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Mutual Diffusion of Asymmetric Block Copolymers with Homopolymers

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ABSTRACT: The mutual diffusion of poly(styrene-*b*-2-vinylpyridine) (PS−PVP) diblock copolymer and PVP-PS-PVP triblock copolymer with polystyrene (PS) homopolymer is measured using secondary ion mass spectrometry. The depth profile of the PVP block in bilayers of PS/PS-PVP films after annealing shows a unique diffusive behavior in that layers of spherical domains of block copolymer are swollen by diffusing homopolymers. We determine the rate of bulk flow across the interface between those layers and find an intrinsic diffusion coefficient of the faster diffusant, i.e., polystyrene. When the molecular weight of PS-PVP ($M_{\mathrm{PS-PVP}}$) is higher than that of PS (M_{PS}), the intrinsic diffusion coefficient agrees well with the self-diffusion coefficient of PS, suggesting that the driving force of the diffusion is mostly translational entropy; interaction between spherical domains (micelles) is negligibly small. When $M_{\mathrm{PS-PVP}} < M_{\mathrm{PS}}$, PS did not diffuse into deuterated PS-PVP but did diffuse into PS-PVP. This result is caused by the enthalpic interaction between PS and deuterated polystyrene (dPS). The intrinsic diffusion coefficient extracted from the experiment with the PS-PVP/PS couple is smaller than the expected self-diffusion coefficient, suggesting that there is an attractive interaction between PS-PVP spheres in a high molecular weight PS matrix. The PVP-dPS-PVP triblock copolymer was swollen only slightly by diffusing low molecular weight PS. The quite different mutual diffusion behavior of diblock copolymer/homopolymer and triblock copolymer/homopolymer couples is attributed to the presence of bridging midblock chains between triblock copolymer domains.

Introduction

It is well-known that diblock and triblock copolymers form unique microphase separated structures. A variety of structures have been discovered experimentally and understood theoretically.[1] On the other hand, the kinetics of formation of such ordered structures as well as the dynamics with which chains can move in such a structure is an important subject whose investigation has just begun.[2] Recently, it has been found that asymmetric diblock copolymers diffuse in spherically ordered diblock copolymer melts by “activated hopping”, where individual diblock copolymer chains hop from one spherical domain to another in the ordered structure.[3,4] This activated hopping is similar to the mechanism by which symmetric diblock copolymers diffuse in their lamellar structure in the direction perpendicular to the lamellae.[5] Essentially, spherical domains (micelles) are immobile in an ordered structure of a mixture of block copolymers with homopolymers. Even in a mixture of an A−B diblock copolymer, whose B block is short, and A an homopolymer, diffusion is dominated by activated hopping diffusion of individual diblock copolymer chains when the volume fraction of diblock copolymer is more than 0.5 even though micelles of the same diblock copolymer can diffuse as individual spheres in dilute mixtures of the diblock copolymer and homopolymer.[6] In addition, the tracer diffusion of the diblock copolymer in homopolymer crosses over from Stokes−Einstein diffusion of micelles to activated hopping diffusion of individual diblock copolymer chains as the concentration of diblock copolymer increases.

Fleischer et al.[7] studied self-diffusion of asymmetric poly(styrene-isoprene) (PS-PI) diblock copolymer by pulsed field gradient nuclear magnetic resonance (PFG-NMR) and found that there are two modes of diffusion. One of these is diffusion of individual spherical domains (micelles), and the other is that of free diblock copolymer chains. They claimed that there is no exchange between free diblock copolymer chains and diblock copolymer chains trapped in spherical domains during the time of the PFG-NMR measurement, in contrast to the activated hopping mechanism mentioned above. The results were attributed to a disordered micellar structure, and the presence of such a structure was supported by small-angle X-ray scattering measurements. This discrepancy may be due to a large difference in glass transition temperature (T_g) between polystyrene (PS) and polyisoprene (PI) in Fleischer's experiment, while PS and poly-2-vinylpyridine (PVP) in our recent experiments have almost the same T_g and monomeric friction coefficients.[8] A high-T_g PS core block would reduce the rate at which diblock copolymer chains escape from one domain and hop to another.

With this background we are ready to investigate the somewhat more complicated, but practically important, mutual diffusion problem. Mutual diffusion between polymers presents interesting issues especially when the intrinsic diffusivities of the two species interdiffusing are greatly different. In the case where two polymers differ only in their molecular weights, Kramer et al.[9] and independently Sillescu[10] derived fundamental equations, and Green et al.[11] showed experimentally that the initial boundary (interface) between the two polymers moves toward the lower molecular weight polymer. This motion, which could be measured by placing inert Au marker particles at the original interface, is attributed to a bulk flow produced as the faster species (low M) diffused into and swelled the slower (high M) species, thus moving the interface markers. From such marker motion, Green et al.[11] extracted tracer diffusion coefficients of low molecular weight polystyrene that were in agreement with tracer diffusion coefficients measured by direct techniques.

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Table 1. Characteristics of Block Copolymers and Homopolymers

code	M_n	f_{PVP}	code	M_n	f_{PVP}
dPS-PVP114	114 000	0.12	PVP-dPS-PVP145	145 000	0.15
dPS-PVP77	77 000	0.14	PS65	65 000	
hPS-PVP97	97 000	0.10	PS600	600 000	

The mutual diffusion between PS-PI diblock copolymer and PS was measured by Koizumi et al.[12] using transmission electron microscopy (TEM) to measure the movement of PI spheres, which can be stained. They observed non-Fickian diffusion profiles and attributed these to a concentration dependence of the mutual diffusion coefficient and the presence of interactions between spherical domains.

Our understanding of the tracer diffusion of the diblock copolymer in the mixture has enabled us to investigate such mutual diffusion problems in detail. We used secondary ion mass spectrometry (SIMS) to observe a depth profile of bilayers of polystyrene and poly(styrene-*b*-2-vinylpyridine) before and after annealing. A great advantage of the SIMS depth profiling is the good depth resolution, which can reveal the ordered structure of the diblock copolymer as well as the volume fraction versus depth profile caused by mutual diffusion. For this particular study, deuteration of the tracer block is not necessary because SIMS can detect CN^- fragments from the PVP block. (We, however, used deuterated diblock copolymers since we have a large selection of such diblock copolymers in stock.) Moreover, we show later in this paper that deuteration may affect the diffusion when the homopolystyrene molecular weight is high. We are able to measure both the mutual diffusion and degree of ordering of the diblock (or triblock) copolymers during mutual diffusion. In this paper we present results on the mutual diffusion between PS-PVP or PVP-PS-PVP block copolymers and PS for a couple of different PS molecular weights and discuss the mechanism of this mutual diffusion.

Experimental Section

Materials. Deuterated polystyrene (dPS)-PVP diblock copolymer, PS-PVP diblock copolymer, and PVP-dPS-PVP triblock copolymer were synthesized via sequential anionic polymerization. Deuterated styrene and styrene were purified with dibutylmagnesium, distilled, and then stored in an argon atmosphere. 2-Vinylpyridine (2VP) was first dehydrated with calcium hydride and distilled under vacuum. 2VP was further purified with a hexane solution of triethylaluminum and then distilled in an argon atmosphere under reduced pressure. Anionic polymerization was carried out in tetrahydrofuran (THF) at −78 °C under an argon atmosphere using *sec*-butyllithium as an initiator for the diblock copolymer. For the triblock copolymer, a living α-methylstyrene tetramer was synthesized by reaction of α-methylstyrene with potassium metal in THF at 0 °C and used as an initiator within a couple of weeks, where α-methylstyrene was purified by the same scheme as styrene. The molecular weight of the dPS or PS block was measured by gel permeation chromatography using standard polystyrene as a reference. Block fractions were measured by elemental analysis, which detects the nitrogen content of the block copolymers. Total molecular weights of the block copolymers were calculated from the molecular weight of the dPS block and the block fractions. M_w/M_n values of the block copolymers were less than 1.15. The results of the characterization of the block copolymers are listed in Table 1. The code (e.g., dPS-PVP114) indicates whether the PS block is deuterated and the number average molecular weight of the entire block copolymer in thousands. PS homopolymers with number average molecular weights of 65 000 and 600 000 and $M_w/M_n < 1.1$ were purchased from Pressure Chemical Co. and used without further treatment.

Sample Preparation. Diffusion couples were prepared on silicon substrates coated with a silicon oxide layer. The silicon oxide layer (~500 nm) was deposited by evaporating silicon oxide using a four-pocket electron beam evaporator (Sharon Vacuum Co., Inc.). This SiO_x layer is sufficiently insulating so that the conditions for charge neutralization using the SIMS electron gun do not change as the SIMS crater approaches the polymer/substrate interface. The block copolymer solution in toluene was spin-cast onto such a silicon oxide substrate to form a block copolymer film. The block copolymer film was annealed at 178 °C for 72 h to allow it to form the ordered spherical domain structures. The film thickness was finely adjusted so that it forms a flat layer without islands or holes on its surface. Then polystyrene in toluene was spin-cast onto a glass substrate, floated off on the surface of a distilled water bath, and then picked up on the preannealed block copolymer film. The bilayer films were cut into several pieces, and each piece of film was annealed for a different time. Prior to SIMS analysis, 1,2-polybutadiene was spin-cast from heptane solution on the specimens to serve a sacrificial layer, ~30 nm thick, so that the SIMS sputtering conditions would become stable before the SIMS crater reached the original surface of the bilayer film.

SIMS Analysis. The SIMS measurements were done with a Physical Electronics 6650 dynamic SIMS using a 3 keV, 20 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, 0.7−1 keV electron beam. Negative ions of H, ^{2}H (D), C, CH, C^{2}H, CN, and Si were monitored from an electrically gated area of less than 10% of the rastered area as a function of time. Under such conditions, we obtain a depth profile with a resolution corresponding to a Gaussian with a full width at half-maximum of ~15 nm. A helpful introduction to the SIMS analysis of polymers has been given by Schwarz et al.[14] By measuring the thickness of the polymer film using an ellipsometer, we convert sputtering time into depth (assuming a steady rate of sputtering). Combining this depth scale with information on the overall chemical composition and volume fraction of each block, we are able to convert the intensities of negative ions into the volume fraction of each block as a function of depth. The normalized CN^- signal was used to obtain a depth profile of the PVP spherical domains (micelles).

Results and Discussion

Mutual Diffusion of dPS-PVP114 and PS65 ($M_{dPS-PVP} > M_{PS}$).

Asymmetric diblock copolymers with a spherical domain structure form layers of spherical domains corresponding to (110) planes of body-centered cubic (bcc) structure on SiO_x surfaces.[4,13] The existence of this layered structure as well as the good depth profiling resolution of SIMS enables us to observe the mutual diffusion of homopolymer PS with the layers of spherical domains of the dPS-PVP114 diblock copolymers. Depth profiles of PS65/dPS-PVP114 bilayers after 0, 10, 20, and 30 min of annealing at 165 °C are shown in Figure 1. The depths of 0, 310, and 640 nm correspond to the initial interfaces between the vacuum and PS65, between PS65 and dPS-PVP114, and between dPS-PVP114 and silicon oxide, respectively. The PVP volume fraction in the unannealed bilayer oscillates with a period of about 30 nm due to the formation of the layered structure of spherical domains on the SiO_x substrate. The extreme maximum in the PVP volume fraction at the silicon oxide surface preceded at a smaller depth by a minimum in the PVP volume fraction is due to the formation of a brush of adsorbed dPS-PVP114 diblock copolymer on the SiO_x substrate.[4] The decay of the oscillation at the center of the unannealed

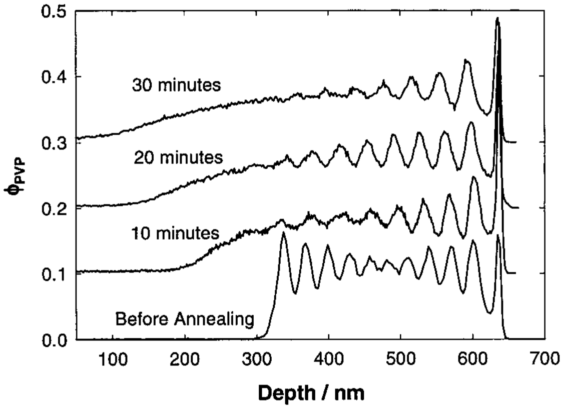

Figure 1. Volume fraction of PVP in a bilayer of PS65 and dPS-PVP114 as a function of depth after annealing for various times at 165 °C. The volume fractions are shifted upward by 0.1 relative to each other for easy comparison.

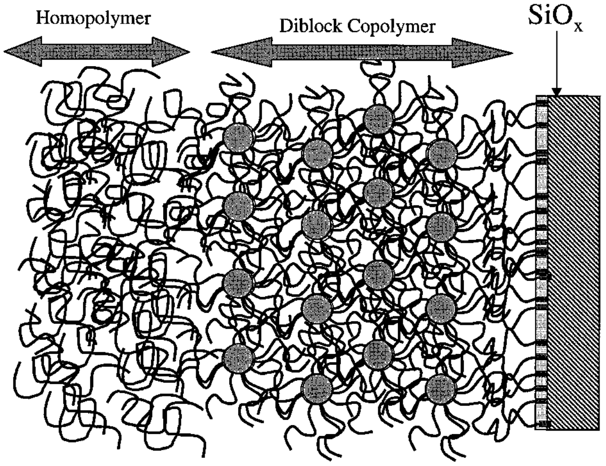

Figure 2. Schematic of the structure of PS-PVP and PS bilayer. Gray areas represent PVP domains, while white areas with dark polymer chains represent PS domains.

film may be due to the competition between the ordering starting from the two surfaces.[15] A peak at the vacuum surface (not shown) is due to an impurity that contains mass 26 fragments at the surface. A schematic picture of the structure of the film before annealing is illustrated in Figure 2. The brush of dPS-PVP114 is formed on silicon oxide, and dPS-PVP114 micelles are assembled on top of the brush so that the (110) plane of the bcc structure aligns parallel to the substrate.[4,13] Such a well-ordered layered structure provides a detailed way to observe the local structure of the diblock copolymer film during the mutual diffusion.

After annealing for 10 min, mutual diffusion takes place, and the spacing between PVP layers increases significantly, while the peaks in ϕ_{PVP} corresponding to these layers decay. The more the annealing time increases the more the spacing between layers of micelles increases. The peaks near the PS65 and dPS-PVP114 interface decay much faster than the peaks far from the interface. The observation nicely illuminates the local diffusion of each layer of spheres caused by dilution with homopolymer as a result of the mutual diffusion between PS65 and dPS-PVP114. The results show that PS65 rapidly diffuses into the dPS-PVP114 film and swells the layered structure of dPS-PVP114. The tracer diffusion coefficient of the dPS-PVP114 diblock copolymer in a mixture with PS of molecular weight 68 000 at a volume fraction of dPS-PVP114 of 0.5 is very small, ca. 1×10^{-15} cm^2 s^{-1} at 178 °C[6] (our annealing temperature is 165 °C). In a PS65/dPS-PVP114 mixture with a volume fraction of dPS-PVP114 greater than 0.5 (equivalent to $\phi_{PVP} = 0.05$ in Figure 1), the diffusion of whole micelles is essentially prohibited within times of 10−30 min. We clearly observe, however, that the positions of the layers of spheres move continuously toward the PS side of our diffusion couple.

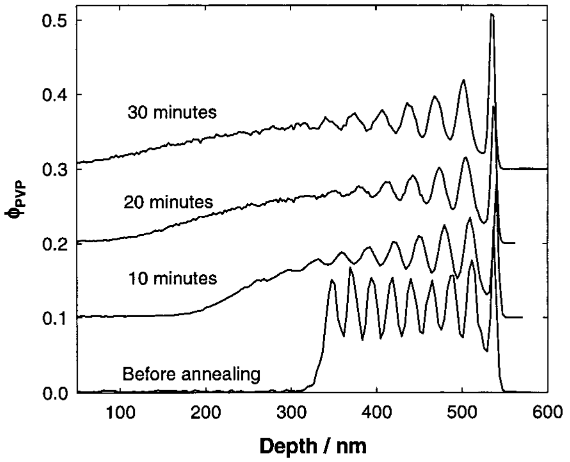

Figure 3. Volume fraction of PVP in a bilayer of PS65 and dPS-PVP77 as a function of depth after annealing for various times at 165 °C. The volume fractions are shifted upward by 0.1 relative to each other for easy comparison.

In Figure 3, the depth profiles for diffusion between PS65 and dPS-PVP77 is shown. The behavior of this couple is essentially identical to that of the couple of PS65 and dPS-PVP114. After annealing, PS and dPS-PVP interdiffuse rapidly, and the oscillation due to the layered structure of the PVP spheres decays as well. Surprisingly the movements of those PVP spheres toward PS65 are identical even though they have different molecular weights or, equivalently, different hydrodynamic radii of the PS-PVP diblock copolymer spheres. The self-diffusion coefficient of PS with M_w = 65 000 is 7×10^{-13} cm^2 s^{-1} at 165 °C,[11] while that of PS-PVP is no more than 1×10^{-15} cm^2 s^{-1},[3] which is an overestimate of the diffusion coefficient since it is at 178 °C and in the mixture of 50% diblock copolymer.[20] With such a big difference in diffusion coefficients between components of a couple, the mutual diffusion coefficient does not reflect the mobility of the slower component but is instead influenced by bulk flow across the initial interface. In this respect the mutual diffusion we measure is similar to that demonstrated by Green and co-workers,[11] where inert gold markers were placed at the initial interface between two PS films with very different molecular weights. It seems to us that the block copolymer micelles in our system act like the very high molecular weight PS in the experiment by Green et al. (We should note, however, that such similarity is limited to time scales much smaller than the time scale for activated hopping of single diblock copolymer chains.[6]) Therefore, we anticipate that diffusion of the faster PS65 homopolymer into an array of PS-PVP micelles across the interface dominates the mutual diffusion. When the intrinsic diffusion coefficient of the faster diffusant D_f is much greater than the diffusion coefficient of the slower diffusant D_s, one can extract the intrinsic diffusion coefficient of the faster diffusant from the velocity of the boundary movement. That is already qualitatively demonstrated by the fact that the molec-

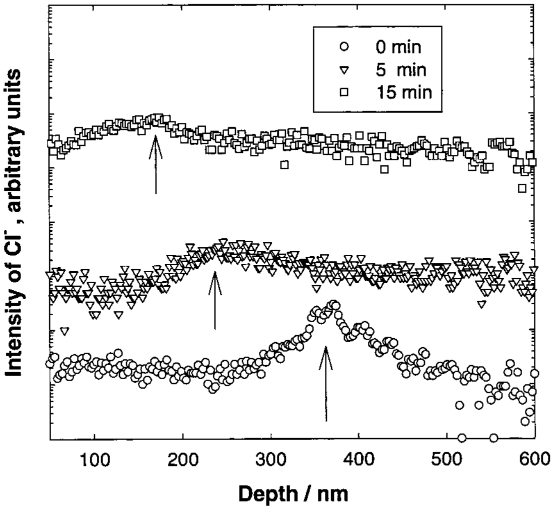

Figure 4. The movement of the Cl^- impurity peak with the moving interface between dPS-PVP and PS. (Note the logarithmic scale for the Cl^- signal.)

ular weight of the diblock copolymer does not affect the profile of the diffusion couple; the mutual diffusion is determined by the diffusion of PS65.

We examine such a hypothesis quantitatively below. The velocity of the marker (the velocity of bulk flow) at the boundary between the two layers with respect to a coordinate system whose origin is fixed at one end of the diffusion couple is given by[9]

$$V = (D_A - D_B)\nabla\phi \tag{1}$$

where D_A and D_B are the intrinsic diffusion coefficients of polymer A and polymer B, respectively, and ϕ is the volume fraction of polymer A. In the absence of interaction between polymer A and polymer B, i.e., $\chi_{AB} = 0$, D_A and D_B are given by

$$D_A = N_A D_A^* \left[\frac{(1-\phi)}{N_A} + \frac{\phi}{N_B}\right] \tag{2}$$

$$D_B = N_B D_B^* \left[\frac{(1-\phi)}{N_A} + \frac{\phi}{N_B}\right] \tag{3}$$

Under the condition where $D_A^* \gg D_B^*$ and $N_A \ll N_B$, V is given by

$$V = D_A^*(1-\phi)\nabla\phi \tag{4}$$

Equation 1 was solved numerically[11] to obtain the following expression:

$$\Delta x_m = C(D_A^* t)^{1/2} \tag{5}$$

where C is 0.48, Δx_m is the displacement of the interface (or markers), and t is time.

To trace the movement of the boundary between PS65 and PS-PVPs, we look for an impurity peak of a mass 35 negative fragment, which is most probably Cl^- from water used for floating the PS65 film to allow it to be picked up to make the diffusion couple. The amount of Cl^- at the interface is tiny; nevertheless, SIMS can detect such a fragment due to a very high sensitivity for Cl^-. We can use this Cl^- as a marker for the position of the initial interface and show an example of the movement of the marker peak in Figure 4. The interface represented by the impurity peak consistently moves toward PS65, suggesting bulk flow (swelling of the dPS-PVP) due to diffusion of PS into the dPS-PVP film. The square of the displacements of the Cl^- markers, Δx_m^2, is plotted against time, t, in Figure 5. The trend is well approximated as a straight line for both dPS-PVP114 and dPS-PVP77. Using eq 5, the intrinsic diffusion coefficient of PS65 is extracted from the slope in Figure 5. Here we treat PS65 as the faster diffusant (polymer A) of the couple and dPS-PVP as the slower diffusant (polymer B) in our notation for eqs 1−5. The extracted tracer diffusion coefficient D_{PS}^* is 6.8×10^{-13} cm^2 s^{-1}, while the self-diffusion coefficient of polystyrene is 7.0×10^{-13} cm^2 s^{-1}. This good agreement suggests the following: (1) The dPS-PVP micelles are practically immobile so that the mutual diffusion is controlled by the diffusion of PS65, which is by far the faster diffusant in the diffusion couple. (The assumption that $D_A \gg D_B$ is correct.) (2) The PS65 diffusing into dPS-PVP swells the ordered structure of the dPS-PVP micelles. This swelling cannot involve a free energy penalty, which would slow the diffusion. (The assumption $\chi_{AB} = 0$ is correct.) Consequently, the mutual diffusion is driven only by translational entropy; neither the enthalpic interaction between dPS-PVP micelles and PS65 nor any other excess free energy of mixing is important.

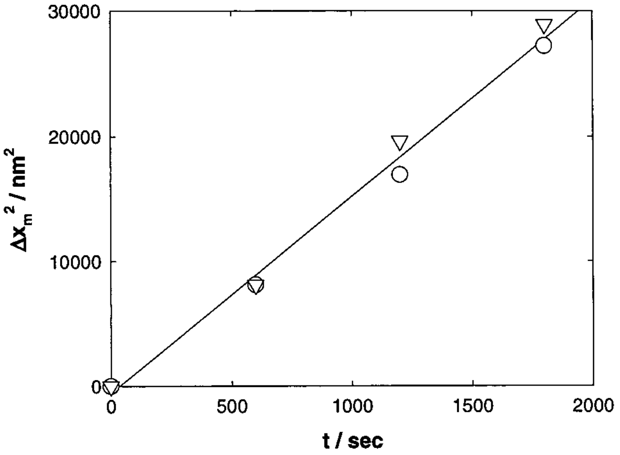

Figure 5. Square of the interface displacement $(\Delta x_m)^2$ vs time t. The slope of the straight line fit can be analyzed using eq 5 to give the tracer diffusion coefficient of the faster diffusing species, in this case PS65. The circles are the results from the couple of PS65 and dPS-PVP114, and the triangles are the results from the couple of PS65 and dPS-PVP77.

Mutual Diffusion of dPS-PVP114 and PS600 ($M_{dPS-PVP} < M_{PS}$). In the couples between the dPS-PVPs and PS65, the molecular weight of polystyrene is always smaller than that of the dPS-PVPs. By analogy to the symmetric lamellar diblock copolymers mixed with homopolymers, the mixture of dPS-PVP with PS65 is in the wet brush limit, in which PS homopolymers penetrate into the corona region and swell it. It is known that the mixtures of symmetric diblock copolymer and homopolymer with higher molecular weight than that of the diblock copolymer phase separate on a macroscopic scale.[16] In such a case, mutual diffusion vanishes at the spinodal within the coexistence curve. Even in the one-phase region, the mutual diffusion is supressed thermodynamically as one approaches the spinodal.[17] The depth profiles of the PS600 and dPS-PVP114 bilayer after annealing are shown in Figure 6. In contrast to the case of the PS65/dPS-PVP114 bilayer, PS600 does not diffuse into the dPS-PVP layer at all.

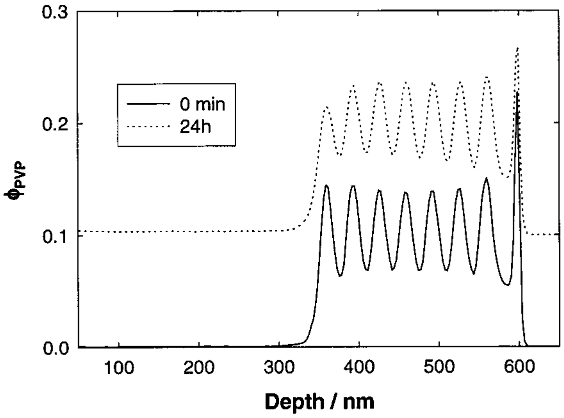

Figure 6. Volume fraction of PVP in a bilayer of PS600 and dPS-PVP114 as a function of depth after annealing for various times at 165 °C. The volume fractions are shifted upward by 0.1 relative to each other for easy comparison. No mutual diffusion between dPS-PVP114 and PS600 is observed.

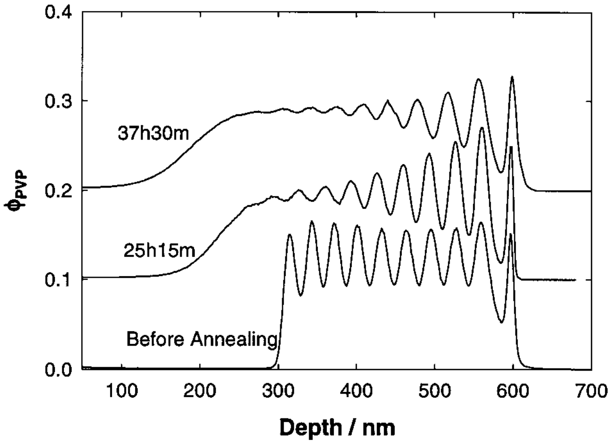

Figure 7. Volume fraction of PVP in a bilayer of PS600 and PS-PVP97 as a function of depth after annealing for various times at 165 °C. The volume fractions are shifted upward by 0.1 relative to each other for easy comparison. In this case PS600 can diffuse into PS-PVP97 and swell the ordered structure.

The system seems to be deep within a two-phase coexistence region. There are two possible explanations for this result. (1) Due to the interaction between dPS and PS (the isotopic $\chi_{\text{dPS-PS}}$), dPS-PVP micelles attract each other in PS.[19] (2) The system is in the so-called "dry brush (micelle)" regime ($M_{\text{dPS-PVP}} < M_{\text{PS}}$); PS does not penetrate into the dPS-PVP corona. Micelles stick together to reduce the total free energy due to the interfacial tension between the corona and the surrounding homopolymer.

To distinguish between these two possiblities, we performed the same mutual diffusion experiment using the couple of PS600 and PS-PVP97. In this couple there are no deuterated blocks or polymers. We are still able to detect the CN^- signal from the PVP blocks. The results from the mutual diffusion experiment on the PS600/PS-PVP97 bilayer are plotted in Figure 7. Surprisingly, PS600 diffuses into PS-PVP97 despite the fact that the corona molecular weight of PS-PVP97 is lower than that of dPS-PVP114. Therefore, the fact that PS600 does not diffuse into dPS-PVP must be due to the interaction between the PS and the dPS block of dPS-PVP. Straightforward calculations to find the critical χ parameter, χ_c for macroscopic phase separation, tell us that an individual dPS block of a single dPS-PVP diblock copolymer is not of high enough molecular weight to cause phase separation given the $\chi_{\text{dPS-PS}}$ measured by small angle neutron scattering (SANS).[19] The micelles of dPS-PVP, however, have much less translational entropy than single dPS-PVP chains and so behave as if they were very high molecular weight dPS. Under these circumstances the small χ between dPS and PS can be large enough to cause macroscopic phase separation. We assume the aggregation number of dPS-PVP in a micelle to be 270, that is, the number derived from the perfect bcc packing with a (110) spacing of 31.4 nm and volume fraction of the minority block of ~0.1. The total number of dPS segments in such a micelle is 270 000, while PS600 has about 6000 segments. We call the number of segments in a micelle N_a and that in PS600 N_b. The critical χ parameter for macroscopic phase separation, χ_c, is obtained from Flory–Huggins free energy[18] and is given by

$$\chi_c = \frac{(\sqrt{N_a} + \sqrt{N_b})^2}{2N_aN_b} \qquad (6)$$

From eq 6 we determine χ_c to be 1.1×10^{-4}. The temperature-dependent χ parameter between PS and dPS has been obtained by Bates and Wignall[19] using SANS and is given by

$$\chi = 0.20(\pm 0.01)T^{-1} - 2.9(\pm 0.4) \times 10^{-4} \qquad (7)$$

which means that $\chi = 1.5 \times 10^{-4}$ at 178 °C. The χ at 178 °C is larger than the critical χ_c computed. Therefore, macroscopic phase separation induced by aggregation of deuterated block copolymers into micelles is a reasonable explanation for the lack of mutual diffusion between the dPS-PVP and PS600 in our study.

We extract the intrinsic diffusion coefficient of PS600 from the experimental results on the PS-PVP97 and PS600 diffusion couple. In this case we could not measure the ^{35}Cl peaks because the annealing time was so long that the impurity peaks disappeared (presumably by diffusion of Cl^-). The diffusion coefficient of PS-PVP micelles in such a high molecular weight matrix (PS600) is expected to be slower than 5×10^{-16} cm^2 s^{-1} even in a dilute mixture, while that of PS600 is 3.5×10^{-14} cm^2 s^{-1}. For instance, in 37 h and 30 min, the micelles can diffuse only approximately $(Dt)^{1/2} = 80$ nm even for dilute micelles in PS600.

The front edge of the PS-PVP volume fraction versus depth profile in Figure 6 is sharper than that of dPS-PVP in Figure 1, suggesting the mobility of micelles of PS-PVP in a low molecular weight PS matrix is higher than that of micelles of PS-PVP in a PS600 matrix. A physical picture for the mutual diffusion of PS-PVP and PS is the following. As PS diffuses into the PS-PVP layer, the spherical domain structure of PS-PVP is swollen. In regions where the local volume fraction of the PS-PVP diblock is above ~0.5, PS-PVP micelles do not diffuse in any molecular weight of the surrounding PS. When the local volume fraction becomes less than 0.5, the PS-PVP micelles start to diffuse at a rate that is determined by the viscosity of the surrounding PS as well as the collision rate between micelles. Consequently, the PS-PVP spherical domains remain immobile until PS diffuses into them and dilutes them. This physical picture is compatible with the measurement by Koizumi et al.,[12] where the mutual diffusion between a 50% blend of PS-PI and PS, and PS was compared with that between pure PS−PI and PS, where $M_{PS} < M_{PS-PI}$. The premixed PS-PI with PS interdiffused faster with PS than pure PS-PI interdiffused with PS. This result was attributed to a concentration-dependent diffusion coefficient and a nonideal free energy of mixing. In our physical picture, premixed PS-PI will reach the volume fraction (~0.5), at which diffusion of micelles is possible, earlier than pure PS-PI; therefore, the apparent mutual diffusion is faster. The concentration dependence cannot be blamed on a nonideal free energy of mixing since we observe that the diffusion is driven by translational entropy even for the couple of PS and dPS-PVP when $M_{PS} < M_{PS-PVP}$. The origin of the concentration-dependent diffusion coefficient is rather the collisions and hydrodynamic coupling between micelles.

From the results in Figure 7 we can roughly estimate the movement of the initial interface by representing it by the front edge of the PVP peaks. We took the position of the initial interface to be where the front edge of the ϕ_{PVP} has its maximum slope. Since the broadening due to diffusion of each micelle is small, that treatment still gives a good approximation of the boundary movement. A rough estimate of the intrinsic diffusion coefficient of PS600 at 165 °C is 1 order of magnitude smaller than the self-diffusion of PS600. A possible interpretation is that the micelles have a slight attractive interaction in PS600 since PS600 is about 6 times higher than PS-PVP in molecular weight and therefore its free energy of mixing with the corona region of PS-PVP is reduced. The criterion for "wet brush" and "dry brush" conditions,[21] which holds for lamellar geometry $M_{PS} < M_{PS-PVP}$ or $M_{PS} > M_{PS-PVP}$, is not directly applicable for this spherical geometry, but in this extreme case where $M_{PS}/M_{PS-PVP} = 6$ we may be approaching a dry brush corona such that diffusion of PS600 into the PS corona region between micelles of PS-PVP will be retarded.

Mutual Diffusion of PVP-dPS-PVP145 and PS65 ($M_{PVP-dPS-PVP} > M_{PS}$). Another important class of block copolymers is the class of ABA triblock copolymers, which are of great practical importance as thermoplastic elastomers. Here we just briefly demonstrate the problem of mutual diffusion between PVP-dPS-PVP145 triblock copolymer and PS65. The length of the PVP-dPS-PVP145 triblock is about double that of the dPS-PVP77 diblock. The domain structure of the ordered triblock copolymer is very similar to that of the dPS-PVP77 diblock copolymer. The major difference is that, in the triblock copolymer, "bridging" copolymer chains[22] connect neighboring domains together. We chose PS65 so that there is no macroscopic phase separation due to the enthalpic interaction between dPS and PS. Bilayer diffusion couples of PS65 and PVP-dPS-PVP145 are measured under the same conditions as the PS65/diblock copolymer diffusion couples. The results are shown in Figure 8. Initially, PS65 diffuses into the triblock copolymer and swells the structure. Then, the swelling seems to stop and the structure does not change further even after very long annealing times. What happens here is similar to swelling of a cross-linked polymer by solvents. Entropy drives the short PS65 to diffuse into the PVP-dPS-PVP145 "gel" and swells the structure. At some volume fraction, the translational entropy gain balances with the elastic free energy loss caused by the stretching of bridging triblock copolymer chains between domains. For the triblock copolymer to swell further, the triblock copolymers bridging between spherical domains have to detach simultaneously. Since even the activation of one chain end costs a significant thermodynamic penalty, it is almost impossible for all the triblock copolymer chains bridging between two particular spherical microdomains to activate one of their end blocks simultaneously and allow the two spherical domains to separate. Therefore, the swollen spherical domain structure of the triblock copolymer persists indefinitely, although it may not be the true equilibrium structure.

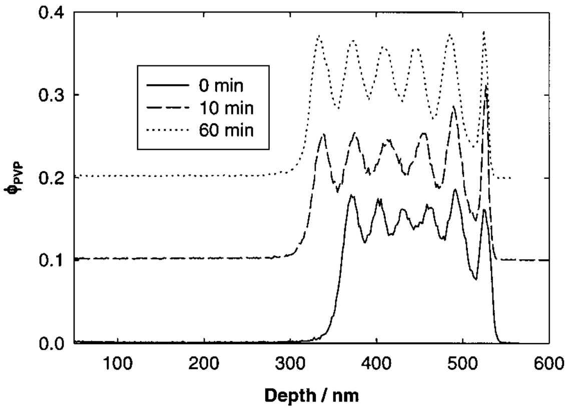

Figure 8. Volume fraction of PVP in a bilayer of PS65 and PVP-dPS-PVP145 as a function of depth after annealing for various times at 165 °C. The volume fractions are shifted upward by 0.1 relative to each other for easy comparison.

Summary

We observed mutual diffusion in diffusion couples between diblock copolymer and homopolymer.

(1) When the molecular weight of the homopolymer is sufficiently low, the homopolymers diffuse into a diblock copolymer layer and swell the ordered structure continuously. The mutual diffusion is dominated by the diffusion of homopolymer across the initial interface compensated by bulk flow of the swollen diblock copolymer. No evidence of an attractive or repulsive interaction between micelles is observed. Diffusive behavior of micelles is only observed at the edge of the moving initial interface where the diblock copolymer concentration is low.

(2) When the molecular weight of homopolymer is much higher than that of the diblock copolymers, subtle enthalpic interactions become important. Deuterium-labeled diblock copolymers should not be used since the interaction between deuterated and nondeuterated polymers is not negligible when the diblock copolymers form micelles. Using unlabeled diblock copolymers, we observed mutual diffusion and found that the behavior is qualitatively similar to that in the case of low molecular weight homopolymers. Homopolymers diffuse into the diblock copolymer film and swell the ordered structure. The velocity of the boundary movement is, however, slower than that expected on the basis of the diffusion of the homopolymer, suggesting the presence of an additional attractive interaction between micelles in this case.

(3) Triblock copolymers do not interdiffuse with homopolymers in the same way diblock copolymers do. Even when the molecular weight of homopolymer is sufficiently low, the presence of bridging chains between micelles limits mutual diffusion. The triblock copolymer film can absorb only a limited amount of homopolymer. The structure is swollen and reaches an "equilibrium"

where translational entropy of homopolymer and elastic free energy of such bridging chains balance.

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(15) Note: The quantization of thickness occurs even in a sphere-forming diblock copolymer thin film. When the film thickness is intermediate (ca. 200−500 nm), the formation of islands and holes is supressed by surface tension and the internal structure of the layered film is slightly distorted. In a fairly thick film, ∼1 μm, such distortions are absorbed by small strains of the internal structure and are too small to be detected experimentally.[13]
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(20) Note: The diffusion coefficient measured at a volume fraction of 0.5 occurs by a mechanism of activated hopping of individual block copolymer chains; therefore, the diffusion coefficient of whole micelles must be smaller than that.[6]
(21) Wet brush stands for a condition where a homopolymer penetrates into an adsorbed brush of diblock copolymer when the molecular weight of the homopolymer is smaller than that of the diblock copolymer. Dry brush describes the condition where a homopolymer does not penetrate into the adsorbed brush of block copolymer when the molecular weight of the homopolymer is larger than that of the diblock copolymer.
(22) The bridging chains may include entangled loops, in which both chain ends reside in the same spherical domain, forming a loop, but the chain is topologically entangled with another loop. “Bridging” and “entangled loops” cannot be easily distinguished.

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