ ($\zeta_{PS-PMMA}(PS) = 2.2 \times 10^{-6}$ Ns/m ($T = 170$ °C)). This confirms the results in Figure 1 which suggested that the PMMA block on the diblock chain was primarily responsible for the comparatively low diffusivity of the diblock chain in the PS phase. It is also noteworthy that ζ_{PS}(PMMA) is comparable to ζ_{PMMA}(PS), a result which is consistent with the fact that $D_{PS-PMMA}$(PS) is comparable to $D_{PS-PMMA}$(PMMA). If we compare the magnitudes of the friction factors for the homopolymers, we find that $\zeta_{PMMA}(PS) \approx 10\zeta_{PMMA}(PMMA)$ in contrast to $\zeta_{PS}(PMMA) \approx 10^3\zeta_{PS}(PS)$.

In one considers a diffusion process such that the block whose translation is energetically most favorable in that phase will first move forward, then the attached block whose friction factor is very large will impeded further motion. Within a mean-field approximation both processes can be treated independently and in series. It follows that the effective friction factor per copolymer chain might be written

$$\zeta_{A-B}(A) = \zeta_{eff} = N_A\zeta_A(A) + N_B\zeta_B(A) \qquad (3)$$

Hence, for an unentangled diblock copolymer diffusing into a homopolymer of type A the tracer diffusion coefficient is

$$D_{Ro(A-B)}(A) = k_BT/\zeta_{eff} \qquad (4)$$

The diffusion coefficient for the entangled diblock is

$$D_{A-B}(A) = \frac{4}{15}\frac{N_e k_B T}{\zeta_{eff}} N_c^{-1} \qquad (5)$$

As one might anticipate, this equation provides reasonable predictions for the diffusivity of a PS–PMMA diblock into PS. The open circles in Figure 2 show the diffusion coefficients calculated using eq 4; they are in good agreement with the measured values. In the WSR, eq 5 should also provide a reasonable description of the diffusion of a diblock parallel to the interfaces in an ordered diblock host.

A few comments might be made concerning the diffusion of PS–PMMA into an ordered diblock of a lamellar morphology. Let us consider a situation in which an A–B diblock diffuses into a highly ordered lamellar structure in a direction that is perpendicular to the lamellar orientation. Further assume that the interlamellar spacing is large compared to the diblock. The diffusion coefficient of the diblock perpendicular to the lamellae would be decreased in relation to its value in a pure homopolymer A-phase by a factor that is

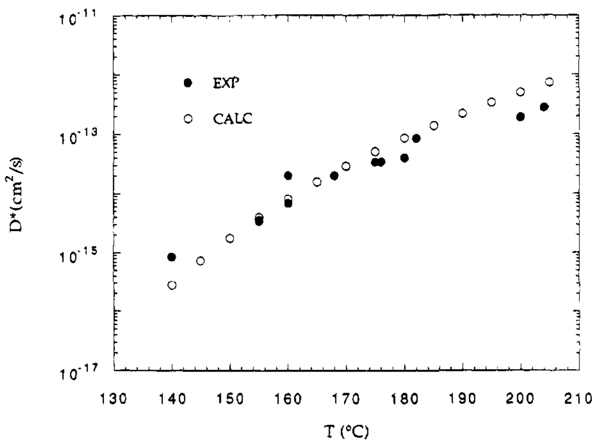

Figure 2. Comparison of the measured and calculated tracer diffusivities of the diblock into PS.

related to the time that it resides in each phase. The diffusion coefficient is therefore

$$D_{A-B}(A-B) = D_{A-B}(A)\frac{N_{e(B)}\zeta_{A-B}(A)}{N_{e(A)}\zeta_{A-B}(B)} \qquad (6)$$

In cases where the lamellar spacing is comparable to that of the diblock, one should still anticipate the same general results. This equation predicts that $D_{A-B}(A-B)$ and $D_{A-B}(A)$ should be comparable in the PS/PMMA system, which is not unexpected based on the data presented here since R is considerably smaller than 1.

A final comment could be made regarding the temperature dependence of diffusion. We would not expect the diffusivity to show a notable transition at the ODT in this system because $\zeta_{PS-PMMA}(PS-PMMA) \approx \zeta_{PMMA}(PS)$. There is however evidence which suggests that this observation is not general.[4]

It should be clear that knowledge of the relevant friction factors of homopolymer chains can yield important insight into the translational dynamics of block copolymer systems. It is hoped that the results of this paper will stimulate considerable discussion of this topic.

Acknowledgment. This work was performed at Sandia National Laboratories and supported by DOE under Contract No. DE-AC04-94AL8500. The author acknowledges discussions with J. Melenkewicz, B. L. Doyle, T. P. Russell, and M. Kent.

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MA945041S