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Diffusion in Mixtures of Asymmetric Diblock Copolymers with Homopolymers

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ABSTRACT: Tracer diffusion of asymmetric diblock copolymer in mixtures with homopolymers has been investigated as a function of the volume fraction of diblock copolymer and the molecular weight of matrix homopolymer. The depth profile of polydeuteriostyrene-*b*-2-vinylpyridine (dPS−PVP) diffusing into the mixture of polystyrene-*b*-2-vinylpyridine (PS−PVP) with polystyrene was measured by forward recoil spectrometry (FRES), and the tracer diffusion coefficient was determined. Secondary ion mass spectrometry (SIMS) was used for depth profiling when better depth resolution (∼15 nm) than that of FRES (∼80 nm) was necessary. The ordered structure of the mixtures was measured by small-angle X-ray scattering (SAXS). In concentrated mixtures of PS−PVP diblock copolymer with polystyrene which exhibit an ordered spherical domain structure, the diffusion coefficients are independent of the molecular weight of polystyrene and are also very close to the diffusion coefficient in a neat diblock copolymer melt. On the other hand, in dilute mixtures exhibiting a disordered arrangement of spherical copolymer micelles in a polystyrene matrix, the diffusion coefficient is strongly dependent on the molecular weight (P) of the matrix polystyrene. In highly dilute systems, the diffusion coefficient, D, scales as $D \sim P^{-3}$, which would be expected for Stokes−Einstein diffusion of spherical micelles in a homopolymer whose viscosity scales approximately as P^3. The crossover from the "activated hopping" diffusion of single diblock copolymers (the diffusion mechanism in the neat diblock copolymer melt) to the Stokes−Einstein diffusion of whole spherical micelles occurs at the volume fraction of the transition between the ordered spherical domain structure and the disordered spherical domain structure.

Introduction

Measuring the diffusion of diblock copolymers is an attractive way to study the fundamentals of polymer chain motion in a periodic potential field resulting from an ordered microphase structure. In addition to the fundamental importance of the diffusion mechanism, the diffusion of diblock copolymers plays a crucial role in the kinetics of ordering (microphase separation) and the viscoelastic properties of diblock copolymers. Most theories[1−5] and experiments[6−14] have focused on the diffusion of symmetric diblock copolymers. Much less attention[15−19] has been paid to the diffusion of asymmetric diblock copolymers that order to a spherical domain microstructure even though those systems are expected to be ideal for investigating the effect of ordering on diffusion. Recent studies of such asymmetric diblock copolymers show that individual copolymers can diffuse from spherical domain to spherical domain by "activated hopping".[16,17] In this mechanism, the shorter core block from a given spherical domain must "hop" through a matrix of the other block in order to move to an adjacent spherical domain. In doing so, it must surmount a thermodynamic barrier $\chi N_{\mathrm{core}} k_{\mathrm{B}} T$ where χ is the Flory−Huggins parameter between the two blocks, N_{core} is the degree of polymerization of the core block, k_{B} is Boltzmann's constant, and T is temperature. Thus, for activated hopping the diffusion coefficient $D \sim \exp(-\chi N_{\mathrm{core}})$. In principle, cooperative diffusion of entire spherical domains could be also possible in the neat diblock copolymer melt; however, such a diffusion mechanism should not depend sensitively on χN_{core}, in contradiction to what is observed in experiment.[18]

Diblock copolymers are also useful in practice as compatibilizers for immiscible polymer blends to improve mechanical properties.[20] The improvement of mechanical properties is primarily due to the segregation of block copolymer at interfaces. Segregating diblock copolymers reduce the interfacial energy of the blends and impede the coalescence of minority phase droplets, stabilizing fine dispersions.[21−30] They also reinforce the interface by forming molecular connections across it.[31−33] Similar segregation has been observed at interfaces of polymers with inorganic solids or vacuum.[28−30] Although over the past decade the segregation of diblock copolymers to various polymer interfaces has been widely investigated, very little is known about the kinetics of segregation of these diblock copolymers. The key to understanding the segregation kinetics is knowledge of the diffusion of diblock copolymer in mixtures of diblock copolymers with homopolymers. However, the diffusion mechanism of diblock copolymer in a homopolymer matrix has only been investigated for the special case where the blocks composing the cores of the spherical domains were near their glass transition temperature.[15]

There are two points we may have to consider in order to understand the diffusion of diblock copolymers in

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such mixtures. First, the structure of the block copolymer in the homopolymer matrix depends on copolymer concentration. Above a certain homopolymer concentration, micelles of diblock copolymer will be placed in a disordered fashion in the homopolymer matrix unless the diblock copolymer and homopolymer show macroscopic phase separation. On the other hand, at very low concentrations of added homopolymer, the structure is expected to be almost the same as that in neat diblock copolymer melts, i.e., a body-centered cubic (bcc) structure. Second, in addition to the diffusion of single diblock copolymer chains observed in neat diblock copolymer melts, cooperative diffusion of individual spherical domains may also be possible in such mixtures.[15] We anticipate that the structure of the mixture will play a crucial role in determining the diffusion mechanism.

In the past, only a few attempts have been made to understand the diffusion of diblock copolymer in homopolymer. Transmission electron microscopy was used to observe the diffusion of spherical diblock copolymer micelles into homopolymer by counting the number of spheres around the interface between the homopolymer phase and diblock copolymer phase.[19] A non-Fickian profile of diblock copolymer was observed and attributed to concentration dependent diffusion coefficients. This made the analysis of mutual diffusion difficult. Measurements of the simpler tracer diffusion of poly(styrene-*b*-isoprene) in a mixture of the diblock copolymer with polyisoprene has been made using forced Rayleigh scattering.[15] In this case, however, diffusion of single diblock copolymers from micelles was restricted by the proximity of the blocks in the micelle cores to their glass transition temperature.

In this paper we investigate the diffusion of diblock copolymer in mixtures of diblock copolymer and homopolymer at a temperature well above the glass transition temperature of both copolymer blocks as a function of the volume fraction and molecular weight of the homopolymer. The system of poly(styrene-*b*-2-vinylpyridine) (PS−PVP) with polystyrene is used since these two polymer species, PS and PVP, have nearly identical monomer friction coefficients and glass transition temperatures.[9] By forward recoil spectrometry (FRES) one can monitor the diffusion of deuterium-labeled PS−PVP diblock copolymer (dPS−PVP) into ordinary PS−PVP diblock copolymer (self-diffusion), into the mixture of PS−PVP and PS, or into pure PS homopolymer under conditions where dPS−PVP and PS−PVP are matched in molecular weight and monomer fraction. For our diblock copolymers (approximately 900 segments of PS and 100 segments of PVP with $\chi \approx 0.1$), the critical micelle concentration ϕ_{cmc} in a matrix of $N = 500-1000$ is expected to be quite low (0.002−0.008 by mean field theory). We measure the tracer diffusion coefficient of the dPS−PVP diblock copolymer as a function of volume fraction in PS from almost 0% to 100% simply by mixing PS−PVP with PS. We are especially concerned with the relationship between the structure of the mixture and the diffusion process; the contributions of two independent diffusion processes, diffusion of a whole spherical domain (micelle) and "activated hopping" diffusion of individual diblock copolymer chains, will be discussed.

Experimental Section

Materials. Asymmetric poly(deuterated styrene-*b*-2-vinylpyridine) and poly(styrene-*b*-2-vinylpyridine) were synthesized by sequential anionic polymerization. Styrene (Aldrich) was dried using calcium hydride and distilled under vacuum followed by further purification by dibutylmagnesium and distillation. Deuterated styrene (Cambridge Isotopes) was purified by dibutylmagnesium and distilled. 2-Vinylpyridine was dried by calcium hydride and distilled under vacuum and then purified by a hexane solution of triethylaluminum followed by distillation under reduced pressure with an argon atmosphere. These monomers were stored under an argon atmosphere prior to the polymerization. The polymerization was carried out with *sec*-butyllithium as an initiator in tetrahydrofuran at −78 °C under an argon atmosphere. The dPS and PS blocks were sampled, and their molecular weights were measured by gel permeation chromatography using polystyrene standards as the reference prior to addition of the second monomer. The block ratio was determined by elemental analysis, and the total molecular weight was calculated. The PS−PVP has a number-average molecular weight $M_{\mathrm{n}} = 97\,000$ g/mol and a f_{PVP}, the volume fraction of PVP, of 0.11, while the dPS−PVP has a $M_{\mathrm{n}} = 114\,000$ g/mol and a $f_{\mathrm{PVP}} = 0.12$. Polystyrenes were purchased from Pressure Chemical and used without further purification. Deuterated polystyrene was purchased from Polymer Standards Service and used without further purification.

Forward Recoil Spectrometry. A bilayer diffusion couple was prepared by the following procedure. PS−PVP, PS, or mixtures of PS−PVP and PS were dissolved in toluene and then cast on native oxide silicon substrates to serve as relatively thick (>1 μm) bottom layers. The bottom layer was preannealed at either 178 or 153 °C for at least 2 days to form the equilibrium structure prior to the diffusion measurement. A very thin (20 nm) film of dPS−PVP was spun-cast on glass and floated onto the surface of a distilled water bath and then picked up on the preannealed bottom layer to serve as a top layer. In that way, we can provide a bottom layer with any volume fraction of PS−PVP and study the diffusion of dilute dPS−PVP into that layer. The diffusion couple was then annealed at 178 °C so that the dPS−PVP diffuses over ~500 nm.

When the polystyrene molecular weight was relatively high, we found that the surface has an effect on the diffusion of dPS−PVP diblock copolymer due to the tendency for the deuterated copolymer to segregate to the surface due to the lower surface energy of dPS block.[34] To avoid such an influence of the surface on the diffusion, a trilayer film was constructed, and the tracer layer of dPS−PVP was placed in the middle of the trilayer.

After annealing the bilayer or trilayer, the depth profile of the dPS−PVP tracer molecules was measured by forward recoil spectrometry (FRES). The details of this depth profiling technique have been described previously.[35−38] The concentration profile of dPS determined from the FRES spectrum was fit to the solution of the diffusion equation with appropriate boundary and initial conditions smeared by a Gaussian (fwhm = 80 nm) to account for the limited instrumental depth resolution of the technique.

The diffusion profiles were fit to solutions of the diffusion equation of the following forms: for the diffusion from surface,

$$\phi(z) = \frac{1}{2}\phi_0\left\{\operatorname{erf}\frac{h-z}{2(Dt)^{1/2}} + \operatorname{erf}\frac{h+z}{2(Dt)^{1/2}}\right\} \tag{1}$$

where z is the depth from the surface ($z > 0$), h is the initial thickness of the tracer layer, D is the diffusion coefficient, $\phi(z)$ is the volume fraction at the depth z, ϕ_0 is the initial volume fraction, t is the time, and erf is the error function. For diffusion from the midlayer of trilayer specimen,

$$\phi(z) = \frac{1}{2}\phi_0\left\{\operatorname{erf}\frac{h/2-z}{2(Dt)^{1/2}} + \operatorname{erf}\frac{h/2+z}{2(Dt)^{1/2}}\right\} \tag{2}$$

where z is the distance from the center of the deposited tracer midlayer in this case. Some of the experimental profiles show non-Fickian diffusion; the reason for the non-Fickian behavior has been discussed elsewhere.[16,17,39]

The initial tracer dPS−PVP layer is an as-cast film, which does not have equilibrium order. But after diffusion corresponding to $(Dt)^{1/2} = 400$ nm, the dPS−PVP is highly diluted and well accommodated within any ordered matrix structure. Actually for diffusion in the neat block copolymer matrix, the accommodation is very rapid, taking place within 10 min at 178 °C.[17]

If the diffusion was too fast to be measured by FRES at 178 °C, as in the case of dilute dPS−PVP in PS, the annealing was done at a lower temperature. As we will show later in this paper, diffusion coefficients of the dilute diblock copolymer in homopolymer follow a WLF temperature dependence so that we are able to shift the diffusion coefficients measured at lower temperature to the standard reference temperature of 178 °C.

Dynamic Secondary Ion Mass Spectrometry (SIMS). Layers of PS−PVP and/or PS were prepared for SIMS analysis by spin-casting toluene solutions of these polymers on a silicon oxide-coated silicon substrate. Multilayered specimens were produced by the same floating technique described above for making FRES specimens. The silicon oxide layer (~500 nm thick) was deposited by evaporating silicon oxide on a silicon substrate using a four pocket electron beam evaporator (Sharon Vacuum Co., Inc.). This SiO_x layer is sufficiently insulating that the conditions for charge neutralization do not change as the SIMS crater nears the SiO_x/polymer interface. SIMS measurements were made with a Physical Electronics 6650 dynamic SIMS using a 3 keV, 10 nA beam of O_2^+ ions at 60° off normal incidence, rastered over a 0.09 mm^2 region. Charge neutralization was accomplished using a static, defocused, 1 keV electron beam. Negative ions of H, ^2H, C, CH, C^2H, CN, and Si were monitored as a function of time from an electronically gated area corresponding to the center 10% of the rastered area. Under such conditions, we obtain a depth profile with a resolution corresponding to a Gaussian distribution with a full width at half-maximum of ~15 nm. Further details of SIMS depth profiling analysis for polymers have been presented by Schwarz et al.[40]

Small-Angle X-ray Scattering (SAXS). SAXS measurements employed Cu Kα radiation ($\lambda = 1.54$ Å) generated by a Rigaku RU-200BVH rotating anode X-ray generator equipped with an 0.2 × 2 mm microfocus cathode and Franks mirror optics. The 2-D image of the SAXS pattern was recorded on a Siemens area detector at the end of a 1.5 m evacuated flight tube. An azimuthal average at each scattering vector was taken to obtain the 1-D SAXS pattern.

Results and Discussion

Diffusion of Diblock Copolymers in the Dilute Limit. The tracer diffusion coefficient of dPS−PVP into polystyrene at 178 and 153 °C, $D^*(0,P)$, is plotted against the molecular weight P of the matrix polystyrene in Figure 1. $D^*(\phi,P)$ stands for the diffusion coefficient of the dPS−PVP diblock copolymer in a mixture of volume fraction ϕ of PS−PVP with the matrix polystyrene of molecular weight of P. The diffusion coefficients measured at 153 °C are scaled to the reference temperature of 178 °C using the WLF temperature dependence of the diffusion coefficients of PS. These scaled $D^*(0,P)$ data from these two temperatures superimpose reasonably well and decrease strongly with increasing P, scaling approximately as P^{-3}. While the temperature scaling is that normally expected for homopolymer self-diffusion, which is the same as the temperature T divided by the monomer friction coefficient, this temperature dependence is significantly different from that for self-diffusion of the diblock copolymer.[16] The diffusion mechanism of the diblock copolymer in the dilute mixture must be different from that in the neat diblock copolymer melt.

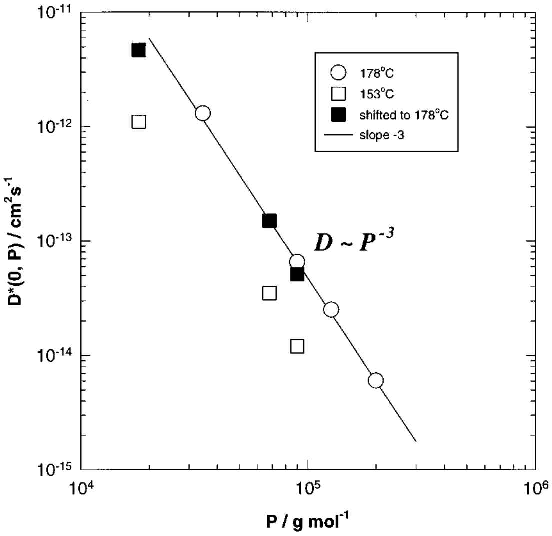

Figure 1. Dependence of tracer diffusion coefficient of PS−PVP diblock copolymer at dilute limit on the molecular weight of the matrix homopolystyrene at 178 °C. The diffusion coefficients measured at 153 °C were shifted to 178 °C vertically by the temperature dependence predicted with the Vogel equation for polystyrene.

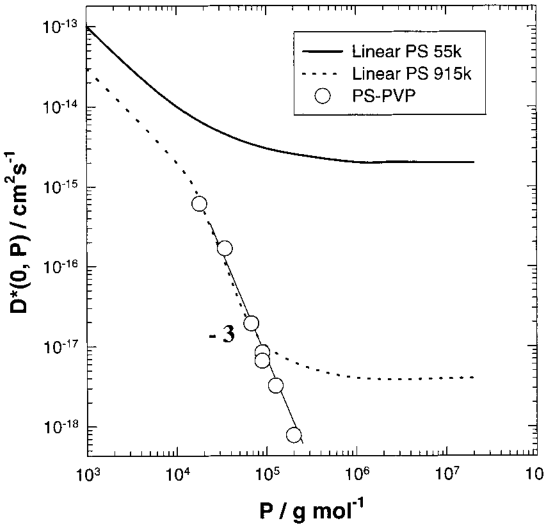

Figure 2. Tracer diffusion coefficient data of the diblock copolymer from Figure 1 shifted to a reference temperature of 125 °C (fractional free volume 0.042) as a function of the homopolymer molecular weight P. These data are compared with the tracer diffusion coefficients of linear polystyrene at 125 °C in homopolystyrene of molecular weight P from ref 37. A solid line represents linear polystyrene with molecular weight of 55 000, and a dotted line represents linear polystyrene with molecular weight of 915 000.

Figure 2 compares the tracer diffusion of the diblock copolymer in the polystyrene matrix with the tracer diffusion of linear polystyrenes as a function of the matrix polystyrene molecular weight. The diffusion coefficients of the diblock copolymer are shifted to the temperature at which the free volume in PS is same as that in ref 37.[41] For the linear polystyrenes, we clearly find two regions above the critical molecular weight for entanglement: the strong P-dependent diffusion at moderate P corresponding to constraint release diffusion of the linear chains, and a P-independent mechanism at high P corresponding to diffusion of linear chains by reptation. However, the diblock copolymer does not show reptation behavior. The diffusion constant depends strongly on P over a wide range of molecular weights, varying approximately as P^{-3}. The (Stokes–Einstein) diffusion of spherical domains (micelles) in PS is the most probable diffusion mechanism giving such strong matrix dependence. Since the viscosity η of the matrix homopolymer scales as $\eta = P^{3-3.4}$, the diffusion coefficients are approximately proportional to η^{-1}, which is the Stokes–Einstein relation. This interpretation is supported by the previous work of Schaertl et al.,[15] who identified a similar mechanism in studies of poly(styrene-*b*-isoprene) (PS–PI) micelles in PS–PI/PI mixtures at temperatures where the PS cores were glassy or relatively immobile. Assuming Stokes–Einstein diffusion of whole spherical domains in the polystyrene matrix, we calculate the hydrodynamic radius, R_h, of a spherical domain by the following equation

$$D^* = \frac{k_B T}{6\pi R_h \eta} \tag{3}$$

where k_B is Boltzmann's constant, T is temperature, and η is the viscosity of polystyrene at 178 °C.[42]

We find the hydrodynamic radius, R_h, is 15 nm for $P = 200\,000$ g/mol and 21 nm for $P = 20\,000$ g/mol. These sizes are reasonable for the dPS–PVP spherical domains given results on the neat diblock copolymer from SAXS (see below), secondary ion mass spectrometry,[17] and transmission electron microscopy:[16] a sphere radius of ~22 nm has been determined by these techniques. The increase in R_h from 15 to 21 nm as P decreases may result from the change from dry brush to wet brush conditions for the dPS block corona of these micelles as P decreases. Schaertl et al.[15] observed a much larger increase in R_h, i.e., 20–70 nm, with decreasing P and attributed it to the same mechanism. We should note, however, that their diffusion measurement was done at a volume fraction of ~50%, where neither the hydrodynamic interaction between micelles nor the interaction due to collisions of micelles is negligible. As well as the reasonable value of R_h, the WLF temperature dependence of diffusion is also consistent with spherical domains diffusing in the viscous homopolymer matrix.

This diffusion mechanism is quite different from that in the neat diblock system we reported previously.[16,17] In the neat diblock copolymer melt with a spherical domain structure, individual diblock copolymer chains diffuse in an array of bcc packed spheres by activated hopping from one domain to another. We found that the diffusion coefficient depends on temperature as $\sim D_0(T) \exp(-1.2\chi(T)N_{\text{core}})$, where $\chi(T)$ is the temperature-dependent interaction parameter between two segments, N_{core} is the number of segments of the core block, and $D_0(T)$ is the diffusion coefficient of PS which has the WLF temperature dependence.[16] The exponential dependence arises from the fact that a thermodynamic potential barrier controls the rate of a hop from a potential minimum to another minimum. The diffusion coefficient is thus reduced exponentially by the thermodynamic barrier, i.e., $D/D_0 \sim \exp(-\Delta F/k_B T)$, where ΔF is the potential barrier and k_B is Boltzmann's constant. ΔF is approximately equal to $\chi N_{\text{core}} k_B T$ in the case where the core block experiences full contact with surrounding corona block segments. Such a strong exponential dependence on $\chi(T)$ adds an extra temperature dependence to the WLF temperature dependence. As homopolymer is added to the block copolymer, the diffusion mechanism must cross over from activated hopping to Stokes–Einstein diffusion of spherical block copolymer domains. How that crossover occurs in the intermediate concentration regime will be presented in the following sections.

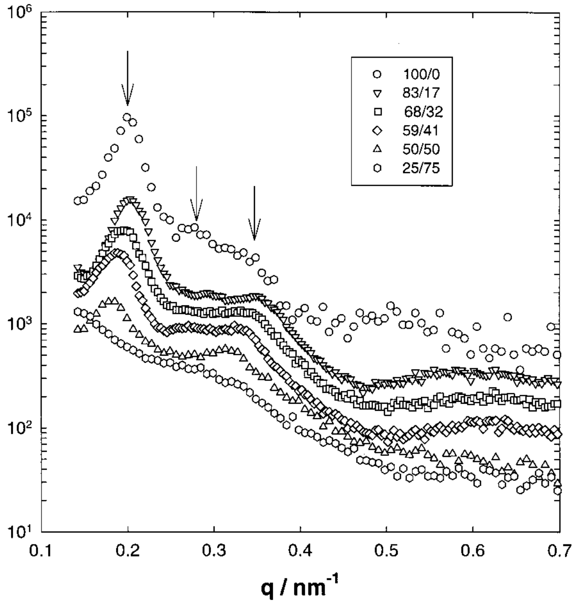

Figure 3. SAXS profile of mixtures of PS–PVP and polystyrene annealed at 178 °C. The index, for example, 25/75 means that the volume fraction of PS–PVP is 25% and PS is 75%.

Structure of Diblock Copolymer in a Mixture of Diblock Copolymer and Homopolymer. Small-angle X-ray scattering (SAXS) reveals the changes in domain structure of the mixture of diblock copolymer and homopolymer as the volume fraction of diblock copolymer is decreased. Figure 3 shows the scattered intensity from several samples as a function of diblock copolymer concentration in a matrix of PS homopolymer with $P = 67\,000$ g/mol. The arrows indicate the expected positions of reflections characteristic of the body-centered cubic structure. These occur at q^*, $2^{1/2}q^*$, and $3^{1/2}q^*$, where q^* is the position of the lowest order nonvanishing reflection. Upon dilution with polystyrene down to a concentration of 59% diblock copolymer, all peaks shift to lower wavenumbers as the structure is swollen by the homopolymer. The bcc packing is apparently preserved. At 50% diblock copolymer, the reflection at $2^{1/2}q^*$ disappears. The structure of mixture may change near 50% of diblock copolymer from bcc to another ordered structure before it attains a completely disordered fluidlike or gaslike packing. At a concentration of 25 wt % diblock, however, all of the Bragg reflections vanish. This result suggests that the ordered structure has been destroyed and that the material consists of a fluidlike or gaslike arrangement of PS–PVP spherical micelles in PS.

We fit the SAXS profile using the structure factor for a spherical PVP domain, assuming a Gaussian distribution of sphere radii.[43–47] The core radius obtained was 9.5–11.5 nm, which is smaller than the hydrodynamic radii estimated from the diffusion coefficients in dilute mixtures of PS–PVP and PS (15–21 nm).[48] Since SAXS detects only the interface separating the PS and PVP blocks, X-ray PVP core radius does not include a contribution from the PS blocks in the micelle coronas, making it a lower limit for the hydrodynamic radius of the micelles. The hydrodynamic radius can also be estimated from SAXS measurements of the unit cell

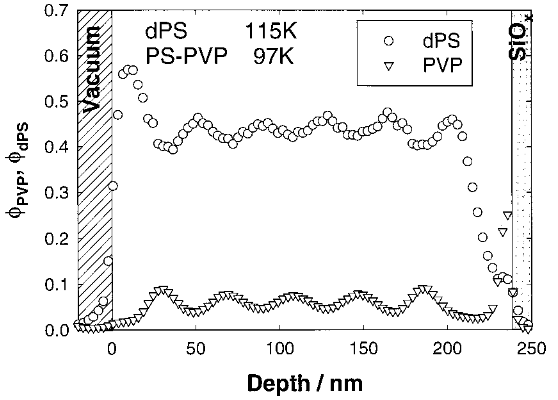

Figure 4. Distribution of deuterated polystyrene (dPS) and poly(2-vinylpyridine) (PVP) of PS−PVP diblock copolymer in a thin film of a mixture of dPS and PS−PVP on a silicon oxide substrate. The film had been annealed at 178 °C for 3 days to equilibrate.

dimension. Each bcc unit cell contains two micelles. If the micellar coronas are swollen by the added PS (as suggested in the preceding paragraph), each micelle occupies half of the unit cell volume. For a bcc unit cell with a (110) spacing of 31.5 nm, this corresponds to a sphere radius of 22 nm, consistent with the diffusion data.

In prior work by Kinning et al.,[49,50] mixtures of a nearly symmetric PS−PI copolymer with PS homopolymer showed a transition from an ordered micellar regime to a liquidlike packing regime as the copolymer volume fraction was reduced. The latter structure appeared at volume fractions of 5−15% copolymer. Our data are of insufficient resolution to identify intermicellar correlations characteristic of such a liquidlike packing, and it is certainly possible that such structure develops in our materials at low copolymer concentrations. In this study, however, our primary emphasis is on the degree to which the presence of lattice order affects the diffusion of block copolymers.

SIMS provides additional evidence for the ordered spherical domain structure and indicates that the homopolystyrene does not undergo macrophase separation. Deuterated polystyrene (dPS) was mixed with PS−PVP diblock copolymer to form a mixture with 53 vol % PS−PVP. By using SIMS to detect ^{2}H negative ions as well as CN negative ions, one can find the depth profile of the PVP spherical domains of the PS−PVP block copolymer and the added dPS simultaneously. The result is shown in Figure 4. Even with dPS of moderate molecular weight ($M_n = 115\ 000$ g mol^{-1}), slightly higher than that of PS−PVP, no evidence of macrophase separation is observed. An oscillatory profile of ϕ_{PVP} suggests layers of spherical domains stacking on top of an adsorbed layer of PS−PVP brush at the SiO$_x$ surface. The ϕ_{PVP} profile of the mixture is similar to the profile of the same diblock copolymer in the neat melt[17] but has lower maxima of the oscillating profile and a larger spacing between maxima. ϕ_{dPS} also shows an oscillation that is out of phase with the oscillation of ϕ_{PVP}. Except for a segregation of dPS to the vacuum surface and a depression of dPS in the PS−PVP brush region, dPS is evenly distributed throughout the corona region of the PS−PVP spherical domains and swells the ordered structure. The spherical block copolymer micelles are well ordered in layers perpendicular to the direction of our depth profiles used for measuring diffusion even in the 50% block copolymer/homopolymer mixture.

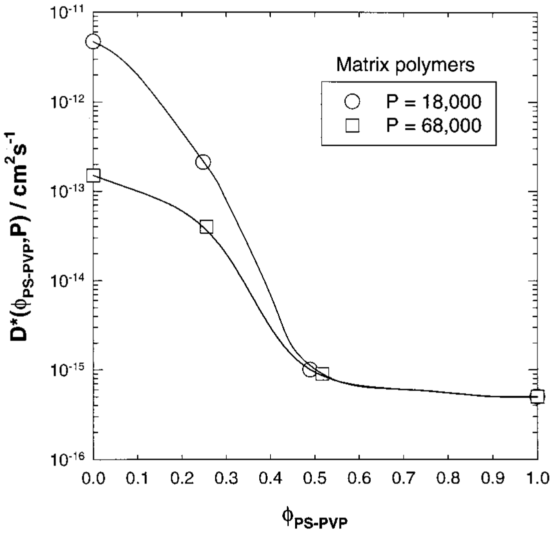

Figure 5. Dependence of tracer diffusion coefficient of dPS−PVP diblock copolymer, $D^*(\phi_{PS-PVP},P)$, on the volume fraction of diblock copolymer, ϕ_{PS-PVP}, for two matrix PS molecular weight, P, at 178 °C. The molecular weights of PSs are smaller than the molecular weight of PS−PVP in any case. The solid lines are guides to the eye.

Diffusion of Diblock Copolymer in Concentrated Mixtures of Diblock Copolymer and Homopolymer. The tracer diffusion of diblock copolymer in the concentrated mixtures was measured by FRES. The tracer diffusion coefficient of the diblock copolymer in the mixture is plotted against the volume fraction of diblock copolymer in Figure 5. Two molecular weights of matrix polystyrene are chosen; both are lower than the molecular weight of the diblock copolymer, but one of them has a molecular weight less than the critical molecular weight for entanglement M_e. The tracer diffusion at the volume fraction of 1 is the self-diffusion of neat diblock system in which "activated hopping" diffusion dominates.[16,17]

We now consider the tracer diffusion at a diblock copolymer volume fraction of 0.5, a volume fraction at which the spherical domain structure is still ordered from the SAXS and SIMS analyses. The tracer diffusion coefficient increases only a relatively small amount from its value for the neat block copolymer. It is also independent of the molecular weight of the matrix polystyrene even though one of these is entangled and the other is not. This independence of D^* with respect to the matrix molecular weight is in sharp contrast to the case of the spherical domain (micelle) diffusion of dilute diblock copolymer in the homopolymers as represented by the values of D^* at low ϕ_{PS-PVP}. The diffusion mechanism for the $\phi_{PS-PVP} = 0.5$ mixture, therefore, cannot be Stokes−Einstein diffusion of spherical PS−PVP micelles. The fact that diffusion is nearly as slow as in the neat diblock copolymer and independent of P suggests that, as long as the ordered domains still exist, the copolymer diffuses by the same "activated hopping" mechanism as in the neat diblock copolymer bcc structure since the thermodynamic (enthalpic) barrier to "activated hopping" diffusion is the interaction of the short PVP block with the PS corona block in the neat copolymer, giving rise to an $\exp(-\chi N_{PVP})$ dependence of D^*. We expect a similar dependence for the spherical micelle structure swollen with PS homopolymer.

For the mixture containing 25% of diblock copolymer, the tracer diffusion shows matrix molecular weight dependence similar to, but less than, that of the dilute mixture. In addition, the diffusion coefficients are more than a magnitude larger than that in the neat diblock copolymer melt. This dramatic change in the tracer diffusion coefficient between $\phi_{PS-PVP} = 0.5$ and $\phi_{PS-PVP} = 0.25$ is consistent with the change in the structure of the mixture from an ordered spherical structure to a fluidlike or gaslike arrangement of spherical domains. The diffusion coefficient in dilute mixture with polystyrene is 2 orders of magnitude larger than that in the neat bulk; therefore, the spherical domains start to diffuse just as soon as the ordered structure "melts". The transient behavior of diffusion in the region of 0−50% is qualitatively similar to the concentration dependence of diffusion of colloid particles in colloidal dispersions.[51] For isolated colloidal particles the diffusivity is determined by the Stokes−Einstein relation; a similar result was obtained for our dilute micelles of diblock copolymers in homopolymer. At higher volume fractions of hard sphere (uncharged) colloids, the long-range diffusivity of particles decreases with the increasing volume fraction ϕ of colloidal spheres approximately as[51]

$$\frac{D(\phi)}{D(0)} = \frac{(1-\phi)^3}{1 + {}^2/_3\phi + 2\phi^2 + 3\phi^3} \tag{4}$$

where $D(0)$ is the $\phi = 0$ (Stokes−Einstein) diffusivity of the colloid. Applying this result to our diblock copolymer micelles gives $D(\phi)/D(0) = 0.26$ at $\phi = 0.25$, in good agreement with our $D^*(0.25, P = 68\,000)/D^*(0, P = 68\,000)$ result (0.27), but greatly overestimates our $D^*(0.25, P = 18\,000)/D^*(0, P = 18\,000)$ result (0.05). The reason for this discrepancy seems clear as the ϕ to be substituted in eq 4 is the volume fraction of micelles (hard sphere colloid). If the micelle coronas are strongly swollen by homopolymer as in the case of the $P = 18\,000$ homopolymer, the volume fraction of the micelles can be much larger than the volume fraction of block copolymer. This hypothesis is qualitatively in accord with the fact that hydrodynamic radius measured in dilute mixtures increases by decreasing the molecular weight of homopolymer.

At higher copolymer volume fractions ($\phi \geq 0.5$) our $D^*(\phi)/D^*(0)$ differs even more significantly from that of the colloidal suspension in that the diffusion coefficient of diblock copolymers remains nonzero and almost constant as the volume fraction of diblock copolymer increases above 50%. Diblock copolymers can still diffuse as individual chains even in an ordered "solid" mixture by the "activated hopping" diffusion mechanism, a mechanism which is not available for colloidal particles.

Diffusion of Diblock Copolymer in High Molecular Weight Matrix Homopolymer. The diffusion of diblock copolymer in a high molecular weight matrix ($P \gg M_{PS-PVP}$) is different from that in a low molecular weight matrix ($P \leq M_{PS-PVP}$). Figures 1 and 2 show that the diffusion coefficient of the dilute diblock copolymer decreases rapidly as P increases.

The diffusion coefficient of the diblock copolymer in PS of molecular weight P will approach the diffusion coefficient of diblock copolymer in the neat diblock copolymer melt at $P_c \approx 460\,000$. Since the elementary step in the diffusion of the neat diblock copolymer is the "activated hopping" of block copolymer chains from spherical domain to spherical domain, it is questionable whether individual diblock copolymer micelles will diffuse in homopolymer at such slow rates. There will be enough time for individual diblock copolymer chains to escape by a very similar activated hopping process into the homopolymer surrounding a micelle in times not very different from those required for hopping from spherical domain to spherical domain in the neat diblock copolymer. The characteristic time for one such hop in the neat diblock copolymer can be estimated from short-range diffusion measurements using secondary ion mass spectrometry (SIMS) to be $\sim 5 \times 10^4$ s.[17] By extrapolating the data in Figure 1 to $P = 600\,000$, for example, we can estimate that an individual micelle will have a diffusion coefficient of $\sim 2 \times 10^{-16}$ cm^2/s at 178 °C. In the time required for one activated hop, such a micelle will diffuse only a distance $\sim (Dt)^{1/2} = 31$ nm, much less than the instrumental resolution of FRES. Thus, we can expect that individual diblock copolymer chains with relatively short PVP blocks (small thermodynamic escape barriers χN_{PVP}) will escape from the micelle and diffuse individually in the homopolymer.

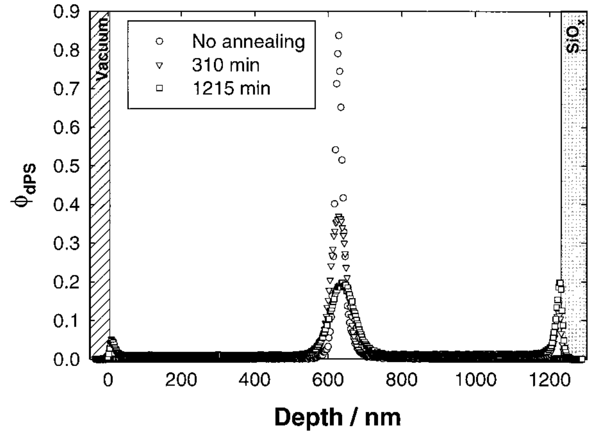

Figure 6. Concentration profile of diffusing dPS−PVP diblock copolymers in polystyrene matrix with $P = 600\,000$ using SIMS. Depth = 0 nm corresponds to a vacuum surface of the film while Depth = 1230 nm corresponds to a silicon oxide surface that attracts the PVP block. A tracer dPS−PVP diblock copolymer layer was placed in the middle of two homopolystyrene layers and then annealed at 178 °C.

The thermodynamic barrier for block copolymers to escape from a micelle into the homopolymer is expected to be similar to that for hopping of the diblock copolymer from domain to domain in the spherical domain structure. We see evidence for this escape and diffusion of individual block copolymer chains for tracer diffusion into the high molecular weight PS homopolymer. The diffusion of a thin layer ($\sim$20 nm) of diblock copolymer (dPS−PVP) sandwiched between thick PS homopolymer layers with $P = 600\,000$ g/mol has been probed using SIMS after a couple of annealing times. The results are shown in Figure 6. $P = 600\,000$ is larger than the crossover molecular weight P_c (= 460 000) from the diffusion of whole micelles to the activated hopping diffusion of block copolymers so that we do not expect observable diffusion of micelles as a whole on the time scale that individual diblock copolymer chains can escape from the micelles. Even after 20.25 h at 178 °C, little diffusion of micelles (which would produce Fickian diffusion broadening of the initial profile) is observed. Instead, we observe a decay of the dPS−PVP volume fraction of the tracer layer with little broadening. The dPS−PVP lost from this tracer layer seems to be uniformly distributed throughout the homopolymer as well as segregated to the vacuum surface and the SiO$_x$ interface. Once the dPS−PVP chains have escaped their micelles, they can diffuse very rapidly in the PS homopolymer with a diffusion coefficient that approaches the diffusion coefficient of polystyrene of the same molecular weight. This fact accounts for the flat dPS profile outside the tracer layer and the buildup of segregation at the both the vacuum and SiO$_x$ surface. Such segregation of diblock copolymer to the silicon oxide and vacuum surface is well-known; these surfaces act as sinks for the diffusing diblock copolymers.[28−30]

Conclusion

We find two different diffusion mechanisms related to the structure in mixtures of asymmetric diblock copolymer and homopolymer. In the concentrated diblock copolymer regime $0.5 \le \phi_{\mathrm{dPS-PVP}} \le 1$, a spherical ordered structure and “activated hopping” diffusion of single diblock copolymers are observed. For dilute diblock copolymer ($\phi_{\mathrm{dPS-PVP}} \approx 0$) we find a gaslike micellar structure and observe Stokes−Einstein diffusion of these micelles. The crossover between these diffusion mechanisms occurs approximately at the volume fraction where the domain structure changes from ordered micelles to disordered micelles. Similar changes in diffusion mechanism were also observed by increasing the molecular weight of the matrix homopolymer while keeping the volume fraction of diblock copolymer low. These crossovers between diffusion mechanisms are related and occur when the time required for the diffusion of a whole micelle exceeds the hopping or escape time of a single diblock copolymer chain.

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