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Interfacial Segregation in Two-Phase Polymer Blends with Diblock Copolymer Additives: The Effect of Homopolymer Molecular Weight

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ABSTRACT: Segregation to interfaces in two-phase blends containing diblock copolymers is fundamental to understanding the properties of these interfaces. In this study, the effect of homopolymer molecular weight on the segregation is examined by forward recoil spectrometry (FRES). In the case of $P_a > N_a$, where P_a and N_a are the polymerization indices of the homopolymer A and the A block of the copolymer, respectively, it is found that the interfacial areal density of block copolymer chains (ν_i) at saturation is not affected significantly by P_a. This situation corresponds to the case where the "brush" of A block chains is not penetrated strongly by the A homopolymer, the so-called dry brush case. However, a lower ν_i is observed in the case of $P_a < N_a$, the so-called wet brush case. While Leibler's brush theory[1] can reproduce the shape of the segregation isotherm if the Flory interaction parameter χ is allowed to vary with P_a, a self-consistent mean-field theory[2] can predict the observed isotherm using a single value of χ. The critical micelle concentration, ϕ_{cmc}, is obtained from the onset of surface segregation and is found to decrease as the molecular weight of the homopolymer matrix increases.

Introduction

Diblock copolymers, which consist of a block of polymer A covalently bonded to a block of polymer B, can behave as surfactants in blends of immiscible homopolymers A and B. Several studies,[1–6] both theoretical and experimental, have reported on the segregation of such block copolymers to the interface between the homopolymers. In addition to decreasing the interfacial tension, the segregation of such block copolymers can lead to a remarkable mechanical strengthening.[7–9] For the particular system in this paper, polystyrene (PS) and poly(2-vinylpyridine) (PVP), Creton and co-workers[7] have shown, for example, that debonding of the PS–PVP interface can be prevented by adding PS–PVP diblock copolymers in small quantities to the blends of the homopolymers. The copolymer chains migrate to the interface where the blocks penetrate into their respective homopolymer phases. By this mechanism, the copolymers serve to strengthen the adhesion at the phase boundary. It has also been demonstrated that the strengthening is a function of both the areal chain density of copolymers at the interface and the polymerization indices of the blocks.[7–9]

However, when the concentration of the copolymer in the homopolymer phase exceeds the critical micelle concentration, diblock copolymer micelles are formed and these micelles make it difficult for the system to come to equilibrium by slowing down the kinetics of segregation. The micellization, therefore, may limit the utility of block copolymers as interfacial agents. Hence, knowledge of both the thermodynamics and kinetics of block copolymer micellization, as well as those of segregation to the interfaces, is necessary for rational interface design.

In this paper, we investigate the effect of one such molecular variable, the molecular weight of the homopolymers. The immiscible polymers polystyrene (PS) and poly(2-vinylpyridine) (PVP) were chosen for this study because of their similarity in chemical structure and resulting physical properties. For example, their glass transition temperatures (~100 °C) and entanglement molecular weights (~20 000) are nearly identical. Diblock copolymers of deuteriopolystyrene (dPS) and poly(2-vinylpyridine) were synthesized by anionic polymerization. The styrene block was deuterated so as to be detectable by forward recoil spectrometry (FRES). The molecular weight of this diblock copolymer is approximately 40 000 for the deuterated polystyrene block and 7000 for the poly(2-vinylpyridine) block converting to the polymerization indices $N_{dPS} = 391$ and $N_{PVP} = 68$. A 100-nm-thick layer of PVP ($P_{PVP} \approx 5100$ for all cases in this study) was spun on a silicon wafer and subsequently spin-coated with a layer of PS, ca. 400 nm thick, doped with small amount of the dPS–PVP copolymer. The thickness of the PVP layer may be chosen for convenience, needing only to be thick enough to eliminate any effects of the Si–PVP interface on the segregation; 100 nm is thick enough for this purpose. The specimens were annealed for at least 8 h at 178 °C after spin-coating, a time sufficient in all cases studied here to allow the system to equilibrate. Details of both the polymerization and the sample preparation have been published elsewhere.[3]

Results and Discussion

Figure 1 shows a schematic of the sample before and after segregation. As shown in this figure, diblock copolymer chains segregate to the interface, mainly driven by the unfavorable enthalpic interaction between the PVP blocks and the PS homopolymers. Depth profiles of diblock copolymer chains were determined using forward recoil spectrometry (FRES) with deuterium-labeled copolymers as previous described.[3] An example of a depth profile is given in Figure 2a. This observed profile represents the actual profile convoluted with the instrumental resolution function, a Gaussian with a full width half-maximum (fwhm) of 550 Å at 2.7-MeV incident beam energy.[10] The energy was normally chosen to be 2.7 MeV rather than 3.0 MeV chosen previously[3] (instrumental resolution fwhm ≈ 800 Å) in order to obtain better

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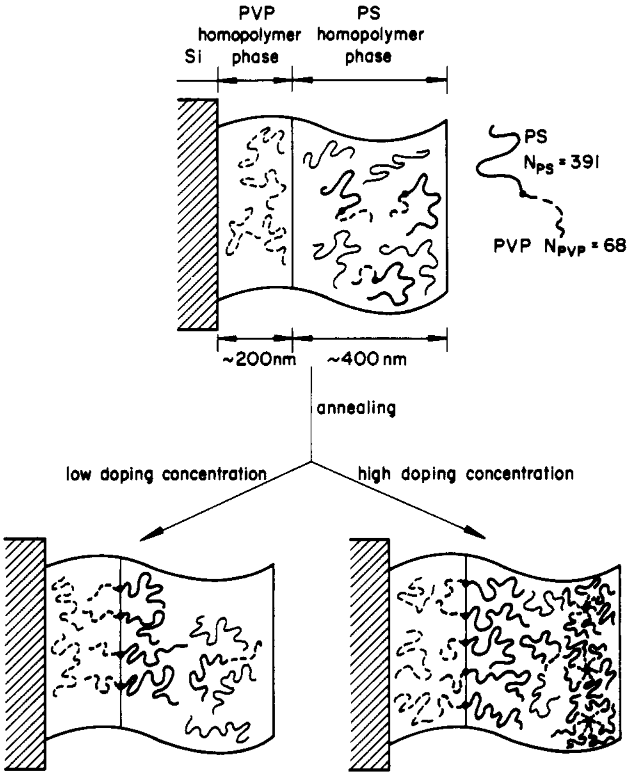

Figure 1. dPS–PVP copolymers added in the PS phase. They may segregate to the interface as a "brush" and to the surface (or interface) as micelles after annealing. In the case of low doping concentration, the copolymer chains segregate to the interface and then stretch their blocks into their respective homopolymer phases (no micellar segregation is observed). In the case of high doping concentration where copolymer micelles are formed in the PS phase, copolymer micelles segregate to the free surface while some of the free copolymer chains still segregate to the interface.

instrumental resolution but yet to provide enough separation between the hydrogen and deuterium surface peaks to allow us to define the plateau of the depth profiles. The peak at a depth of 3900 Å indicates a high concentration of diblock copolymer chains at the interface between the two homopolymers.

When the initial concentration of copolymer in PS is high enough, i.e., when it exceeds the critical micelle concentration (cmc), segregation to the surface is also observed in this experiment, as shown in Figure 2b.

The interfacial excess is defined as

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

where $\phi(x)$ and ϕ_∞ are the volume fractions of block copolymer at depth x and in the bulk PS phase, respectively, and where the integral is computed over a range of x near the interface. In Figure 2, the crosshatched areas represent the interfacial or surface excess. Using the interfacial excess, the areal density of diblock copolymer chains at the interface can be determined from the formula

$$\nu_i = z_i^* \rho_0 / N_c \qquad (2)$$

where ν_i is the number of copolymer chains per unit interfacial area, and N_c and ρ_0 are the polymerization index and segment density of the copolymer, respectively. Here a segment is defined as a repeat unit for the appropriate polymer chain, and the segment density is defined as the number of segments per unit volume. Since PS and PVP have nearly the same segment density, ρ_0 is taken to be the segment density of PS, i.e., 9.4×10^{-3} mol/cm^3 at 178 °C.[11]

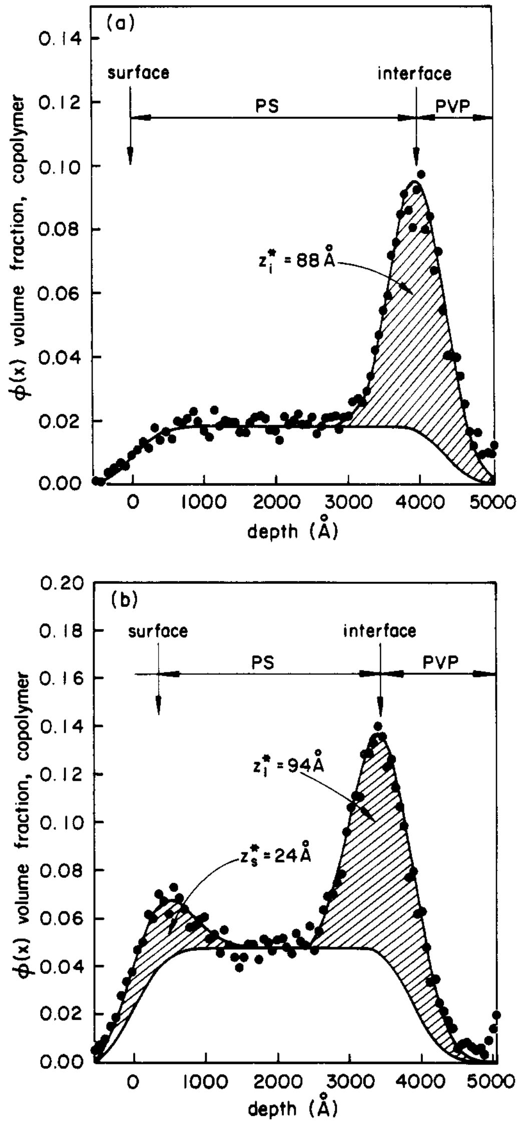

Figure 2. Volume fraction profile of copolymer from a blend containing dPS–PVP ($N_{PS} - N_{PVP}$ = 391 – 68) and PS (P_{PS} = 2000) after an 8-h anneal at 178 °C. (a) Volume fraction of the diblock copolymer in the PS phase for $\phi_\infty = 0.019$, where only interfacial segregation is observed. The interfacial excess z_i^* = 88 Å is represented by the shaded area. (b) When $\phi_\infty = 0.051$ both interfacial and surface segregation are observed yielding an interfacial excess z_i^* = 94 Å and a surface excess z_s^* = 24 Å.

The chemical potential of block copolymer, μ_c, completely determines the equilibrium distribution of the block copolymers. Because the volume fraction of PVP in the PS matrix phase is negligible, the copolymer chemical potential is approximately given by[2]

$$\mu_c/k_B T \cong \ln \phi_\infty - \phi_\infty + \chi N_{PVP} + 1 - N_c/P_{PS} \qquad (3)$$

where k_B is the Boltzmann constant, χ is the Flory interaction parameter between PS and PVP, and N and P represent the polymerization indices of the copolymer and the homopolymer, respectively. The subscripts c, PS, and PVP refer to the entire copolymer, the PS block or homopolymer, and the PVP block or homopolymer, respectively. The volume fraction ϕ_∞ of copolymer in the PS phase is the parameter which controls the segregation through its influence on μ_c. The analogue of eq 3 for the PVP phase shows that, for the asymmetry and χ of our block copolymer, its volume fraction in the PVP phase will be entirely negligible at equilibrium; hence, we concentrate our attention on the PS phase. Figure 3a shows the interfacial excess and areal density of diblock

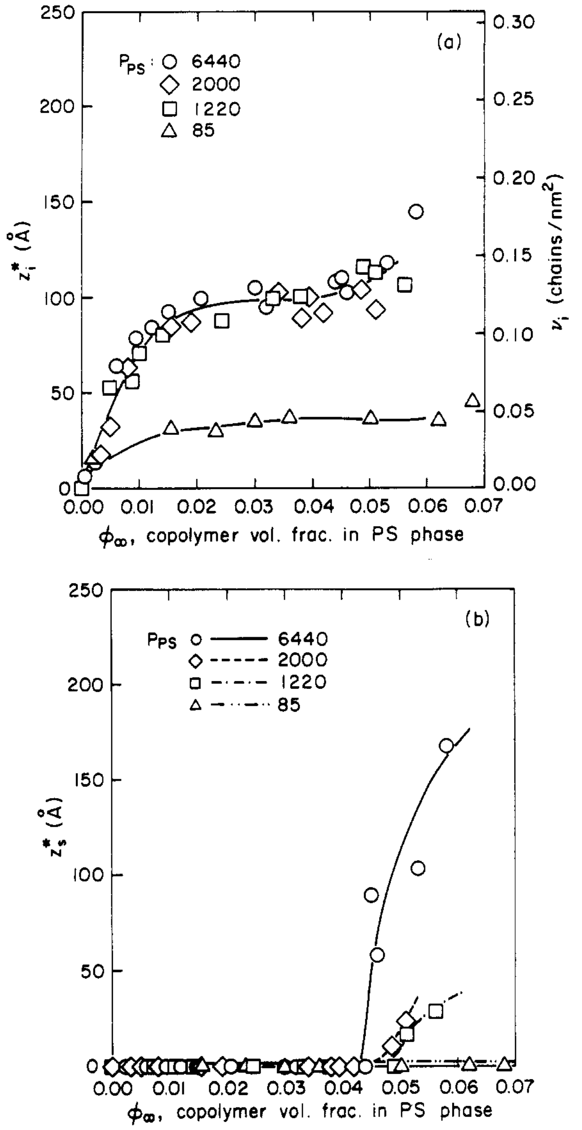

Figure 3. (a) Interfacial excess and areal chain density of copolymer, $N_{PS} - N_{PVP} = 391 - 68$, as a function of ϕ_∞ for various P_{PS} while $P_{PVP} \approx 5120$ maintains unchanged. The solid line is a guide to the eye for defining the three regimes: the initial stage at low ϕ_∞, the plateau at intermediate ϕ_∞, and the final stage at high ϕ_∞. (b) Surface excess and chain density as a function of ϕ_∞ for corresponding molecular variables. The onsets of surface segregation are marked by lines.

copolymer chains as a function of ϕ_∞ for four different homopolymer polymerization indices P_{PS}. Figure 3b shows a corresponding plot of the surface excess.

The interfacial segregation can be divided into three regimes, an initial stage, a plateau, and a final stage, as ϕ_∞ is increased. In the initial stage which is the regime of low ϕ_∞, the interfacial excess is increasing with increasing concentration of the diblock copolymer, and there is no detectable surface excess. A fraction of the diblock copolymer chains migrates to the interface, forming an adsorbed layer in equilibrium with ϕ_∞. As ϕ_∞ is increased, more of the block copolymers segregate to the interface. Above a certain ϕ_∞, the interfacial excess reaches a plateau and there is still no visible surface excess. This plateau suggests that the copolymer enrichment at the interface is approaching saturation. This saturation can be explained by the limited packing of copolymer chains at the interface and is predicted by the models of segregation to be discussed below. As the saturation density is approached, most of the copolymer chains accumulate in the bulk PS phase without migrating to the interface and finally micelles are formed. The onset of surface segregation, which is believed to occur at the critical micelle concentration, defines the final stage and the interfacial excess may rise again in this regime as micelles segregate also to the brush. The formation of micelles at the surface and at the brush has been observed directly using transmission electron microscopy by Shull et al.[12] Shull and co-workers[3,12] have demonstrated that this segregation is due to the block copolymer micelles which segregate to the surface (PS–vacuum interface) or to the brush due to an attractive interaction between the corona of the micelles and the free surface or the brush. In the case of the surface the origins of this attractive interaction are believed to be (1) the lower surface energy of deuterated polystyrene compared to hydrogenated polystyrene and (2) the loss of entropy of homopolymer matrix chains in the vicinity of both the micelle corona and the surface, a loss that is reduced if the micelles migrate to the interface.[12] [The attractive interaction to the brush is similarly thought to have two contributions: (1) a reduction in the interfacial energy between dPS and PS (isotope effect) and (2) a reduction in the loss of entropy of homopolymer in the vicinity of the brush and the corona.[13]] In any case the surface segregation is a consequence of the formation of micelles and the volume fraction of diblock copolymer chains in the bulk at the onset of the surface segregation roughly corresponds to ϕ_{cmc}.[14] On the basis of the segregation study, the critical micelle concentrations of the polymer blends with various P_{PS} are obtained from Figure 3b and summarized in Table I.

Table I
Dependence of the Critical Micelle Volume Fraction ϕ_{cmc} on PS Molecular Weight

degree of polymzn of PS homopolymer (P_{PS})	ϕ_{cmc}	μ_{cmc} from z^*	μ_{cmc} from Leibler's micellar theory
6440	~0.045	~4.92	3.5
2000	~0.049	~4.85	3.5
1220	~0.051	~4.74	3.5
85	>0.068	~0.12	-1.2

As indicated in Table I, the ϕ_{cmc} decreases as the P_{PS} increases. This tendency is due to the larger combinatorial entropy for the mixing of the unfavorable blocks of the diblock copolymers with the shorter homopolymer chains, which thus delays the onset of micelle formation to larger block copolymer concentrations. The surface segregation of the blend with short homopolymer chains, $P_{PS} = 85$, has not been observed up to $\phi_\infty = 0.068$, as shown in Figure 3b. This result implies either that the micelles have not yet formed at this volume fraction or that the micelles do not migrate to the interface and/or the surface because the attraction between brushes no longer exists in this case.[13] Due to its insensitivity to N_{PVP} and χ relative to ϕ_{cmc}, the observed μ_{cmc} is best compared to theory. Two regimes may be defined, the dry brush regime and the wet brush regime, depending on the extent of penetration of homopolymer chains into the copolymer brush, in this case the corona of the micelle. When the homopolymer chains are much longer than the chains of the corona, these are excluded from the corona, whch is thus "dry", and when the homopolymer chains are much shorter, these penetrate into the corona, which becomes "wet". As seen in Table I, the predicted μ_{cmc} in the dry brush case[1] is lower than those observed and is independent of P_{PS} whereas the observed μ_{cmc} increases a small amount over this range of P_{PS}. The underestimation of μ_{cmc}, previously also noted by Shull et al.,[3] may be attributed to some of the simplications (e.g., uniform chain stretching) of the Leibler theory of micelles. In the wet brush case, the prediction of the Leibler, Orland, and Wheeler model[15] is similarly considerably lower than the lower limit that we have established for μ_{cmc}.

Leibler has also suggested a simple theory of interfacial copolymer segregation and energetics.[1] By analogy to the case of the micelles, two regimes are defined, the dry brush and the wet brush, depending on the extent of penetration of homopolymer chains into the copolymer brush at the interface. In the following derivation, slightly different formulae are obtained as compared to Leibler's original brush model because we eliminate the assumption which is made by Leibler that $\rho_0 \approx 1/a^3$ where a is the statistical segment length.

(A) Dry Brush Model. In this regime, the homopolymer chains (PS) do not significantly penetrate the similar block chains (PS) if

$$P_{\mathrm{PS}}^{3/2} > N_{\mathrm{PS}} \text{ and } \nu_{\mathrm{i}} a^2 P_{\mathrm{PS}}^{1/2} > 1 \tag{4}$$

leading to the following simple relations

$$z_{\mathrm{i}}^* = \frac{a}{3}\left[2N_{\mathrm{c}}\frac{\mu_{\mathrm{c}}}{k_{\mathrm{B}}T}\right]^{1/2} \tag{5}$$

and

$$\gamma = \gamma_0 - \frac{\rho_0 a}{9}\left\{\frac{8}{N_{\mathrm{c}}}\left[\frac{\mu_{\mathrm{c}}}{k_{\mathrm{B}}T}\right]^3\right\}^{1/2} k_{\mathrm{B}}T \tag{6}$$

where γ and γ_0 is the interfacial tension in the presence and the absence of the copolymers, respectively. It has been reported that the chain dimensions of PS and PVP are not significantly different in a Θ solvent.[16] Therefore, a is taken to be the statistical length of a PS segment of 6.7 Å.[17] As a consequence of assuming that the homopolymer chains do not penetrate into the copolymer brush, only the chain stretching free energy of the copolymers will contribute to the overall free energy of the interfacial region. This assumption leads to an analytical expression for the interfacial excess as a function of ϕ_∞, i.e., eq 5. It has been demonstrated that this assumption is not rigorously correct and can lead to significant errors, as for example it leads to a serious overestimation of the decrease in interfacial tension.[2] However, this model captures the important features of interfacial segregation without requiring complicated computer calculations, which are necessary for more rigorous methods, e.g., the various self-consistent mean-field models.

(B) Wet Brush Model. In the case of short homopolymer chains which penetrate into the copolymer brush appreciably, it is necessary to include the contribution of the combinatorial entropy to the free energy in order to describe the interfacial excess properly. According to Leibler, the free energy per chain of the PS or PVP brush is approximated as

$$\frac{g_j}{k_{\mathrm{B}}T} = \ln\left[N_j\frac{\nu_{\mathrm{i}}}{\rho_0 a}\right] + \frac{3^{4/3}}{2^{5/3}}\frac{N_j}{P_j^{2/3}}\left(\frac{\nu_{\mathrm{i}}}{\rho_0 a}\right)^{2/3} \quad \text{where } j = \text{PS or PVP} \tag{7}$$

when the following condition is satisfied

$$P_j^{1/2} < \frac{1}{\nu_{\mathrm{i}} a^2} < \frac{N_j^{3/2}}{P_j} \tag{8}$$

and leads to an analytical relation between the interfacial chain density and the chemical potential which is

$$\frac{\mu_{\mathrm{c}}}{k_{\mathrm{B}}T} = 2 + \ln\left\{\left[N_{\mathrm{PS}}N_{\mathrm{PVP}}\left[\frac{\nu_{\mathrm{i}}}{\rho_0 a}\right]^2\right\} + \left[\frac{375}{32}\right]^{1/3}\left[\frac{N_{\mathrm{PS}}}{P_{\mathrm{PS}}^{2/3}} + \frac{N_{\mathrm{PVP}}}{P_{\mathrm{PVP}}^{2/3}}\right]\left[\frac{\nu_{\mathrm{i}}}{\rho_0 a}\right]^{2/3} \tag{9}$$

Leibler ignored the logarithmatic term in eq 9 so as to obtain the following analytical formula for ν_{i} in terms of μ_{c}:

$$\nu_{\mathrm{i}} = \left(\frac{32}{375}\right)^{1/2}\left(\frac{N_{\mathrm{PS}}}{P_{\mathrm{PS}}^{2/3}} + \frac{N_{\mathrm{PVP}}}{P_{\mathrm{PVP}}^{2/3}}\right)^{3/2}\left(\frac{\mu_{\mathrm{c}}}{k_{\mathrm{B}}T}\right)^{3/2}\rho_0 a \tag{10}$$

It must be pointed out that this approximation leads to a serious distortion of the solution of eq 9. This transcendental equation must be solved directly in order to compare this model correctly with the experiment. Using eqs 3 and 9, one can establish the relation between the interfacial chain density ν_{i} and ϕ_∞ more accurately. Associated with the solution of eq 9 for ν_{i}, one can evaluate the interfacial tension γ by the formula

$$\gamma = \gamma_0 - \left[2 + \frac{3^{1/3}}{2^{2/3}}\left(\frac{N_{\mathrm{PS}}}{P_{\mathrm{PS}}^{2/3}} + \frac{N_{\mathrm{PVP}}}{P_{\mathrm{PVP}}^{2/3}}\right)\left(\frac{\nu_{\mathrm{i}}}{\rho_0 a}\right)^{2/3}\right]\nu_{\mathrm{i}} k_{\mathrm{B}}T \tag{11}$$

(C) Wet–Dry Brush Case. It should be noted that the previous two models are used to describe cases in which either both wet or both dry brushes are found on each side of the interface. The asymmetric case in which a brush of one block is wet ($P_{\mathrm{a}} < N_{\mathrm{a}}$) on one side of the interface and a brush of the other block is dry ($P_{\mathrm{a}} > N_{\mathrm{a}}$) on the other side of the interface will be referred to the wet–dry brush case in this paper. On the basis of Leibler's brush model, we derive the following expression for μ_{c} as a function of ν_{i} in this special case.

$$\frac{\mu_{\mathrm{c}}}{k_{\mathrm{B}}T} = 1 + \ln\left[N_{\mathrm{wet}}\frac{\nu_{\mathrm{i}}}{\rho_0 a}\right] + \left[\frac{375}{32}\right]^{1/3}\left[\frac{N_{\mathrm{wet}}}{P_{\mathrm{wet}}^{2/3}}\right] \times \left[\frac{\nu_{\mathrm{i}}}{\rho_0 a}\right]^{2/3} + \frac{9}{2}N_{\mathrm{dry}}\left[\frac{\nu_{\mathrm{i}}}{\rho_0 a}\right]^2 \tag{12}$$

This equation is solved to obtain the interfacial excess as a function of ϕ_∞. In association with the solution of eq 12, one should be able to establish the relation between the interfacial tension γ and ϕ_∞ with the aid of eq 13. The

$$\gamma = \gamma_0 - \left[\left(\frac{\nu_{\mathrm{i}}}{\rho_0 a}\right)^2 + 1 + \frac{3^{1/3}}{2^{2/3}}\left(\frac{N_{\mathrm{wet}}}{P_{\mathrm{wet}}^{2/3}}\right)\left(\frac{\nu_{\mathrm{i}}}{\rho_0 a}\right)^{2/3}\right]\nu_{\mathrm{i}} k_{\mathrm{B}}T \tag{13}$$

results, based on eqs 2, 3, 12, and 13, are also used to test the validity of the wet brush model.

As shown in Figure 3a, the interfacial excesses in blends of block copolymer and PS with P_{PS} = 6440, 2000, and 1220 level off at nearly the same value of z_{i}^* = 100 Å and ν_{i} = 0.12 chains/nm^2. The interfacial areal chain densities at saturation for these three blends are considered to be the same within the experimental uncertainty. According to Leibler's theory, these three blends fall in the category of the dry brush model. Our result is consistent with this assumption since, in the dry brush model, the saturation chain density is controlled mainly by the PVP block length of the diblock copolymer and the Flory parameter χ. Moreover, since the dependence of μ_{c} on P_{PS} in eq 3 is small at large P_{PS}, the interfacial excesses, of all three dry brush cases, should not be significantly different in the first two regimes up to the critical micelle concentration.

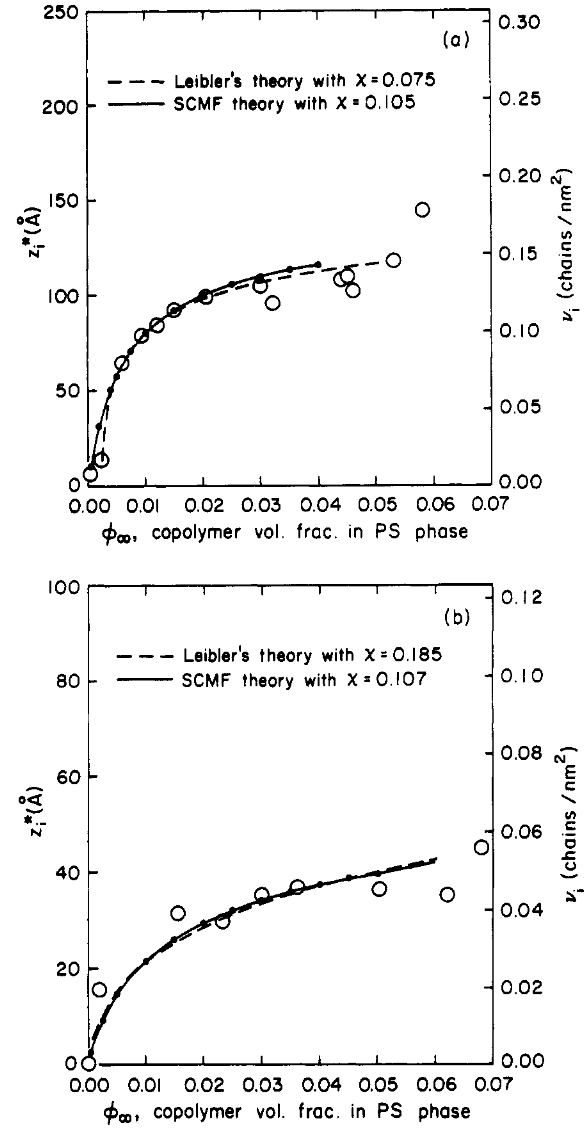

Figure 4. Interfacial excess of the copolymer for (a) PS blends with P_{PS} = 6440, the dry brush case, and (b) PS blend with P_{PS} = 85, the wet–dry brush case, as a function of ϕ_∞ and the predictions from the SCMF theory and from Leibler's brush model. The χ parameter is adjusted in each case to produce the best fit of the theory to the data.

In the case of the blend with a PS homopolymer of P_{PS} = 85, the significant penetration of PS homopolymer chains into the PS brush (wet–dry brush case) results in higher combinatorial entropy, as compared to the dry brush case, in the vicinity of the interface. This entropic contribution partly compensates for the unfavorable enthalpic interaction between the PVP blocks and PS homopolymers, with the consequence that this blend has a lower interfacial excess at saturation.

For the higher molecular weight homopolymers (P_{PS} = 6440, 2000, and 1220), we can force fair agreement between Leibler's dry brush model of the interfacial excess and the experimental data by adjusting the χ parameter, with the exception that the theory does not accurately represent the data for very small ϕ_∞'s. This discrepancy is due to the fact that Leibler's theory can not be valid at low copolymer chemical potential. For the sake of clarity, only one of the three dry brush cases is shown in Figure 4a; the other predictions (for the same χ) are not significantly different. For comparison, we have used a more exact self-consistent mean-field theory (SCMF theory[2]) to predict the interfacial excess for P_{PS} = 6440, and this prediction is shown as the solid curve on Figure 4a. It should be noted that the interaction parameter χ used in the SCMF theory fitting, i.e., 0.105, is very close to the estimated value 0.1.[3] In contrast, a lower χ is necessary to allow Leibler's theory to fit the experimental data by compensating for its overestimation of the chemical potential of the diblock copolymer at a given ν_i, an overestimation which arises from only considering the chain stretching contribution. The comparison of segregation isotherms between the wet–dry brush model and the experimental data is shown in Figure 4b. Fair agreement is found provided a χ parameter of 0.185 is used for the data fitting (the estimated value is ~0.1[3]).

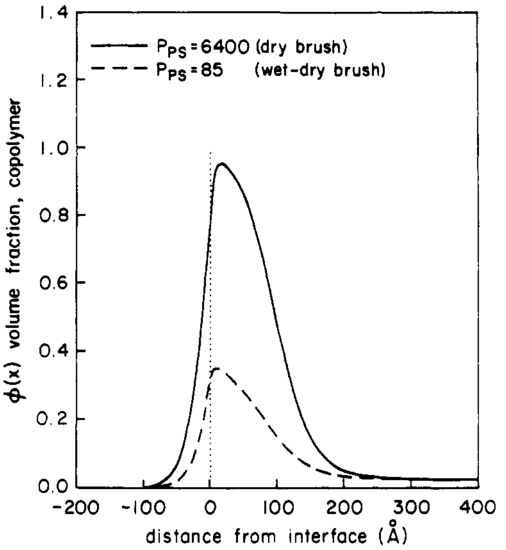

Figure 5. Depth profiles of diblock copolymer ($N_{dPS} - N_{PVP}$ = 391 − 68) calculated using the SCMF theory at ϕ_∞ = 0.03. Solid line: dry brush case with P_{PS} = 6440. Dashed line: wet–dry brush case with P_{PS} = 85.

The depth profiles of copolymers, calculated from the SCMF theory and shown in Figure 5, provide a clear elucidation of the concept of dry and wet brushes. As indicated, the penetration of the homopolymer chains is much more significant in the wet brush (dashed line) as compared to the dry brush (solid line). Moreover, the phase boundary between the brush and the bulk phase is more diffuse; i.e., there is a smaller gradient in volume fraction near the interface in the wet brush case than in the dry brush case. Therefore, the step brush assumed in Leibler's theory may not be a good approximation to the real profile in this case (wet brush case), and thus we believe this approximation is mainly responsible for the large discrepancy in χ parameters between Leibler's theory and the SCMF theory.

The SCMF theory as well as Leibler's theory may be further tested by fitting the experimental data for both the dry and the wet brush cases. If theory is satisfactory, it should be able to fit the data with the same interaction parameter χ. For the SCMF theory, the χ used for the high P_{PS} case (0.105) and that used for the low P_{PS} (0.107) are not significantly different as seen in Figure 4a,b. This agreement indicates that the SCMF theory may provide a reliable way to predict the interfacial segregation and energetics for general cases. For Leibler's theory, in contrast, the χ used for the high P_{PS} case (0.075) is very different from that needed in the low P_{PS} case (0.185). This discrepancy is expected because varying χ is necessary to compensate the error caused by the oversimplified assumption on the overall free energy. But, as long as χ is allowed to vary with P_{PS}, Leibler's theory can reproduce the form of segregation isotherms reasonably well.

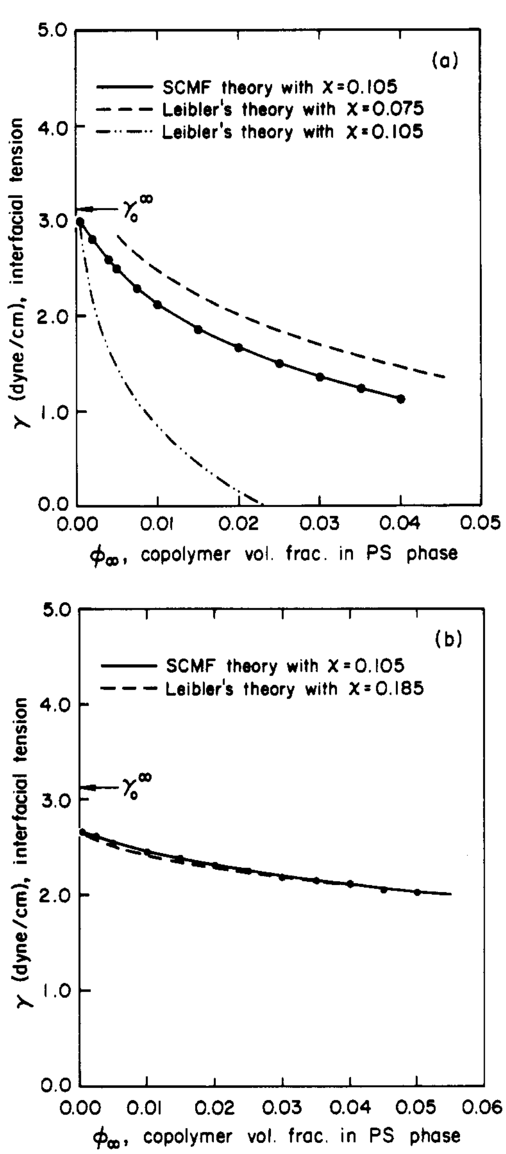

Figure 6. Interfacial tension as determined by the SCMF theory with $\chi \approx 0.105$ for (a) PS blends with $P_{PS} = 6440$, the dry brush case, and (b) PS blends with $P_{PS} = 85$, the wet–dry brush case, and the prediction from Leibler's brush model. γ_0^∞ is the interfacial tension for infinite molecular weight in the absence of copolymer.

The interfacial tension as estimated by the SCMF theory and the Leibler theory are shown in parts a and b of Figure 6 for the dry brush and the wet–dry brush case, respectively. As shown in Figure 6a, Leibler's theory greatly overestimates the decrease in the interfacial tension for the estimated value of χ ($\sim$0.1) and even leads to a negative value of γ before the measured ϕ_{cmc} is reached. However, with the interaction parameter χ (0.075) used for fitting the interfacial excess data, the difference between the SCMF theory and the Leibler theory is narrowed. Leibler's theory also shows good agreement with the SCMF theory in the wet–dry brush case, as shown in Figure 6b. One should be aware that the evaluation of interfacial tension (the dashed line in Figure 6) by Leibler's theory may lead to nonreal values at small ϕ_∞ for both dry and wet–dry cases, which suggests that the arbitrary adjustment of the χ parameter may cause errors. Therefore, we suggest the SCMF theory is necessary to evaluate the interfacial tension accurately. However, it is important to point out that the simplicity of Leibler's theory provides a useful starting point for segregation studies.

Conclusions

(1) The interfacial excess is divided into three regimes with respect to ϕ_∞: the initial stage, the plateau, and the final stage. In the regime of the initial stage, the interfacial excess increases with the increasing ϕ_∞. The saturation of the copolymer packing at the interface is responsible for the observed plateau, the magnitude of which is very useful in the design of interfaces. The final stage is a regime of increasing interfacial excess caused by micelle segregation to the brush.

(2) The interfacial excesses of the diblock copolymer in the dry brush cases are not affected appreciably by the P_{PS} in the first two regimes, resulting in nearly the same areal chain density at saturation.

(3) The penetration of lower molecular weight homopolymer chains into the brush at the interface (wet–dry case) results in lower interfacial excess, as well as lower areal chain densities at saturation.

(4) The critical micelle concentration ϕ_{cmc} is obtained from the onset of the surface segregation and increases as the P_{PS} decreases.

(5) While Leibler's brush theory[1] can reproduce the shape of the segregation isotherms if the Flory interaction parameter χ is allowed to vary with P_{PS}, a SCMF theory[3] can predict the observed isotherms using a single value of χ ($\sim$0.105) which is very close to the estimated value of 0.1.

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