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Self-Diffusion of Asymmetric Diblock Copolymers with a Spherical Domain Structure

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ABSTRACT: The temperature and molecular weight dependence of the self-diffusion coefficient of asymmetric diblock copolymers (polystyrene-*b*-2-vinylpyridine) (PS−PVP) with a spherical PVP domain structure has been measured by forward recoil spectrometry. The self-diffusion coefficient D is decreased by up to a factor of 10^{-4} by the existence of the ordered spherical microstructure. The normalized diffusion coefficient D/D_0, where D_0 is the diffusion coefficient of homopolystyrene with same molecular weight, depends strongly on the product of the interaction parameter χ between PS and PVP and N_{PVP}, the number of segments in the shorter PVP block, scaling approximately as $\exp(-1.2\chi N_{\mathrm{PVP}})$. Our results suggest that the diffusion process is governed by the thermodynamic barrier for moving PVP blocks from one spherical domain to another in contrast to the normal reptation mechanism seen for homopolymer self-diffusion.

Introduction

The diffusion process of diblock copolymers plays an important role in both the rheological properties of these materials and the kinetics of their microphase separation. The dynamics of block copolymers is closely related to their ordered microstructure as well as the architecture of the molecules themselves.

The existence of the ordered domain structure and, in turn, the Flory parameter χ creates a periodic potential field that will act on any diffusing block copolymer molecule. In a domain structure with long range order, this periodic potential field can be either anisotropic or isotropic. In a lamellar domain structure, for example, the block copolymer molecules can, in principle, diffuse parallel to the lamellae without any change in this potential[1] but will see a large potential variation if they diffuse perpendicular to the lamellae. Several papers have reported on the diffusion of nearly symmetric diblock copolymers melts and concentrated solutions as measured by forced Rayleigh scattering (FRS),[2−8] forward recoil spectrometry (FRES),[9] dynamic light scattering (DLS),[10,11] and nuclear magnetic resonance (NMR).[12] Near the order−disorder transition (ODT), there was no discontinuity of the diffusion coefficients of nearly symmetric diblock copolymers. This remarkable insensitivity of diffusion to the order−disorder transition has been observed in several different polymer systems by several different techniques.[4,5,9,12] Recent evidence suggests that such insensitivity arises in part due to the fact that diffusion is already slowed somewhat well above the ODT by composition fluctuation trapping. For asymmetric diblock copolymers, only a few attempts have been made to measure diffusion in the melt.[13,14] Those results are, however, limited to the case where the glass transition temperature and friction coefficients of the blocks differ greatly. In solutions where micelles are formed, large decreases in diffusion coefficient with increasing concentration of triblock copolymer have been observed.[15]

Here, for convenience, the ordered morphology is divided into three regimes: the weak segregation limit (WSL), the intermediate segregation regime (ISR), and the strong segregation limit (SSL). Below the ODT, the diffusion coefficient in the lamellar domain structure decreases as one progresses from the WSL to the ISR.[2] Anisotropy of diffusion in these lamellar block copolymers has also been demonstrated where a single crystalline lamellar texture was produced by shear alignment.[2] The diffusion coefficient is smaller in a direction normal to the lamellae than parallel to them. Nevertheless these results must be considered a lower limit for the anisotropy since, as the perpendicular diffusion coefficient decreases relative to the parallel one, defects such as dislocations can serve as short-circuiting paths and thus increase the perpendicular diffusion coefficient above its value in a perfect set of lamellae. These potential difficulties become more worrisome as the SSL is approached.

The spherical domain morphology of asymmetric copolymers has the advantage that it is insensitive to the presence of defects. There is no way for a block copolymer chain to move from one spherical domain to another without the short block penetrating the matrix surrounding the spheres. The diffusion should be isotropic and sensitive to the χN_{core} where N_{core} is the degree of polymerization of the short block that forms the spheres.

Accordingly we have concentrated on measuring self-diffusion in asymmetric diblock copolymers with a spherical domain structure. To measure very low diffusion coefficients and thus explore further into the SSL, we have used forward recoil spectrometry to depth profile isotopically labeled block copolymers. These labeled block copolymers have been allowed to diffuse for a certain time after they were initially deposited as a thin layer on a previously ordered block copolymer with the same spherical domain structure. As a result, we will report diffusion coefficients that are as much

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Table 1. Characteristics of the Block Copolymers (PS−PVP)

	M_n	f_{PVP}	N_{PS}	N_{PVP}
dPS−PVP32	32 000	0.113	273	34
hPS−PVP36	35 500	0.110	304	37
dPS−PVP46	46 400	0.095	404	42
hPS−PVP49	48 500	0.087	426	40
dPS−PVP77	76 800	0.146	631	107
hPS−PVP70	69 800	0.129	585	86
dPS−PVP114	114 000	0.116	971	126
hPS−PVP97	97 000	0.109	832	100

as 10 000 times lower than those of the corresponding homopolymers at the same temperature. We will analyze these results in terms of the free energy barrier that exists for motion of the short block from one spherical domain to another spherical domain.

Experimental Section

1. Materials. The diffusion couples are made up of poly(deuterated styrene-*b*-2-vinylpyridine) (dPS−PVP) and poly(styrene-*b*-2-vinylpyridine) (hPS−PVP) that have a short PVP block and thus a domain structure where the PVP forms a spherical core in a dPS or hPS matrix. The series of dPS−PVP and hPS−PVP diblocks are nearly matched in degree of polymerization, N, and PVP fraction, f_{PVP}. This system is particularly useful in that the glass transition temperatures of PS and PVP are the same; in addition the diffusion coefficients (at comparable N) and monomer friction coefficients of these polymers are similar in both magnitude and temperature dependence. Indeed symmetric PS−PVP diblock copolymers that are short enough to be disordered (above their ODT) have almost the same diffusion coefficient as that of PS of the same total N.[5]

Deuterated (d_8-) styrene (atomic fraction of ^{2}H > 0.98) was purchased from Cambridge Isotope Labs and purified with dibutylmagnesium, followed by high-vacuum transfer. Styrene (Aldrich) was first distilled using calcium hydride as drying agent and then further purified by the same scheme as d_8-styrene. 2-Vinylpyridine (Aldrich) was distilled from calcium hydride and then purified using a triethylaluminum heptane solution, followed by distillation at reduced pressure under an argon atmosphere. All of these monomers were stored under a high-purity argon atmosphere in securely sealed containers and used within a week. Sets of dPS−PVP and PS−PVP were synthesized via sequential living anionic polymerization in which styrene was polymerized first and 2-vinylpyridine second using tetrahydrofuran as a solvent under an argon atmosphere at −78 °C. The reaction was carried out using *sec*-butyllithium as initiator. Prior to the addition of 2-vinylpyridine, a sample of the polystyrene precursor was taken to determine the molecular weight of the dPS or hPS block. The molecular weight of the PS precursors was measured by gel permeation chromatography (GPC) using polystyrene standards as reference polymers. The block copolymers were also analyzed by GPC to determine their polydispersity index. In all cases the polydispersity index (M_w/M_n) was less than 1.12. The fraction f_{PVP} of PVP in the block copolymer was determined from the nitrogen content obtained by elemental analysis. The degree of polymerization of the entire block copolymer was then computed from that of the dPS or PS precursor and f_{PVP}. 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 average molecular weight of the entire block copolymer in thousands.

2. Sample Preparation. Diffusion couples consisting of 20 nm thick top layers of dPS−PVP copolymer on thick (>1 μm) bottom layers of hPS−PVP were prepared by the following procedure. These dPS−PVP and hPS−PVP copolymers were matched as closely as possible in M_n and f_{PVP}. Thick hPS−PVP layers were spun cast directly on smooth silicon substrates from toluene solutions to serve as a bottom layer. The bottom layers were preannealed under vacuum for at least 48 h at the temperature at which the subsequent diffusion would be carried out in order to allow an ordered spherical domain microstructure to form. The ordered nature of these structures was confirmed by transmission electron microscopy (TEM); TEM micrographs of this structure for two diblock copolymers are shown in Figure 1. Note that even the low molecular weight diblock copolymer, hPS−PVP36, has an ordered spherical domain structure at 150 °C. Next, thin (~20 nm thick) dPS−PVP layers were spun cast on glass or polished NaCl crystals from toluene solution and allowed to dry. The thickness of the top film was measured by ellipsometry while that of the thicker bottom film was measured using a profilometer. These thin films were then floated off onto the surface of a distilled water bath and picked up on top of the preannealed hPS−PVP bottom layers.

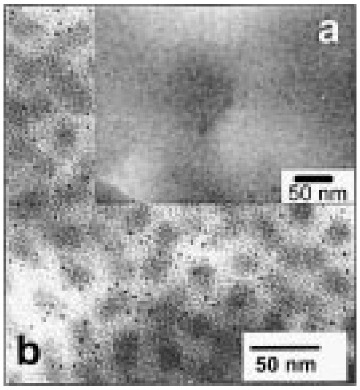

Figure 1. TEM micrographs of PS−PVP diblock copolymers in which the spherical PVP domains are stained by exposure to I_2 vapor. (a) hPS−PVP36, (b) hPS−PVP97.

The couples were then annealed under vacuum at various temperatures and allowed to diffuse. Annealing times were chosen so that the typical diffusion distance is from 300 to 500 nm so that the initial nonequilibrium morphology near the surface due to unannealed top layer (~20 nm) will have little impact on the results. We observed that the thin top layer is rapidly absorbed by the top layer of spherical PS−PVP micelles of the underlying, previously annealed film.[16] Nevertheless, the diffusing species are still far away from the silicon substrate so that this substrate should have negligible effect on diffusion.[17] In some cases, inverse diffusion couples were prepared in which thin hPS−PVP layers were placed on thick dPS−PVP films. The diffusion results from such couples were used to check whether any isotope effect, especially one binding dPS to the surface (dPS is known to have a lower surface energy than hPS[18]), exists that would complicate the diffusion results; none was found.

3. Preparation and Observation of Samples by TEM. TEM was used to ensure that all samples had a spherical microdomain structure. Thin (~50 nm) hPS−PVP copolymers were spun cast onto NaCl crystals from toluene solution and annealed at 150 °C for 3 days under vacuum. The film was floated off onto the surface of a water bath and subsequently picked up onto a gold grid. The film was then exposed to iodine vapor for 12 h to selectively stain the PVP phase. A JEOL 1200EX TEM operating at 120 keV was used for the morphology observations.

4. Diffusion Measurement. The deuterium volume fraction as a function of depth in annealed diffusion couples was determined by FRES as described elsewhere in detail.[19−22] The profile obtained is averaged laterally over the area irradiated by the ion beam (~1 mm × 5 mm). In the case of the inverse diffusion couples, the hydrogen volume fraction was determined and analyzed in a same way.[19] To extract diffusion coefficients, the concentration profiles obtained by FRES were fitted to the solution to the diffusion equation convoluted with a Gaussian factor which represents the instrumental depth resolution of 80 nm.

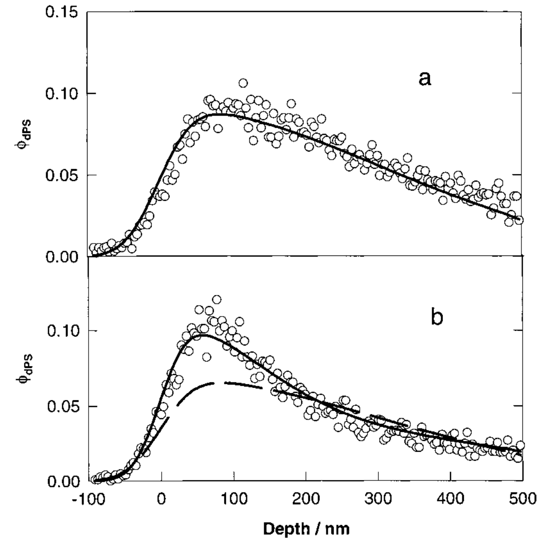

Figure 2. (a) Depth profile of dPS−PVP32 diblock copolymer diffusing into a well-ordered spherical domain structure of hPS−PVP36 at 159 °C. (b) Depth profile of dPS−PVP77 diblock copolymer diffusing into a well-ordered spherical domain structure of hPS−PVP70 at 178 °C. The dashed line is the best fit of the data to eq 1, i.e., to Fickian diffusion. The solid line shows a non-Fickian diffusion profile consisting of a weighted sum of three Gaussians as described in the text.

Results

Typical dPS−PVP volume fraction vs depth profiles from diffused diblock copolymer films are shown in Figure 2. The data for the lowest molecular weight set of diblocks dPS−PVP33/hPS−PVP36 diffused at 159 °C for 5 min are shown in Figure 2a. The solid line represents a fit to the solution of the diffusion equation for a thin top layer (thickness h) diffusing into an infinitely thick bottom layer.

$$\phi(x) = \frac{\phi_o h}{\sqrt{4\pi D t}} \exp\left(-\frac{x^2}{4Dt}\right) \tag{1}$$

Here ϕ_o is the initial volume fraction of the dPS−PVP diblock copolymer, D is the diffusion coefficient, x is the distance from the surface, and t is the annealing time. The result from eq 1 was convoluted with a Gaussian (full-width at half-maximum = 80 nm) which represents the instrumental depth resolution of FRES to obtain the solid line in Figure 2a.

Data for a longer diblock copolymer pair dPS−PVP77/hPS−PVP70 diffusing for 480 min at 178 °C are shown in Figure 2b. Despite the fact that this diblock copolymer pair is only a factor of 2 longer than that in Figure 2a and diffusion is taking place at a significantly higher temperature, a diffusion coefficient of 1×10^{-14} cm^2/s—more than a factor of 100 times lower than that for the dPS−PVP33/hPS−PVP36 of Figure 2a—is needed to produce the approximate fit to the data shown by the dashed line using eq 1. The fit is poor. We believe that this poor fit is caused by the residual polydispersity of the block copolymer and the resulting variation within the sample of N_{PVP} of the dPS−PVP77 block copolymer. As we show below, the self-diffusion coefficient of the diblock copolymer decreases exponentially with χN_{PVP} in the higher N_{PVP} range. Consequently a rather small polydispersity in N_{PVP} will translate into a large dispersion in diffusion coefficient of the higher N_{PVP} block copolymers and will be reflected as a non-Fickian diffusion profile. To analyze these data we fitted the profiles to a sum of three Gaussian solutions (eq 1) with different diffusion coefficients and an initial volume fraction ϕ_i such that $\sum\phi_i = 1$ and report an average diffusion coefficient given by

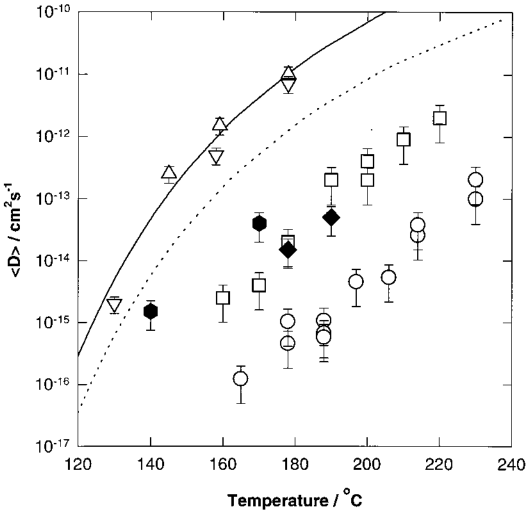

Figure 3. Self-diffusion coefficients as a function of temperature for dPS−PVP32 (upward-pointing triangle), dPS−PVP46 (downward-pointing triangle), hPS−PVP70 (hexagon), dPS−PVP77 (square), hPS−PVP97 (diamond), and dPS−PVP114 (circle). Open symbols represent dPS−PVP diffusion into hPS−PVP. Filled symbols represent hPS−PVP diffusion into dPS−PVP.

$$\langle D\rangle = \sum_i \phi_i D_i \tag{2}$$

The solid line in Figure 2b is such a fit with $\phi_1 = 0.3$, $\phi_2 = 0.4$, $\phi_3 = 0.3$, $D_1 = 5 \times 10^{-15}$ cm^2/s, $D_2 = 1 \times 10^{-14}$ cm^2/s, and $D_3 = 3 \times 10^{-14}$ cm^2/s. A more detailed analysis of the diffusion profile expected for dPS−PVP with a slightly polydisperse PVP block gives results in reasonable agreement with the observed profile.[16]

The average self-diffusion coefficients, $\langle D\rangle$, of the various PS−PVP diblock copolymers are plotted versus annealing temperature in Figure 3. The error bars correspond to the range of D_1 and D_3 used in eq 2. Also shown in this figure are the self-diffusion coefficients of polystyrene with (a) an N corresponding to the smallest N (= 300) of the diblock copolymers (solid line) and (b) an N corresponding to the largest N (= 1100) of the diblock copolymers (dashed line).

The block copolymer with the lowest molecular weight and shortest PVP block, dPS−PVP32, has a $\langle D\rangle$ very similar to that of polystyrene of same molecular weight, despite the fact that it is well ordered into a spherical domain structure as observed by TEM. A very similar result was found by Eastman and Lodge[5] for a short symmetric diblock copolymer of PS and PVP that formed an ordered lamellar structure. The similarity of the $\langle D\rangle$ to that of PS is expected if the monomer friction coefficients of PS and PVP are similar and if the ordered domain structure produces only a weak barrier to the diffusion of the short dPS−PVP32 diblock copolymer.

On the other hand, $\langle D\rangle$ of the diblock copolymer, dPS−PVP114, with the highest molecular weight and longest PVP block is much lower than that of polystyrene with the same M_w. The diffusion of this diblock copolymer

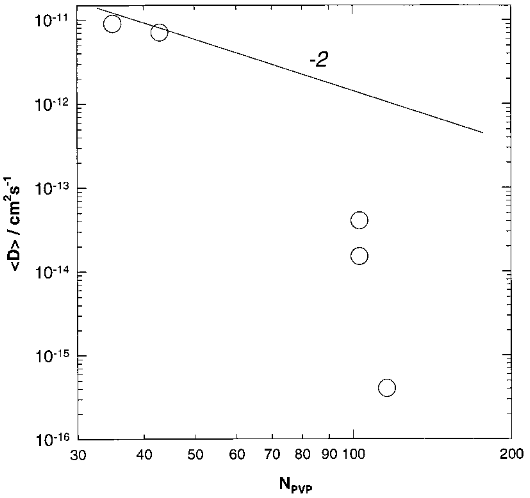

Figure 4. Self-diffusion coefficients at 178 °C plotted against the number of segments of PVP core block.

is slower by a factor of approximately 10^4. The temperature dependence of its diffusion is also different from that of PS and cannot be fit, as can the $\langle D\rangle$ of PS, by the Vogel-Fulcher or WLF form.[23] Both the magnitude of $\langle D\rangle$ and its temperature dependence thus suggest that the resistance to diffusion in the diblock copolymer does not originate in the segmental motion of the chain but in the thermodynamic barrier to copolymer motion presented by its spherical domain microstructure.

The other diblock copolymers, those with intermediate molecular weights between dPS−PVP32 and dPS−PVP114, have intermediate values of $\langle D\rangle$, but in all cases these are considerably lower than the polystyrene homopolymer of equal degree of polymerization. For these block copolymers, as for the dPS−PVP114, it seems that the thermodynamic barrier to block copolymer motion due to the spherical domain microstructure is important.

Another way to demonstrate the strong effect of the ordered microstructure on diffusion is to plot the logarithm of $\langle D\rangle$ versus the logarithm of N_{PVP} at a constant temperature, 178 °C, as shown in Figure 4. Since all the block copolymers have an $f_{PVP} \approx 0.1$, the slope of this plot would be −1 if the diffusion were controlled by Rouse motions of the polymer chains and −2 if the diffusion were controlled by reptation. The N_{PVP} dependence of the longer block copolymers is much stronger than would be predicted from either the Rouse or reptation models.

Discussion

In discussing the possible mechanisms of self-diffusion of the diblock copolymers, one can distinguish two possible mechanisms, at least in theory. One such mechanism is diffusion by motion of individual block copolymer chains so that the PVP block that forms part of the core of one spherical domain “hops” from that domain to another spherical domain. A second mechanism is by motion of an entire spherical domain (“melt micelle”) in the ordered domain structure. This second mechanism is the formal equivalent of the diffusion of atoms in an ordered solid with diffusion of micelles replacing diffusion of atoms. While diffusion of whole micelles in a homopolymer melt has been observed,[14,24] it seems extremely unlikely in the ordered spherical domain structure of the block copolymer. Micelle “vacancy” or “interstitial” diffusion mechanisms would seem to be ruled out for such large aggregates on purely energetic grounds, and “ring” mechanisms would carry with them such a very strong entropic penalty for the concerted motion necessary as to make them prohibitively improbable.[25] Therefore in what follows we discuss the first possible mechanism: diffusion of individual block copolymer chains.

If an individual block copolymer chain moves so that its short PVP block moves from the core of one spherical domain to another, this block must pass through a matrix consisting of PS block chains. For the case where the PS matrix has a PS volume fraction = 1, i.e., in the strong segregation limit, and the PVP block is so short that it must be entirely surrounded by PS segments as it passes from core to core, the copolymer will have to surmount a free energy barrier corresponding to the unfavorable interaction of N_{PVP} PVP segments with PS every time it moves from one core to another. This free energy barrier will be $\Delta G^* = \chi N_{PVP} k_B T$, where χ is the Flory segmental interaction parameter between PVP and PS. For thermal activation over this barrier,[26] $\langle D\rangle$ should be given by

$$\langle D\rangle \sim D_0 \exp(-\alpha\chi N_{PVP}) \tag{3}$$

where the prefactor D_0 is the self-diffusion coefficient of the dPS−PVP chain in a (hypothetical) disordered PS−PVP phase at the temperature of our interest and α is a constant of order 1. The proportionality constant in eq 3, which we do not include in our equation, should depend on the shape of the potential and the mechanism of chain motion (i.e., Rouse or reptation) in the absence of the potential.[26] Following the arguments given above, we set D_0 equal to D for PS of the same degree of polymerization as the block copolymer. The temperature-dependent Flory parameter $\chi(T)$ for PS−PVP is given by

$$\chi(T) = -0.033 + (63/T) \tag{4}$$

from measurements of the segregation of similar asymmetric dPS−PVP diblock copolymers to interfaces between PS and PVP.[27] In eq 3, each segment of free PVP block is assumed to make contact with the surrounding PS corona in the activated state. While it is possible that the PVP block could collapse on itself to form a tiny sphere,[28] causing ΔG^* to scale as $\chi^{1/2}N_{PVP}^{2/3}$ instead of as χN_{PVP}, our calculation outlined in the Appendix shows that such collapse is not likely in our experimental range of χ and N_{PVP}.

According to eq 3 a plot of the logarithm of $\langle D\rangle/D_0$ versus χN_{PVP} should yield a straight line. Such a plot containing the data for all copolymers and all temperatures is shown in Figure 5. Note that all the data for the longer diblock copolymers, those with $\chi N_{PVP} > 9$, do indeed cluster closely around a single line with a slope of about −1.2. Note also that data for hPS−PVP diblock copolymers diffusing into dPS−PVP ordered spherical domain structures, which are represented by the solid points, follow the same trend. Therefore we can show that our results are not caused by the labeling of the diffusing polymer with deuterium or hydrogen, i.e., there is no surface isotope effect giving rise to an apparent slower diffusion of the dPS−PVP species.

Finally we note that the data for the shortest diblock copolymer, that with $\chi N_{PVP} \approx 4$, falls well below the extrapolation of the line that describes the larger diblock

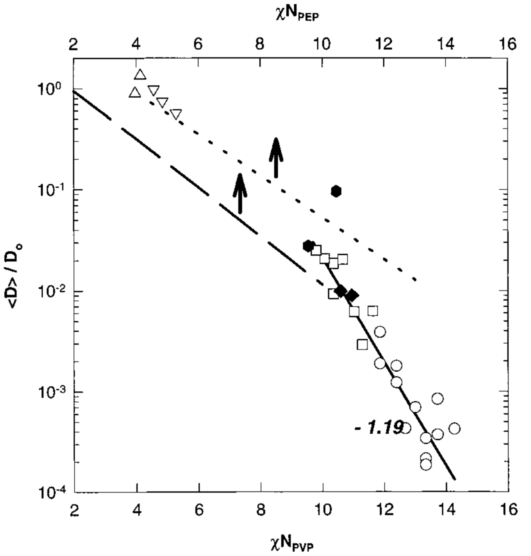

Figure 5. Universal χN_{PVP} dependence of the normalized diffusion coefficients $\langle D\rangle/D_0$, where D_0 is the diffusion coefficient of polystyrene with same degree of polymerization as the diblock copolymers at the temperature. Symbols are the same as in Figure 3. The dotted and dashed lines represent the data of Lodge and co-workers on the symmetric PEP−PEE diblock copolymer diffusing parallel to and perpendicular to the lamellae, respectively.

copolymers. This extrapolation would be unphysical in any case since it would suggest that the ordered diblock copolymer would diffuse faster than the disordered diblock copolymer (or the PS homopolymer). Clearly as χN_{PVP} decreases, the controlling resistance to diffusion must change from an "activated hopping" of individual block copolymer chains controlled by the free energy barrier to motion of the PVP block through the PS block matrix to the normal resistance that any polymer chain experiences due to its interaction with neighboring chains. This transition seems to occur somewhere between $\chi N_{\mathrm{PVP}} = 5$ and $\chi N_{\mathrm{PVP}} = 9$. It is instructive to compare our results with those of Lodge and co-workers[2] on diffusion of symmetric poly(ethylenepropylene)−poly(ethylethylene) (PEP−PEE) diblock copolymers (Figure 5). The dotted line represents their data for diffusion parallel to the lamellae while the dashed line represents their data for diffusion perpendicular to the lamellae. To be consistent with our treatment, we have plotted their data versus χN_{PEP} (top scale). Their data can also be represented by eq 3 (as they observed in their original paper) but the value of α that must be used to describe either the parallel or perpendicular diffusion is about 0.5, much smaller than the value of α (≈1.2) we need to fit our data for the asymmetric dPS−PVP diblock copolymers with $\chi N_{\mathrm{PVP}} > 9$.

One possible reason for the difference in the Lodge data for symmetric diblock copolymers and ours for asymmetric ones is simply that the values of χN_{PVP} explored by us are larger than χN_{PEP} explored by Lodge and co-workers. (The extent of the dotted and dashed lines in Figure 5 represents the extent of their data.) It is certainly possible, and perhaps even likely, that dPS−PVP asymmetric diblock copolymers with χN_{PVP} between 6 and 9 will have $\langle D\rangle/D_0$ ratios that are approximately described by a line parallel to, but above, the dashed line in Figure 5. But there is another possible cause for the difference based on the size of the PVP block relative to the PS region it must diffuse through to reach another spherical core. Except near the interface of the spheres, the PVP block experiences almost pure PS surroundings as it diffuses. Consequently its free energy depends little on the internal coordinates of its chain. The blocks of the PEP−PEE symmetric diblock copolymer are much longer relative to the lamellae through which they must diffuse, and their free energy as they are dragged through unfavorable lamellae can be expected to depend significantly on internal chain coordinates. A extreme example of this dependence is the mechanism first proposed by Helfand[29] in which he showed that it was energetically favorable for a symmetric block copolymer to diffuse in a direction perpendicular to its lamellae by stretching the chain of the block diffusing through the unfavorable domain so that not all the segments of that block are simultaneously exposed to the unfavorable segment−segment interaction. While this mechanism (which should only be valid in the extremely strong segregation limit) may not apply directly to the results of Lodge and co-workers, the effects of changing the internal chain coordinates should be much more important for symmetric as opposed to asymmetric diblock copolymers.

Conclusions

The self-diffusion of asymmetric dPS−PVP diblock copolymers with a spherical domain microstructure can be extremely slow, being reduced by nearly a factor ($\langle D\rangle/D_0$) of 10^{-4} with respect to the diffusion of PS homopolymer with the same degree of polymerization. We demonstrate that the reduction faction $\langle D\rangle/D_0$ scales as $\exp(-1.2\chi N_{\mathrm{PVP}})$ for copolymers with long enough PVP blocks and suggest that this form comes about because the diblock copolymer diffusion process is controlled by the activated hopping of individual block copolymer chains with an "activation free energy", χN_{PVP}, which is the thermodynamic penalty a PVP core block must pay being in a PS corona region.

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Appendix

Does the PVP Block Coil Collapse in PS? The configuration of the PVP block coil in the PS corona may not be a Gaussian coil in order to reduce the unfavorable contact between PVP and PS segments. The PVP block coil may collapse in the PS corona to reduce such contact. We derive the free energy of this case and compare it to the full contact free energy, χN_{core}, and the degree of polymerization of the core block, N_{core}, which in our case is N_{PVP}.

To derive the free energy of collapsed coil, we assume a spherical shape for the coil. The radius of this sphere is given by

$$R = \left(\frac{3}{4\pi}\frac{N_{\mathrm{core}}}{\rho_0}\right)^{1/3} \tag{A1}$$

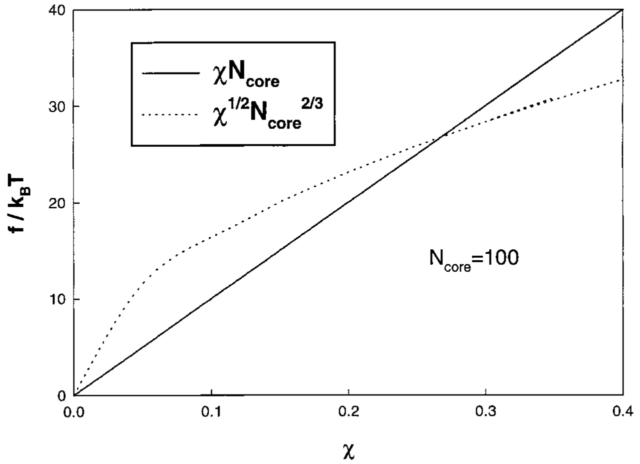

Figure 6. Comparison of the free energy of the collapsed coil (eq A3) with the full contact free energy (χN_{core}).

where R is the radius of the sphere and ρ_0 is the number density of core block segment. The interfacial energy between this sphere and its surroundings is assumed to have the Helfand–Tagami form[30] appropriate for the strong segregation limit. This interfacial energy is given by

$$\frac{\gamma_0}{k_{\mathrm{B}}T} = a\rho_0\sqrt{\frac{\chi}{6}} \tag{A2}$$

where γ_0 is the interfacial energy, a is the segment length, and χ is the interaction parameter. Using this interfacial energy, the single-chain sphere with surface area of $4\pi R^2$ has a free energy per chain, f, given by

$$\frac{f}{k_{\mathrm{B}}T} = 4\pi\left(\frac{3}{4\pi}\frac{N_{\mathrm{core}}}{\rho_0}\right)^{2/3} a\rho_0\sqrt{\frac{\chi}{6}} \tag{A3}$$

We have not taken into account the entropies of configuration and packing as well as bending energy of the core chain to form a sphere. Therefore, the free energy given here should be a lower limit for the actual free energy of the sphere. Equation A3 shows that the free energy of the collapsed coil should scale as $\chi^{1/2}N_{\mathrm{core}}{}^{2/3}$ rather than χN_{core} appropriate for the uncollapsed coil. We compare the free energy in eq A3 with full contact free energy χN_{PVP} with the parameters of our system. In Figure 6 we show a comparison of the free energy of the collapsed sphere with full contact free energy χN_{core} using $\rho_0 = 6$ nm^{-3}, $a = 0.67$ nm, and $N_{\mathrm{core}} = 100$—parameters that are characteristic of polystyrene. Our χ range is from about 0.09 to 0.12 for our experimental temperature range of 130~230 °C. Over this range the collapsed coil free energy is always higher than the full contact free energy. We therefore use the full contact free energy in computing the free energy barrier to diffusion of our block copolymer chain, leading to eq 3.

References and Notes

(1) Note, however, that highly entangled block copolymers may diffuse parallel to the lamellae by executing some motion perpendicular to the lamellar interface.[2]
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