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Segregation Study of a BAB Triblock Copolymer at the A/B Homopolymer Interface

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ABSTRACT: The segregation of a poly[(2-vinylpyridine)-*b*-styrene-d_8-*b*-(2-vinylpyridine)] triblock copolymer (PVP-dPS-PVP) to a planar interface between the homopolymers PS and PVP is determined by forward recoil spectrometry (FRES). Compared to a diblock copolymer of dPS-PVP with the same mole fraction of PVP (~0.15) and total degree of polymerization (~500), we find that the triblock copolymer interfacial excess z_i^* at saturation is roughly half that of the diblock copolymer. Self-consistent mean field theory produces a segregation isotherm in fair agreement with the experimental results for the triblock copolymer using the same value of the Flory parameter χ deduced for the diblock copolymer. Both triblock and diblock copolymers show an increase in z_i^* beyond the saturation plateau which is due to the condensation of block copolymer micelles adjacent to the interface in the PS phase. This increase for the triblock copolymer occurs at a copolymer volume fraction $\phi_\infty = 0.15$ in the PS phase, whereas for the diblock copolymer it occurs at a much lower volume fraction, 0.05. This result indicates that the triblock copolymer has a larger critical micelle concentration (CMC) than the diblock copolymer. While the condensation of diblock copolymer micelles at the surface occurs above the CMC, no such preferential segregation is observed for the triblock copolymer. Transmission electron microscopy was used to examine the structure of the triblock copolymer micelles at and near the interface.

Introduction

Physical blending of homopolymers is known as one of the most convenient methods to produce a polymer with properties specifically tailored to individual needs. For an immiscible polymer blend, the blend composition and its morphology are both important factors controlling the resulting properties of the blend. For such a phase-separated polymer blend, block copolymer can be added as a compatibilizer to provide a finer dispersion of the second phase[1–3] and to improve the mechanical strength of the polymer/polymer interface.[4–8] These improvements of properties originate from the segregation of block copolymers to the polymer/polymer interface,[9–11] leading to a reduction in the interfacial tension[12] and an increase in covalent bond connections across the interface by virtue of the entanglement of the copolymer blocks with the homopolymer. In practice, a fraction of the copolymer added to the polymer blends is expected to segregate to the polymer/polymer interface to serve as an effective compatibilizer while the rest of block copolymer additive remains in either or both of the homopolymer phases. However, if the volume fraction of block copolymer additive in a given homopolymer is beyond the critical micelle concentration (CMC), micelles form. The micelles, besides limiting the chemical potential of the block copolymer which drives the segregation, also lead to a dramatic decrease in the kinetics of segregation.[9] Hence, micellization lowers the efficiency of the block copolymer as a compatibilizer. In this regard, triblock copolymers are thought to be better compatibilizers than diblock copolymers due to the fact that triblock copolymers have a higher CMC for the same copolymer composition and total molecular weight.[13,14] The objective of this work is to explore the difference in the segregation between the diblock and triblock copolymers. In addition, this study may provide some understanding of the chain conformation of the triblock copolymer at the interface.

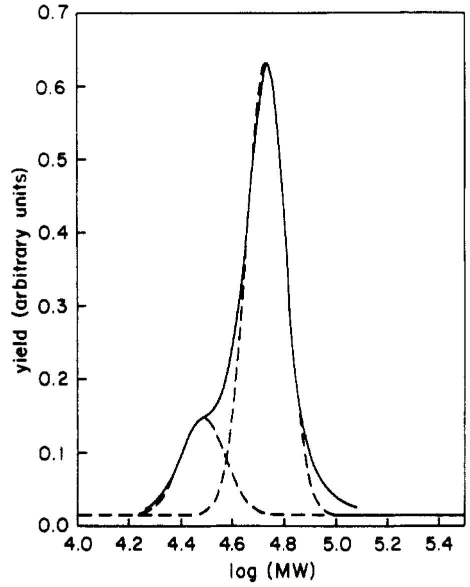

Figure 1. SEC trace of the triblock copolymer. The dashed lines represent two Gaussian functions used to separate the shoulder from the main peak.

Experiments

Materials. A triblock copolymer of poly(2-vinylpyridine-*b*-styrene-d_8-*b*-2-vinylpyridine) (PVP-dPS-PVP) was synthesized via anionic polymerization using a difunctional initiator, (α-methylstyryl)potassium.[15] A small amount of excess initiator was added to the reactor as a rose-red color indicator to ensure the absence of impurities (zero point) prior to the polymerization reaction. A small fraction of the difunctional initiator may thus be converted to the monofunctional initiator by this procedure. Therefore, the resulting triblock copolymer may contain a small fraction of diblock copolymer. Such a diblock copolymer is believed to be responsible for the shoulder observed close to the peak on the size exclusion chromatography (SEC) trace,[16] as shown in Figure 1, and estimated to be approximately 12% of the total copolymer. The difference of retention time between the PS and PVP homopolymer leads to an underestimation in the overall molecular weight of the PS-PVP copolymer when PS with a narrow molecular weight distribution is used as the SEC

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standard; it is found that this underestimation is 4–6% for the copolymer with a PVP fraction less than 20%. The overall molecular weight of the triblock copolymer is then determined to be approximately 57 000, which is approximately twice the molecular weight of the diblock copolymer estimated from the shoulder of the SEC trace. The PVP fraction is determined by ^{13}C NMR to be approximately 15%, which is consistent with the ratio of deuterium to hydrogen measured by forward recoil spectrometry (FRES). Hence, the degree of polymerization of the resulting triblock copolymer is determined to be 37/434/37 (PVP/dPS/PVP).

FRES Measurements. A 100-nm-thick film of PVP homopolymer with degree of polymerization $P_{\mathrm{PVP}} = 5100$ was spun cast on a silicon wafer and used as the substrate for the segregation measurement with FRES. The blends of PS homopolymer ($P_{\mathrm{PS}} = 2240$) with various volume fractions of the triblock copolymer were spun on the PVP precoated substrates. The bilayer specimens were then annealed at 178 and 200 °C, respectively, for at least 12 h in vacuum to allow the triblock copolymer to segregate to the interface between the PS and PVP homopolymers. This segregation is mainly caused by the immiscibility between the PVP block and the PS homopolymer. FRES is used to probe the labeled dPS block to determine the profile of block copolymer volume fraction versus depth (perpendicular to the interface). The interfacial excess z_i^* of the triblock copolymer is thus computed from the depth profile as a function of ϕ_∞, the volume fraction of block copolymer far from the interface, to construct the segregation isotherm.

TEM Observations. The specimens for the examination of morphology were prepared using the same method as described in the previous paragraph except that the silicon wafer was replaced by a piece of salt crystal (NaCl) and a film of the PVP homopolymer with a larger thickness of few microns was used. After the anneal, the specimen was divided into two parts which were then examined by FRES and transmission electron microscopy (TEM), respectively. Such a parallel examination provides an unambiguous way to correlate the observed morphology with its corresponding interfacial excess of triblock copolymer. The film for the TEM observation was floated on the water surface where the rock salt was completely dissolved and then picked up by a PVP substrate (2 × 2 × 200 mm). This piece was dried in the air for few hours and followed by an anneal at 110 °C for approximately 5 min. Such an anneal is to provide necessary adhesion ("healing") between the PVP homopolymer of the film and the PVP substrate, without affecting the interfacial structure. The resulting piece was embedded in epoxy resin and cured at room temperature so as to provide a sample with the appropriate geometry to fit into the specimen holder of the microtome. A thin section (~100 nm) was cut from the portion of the film specimen beyond the epoxy by microtoming using a glass knife at room temperature. Using this method, sections were cut from a portion of the film specimen whose morphology was not affected by the surrounding epoxy resin. The microtomed film was then floated on a water surface and flattened by briefly exposing it to the solvent vapor (toluene/chloroform = 4/1). The film was subsequently picked up onto a copper grid and dried in vacuum. The resulting grid was exposed to iodine vapor at room temperature for several hours to selectively stain the PVP phase. Such staining results in an enhancement of electron scattering from the PVP phase and thus leads to a "darkening" of the PVP phase which can be easily distinguished by TEM observation.[7] A JEOL 1200EX transmission electron microscope operating at 120 keV was used for the morphology observations.

Theory

Brush Theory. A segregation theory of a BAB triblock copolymer to the homopolymer interface is formulated in this section. This theory is based on the concept of the "dry brush" proposed by Leibler,[17] in which the term "brush" is used to describe the conformation of the segregated AB diblock copolymer chains at the interface and "dry" refers to the assumption that no homopolymer penetrates into the brush. This brush theory allows a quick estimation of the segregation isotherm, namely the interfacial excess z_i^* versus the volume fraction of copolymer far from the interface ϕ_∞. The interfacial excess z_i^* is defined as

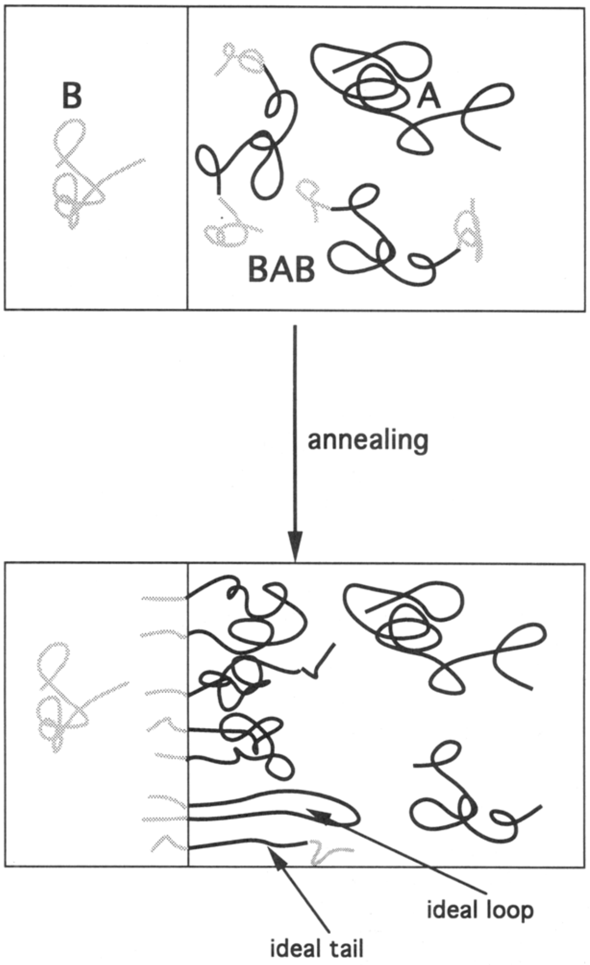

Figure 2. Schematic of the segregation system, showing the loop and tail conformations of a triblock copolymer at the interface.

$$z_i^* = \int_{\mathrm{interface}} [\phi(x) - \phi_\infty]\,\mathrm{d}x \qquad (1)$$

where $\phi(x)$ is the volume fraction of block copolymer at depth x. A schematic of the triblock copolymer segregation is shown in Figure 2; a fraction of the triblock copolymer migrates to, and accumulates at, the interface after annealing while the other fraction remains in the bulk phase away from the interface. Given that ϕ_∞ is experimentally measurable, the chemical potential of the triblock copolymer μ_c can be defined approximately from the Flory–Huggins expression for the free energy of mixing

$$\frac{\mu_c}{kT} = \ln \phi_\infty + 1 + \chi(2N_{\mathrm{cb}}) \qquad (2)$$

where N_{cb}, k, and χ are the degree of polymerization of each B block, the Boltzmann constant, and the Flory interaction parameter between polymers A and B, respectively. This approximation is valid at very small ϕ_∞.

The triblock copolymer chains segregating to the interface are assumed to form a "dry brush" type structure consisting of a mixture of two conformations, loop (hairpin) and tail, as depicted in Figure 2. The loop conformation describes the copolymer chain both of whose end blocks reside at the interface; the tail conformation describes the copolymer chain with only one of the end blocks residing at the interface while the other dangling end block is embedded in the host A phase. The free energy of the dry brush in the A phase can be written as

$$\frac{F_A}{kT} = \frac{\gamma A_i}{kT} + Q\left\{\left[1.1f\ln\left(\frac{R_g}{\delta}\right) + 1.1(1-f)\ln\left(\frac{R_g}{\sqrt{2}\delta}\right)\right] + \left[\frac{3}{2}f\frac{z_i^*}{N_{ca}\mathbf{a}^2} + 3(1-f)\frac{z_i^*}{(N_{ca}/2)\mathbf{a}^2}\right] - \left[\frac{(1-f)}{2}\ln(\pi\chi N_{ca})\right] + [f\chi N_{cb}] + [f\ln f + 2(1-f)\ln[2(1-f)] - (2-f)\ln(2-f)]\right\} \quad (3)$$

where f is the fraction of the triblock copolymer chains in the brush with the tail conformation; Q is the number of copolymer chains in the brush; A_i is the interfacial area; γ is the interfacial tension; N_{ca}, R_g, and $\mathbf{a}$ are the degree of polymerization, the radius of gyration, and the statistical segment length of the copolymer block A, respectively; ρ is the segment density of the polymer (here we assume $\rho_a = \rho_b = \rho$ to simplify the algebra); and δ is the thickness of the interface which defines the confinement of the copolymer joints.[18] The interfacial thickness between immiscible homopolymers with infinite molecular weights derived by Helfand and Tagami is given in eq 4.[19] The

$$\delta = 2\mathbf{a}/\sqrt{6\chi} \quad (4)$$

terms in the first set of brackets of eq 3 account for the fact that the copolymer joints are not strictly placed at the interface but are within a narrow region of the interface.[20,21] The expression in the second set of brackets accounts for the deformation free energy of the copolymer chains due to stretching, namely that arising from the elastic entropy.[17,18] The expression in the third set of brackets accounts for the entropic loss associated with the return of a polymer chain with a Gaussian configuration to an infinite flat interface with a thickness of δ (entropy loss due to the formation of a loop);[14] although the segments of the copolymer chains near the interface certainly deviate from the Gaussian distribution, the level of this approximation is the same as that used to calculate the deformation energy. The terms in the fourth set of brackets account for the unfavorable enthalpic interaction between dangling end block B and polymer A. The combinatorial entropy arising from the mixing between the loop and tail chains in the plane of the interface is given in the fifth set of brackets, with the derivation provided in Appendix A.1.

For the sake of simplifying the algebra, end block B is assumed to be short in comparison with midblock A (an assumption which matches our experimental condition) and thus the contribution to the overall free energy from the B phase in the brush can be neglected. Therefore, the chemical potential per copolymer chain residing in the brush (μ_c) can be approximated solely by the derivative of eq 3 with respect to Q while A_i is held constant, i.e.:

$$\frac{\mu_c}{kT} = 2.2\ln\left(\frac{\sqrt{2}R_g}{\delta}\right) + 3\left(\frac{z_i^*}{R_g}\right)^2 - \frac{1}{2}\ln(\pi\chi N_{ca}) + 2\ln\left[\frac{2(1-f)}{2-f}\right] \quad (5)$$

where f can be found by minimizing the free energy F_A with respect to f. Since the triblock copolymer segregated to the interface is in equilibrium with the triblock copolymer in the bulk phase, this chemical potential (for the triblock copolymer in the brush) must be equal to the chemical potential defined by eq 2. Thus the segregation isotherm ($z_i^* = f(\phi_\infty)$) can be obtained by numerically solving eq 2 and 5.

Self-Consistent Mean Field Theory. A self-consistent mean field theory (SCMF) reported by Shull and Kramer[21] describing the segregation of diblock copolymers to the homopolymer interface is modified to describe the segregation of triblock copolymers. This SCMF theory is briefly outlined in this section; for the details, the reader is referred to the paper by Shull et al.[18,21] The main revision of the theory is to modify the distribution function q to account for the connectivity of repeat units in a triblock copolymer, as shown in eq 6.

$$q_c(i,j) = \left\{\frac{2}{3}q_c(i,j-1) + \frac{1}{6}q_c(i-1,j-1) + \frac{1}{6}q_c(i+1,j-1)\right\}\exp\left(\frac{-w(i)}{kT}\right) \quad (6)$$

where

$$w(i) = \begin{cases} w_a(i) & N_{cb} < j < N_{ca} + N_{cb} \\ w_b(i) & 0 < j < N_{cb},\ N_{ca} + N_{cb} < j < N_c \end{cases}$$

and where $q_c(i,j)$ is the probability of finding a jth segment of the copolymer at layer i where the space in the segregation system is divided into layers parallel to the interface. The local mean field w for the appropriate segment (A or B) is

$$w_k(i) = kT(\chi(\phi_{ck}(i) + \phi_{hk}(i))^2 - K_\phi(i)) - \Delta w(i) \qquad \mathrm{k = a, b} \quad (7)$$

where $K_\phi = \phi_{ha}/N_{ha} + \phi_{hb}/N_{hb} + \phi_c/N_c$. The subscripts ha, hb, ca, cb, and c correspond to homopolymer A, homopolymer B, copolymer block A, copolymer block B, and the entire block copolymer, respectively. The local mean field represents the free energy required to place the specific segment in the local environment whereas the chemical potential μ_c represents the free energy required to place an entire chain in a corresponding homogeneous phase. Δw is introduced to account for the incompressibility of the polymer and ensures that the total volume fraction of both A and B segments add to 1. The volume fraction of the copolymer can be computed from the distribution function q_c via the following relationships:

$$\phi_{cb}(i) = \left[\sum_{1}^{N_{cb}} q_c(i,j)\, q_c(i,N_c - j) + \sum_{N_{ca}+N_{cb}+1}^{N_c} q_c(i,j)\, q_c(i,N_c - j)\right]\frac{\exp\left(\frac{\mu_c}{kT} - 1\right)}{N_c} \quad (8)$$

$$\phi_{ca}(i) = \left[\sum_{N_{cb}+1}^{N_{ca}+N_{cb}} q_c(i,j)\, q_c(i,N_c - j)\right]\frac{\exp\left(\frac{\mu_c}{kT} - 1\right)}{N_c} \quad (9)$$

where ϕ_{ca} and ϕ_{cb} are the volume fraction of copolymer block A and B, respectively.

The equations for the homopolymers, equivalent to eqs 6–9, can be formulated as listed below:

$$q_{ha}(i,j) = \left\{\frac{2}{3}q_{ha}(i,j-1) + \frac{1}{6}q_{ha}(i-1,j-1) + \frac{1}{6}q_{ha}(i+1,j-1)\right\}\exp\left(\frac{-w_a(i)}{kT}\right) \quad (10)$$

$$q_{hb}(i,j) = \left\{\frac{2}{3}q_{hb}(i,j-1) + \frac{1}{6}q_{hb}(i-1,j-1) + \frac{1}{6}q_{hb}(i+1,j-1)\right\}\exp\left(\frac{-w_b(i)}{kT}\right) \quad (11)$$

$$\phi_{ha}(i) = \left[\sum_{1}^{N_{ha}} q_{ha}(i,j)\, q_{ha}(i,N_{ha}-j)\right]\frac{\exp\left(\frac{\mu_{ha}}{kT} - 1\right)}{N_{ha}} \quad (12)$$

$$\phi_{hb}(i) = \left[\sum_{1}^{N_{hb}} q_{hb}(i,j)\, q_{hb}(i,N_{hb}-j)\right]\frac{\exp\left(\frac{\mu_{hb}}{kT} - 1\right)}{N_{hb}} \quad (13)$$

The chemical potential μ_k is given by:

$$\frac{\mu_k}{N_k} = \frac{\partial(\mathbf{f}/\rho)}{\partial\phi_k} + \frac{\mathbf{f}}{\rho} - \sum_k \phi_k \frac{\partial(\mathbf{f}/\rho)}{\partial\phi_k} \qquad k = \text{ha, hb, c} \quad (14)$$

where ρ is the segment density and where the derivatives with respect to a particular ϕ_k are to be taken with $\phi_{j\neq k}$ held constant. The free energy density $\mathbf{f}$ is given in the Flory–Huggins form as

$$\frac{\mathbf{f}}{kT\rho} = \chi(\phi_{ha} + \phi_{ca})(\phi_{hb} + \phi_{cb}) + \sum_k \frac{\phi_k \ln \phi_k}{N_k} \quad (15)$$

For a particular χ parameter and with the appropriate initial conditions, e.g. $q_c(i,1) = 1$, and boundary conditions, e.g. $q_c(-\infty,j) = \exp(-(N_{ca}w_a(-\infty) + N_{cb}w_b(-\infty))/kT)$ and $q_c(\infty,j) = \exp(-(N_{ca}w_a(\infty) + N_{cb}w_b(\infty))/kT)$, eq 6–15 can be solved self-consistently for the distribution functions and the segment density profiles. A computer iteration algorithm[21] based on a relaxation scheme is employed to solve for the equations to obtain the following information at a specific chemical potential (or ϕ_∞): the segment density distributions (volume fraction profiles), the interfacial excess z_i^*, and the interfacial tension.

Results and Discussion

Block copolymers segregate to the interface, mainly driven by the unfavorable enthalpic interaction between the PVP blocks and the PS homopolymers. The amount of segregated block copolymer is determined from the volume fraction versus depth profile measured by FRES. An example of such a depth profile is given in Figure 3. The interface excess z_i^* of copolymer, shown as the hatched area in Figure 3, is evaluated by eq 1 for which the integral is computed over a range of x near the interface. The surface excess of block copolymer, z_s^*, is defined similarly to eq 1 except the integration is performed over a range of x near the surface, i.e. the polymer/vacuum interface.

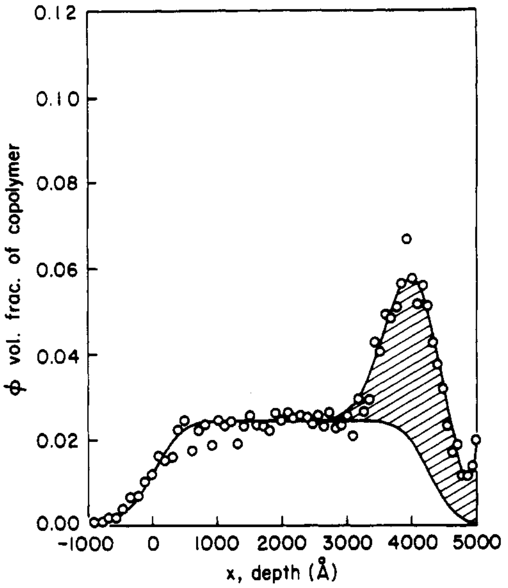

Figure 3. Profile of the triblock copolymer volume fraction versus the depth measured by FRES where $\phi_\infty \approx 0.025$ and $z_i^* = 42$ Å where the z_i^* is indicated by the hatched area.

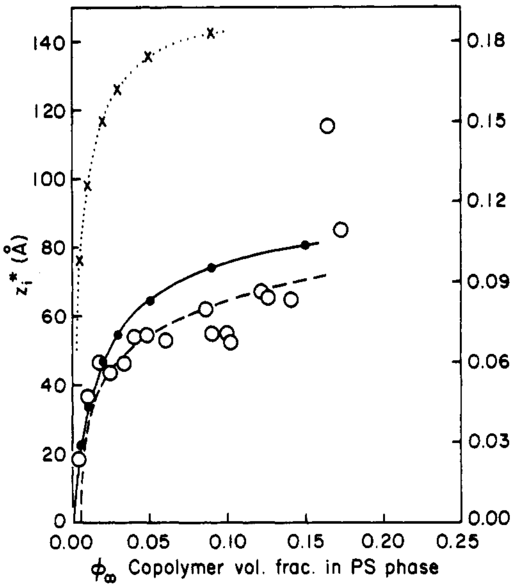

Figure 4. Segregation isotherm of a PVP/dPS/PVP triblock copolymer with the degree of polymerization 37/434/37 at 178 °C: (O) experimental data; (–•–) prediction from the SCMF theory with $\chi = 0.105$; (– – –) prediction from the brush theory with $\chi = 0.065$; (···X···) prediction from the SCMF theory for a 434/74 diblock copolymer.

Figure 4 shows the z_i^* and areal chain density Σ_i of the triblock copolymer at the interface as a function of ϕ_∞ (this plot is referred to as the segregation isotherm). No surface segregation is observed up to $\phi_\infty \approx 0.22$. The average areal chain density of the block copolymer can be estimated from the interfacial excess z_i^* via the following formula:

$$\Sigma_i = z_i^* \rho / N_c \quad (16)$$

where ρ, the segment density of the block copolymer, is approximated by its value for PS[22] of 0.0094 mol/cm³ since the segment densities of PS and PVP are nearly identical.[9] For the purpose of comparison, the corresponding segregation isotherm for a dPS-PVP diblock copolymer with degree of polymerization 391/68 (dPS/PVP)[9] is given in Figure 5. It should be noted that these two block copolymers have comparable overall molecular weights (~50k) and PVP fractions (~0.15). As seen, the interfacial excesses of both the block copolymers increase with increasing ϕ_∞ in the low ϕ_∞ regime, which is followed by a regime of ϕ_∞ where little change of interfacial excess

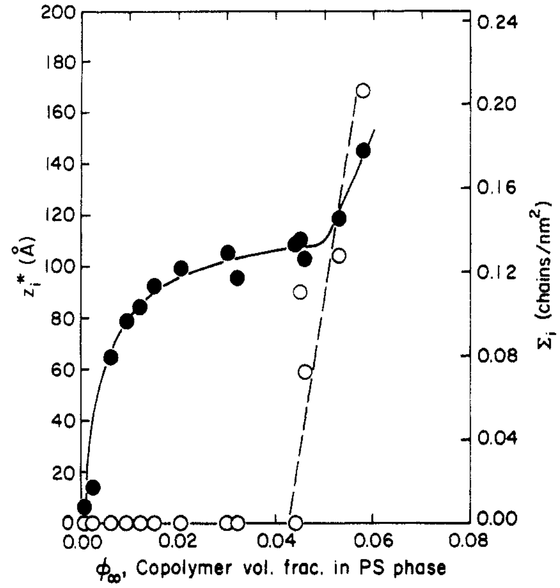

Figure 5. Segregation isotherm of the dPS-PVP diblock copolymer with the degree of polymerization 391/68 at 178 °C. ● and ○ represent the interfacial and surface excess, respectively.

occurs (an apparent saturation plateau), which is followed by a second abrupt increase in the interfacial excess. This upturn of interfacial excess in the postplateau regime for the segregation of diblock copolymer is found to be accompanied by the strong segregation of the diblock copolymer to the surface. No surface segregation of the triblock copolymer is observed in the corresponding regime.

The initial increase of the interfacial excess is due to the accumulation of individual segregated copolymer chains, which locate one or both of the joints between their blocks at the interface forming a "brush" structure at the interface, as depicted in Figure 2. The segregation process is then impeded as more block copolymer chains accumulate at the interface because the existing chains in the brush must stretch, and lose entropy, to accommodate the incoming segregating chains. The deformation free energy due to chain stretching scales as the square of z_i^* (analogous to the deformation of a spring). Thus, the deformation demands more free energy for the same amount of stretching at a higher z_i^*. In addition, the increase in chemical potential due to the increase in ϕ_∞ is leveling off. Hence, these two factors lead to the resulting plateau (saturation) in the segregation isotherm.

The prediction from the brush theory with a χ parameter of 0.065 is shown in Figure 4 as a dashed line. This prediction is in good agreement with the observed isotherm, although the χ parameter is less than its previously reported value of ~0.11.[9,10] The need to use a lower value of χ to fit the data is expected in the brush theory because the copolymer joints in the dry brush are assumed to be ideally located at the interface and thus the enthalpic gain by placing a copolymer chain at the interface is overestimated. This reported value of χ (~0.11) was deduced from the segregation experiments of diblock copolymers.[9,10] The prediction from SCMF with $\chi = 0.105$ for the segregation isotherm of the triblock copolymer is shown as – · · – in Figure 4. As seen, the SCMF theory can indeed reproduce the shape of the observed segregation isotherm. Considering the uncertainty associated with the molecular weight determination by SEC, the SCMF prediction is in good agreement with the measured isotherm except that the plateau level is slightly higher than that observed. It should be noted that this discrepancy is unlikely to be due to the 12% diblock in the triblock copolymer. We have estimated, using SCMF, the approximate segregation isotherm expected for the triblock copolymer containing 12% diblock (details in Appendix 2) which shows a negligible difference from that predicted for a pure triblock copolymer. Nevertheless, for a better test of the theory it will be necessary in the future to use a "clean" triblock copolymer to avoid such complications.

The number density of the copolymer excursions across the interface is defined as the areal joint density. The areal joint density of a diblock copolymer is approximately equal to its areal chain density Σ_i, while that of a triblock copolymer is between Σ_i (tail) and $2\Sigma_i$ (loop) depending upon the fraction f of tail and loop conformations at the interface. As observed from Figures 4 and 5, the plateau Σ_i of the 37/434/37 triblock copolymer is much lower than that of the 391/68 diblock copolymer. Since these two block copolymers have comparable total degrees of polymerization and PVP fractions, this result indicates the significant effect on the saturation excesses due to the difference in the interfacial structures of diblock and triblock copolymers. This point is further supported by the result of a SCMF simulation for a diblock copolymer (434/74) and the same degree of polymerization of the PS and PVP blocks as the triblock copolymer; the predicted isotherm by the SCMF theory is shown as (···×···) in Figure 4. As seen, the saturation excess predicted for this 434/74 diblock copolymer is nearly twice that of the 37/434/37 triblock copolymer. Figure 6 shows the volume fraction of PVP block in the triblock copolymer versus depth profile predicted from the SCMF theory for various ϕ_∞. A second peak on the PS side of the interface gradually develops as ϕ_∞ increases, which is mainly due to the PVP blocks of the triblock copolymer in the "tail" conformation. The fraction f of the triblock copolymer chains with the tail conformation can be estimated by the following formula:

$$f = \frac{2z_{\mathrm{cb}}^*(x \geq x_{\mathrm{d}})}{z_{\mathrm{cb}}^*} \qquad (17)$$

where z_{cb}^* is defined similar to eq 1 with the volume fraction of copolymer replaced by the volume fraction of the B block and the numerator $z_{\mathrm{cb}}^*(x \geq x_{\mathrm{d}})$ is computed over the range where $x \geq x_{\mathrm{d}}$. Here, x_{d} corresponds to the position where the minimum volume fraction of the PVP blocks between these two peaks occurs. The position x_{d} does not vary significantly with ϕ_∞ (the change is less than the statistical segment length **a**). We thus determine x_{d} from the computed segment density profile at high ϕ_∞, a condition under which the minimum is really apparent. x_{d} is found to be ~35 Å, which is approximately half R_{g} of the copolymer. The cross-hatched area shown in Figure 6b represents $z_{\mathrm{cb}}^*(x \geq x_{\mathrm{d}})$ for $\phi_\infty = 0.15$. The solid line in Figure 7 shows the f evaluated using this scheme as a function of ϕ_∞. It is seen that the f monotonically increases from ~0.2 to ~0.4 as ϕ_∞ increases. This result indicates that even at relatively large χN_{cb} (~3.9 in this case for the triblock copolymer), a significant fraction (0.4 for this triblock copolymer) of the triblock copolymer chains at the interface has the tail conformation at saturation. The prediction from the brush theory, with $\chi = 0.065$ obtained from the best fit of the brush theory to the segregation isotherm, is also plotted in Figure 7 for comparison. As seen, this predicted f also shows a monotonic increase of f with ϕ_∞; a larger value of f however is obtained at higher ϕ_∞, as compared to that predicted by SCMF theory.

When the initial concentration of diblock copolymer added in the PS host exceeds the CMC, the diblock

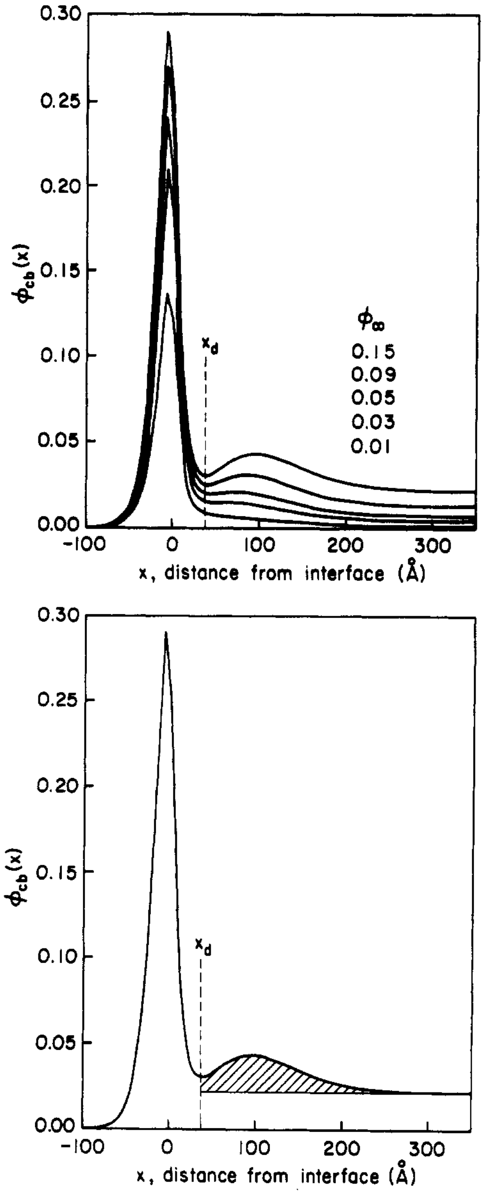

Figure 6. Volume fraction of the PVP block of the 37/434/37 triblock copolymer versus depth profile predicted from SCMF theory for various ϕ_∞ from 0.01 to 0.15. The hatched area shown in (b) represents $z_{cb}(x \geq x_d)$ for $\phi_\infty = 0.15$.

copolymer forms micelles with the corona fully composed of dPS, whose structure is depicted in Figure 8. It is known that dPS has a lower surface energy than PS due to the lower polarizability of the C–D bond as compared to that of the C–H bond.[23] Therefore, these micelles with lower energy surfaces aggregate to the surface and may be responsible for the observed surface segregation shown in Figure 5. Furthermore, in the case of a dry brush (homopolymer $N \gg$ block N) the interaction between the interfacial and the corona brushes is attractive,[18,24] which also causes the micelles to segregate to the interface,[25] and in turn these micelles contribute to the observed upturn of the segregation isotherm for ϕ_∞ above the plateau. However, as pointed out by Semenov[26] and also by Shull,[27] the formation of micelles needs to overcome a nucleation barrier, a barrier which they suggest should be lower at an interface or surface if the interfacial or surface energy of the copolymer is lower than that of the host homopolymer. Therefore, it is suggested that the micelles may preferentially nucleate at the interface and the surface. The onset of this abrupt increase of the interfacial or surface excess is a signature of micellization and is close to, although probably above, the CMC.[26,27] However, the increase of interfacial excess of the triblock copolymer in the postplateau regime is not accompanied with any surface segregation. We believe this difference arises from the significant fraction of tail conformations of triblock copolymer at the interface (either that between the homopolymers or that between the corona of the micelles and the PS homopolymer). There are two possible explanations: (1) The corona of an isolated triblock copolymer micelle, as depicted in Figure 8a, consists of mostly dPS blocks with some PVP blocks in the tail conformation on its outer shell, in contrast to the corona of a diblock copolymer micelle which is wholly composed of dPS. These PVP segments preclude the triblock copolymer micelle from forming a low energy micellar surface and thus prevent the segregation of triblock copolymer micelles to the surface. (2) The unfavorable contacts (an unfavorable enthalpic interaction) between the dangling ends of the PVP tails and the surrounding PS can be further decreased by forming a "bridge" conformation, which for the copolymer chain goes from one micellar core to its neighbor. An important consequence of the attraction originating from this bridging conformation is that a micelle will prefer to form next to another micelle, or next to the adsorbed layer of the triblock copolymers, as depicted in Figure 8b. The consequent decrease in free energy may lead to the formation of micelles (spherical microdomains) condensed against the interface at a chemical potential less than that needed to form isolated micelles. Hence, the dangling PVP tails act as nuclei for micelle formation. From this scenario, a condensation of micelles at the adsorbed triblock copolymer layer is thus responsible for the observed upturn of the segregation isotherm. No surface segregation is observed due to the unfavorable interaction of the PVP tails with the surface as described in (1) above.

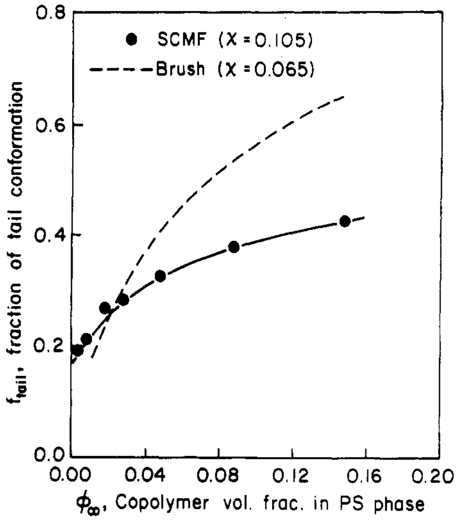

Figure 7. Fraction of the 37/434/37 triblock copolymer chains in tail conformations as a function of ϕ_∞ predicted from the SCMF and the brush theories. The solid line is a guide to eye.

To verify our interpretation of the observed segregation isotherms of the triblock copolymer, TEM was used to examine the morphology of the interfacial region for specimens with various ϕ_∞'s and z_i^*'s. Three representative micrographs are given in Figure 9. The corresponding z_i^* and ϕ_∞ for each micrograph are marked by an arrow on the segregation isotherm shown in the same figure. The dark and bright regions, which result from iodine staining, are the PVP rich and PS rich regions, respectively. Figure 9A shows a sharp interface between the PS and PVP homopolymer phases for a sample in which the z_i^*

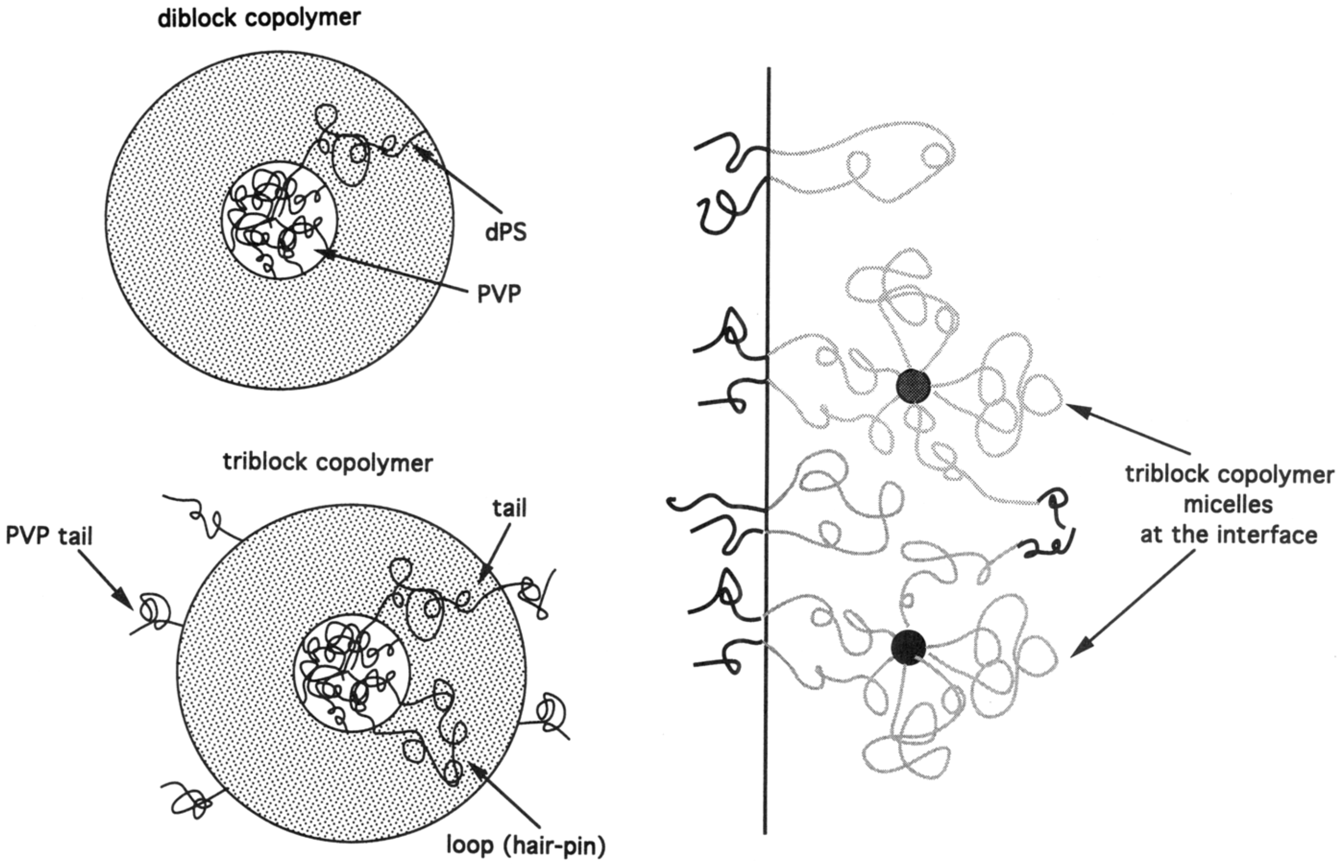

Figure 8. Schematics of (a, left) the isolated micelle structure for diblock and triblock copolymers and (b, right) triblock copolymer micelles adsorbed onto an interfacial brush of triblock copolymers.

corresponds to a value on the segregation plateau. As seen in Figure 9B whose morphology corresponds to a z_i* just above the onset of the upturn of the segregation isotherm, the interface is covered by dark "spheres" (micellar cores consisting of PVP), indicating the presence of micelles at the interface. Due to technical difficulties of specimen preparation, the resolution of the micelle structure in this micrograph is not very good yet when it is compared to Figure 9A, it unambiguously shows the presence of micellar microdomains at the interface. These features are clearly seen in Figure 9C whose morphology corresponds to a z_i* of ~300 Å. A few layers of the interfacial micelles and larger clusters are observed. The TEM observations allow us to correlate the micelle morphology with the measured interfacial excess and strongly support our claim that the upturn in the interfacial excess is due to the condensation of micelles at the interface.

Furthermore, as seen in Figure 9B,C, in the region far from the interface, the collection of the micelles forms a cluster structure with a size on the order of 100 nm. The observation of such aggregates of micelles bolsters the argument that the interaction between the brushes is attractive due to "bridging". In addition, the survival of such aggregates after a long time anneal implies that these micelles are interconnected. The interconnection via bridging thus prevents the migration of individual micelles from the aggregate to the interface.

By inspecting Figures 4 and 5, we found that the upturn in the interfacial excess for the triblock copolymer occurs at a ϕ_∞ of around 0.15 whereas it occurs at a much lower volume fraction of 0.05 for the diblock copolymer. This result indicates that the triblock copolymer has a higher CMC than the diblock copolymer. Since these two copolymers have comparable molecular weights and PVP fractions, the shift of this critical ϕ_∞ indicates that the loop conformation significantly influences the formation of micelles.

Figure 10 shows the segregation isotherm of the triblock copolymer at annealing temperatures of 178 °C (as in Figure 4) and 200 °C, respectively. As illustrated in the figure, the segregation plateau at 200 °C shows a negligible difference from that at 178 °C. However, the critical ϕ_∞ for the micelle formation is higher at 200 °C as compared to that at 178 °C due to a decrease in the interaction parameter χ. The prediction from the SCMF theory (using χ parameters deduced from the segregation experiment of a diblock copolymer for each temperature) gives the difference of ~3 Å between the saturation excess at 178 and 200 °C which cannot be resolved by FRES and thus agrees with this observation. In comparison with the observed temperature dependence of the segregation isotherm for a diblock copolymer with degree of polymerization 597/59 (dPS/PVP),[28] the segregation plateau of the triblock copolymer is less sensitive to the annealing temperature. This result may be explained by the additional entropy arising from the mixing of the tails and loops which reduces the dependence of the saturation excess on the χ parameter.

Conclusions

(1) Segregation theories for triblock copolymers to the polymer/polymer interface based on the brush scheme and self-consistent mean field calculations produce predictions in fair agreement with the observed isotherm if χ is treated as a fitting parameter. It should be noted that the small fraction of the diblock (with half the N and the same PVP mole fraction of the triblock copolymer) in the triblock

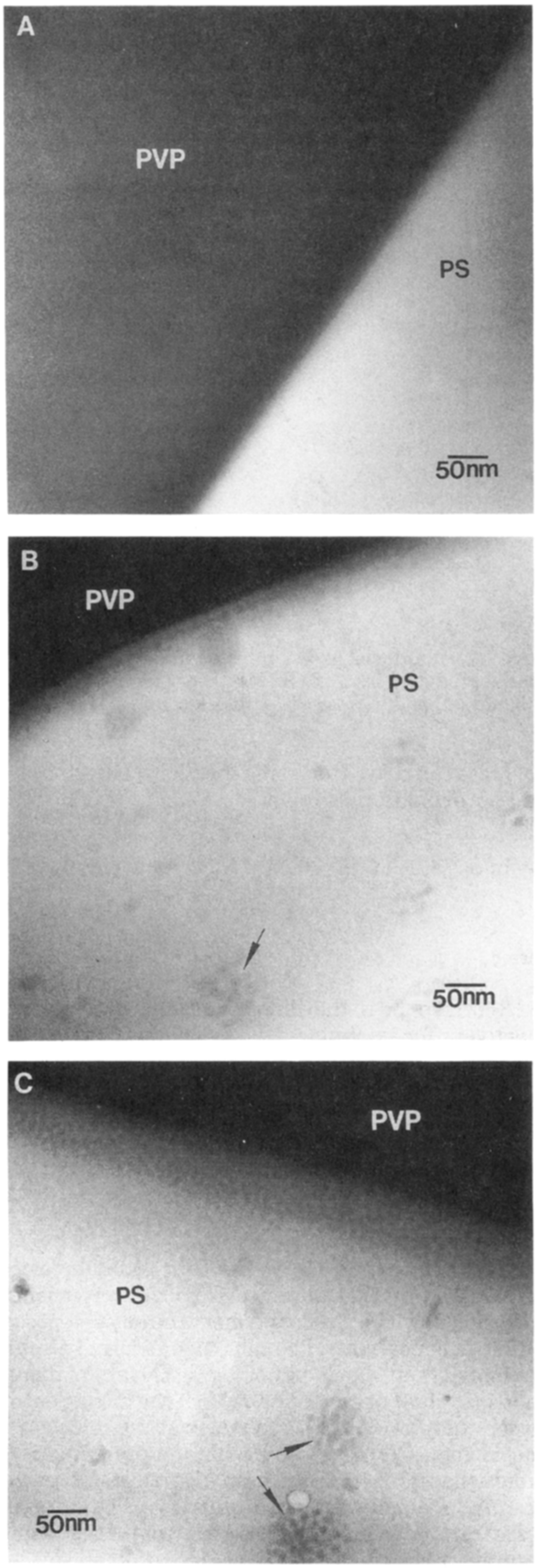

Figure 9. TEM micrographs of the morphology near the interface for z_i^* corresponding to that (A) on the segregation plateau, $z_i^* \approx 60$ Å, (B) just above the onset of the upturn, $z_i^* \approx 120$ Å, and (C) on the upturn of the segregation isotherm, $z_i^* \approx 300$ Å.

copolymer is expected to have a negligible effect on the segregation isotherm.

(2) Both triblock and diblock copolymers show an increase in z_i^* beyond the saturation plateau which is due to the condensation of block copolymer micelles adjacent to the interface in the PS phase. This increase for the triblock copolymer occurs at a ϕ_∞ of around 0.15, whereas it occurs at a much lower value of 0.05 for the diblock copolymer. This result indicates that the triblock copolymer has a lower CMC than the diblock copolymer. While the condensation of diblock copolymer micelles at the surface occurs above the CMC, no such preferential segregation is observed for the triblock copolymer.

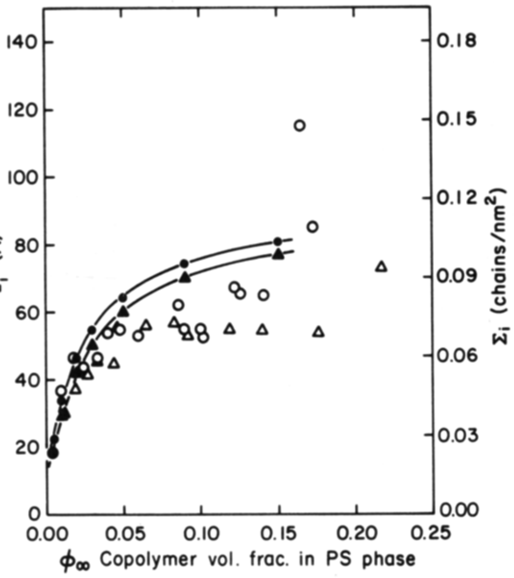

Figure 10. Segregation isotherm of the triblock copolymer at 178 °C (○) and 200 °C (△), respectively. The filled symbols represent the SCMF predictions for 178 and 200 °C, respectively (with the corresponding χ parameter at each temperature[28]). The lines are guides to the eye.

(3) On the basis of our TEM observations, the condensation of micelles indeed coincides with the upturn in the interfacial excess. The triblock copolymer micelles appearing in the host PS phase away from the interface always form aggregates, which probably results from the bridging of triblock copolymer chains between the micelles.

(4) The segregation of a triblock copolymer at 178 and 200 °C exhibits a negligible difference in saturation excess, and yet a higher critical ϕ_∞ for micelle formation is observed for the one annealed at 200 °C.

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Appendix

A.1. Combinatorial Entropy for a Bimodal Brush Consisting of the Copolymer Chains with Tail and Loop Conformations at the Interface. The copolymer joints at the interface possess a two-dimensional freedom in the plane of the interface, as illustrated in Figure A.1. This results in a combinatorial entropy arising from the mixing between the loop conformations and tail conformations. To compute this entropy, the interface is divided into a square lattice in which each cell can be occupied by a copolymer joint. The total number of arrangements Ω

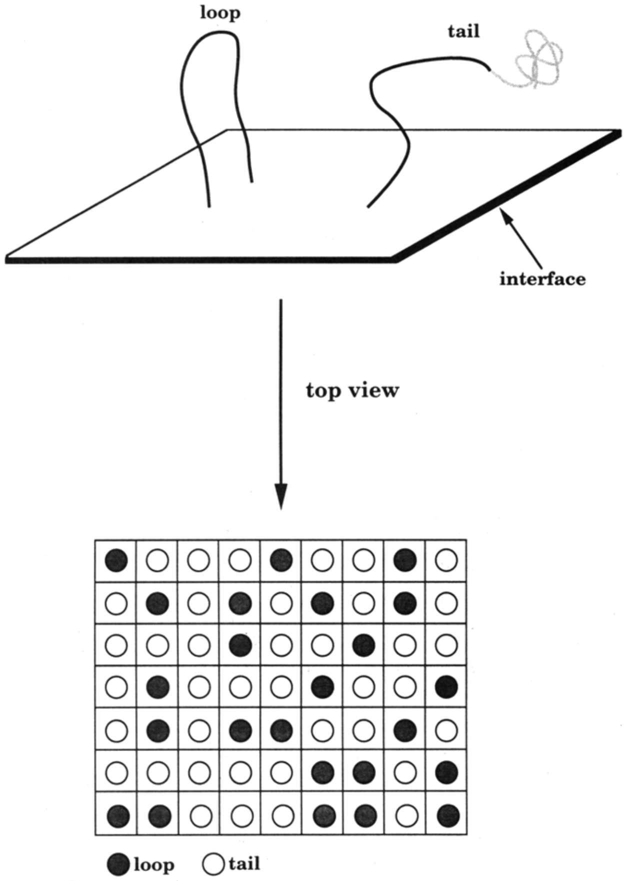

Figure A1. Schematic representation of the two-dimensional translational freedom of the adsorbed triblock copolymer in the plane of the interface.

for the occupancy is given by

$$\Omega = n_0!/n_1!n_2! \qquad (A.1)$$

where n_0, n_1, and n_2 are the total number of cells, number of cells occupied by the copolymer loops, and number of cells occupied by the copolymer tails, respectively. These quantities can be written as

$$n_0 = fQ + 2(1-f)Q \qquad n_1 = fQ \qquad n_2 = 2(1-f)Q \qquad (A.2)$$

The combinatorial entropy is defined as

$$\Delta S = k \ln \Omega = k \ln\{[(2-f)Q]!/(fQ)![2(1-f)Q]!\} \qquad (A.3)$$

With Stirling's approximation $\ln(n!) = n \ln(n) - n$, the free energy associated with this 2D translational freedom can be obtained from eq A.3 and is

$$\frac{F_{2D}}{kT} = Q\{f \ln f + 2(1-f) \ln[2(1-f)] - (2-f) \ln (2-f)\} \qquad (A.4)$$

It should be noted that this calculation overestimates the number of possible arrangements because the correlation between the two cells occupied by the same triblock copolymer with loop conformation is not accounted for. Nevertheless, the correction for this overestimation becomes less important as N of the midblock increases.

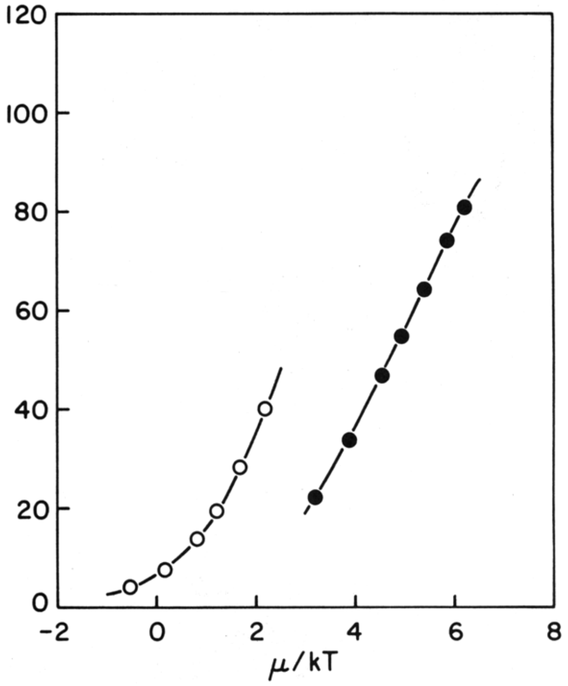

Figure A2. Interfacial excess z_i^* as a function of the chemical potential predicted from the SCMF theory for a 217/37 diblock copolymer (○) and a 37/434/37 triblock copolymer (●), respectively.

A.2. Effect of the Diblock Fraction in the Triblock Copolymer on the Segregation Isotherm. In this section, we have examined the effect of the diblock fraction in the triblock copolymer on its segregation isotherm. The chemical potentials of the diblock and triblock copolymers in this case can be written using the Flory–Huggins mean-field approximation as follows:

$$\frac{\mu_k}{kT} = \ln \phi_{k\infty} + 1 - N_k K_\phi + N_k \chi (N_{ka} \phi_b^{\,2} + N_{kb} \phi_a^{\,2}) \qquad k = 2,3 \quad (A.5)$$

where $\phi_a = \phi_{ha} + \phi_{2a} + \phi_{3a}$, $\phi_b = \phi_{hb} + \phi_{2b} + \phi_{3b}$, and $K_\phi = \phi_{ha}/N_{ha} + \phi_{hb}/N_{hb} + \phi_2/N_2 + \phi_3/N_3$. Here the subscripts 2 and 3 correspond to the diblock and triblock copolymers, respectively; for example, ϕ_{2a} is the volume fraction of the A block of the diblock copolymer. $\phi_{k\infty}$ is the volume fraction of copolymer k far from the interface in the PS host phase. The overall interfacial excess z_i^* is the summation of the individual iinterfacial excesses contributed by each block copolymer, z_2^* and z_3^*. Thus,

$$z_i^* = z_2^* + z_3^* \qquad (A.6)$$

z_2^* is a function of μ_2 where this function can be approximated by that obtained from the corresponding segregation in which the copolymer is purely composed of the diblock copolymer. The same method can be applied to estimate z_3^*. It should be noted that this approximation is valid only if z_2^* or $z_3^* \ll z_i^*$ in which the mixing entropy between these two block copolymers at the interface can be neglected. We have used such an approximation to compute the segregation isotherm for a triblock copolymer containing a small fraction of diblock. The interfacial excesses estimated in this way as a function of the chemical potential for the corresponding segregation of 37/434/37 triblock and 217/37 diblock copolymers are shown in Figure A.2. The fraction of diblock copolymer in the triblock copolymer imposes a constraint in the calculation through the following relation:

$$\text{fraction of diblock copolymer} = \frac{\phi_2}{\phi_2 + \phi_3} \qquad (A.7)$$

Here ϕ_2 is the total volume fraction of diblock copolymer

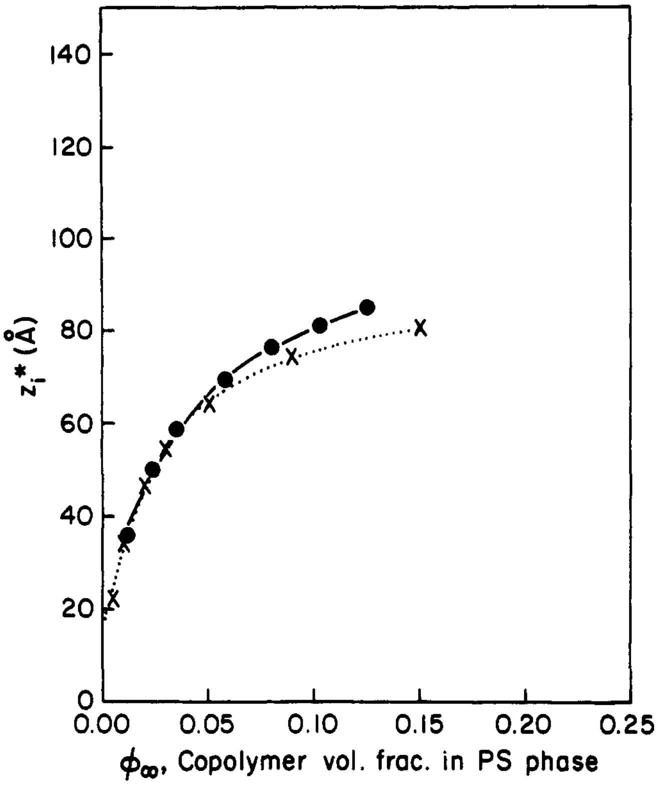

Figure A3. Segregation isotherm for a 37/434/37 triblock copolymer containing a 12% fraction of a 217/37 diblock copolymer (●); the isotherm of the pure triblock copolymer is also plotted for comparison (×). A negligible difference between these two isotherms is seen. The lines are guides to the eye.

and can be estimated by $\phi_{2\infty} + z_2^*/L$. L is the film thickness of the host PS and is taken to be 4000 Å in our calculation to match our experimental conditions. No significant change of the resulting isotherm is found (as long as L is relatively large and thus z_2^*/L is negligible). ϕ_3, the total volume fraction of triblock copolymer, is also evaluated in this way. The segregation isotherm of the 37/434/37 triblock copolymer containing 12% 217/37 diblock copolymer calculated by the above method is shown as solid circles in Figure A.3. The difference between this segregation isotherm and that computed for the triblock copolymer alone (shown by the crosses in Figure A.3) is not significant. This result indicates that the small fraction of diblock copolymer in the triblock copolymer in this specific case does not affect the segregation isotherm in a measurable way.

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