Diffusion of Triblock Copolymers in a Spherical Domain Structure

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ABSTRACT: Self-diffusion and tracer diffusion (diffusion in a fixed diblock copolymer matrix) of ABA triblock copolymers of styrene and 2-vinylpyridine (PVP-PS-PVP) have been measured in a spherically ordered domain structure and compared to that of diblock copolymers. In most of the cases, the self-diffusion and tracer diffusion of the triblock copolymer is controlled by a "walking" diffusion mechanism in which one PVP end block is activated at a time, giving rise to an exponential decrease in D/D_0 as $\exp(-\chi N_{\mathrm{PVP}})$, where D is the diffusion coefficient of the triblock copolymer, D_0 is the diffusion coefficient of the triblock copolymer in a (hypothetical) disordered phase, χ is the interaction parameter, and N_{PVP} is the number of segments in each PVP end block. The normalized diffusion coefficients of the triblock copolymers are not so different from those of diblock copolymers with the same χN_{PVP}. Nevertheless, if one compares the diffusion of triblock and diblock copolymers with the same total molecular weight, the triblock copolymer diffuses much faster. However, when $\chi N_{\mathrm{PVP}} < 6$ and the spacing of the matrix domains is much larger than the natural domain spacing of the triblock copolymer domains, the normalized tracer diffusion coefficient D/D_0 decreases exponentially as $\exp(-2\chi N_{\mathrm{PVP}})$. In this case we propose that the diffusion occurs by both end blocks being activated at the same time, a mechanism we call "double activation".

Introduction

Asymmetric diblock or triblock copolymers with relatively short minority blocks form an ordered body centered cubic (bcc) structure of spherical domains in contrast to the hexagonal cylinder, lamellar, and bicontinuous structures formed by more nearly symmetric diblock or triblock copolymers.[1] The diffusion mechanism of diblock copolymers in a bcc "crystal" is quite different from that of atoms in a bcc atomic solid, since no mechanism analogous to a vacancy or interstitial diffusion is possible for the block copolymers.[2]

In fact a better analogy is the case of diffusion of uncharged colloidal suspensions. Such suspensions show negligible diffusion in a "crystalline" state and only very slow diffusion at lower volume fractions of colloid where the colloidal crystals melt to form a colloidal fluid. This slow diffusion of individual colloidal particles is due to the "cage effect" of the surrounding particles as well as the hydrodynamic interaction between particles.[3] A similar very slow diffusion of individual spherical micelle domains has been observed for mixtures of diblock copolymers and homopolymers but is not observed for the ordered bcc structure.[4] Such diffusion of triblock spherical domains must be even less likely due to the bridging of triblock copolymers from one domain to the next. The other possible diffusion mechanism for diblock copolymers in a spherical domain structure is by diffusion of single diblock copolymer chains.[5] A single diblock copolymer chain can hop from one spherical domain to another by surmounting a free energy barrier ΔF without disturbing the overall spherical domain structure. This "activated hopping" diffusion decreases exponentially with $\Delta F/k_{\mathrm{B}}T$, where k_{B} is Boltzmann's constant and T is temperature. ΔF is given in general by some function of the product of an interaction parameter between immiscible block segments, χ, the number of total segments, N, and the fraction of the minority block, f. When the minority block is very short, so that a spherical domain structure is formed, $\Delta F \approx \chi N f k_{\mathrm{B}}T$ or equivalently $\Delta F \approx \chi N_{\mathrm{core}} k_{\mathrm{B}}T$, where N_{core} is the number of segments in a minority block. This expression for ΔF is a good approximation since the core block experiences full contact with the surrounding corona block in an activated state, where the total number of contacting segments is approximately N_{core} and the excess free energy of each contact is $\chi k_{\mathrm{B}}T$. The activated hopping mechanism of self-diffusion of asymmetric poly(styrene-*b*-2-vinylpyridine) (PS-PVP) diblock copolymers has been observed[5] in diblock copolymer melts. Deuterium labeled PS-PVP (dPS-PVP) was used as a tracer for forward recoil spectrometry (FRES), which can detect the depth profile of the deuterated diblock copolymers. Similar results are observed for the diffusion of symmetric diblock copolymers with a lamellar structure.[6−8] Both symmetric and asymmetric diblock copolymers have self-diffusion coefficients that decrease exponentially with χN.

ABA triblock copolymers show phase behavior similar to that of diblock copolymers depending on the fraction f and the product χN.[9,10] The conformation of individual triblock copolymers, however, must differ from that of diblock copolymers. Triblock copolymers either bridge between neighboring spherical domains or make a loop with both chain ends in a same spherical domain. One might expect that the diffusion of triblock copolymers would differ greatly from that of diblock copolymers due to such differences in their chain topology. We report here diffusion measurements of asymmetric PVP-PS-PVP triblock copolymer in a bcc ordered spherical domain structures. Both self-diffusion and tracer diffusion (of triblock copolymer in diblock copolymer matrixes) show that under most circumstances triblock copolymers and diblock copolymers with the same end block length diffuse at similar rates; i.e., activated hopping of single end blocks is the rate controlling step

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Table 1. Characterization of Polymers

code tracers	M_n	f_{PVP}	code matrix	M_n	f_{PVP}
dPS-PVP32	32 000	0.113	PS-PVP36	35 500	0.110
dPS-PVP46	46 400	0.095	PS-PVP49	48 500	0.087
dPS-PVP78	78 200	0.056	PS-PVP70	69 800	0.130
dPS-PVP77	76 800	0.146	PS-PVP97	97 000	0.110
dPS-PVP114	114 000	0.116	PS-PVP296	296 000	0.088
PVP-dPS-PVP67	66 800	0.132	PVP-PS-PVP67	67 100	0.076
PVP-dPS-PVP78	78 400	0.090	PVP-PS-PVP84	84 300	0.108
PVP-dPS-PVP130	129 000	0.084	PVP-PS-PVP101	101 000	0.152
PVP-dPS-PVP135	135 000	0.179	PVP-PS-PVP151	151 000	0.170
PVP-dPS-PVP170	170 000	0.146			

in diffusion. This discovery implies that triblock copolymer chains normally must bridge from one domain to another to diffuse.

Experimental Section

Materials. We synthesized both deuterated and nondeuterated poly(styrene-*b*-vinylpyridine) diblock (dPS-PVP and PS-PVP) and triblock copolymers (PVP-dPS-PVP and PVP-PS-PVP), where the details of the anionic synthesis of the diblock copolymer have been described elsewhere.[5] Metallic potassium was reacted with α-methylstyrene in tetrahydrofuran at 0 °C to provide a difunctional initiator for making the triblock copolymer. α-Methylstyrene was purified with dibutylmagnesium and distilled prior to the reaction. Except for the difunctional initiator, the polymerization of PVP-PS-PVP and PVP-dPS-PVP triblock copolymers was carried out using the same method as that for PS-PVP diblock copolymers previously described.

A great advantage of the PS-PVP system is that PS and PVP have almost the same friction coefficients[12] as well as the same glass transition temperatures; therefore, we are able to isolate the effects of the ordered domain structures on the diffusion without having to correct for a difference in the friction coefficients of the two blocks. The characteristics of copolymers and homopolymer used in this study are listed in Table 1. The polydispersity indices (M_w/M_n) of diblock copolymers are less than 1.12, and those of triblock copolymers are less than 1.16, where M_w is the weight average molecular weight and M_n is the number average molecular weight.

Sample Preparation. Diffusion couples consisting of 20 nm thick top layers of dPS-PVP diblock copolymer or PVP-dPS-PVP triblock copolymer on thick (>1 μm) bottom layers of PS-PVP or PVP-PS-PVP were prepared by the following procedure. Two sets of experiments were designed. (1) Self-diffusion experiments: The pairs of dPS-PVP and PS-PVP diblock copolymers and the pairs of PVP-dPS-PVP and PVP-PS-PVP triblock copolymers were matched as closely as possible in the number average molecular weight M_n and PVP fraction f_{PVP}. (2) Tracer diffusion experiment: A high molecular weight PS-PVP diblock copolymer (PS-PVP296), which had a $\chi N \approx 300$ (in the strong segregation regime), was chosen as the matrix diblock copolymer. The dPS-PVP diblock copolymers and PVP-dPS-PVP triblock copolymers were diffused into the matrix.

The following procedure was applied for both the self-diffusion and tracer diffusion experiments: Thick PS-PVP or PVP-PS-PVP layers were 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. Next, thin ($\sim$20 nm thick) dPS-PVP or PVP-dPS-PVP thin films were spun cast from toluene solution on glass or polished NaCl crystals 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. The thin top films were then floated off onto the surface of a distilled water bath and picked up on top of the preannealed PS-PVP or PVP-PS-PVP bottom layers.

The couples were then annealed under vacuum at various temperatures and allowed to diffuse. Annealing times were chosen so that the typical diffusion distance was from 300 to 500 nm, so that the initial nonequilibrium morphology near the surface due to an unannealed top layer ($\sim$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.[13] Even after diffusing 500 nm, the diffusing block copolymers are still far away from the silicon substrate so that this substrate should have negligible effect on the diffusion.[14,15]

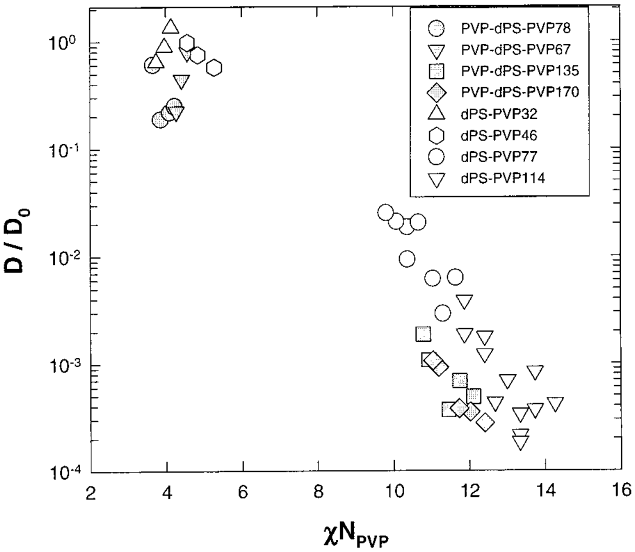

Figure 1. Dependence of normalized self-diffusion coefficient D/D_0 as a function of the thermodynamic barrier to diffusion χN_{PVP}. Gray symbols are the diffusion coefficients of PVP-PS-PVP triblock copolymers, while white symbols are that of diblock copolymers.

Diffusion Measurement. The deuterium volume fraction as a function of depth in the annealed diffusion couples was determined by forward recoil spectrometry (FRES), as described elsewhere in detail.[16–19] The profile obtained is averaged laterally over the area irradiated by the ion beam ($\sim$1 mm × $\sim$5 mm). 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. The details of the analysis are described elsewhere.[5]

Results

Self-Diffusion of Triblock Copolymers. Self-diffusion coefficients of PVP-PS-PVP triblock copolymers are plotted in Figure 1 along with the results of PS-PVP diblock copolymers, results which have already been published in our previous paper.[5] Each self-diffusion coefficient D was normalized by the hypothetical diffusion coefficient D_0 in a disordered phase. The value of D_0 was taken as the diffusion coefficient of polystyrene[16] for our particular PS-PVP diblock and PVP-PS-PVP triblock copolymers since the friction coefficients of PS and PVP are almost the same.[12] We should note here that D_0 has a WLF or Vogel−Fulcher−Tammen temperature dependence and depends on molecular weight as M_n^{-2}. The normalized diffusion coefficient, D/D_0, is plotted in Figure 1 against the free energy barrier χN_{PVP}, where χ is the interaction parameter between PS and PVP and N_{PVP} is the number of monomers in a single PVP block of a triblock copolymer or in the PVP block of a diblock copolymer. With this definition of N_{PVP}, the triblock copolymers are twice as long as the diblock copolymers at the same χN_{PVP}. The temperature dependence of χ between PS and PVP [based on the PVP-mer volume] is given by eq 1.[21]

$$\chi = -0.033 + \frac{63}{T} \qquad (1)$$

The white symbols in Figure 1 represent diblock copolymer self-diffusion coefficients, and the gray symbols represent triblock copolymer self-diffusion coefficients. In the region where χN_{PVP} is between 3 and 6, there is a relatively large scatter of D/D_0 since the diffusion coefficients are close to the upper (faster) limit of the FRES depth profiling measurement. At larger χN_{PVP} (>10), the slope of the scattered data on the log(D/D_0) vs χN_{PVP} plot is approximately −1 for both diblock and triblock copolymers. The D/D_0 values of the triblock copolymers in this range are about a factor of 3 smaller than those of the diblock copolymers. Unfortunately, we were not able to prepare a pair of block copolymers that fill the gap of χN_{PVP} between 6 and 10 due to difficulties in controlling the fractions of the blocks, f_{PVP}, and total molecular weights for small quantities of copolymers.

Tracer Diffusion of Diblock and Triblock Copolymers in Diblock Copolymer Matrix. For our self-diffusion measurements, some aspects of the state of order of the block copolymer matrix, e.g. its domain size or interfacial thickness, change continuously as the molecular weight of the diblock or triblock copolymer increases. Such changes make it difficult to discuss the results with simple theories. It is theoretically much simpler to model the tracer diffusion of several different block copolymers into a fixed block copolymer matrix.

The measured tracer diffusion coefficients of diblock copolymers and triblock copolymers in a fixed diblock copolymer matrix of PS-PVP296 are normalized by the diffusion coefficient of PS and plotted against χN_{PVP} in Figure 2. The tracer diffusion coefficients of diblock copolymers are represented as white symbols, while those of triblock copolymers are represented as gray symbols. Each different symbol corresponds to a different copolymer in Table 1 (different N_{PVP}), and each set of the same symbols represents the χ (temperature) dependence of D/D_0 of the copolymer.

In the large χN_{PVP} region ($\chi N_{PVP} \geq 10$), we find a universal dependence on the product χN_{PVP} for either diblock copolymer or triblock copolymer. The normalized diffusion coefficients, surprisingly, fall onto the same line; moreover, the slope of this line on the plot of log(D/D_0) versus χN_{PVP} is approximately −1. Due to the large scatter of the data, it is impossible to conclude that the small difference in the slope between diblock copolymers and triblock copolymers is real. The diffusion coefficients are, therefore, scaled by

$$D/D_0 \sim \exp(-\chi N_{PVP}) \qquad (2)$$

It is quite remarkable that the difference in diffusion coefficients of diblock and triblock copolymers is only through the difference in D_0 (D_0 depends on molecular weight dependence as M^{-2}).

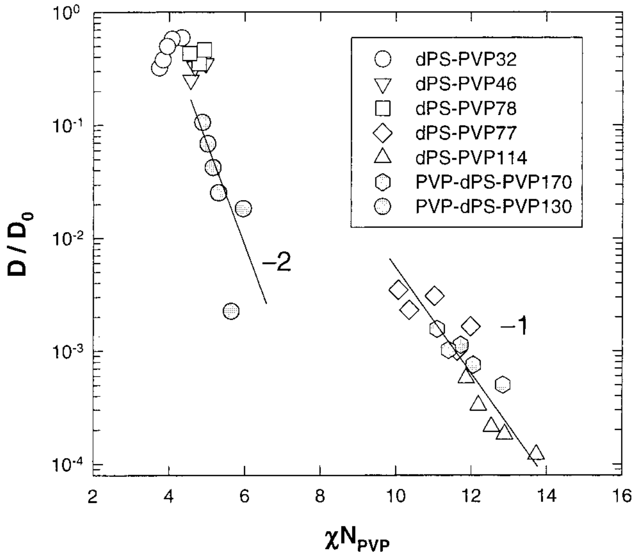

Figure 2. The dependence of normalized diffusion coefficient D/D_0 in a high molecular weight diblock copolymer (PS-PVP296) matrix (tracer diffusion) as a function of thermodynamic barrier of diffusion χN_{PVP}. Gray symbols are the diffusion coefficients of PVP-PS-PVP triblock copolymers, while white symbols are those of diblock copolymers.

In the small χN_{PVP} region ($\chi N_{PVP} \leq 6$), D/D_0 of the diblock copolymers is close to 1; the effect of ordered structure of the long diblock copolymer matrix is very small. On the other hand, the triblock copolymer has much smaller values of D/D_0 than those of the diblock copolymer. The ordered structure of the long diblock copolymer matrix has a strong effect on D/D_0 of the short triblock copolymer. Moreover, D/D_0 of the triblock copolymer depends very strongly on χ (temperature) with log(D/D_0), decreasing approximately as $-2\chi N_{PVP}$, where N_{PVP} is the PVP block length (52) of PVP-dPS-PVP130 block copolymer.

Comparing the Self-Diffusion and Tracer Diffusion of Diblock and Triblock Copolymers. The self-diffusion of diblock copolymer and tracer diffusion of diblock copolymer in a high molecular weight diblock copolymer (PS-PVP296) matrix are compared in Figure 3. The self-diffusion of triblock copolymer and tracer diffusion of triblock copolymer in a high molecular weight diblock copolymer (PS-PVP296) matrix are compared in Figure 4.

Discussion

While one might expect that the diffusion of triblock copolymers will be much slower than that of the diblock copolymers, our results do not confirm this expectation in most circumstances. As seen in the previous sections, the normalized diffusion coefficients of the triblock copolymers are not so different from those of diblock copolymers with the same χN_{PVP}. In fact, if one compares the diffusion of triblock and diblock copolymers with the same total molecular weight, the triblock copolymer diffuses much faster. This triblock copolymer has PVP end blocks half the length of the PVP end block of the diblock copolymer.

The diffusion behavior of the diblock copolymers is well-explained by the idea of activated hopping diffusion previously reported.[5,13] For triblock copolymers, we can

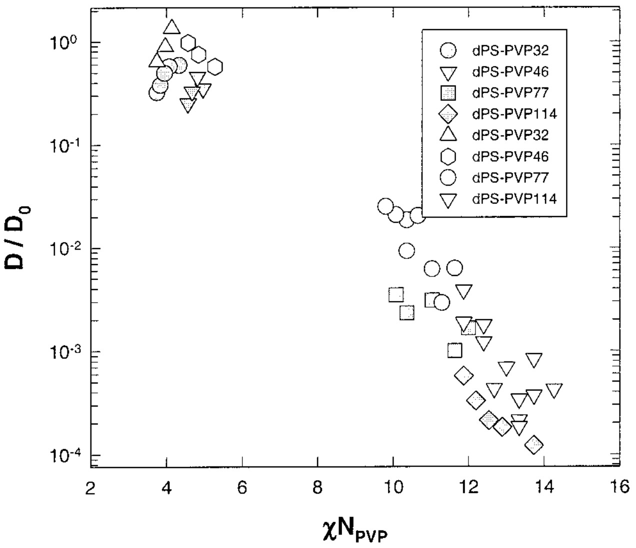

Figure 3. Dependence of normalized diffusion coefficient D/D_0 of diblock copolymers as a function of thermodynamic barrier of diffusion χN_{PVP} in a self-similar matrix (self-diffusion) and a high molecular weight diblock copolymer (PS-PVP296) matrix (tracer diffusion). Gray symbols are the tracer diffusion coefficients, while white symbols are the self-diffusion coefficients.

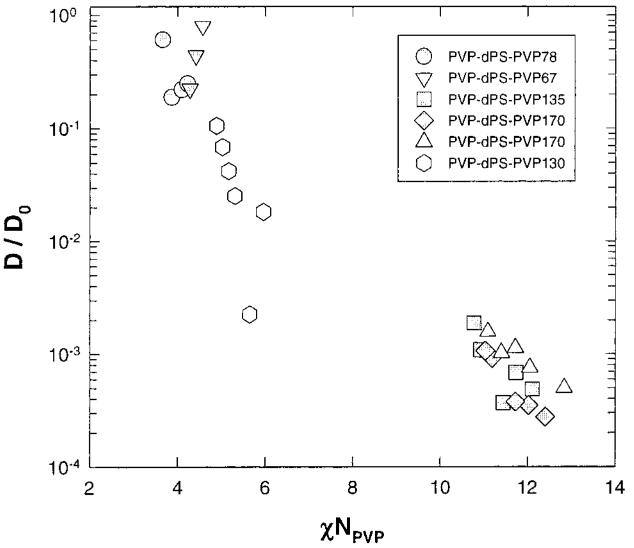

Figure 4. Dependence of normalized diffusion coefficient D/D_0 of triblock copolymers as a function of thermodynamic barrier of diffusion χN_{PVP} in a self-similar matrix (self-diffusion) and a high molecular weight diblock copolymer (PS-PVP296) matrix (tracer diffusion). White symbols are the tracer diffusion coefficients, while gray symbols are the self-diffusion coefficients.

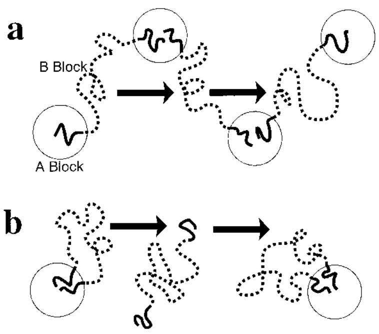

Figure 5. Schematic picture of two possible diffusion mechanisms of the ABA triblock copolymer: (a) "walking" diffusion by a thermodynamic activation of a single end block at a time; (b) "double activation" diffusion by a thermodynamic activation of both end blocks at a time. Gray circles represent PVP spherical domain. Solid lines are PVP block chains, and dotted lines are PS middle block chains. The white background represents the surrounding PS corona block chains, which are not drawn.

imagine two possible mechanisms for the activated hopping diffusion. One is simultaneous activation of both end blocks which encounters a thermodynamic barrier $2\chi N_{\mathrm{PVP}}$, which is called "double activation". In this case the triblock copolymer chain block ends are completely free from spherical core domains in the activated state, but this conformation requires a double thermodynamic penalty. The other possibility is that the triblock copolymers bridge between spherical domains and activate only one end block at a time from one domain to one of neighboring domains, a mechanism we call "walking" diffusion. For "walking" diffusion the thermodynamic penalty in the activated state is given by χN_{PVP} since only one end is surrounded by the unfavorable block in this state. Those two possible diffusion mechanisms are schematically shown in Figure 5, walking diffusion in a and double activation in b, respectively.

In Figure 1, the self-diffusion of triblock copolymers is always slower than that of the diblock copolymers. The similar dependence of D/D_0 of the triblock copolymers on χN_{PVP} to that of the diblock copolymers, $\exp(-\chi N_{\mathrm{PVP}})$, in the large χN_{PVP} region, suggests that the triblock copolymers diffuse by walking instead of double activation, which costs the thermodynamic penalty of $-2\chi N_{\mathrm{PVP}} k_{\mathrm{B}} T$. The difference between triblock and diblock copolymer diffusion may be due to an entropic barrier for the walking diffusion of the triblock copolymers. The entropic barrier may be caused by topological constraints; i.e., the triblock copolymer chains that bridge between different domains cannot cross each other in the process of diffusion. Such entropic barriers for diffusion reduce D/D_0 but do not change the temperature (χ) dependence.

Before discussing the tracer diffusion of the triblock copolymer, we need to evaluate the effect of the matrix molecular weight on the tracer diffusion of the diblock copolymers. From Figure 3, we find that the tracer diffusion of diblock copolymer in the PS-PVP296 matrix is always slower than the self-diffusion. Since the PS-PVP296 has higher molecular weight than the tracer diblock copolymers, the potential field that the tracer diblock copolymers experience during diffusion is more steplike. In the simple picture of activated hopping diffusion, such a shape of the potential field cannot be included in the χN_{PVP} dependence. However, our numerical simulation[22] of diffusion of diblock copolymers in a static potential field using Langevin dynamics showed that the steeper the interface of the potential field between domains, the slower the diffusion of the diblock copolymer is. The bigger and sharper spherical domains of the higher molecular weight PS-PVP296 matrix work as stronger traps for the diffusing diblock copolymer chains than the spherical domains of the matrixes used for the self-diffusion measurements.

As seen in Figure 2, the tracer diffusion of triblock copolymers in the PS-PVP296 diblock copolymer shows a very similar dependence on χN_{PVP} to that of the diblock copolymers in the region where $\chi N_{\mathrm{PVP}} > 10$. The slope of -1 in a region $\chi N_{\mathrm{PVP}} \geq 10$ for triblock copolymers is consistent with the walking diffusion mechanism, which requires that only one end block be

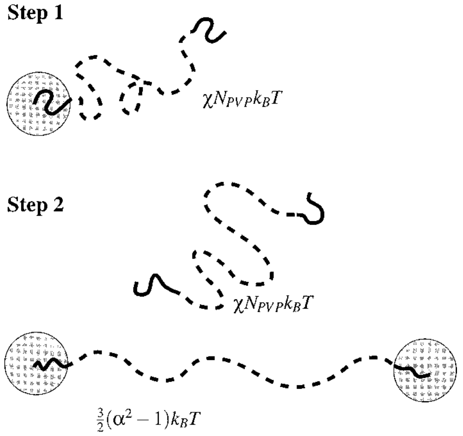

Figure 6. Illustration of the diffusion mechanisms of triblock copolymer and the approximate thermodynamic barrier for an each step of diffusion. Solid lines represent PVP, and dotted lines represent PS blocks, respectively.

activated for a step of the walking diffusion process. In this region, the D/D_0 of the triblock copolymer is almost the same as that of the diblock copolymers. The direct comparison between the tracer diffusion of triblock copolymers in the PS-PVP296 matrix and the self-diffusion of triblock copolymers in Figure 4 indicates that little effect of the matrix is observed for triblock copolymer diffusion (for $\chi N_{PVP} > 10$) in contrast to the diblock copolymer diffusion (Figure 3). In this comparison, however, in addition to the difference in the molecular weight of the matrix (the size and shape of the spherical domain), the matrix is changed from diblock to triblock copolymer. While the large diblock copolymer matrix has a sharper interface between the PVP spheres and the surrounding PS corona, the triblock copolymer matrix has stronger topological constraints (or entropic barrier) to diffusion of the triblock copolymer. Those two effects may work against each other and result in the similar values of D/D_0 for the triblock copolymer diffusion seen in Figure 4.

The slope of -2 in the region $\chi N_{PVP} \leq 6$ in Figure 2 suggests that the triblock copolymer activates both end blocks simultaneously (double activation) as illustrated in Figure 5. For double activation, both end blocks of the triblock copolymer chain have to pay a thermodynamic penalty for the undesirable contact with surrounding dissimilar middle blocks; the chain configuration, however, is not restricted and even may be favorable since the middle block does not have to stretch to allow bridging between domains. The approximate free energy barrier for the double activation is given by

$$\Delta F_{DA} = 2\chi N_{PVP} \tag{3}$$

Why is this different mechanism only observed for PVP-dPS-PVP129? One reason may be the larger spacing between the spherical domains of PS-PVP296 as compared to the end-to-end distance of PVP-dPS-PVP129 chains. We demonstrate here the crossover from the walking diffusion mechanism to the double activation diffusion mechanism depends on the spacing between the spherical domains and χN_{PVP} using a simple model. For either walking or double activation diffusion, it is essential that one of the end blocks be activated from the spherical domain as shown in Figure 6 (step 1). For step 2 of the walking diffusion, the triblock copolymer has to bridge between spherical domains, which incurs a free energy cost $U_b(r)$ of

$$U_b(r) = \frac{3k_B T}{2N_{PS}b^2}(r^2 - \bar{r}^2) = \frac{3}{2}(\alpha^2 - 1)k_B T \tag{4}$$

where k_B is Boltzmann's constant, b is the statistical segment length, N_{PS} is the total number of segments in the middle PS block, r is the end-to-end distance when the triblock copolymer bridges between spherical domains, $\bar{r}^2$ is the unperturbed mean square end-to-end distance of the PS midblock, and α is defined as $\alpha \equiv r/\bar{r}$. The other option for the triblock copolymer in step 2 of Figure 6 is for the other end block to be activated, which incurs a free energy cost of

$$U_a(r) = \chi N_{PVP} k_B T \tag{5}$$

Step 2 of the diffusion process determines the mechanism of diffusion of triblock copolymers. The crossover between the two diffusion mechanisms occurs when the two free energies $U_b(r)$ and $U_a(r)$ become comparable in magnitude.

When χN_{PVP} is fairly large, such as $\chi N_{PVP} = 12$, from eqs 4 and 5 one can obtain a crossover chain stretch ratio, $\alpha_c \approx 3.0$. When χN_{PVP} is smaller, such as $\chi N_{PVP} = 5$, $\alpha_c \approx 2.1$. When $\alpha > \alpha_c$, the triblock copolymer cannot bridge between neighboring spherical domains and diffuses by the double activation mechanism. When $\alpha < \alpha_c$, the triblock copolymer bridges between neighboring spherical domains and diffuses by the walking mechanism. To estimate α of the triblock copolymers in the PS-PVP296 matrix, we compare the unperturbed end-to-end distances of midblocks of these triblock copolymers and PS-PVP296. We assume that the domain structure of PS-PVP296 is approximately the same as that of the triblock copolymer with double the molecular weight of the diblock copolymer and compare the end-to-end distance of the midblock of the matrix triblock copolymer with PVP-dPS-PVP129 and PVP-dPS-PVP170. Equation 6 is used for the unperturbed

$$\bar{r} = aN_{PS}^{1/2} \tag{6}$$

root mean square end-to-end distance $\bar{r}$, where a is 0.67 nm for PS. We find values for $\bar{r}$ of 23, 25, and 48 nm for PVP-dPS-PVP129, PVP-dPS-PVP170, and the matrix, respectively. The approximate α is given by $\bar{r}_{matrix}/\bar{r}_{tracer}$. We find that α is 2.1 and 1.9 for PVP-PS-PVP129 and for PVP-PS-PVP170, respectively. Since $\alpha_c = 2.1$ for PVP-PS-PVP129 but $\alpha_c = 3.0$ for PVP-PS-PVP170, the crossover is expected only for PVP-PS-PVP129. This calculation is only a rough estimate but qualitatively captures the crossover between the two different diffusion mechanisms of the triblock copolymers in the PS-PVP296 diblock copolymer matrix. In general, it is quite difficult to achieve the criteria for the double activation diffusion of triblock copolymers. Unless the tracer triblock copolymer is very different from the matrix copolymer, the triblock copolymer will diffuse by the walking diffusion mechanism, giving a D/D_0 which scales $\exp(-\chi N_{PVP})$. For walking diffusion, D/D_0 is not much different from that of a diblock copolymer with half the molecular weight but faster than that of a diblock copolymer with the same molecular weight.

Conclusions

In summary, diffusion mechanisms of triblock copolymer have been suggested. In the large χN_{PVP} regime

($\chi N_{PVP} \geq 10$) (under conditions where the spacing of the matrix domains is not much different from the natural spacing of the triblock copolymer domains), triblock copolymers walk on an array of spherical domains, giving a universal scaling for $D/D_0 \sim \exp(-\chi N_{PVP})$ that is similar to the results for diblock copolymers. In the small χN_{PVP} regime ($\chi N_{PVP} \leq 6$) (under conditions where the spacing of the matrix domain is much larger than the natural spacing of the triblock copolymer domains), the diffusion seems to crossover to double activation; i.e., $D/D_0 \sim \exp(-2\chi N_{PVP})$. In general, unless the tracer triblock copolymer is very different from the matrix copolymer, the triblock copolymer will diffuse by the walking diffusion mechanism.

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