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Brush Formation by Symmetric and by Highly Asymmetric Diblock Copolymers at Homopolymer Interfaces

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ABSTRACT: Nuclear reaction analysis (NRA) was used to study the segregation of polyisoprene (PI)–deuterated polystyrene (dPS) diblock copolymers to the interfaces formed by high molecular weight (M) polystyrene (PS, $M = 3 \times 10^6$) with vacuum, silicon, and gold. Two types of diblock copolymers, a symmetric PI(M=10^4)–dPS(M=10^4) diblock and a strongly asymmetric PI(M=10^4)–dPS(M=10^6) diblock, were investigated, and their segregation isotherms were determined as a function of their bulk concentration within the PS homopolymer. Isotherms were analyzed in terms of a mean-field approach due to de Gennes and Leibler and the numerical results of a self-consistent mean-field model. Both approaches were found to provide a consistent description of the data.

I. Introduction

In the past few years there has been much attention devoted to the surface and interfacial segregation of A–B block copolymers.[1] This interest has arisen due to many possible applications, including compatibilization,[2] polymeric surfactants,[3] and modification of friction and wear properties.[4]

The basic structural element of the segregated copolymers is a polymeric brush. A single B brush is created when an A block attaches at the surface of a polymeric (or solvent) host and only the B block dangles out to form a brushlike layer.[5–7] Double A brush–B brush systems occur for A–B diblocks located at an A/B or A/C interface separating macroscopic phases A and B (or C),[8–10] or a microdomain droplet A phase from the host phase B(C).[3,11] Here C could be a phase compatible with B but not with A. One can also envisage a micelle built solely of A blocks of the copolymer[12–14] as a microdomain phase.

In a recent paper[7] related to the present report, we studied the segregation of an asymmetric diblock copolymer, consisting of polyisoprene (PI, M = 10^4)/deuterated polystyrene (dPS, $M = 10^5$) blocks, to the interfaces formed by polystyrene (PS) homopolymer with various phases. In all cases the diblocks attach to the interface by their PI moieties alone, to form a brushlike structure of end-attached dPS tails. This adsorption is driven by the lower surface energies associated with PI as compared to PS segments located at the interface, and also by the large enthalpic penalty paid by each segment of the PI block embedded in PS homopolymer resulting from an unfavorable segmental interaction parameter $\chi_{\rm PIPS}$. The overall energy gain of a diblock segregating to the interface may be described by an adsorption parameter β', defined as $\beta'_{\rm i} = N'_{\rm PI}\chi_{\rm PIPS} - \Delta_{\rm i}$, where $N'_{\rm PI}$ is the effective number of PI segments in the diblock and $\Delta_{\rm i}$ represents (mainly) the surface energy change due to a PI block at the interface i (i = polymer/vacuum or polymer/substrate). β' turns out[7] to be a central parameter in describing the thermodynamics of brush formation from these diblocks.

Each PI–dPS copolymer segregating to the PS interface creates a separate PI patch which reduces the interfacial tension. This results in a constant contribution to the adsorption parameter β' as long as the PI blocks do not overlap with each other. Once a continuous dense PI pancake is created at the PS interface, an additional segregating PI–dPS copolymer does not lower further the interfacial tension. The critical interfacial diblock density $\sigma_{\rm c}$, separating these two regimes of low ($\sigma \ll \sigma_{\rm c}$) and high ($\sigma \gg \sigma_{\rm c}$) density, corresponds to one copolymer chain occupying the area Σ described by the PI radius of gyration; i.e., $\sigma_{\rm c} = a^2/\Sigma = a^2/\pi R_{\rm gPI}{}^2$, where a is the statistical segment length.

In the present study we extend our previous investigation of an asymmetric PI–dPS diblock (asymmetry ratio ≈ 10) to a very asymmetric PI(M=10^4)–dPS(10^6) diblock as well as to a symmetric PI(M=10^4)–dPS(10^4) copolymer. We study their segregation to the interfaces of a PS homopolymer melt ($M = 3 \times 10^6$). For the long and short diblocks, we find that the brushes are formed at areal densities $\sigma \cong 0.2\sigma_{\rm c}$ and $\sigma \cong 2.3\sigma_{\rm c}$, respectively. This allows us to compare segregation isotherms and the β' parameters both for the case of low areal densities and at the onset of high coverage. The segregation of block copolymers with different block length ratios has been studied previously[9,15,16] but to our knowledge the block length ratio has never exceeded 10 or so. Here we study the segregation of diblock copolymers with ratios which differ by 2 orders of magnitude. In section II we describe the experimental method, based on composition–depth profiling using nuclear reaction analysis. The results are presented in section III, and in section IV we discuss the experimentally measured surface-excess isotherms of the diblocks, primarily in terms of a Flory-type mean-field model due to Leibler and de Gennes; some comparison with a self-consistent mean-field model due to Shull is made, and it is shown that both models are able to describe our results in a consistent manner.

II. Experimental Section

Polyisoprene–deuterated polystyrene block copolymers were synthesized by anionic polymerization using *tert*-butyllithium as the initiator and methanol as the terminator.[17] Two types

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Table 1. Molecular Weights and Polydispersities (Expressed as the Ratio of Weight to Number Average) of Materials Used in This Study

polymer	M_w	M_w/M_n
PS(3×10^6)[a]	2 890 000	1.09
dPS(10^4)[b]	10 500	1.02
dPS(10^6)[b]	1 000 000	1.18
PI(10^4)–dPS(10^4)[c]	20 000	1.03
	hPI = 10 000	1.03
	dPS = 10 000	
PI(10^4)–dPS(10^6)[c]	1 080 000	1.03
	hPI = 10 300	1.02
	dPS = 1 069 700	

[a] Obtained from Tosoh (Japan) and characterized by them. [b] Obtained from Polymer Laboratories (U.K.) and characterized by them. [c] Synthesized by us and characterized by light scattering and size exclusion chromatography.

of diblocks were obtained: a short, symmetric PI(10^4)–dPS(10^4) copolymer and a long, asymmetric PI(10^4)–dPS(10^6) copolymer (see Table 1 for details). In both cases the isoprene was polymerized first, and thus all PI blocks have a *tert*-butyl end group. Nearly monodisperse homopolystyrene ($M = 3 \times 10^6$) was used as a matrix material. In addition, perdeuterated homopolystyrene samples with molecular weights of 10^4 and 10^6 were used for control measurements. Polished silicon (Si) wafers were purchased from Aurel GmbH, Germany (the wafers were p-doped; 100 orientation; resistivity 1–30 Ω·cm). All solvents used were analytical grade.

Films of the PS incorporating different PI–dPS concentrations were prepared by spin-casting a toluene solution containing the appropriate homopolymer/diblock ratios onto the Si wafers (cut to dimensions ca. 1×2 cm^2) to thickness in the range 350–500 nm. Where segregation at the Au/PS interface was studied, a 5–15 nm thick gold layer was evaporated on a Si wafer or glass, on top of which the PS layer was spin-cast; following this, the Au/PS sandwich was floated off onto distilled water and mounted on the Si wafer with reversed geometry, i.e., with the Au layer on the top. Samples were sealed in glass ampules under vacuum (10^{-5} Torr) and annealed at a temperature of 190 °C (±0.5 °C) for periods up to 15 days. Control experiments were carried out to examine the questions of equilibrium and of the role of isotope labeling of the PS block of the copolymers, as will be described in the following section.

The composition–depth profile of the deuterated styrene segments of the dPS block of the copolymer was determined using nonresonant nuclear reaction analysis (NRA). The technique has been described in detail earlier.[18-20] Briefly, a beam of ^{3}He ions accelerated to energy $E_{3,0}$ is incident at a low angle on the polymer film. The nuclear reaction

$$^3\text{He} + {}^2\text{H} \rightarrow {}^4\text{He} + {}^1\text{H} + Q \qquad (Q = 18.3\ \text{MeV}) \qquad (1)$$

takes place within the sample. From the energy spectrum of the forward-emitted ^{4}He or ^{1}H particles and the known energy losses and reaction cross section, the concentration of the deuterium (^{2}H) atoms (and thus of deuterated styrene segments) is directly obtained as a function of depth. The depth range and the depth resolution of this method depend strongly on $E_{3,0}$. A ^{3}He beam with an incident energy of 900 keV was used, enabling depth probing up to ca. 650 nm. The ^{4}He particles detected at a forward geometry (scattering angle of 30°) yield a resolution of some 9 nm HWHM at the sample surface, deteriorating due to straggling to some 35 nm HWHM at a depth of 500 nm. ^{1}H particles detected at a backward geometry (scattering angle = 175.2°) provide a resolution comparable with ^{4}He at the sample surface but better than ^{4}He at depths up to 250 nm in the PS sample. In the present report protons were used to determine profiles of the PS samples covered with a gold film. A 15 nm thick Au layer results in energy losses comparable with those caused by a 73 nm PS film.[21] In addition, we took advantage of the lower stopping power for ^{1}H as compared with ^{4}He in the gold layer as well as of the reduced scattering background in the backward geometry.

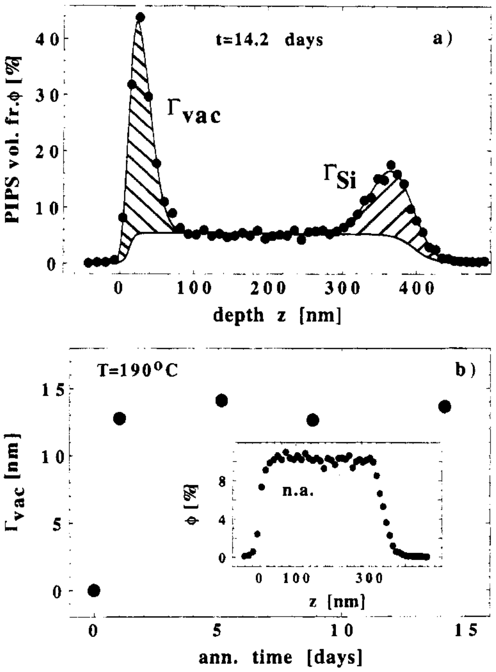

Figure 1. (a) Composition–depth profile for the long, asymmetric (PI(10^4)–dPS(10^6)) diblock at bulk volume fraction ϕ_b = 5.3% in a layer of PS(M=3×10^6) mounted on a silicon wafer, following 14.2 days of annealing at 190 °C. The shaded areas are the interfacial excesses as defined in eq 2; the vacuum interface is at z = 0, while the Si interface is at $z \cong$ 395 nm. The values of copolymer excess at the vacuum/PS interface Γ_{vac} determined for the same system at this and shorter annealing times are shown in plot b. The inset to (b) (n.a. = not annealed) indicates no interfacial excess and a uniform PI–dPS distribution within a PS layer prior to annealing.

The overall excess Γ of the copolymer chains segregated at any PS interface could be determined from the profile, as shown in Figure 1a by the hatched areas for the PS/vacuum and PS/Si interfaces, where

$$\Gamma = \int_0^{z_b} (\phi(z) - \phi_b)\, dz \qquad (2)$$

Here ϕ_b is the bulk copolymer volume fraction $\phi(z)$ at depth z_b. The units of Γ are in nanometers: the surface excess is equivalent to a notional thickness Γ of the pure copolymer at the interface. The absolute values of the volume fractions are derived from the known overall amount of the deuterated polystyrene segments in the cast films.

III. Results

The primary output of our experiments are the NRA composition–depth profiles, from which the interfacial excess Γ of the segregated copolymers is extracted. These results are later discussed in terms of equilibrium models, and care was taken to ensure that the profiles attained their limiting (steady state) values. The dependence of the excess Γ on annealing time, determined for PI(10^4)–dPS(10^6) copolymers at the vacuum/PS interface (see Figure 1b) assures us that after 1–2 days of annealing at 190 °C we should reach a situation close to thermodynamic equilibrium.

While the spectrum of the as-cast (unannealed) matrix homopolymer layer with PI(10^4)–dPS(10^6) (inset to Figure 1b) indicates a uniform distribution in the film, the analogous profile for the shorter, symmetric diblock (Figure 2a) shows that the short copolymer migrates to the PS interface already during the spin-

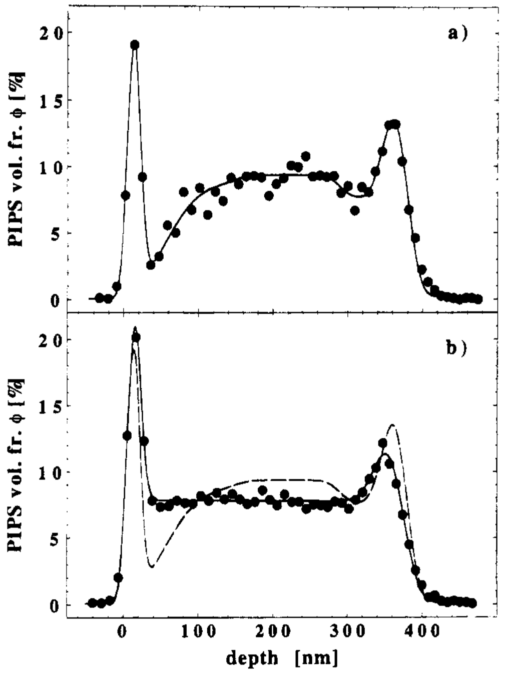

Figure 2. Composition–depth profile for the short, symmetric PI(10^4)–dPS(10^4) diblock at initial concentration ϕ_b = 8.6% in a PS(M=3×10^6) layer as cast (prior to annealing (a) and after 3.2 days of annealing at 190 °C (b). The dashed line in (b) corresponds to the profile of (a).

casting process and could contribute up to 70% of the equilibrium excess values (see Figure 2b). Apparently, the mobility of the longer diblocks in the ternary system (solvent + PS + PI-dPS) is low enough to prevent this. Earlier we found that a PI(10^4)–dPS(10^5) copolymer with molecular weight and block length ratio intermediate to those of the present study did segregate during the PS film preparation, but only to the PS/Si and not to the vacuum/PS interface. Similar effects occurring during spin-casting were also observed by other groups.[15]

As noted in the Introduction, the PI–dPS chains are driven to the PS homopolymer interfaces by a combination of repulsive PI/PS interactions and a lowering of the interfacial tension by the PI. In Figure 3 we show this segregation for both the short and the long diblocks. We note that the surface excess increases monotonically from the lowest concentrations ($\phi_b \cong 1\%$), with no traces of a critical micelle concentration transition,[9,15,22] up to the highest concentrations studied ($\phi_b \cong 6\%$ for the long diblock and $\phi_b \cong 14\%$ for the short diblock) as indicated in Figure 3 and the segregation isotherms later in this section. These results are also consistent with the electron microscopy study of Hasegawa and Hashimoto[14] on the surface segregation of PI–PS diblocks.

Control experiments were carried out with perdeuterated PS homopolymers incorporated in the PS matrix to check the effect of isotopic substitution in driving the labeled diblock to the interfaces. No segregation of a deuterated PS ($M = 10^4$) analogue of the short PI–dPS diblock was observed (Figure 4a), in contrast to the interfacial excess observed for short PI–dPS copolymers in the same matrix (Figure 3a) for annealing times of a few days at 190 °C. This shows directly that for the short PI–dPS diblock it is the PI moiety only that drives the copolymer to interfaces.

Deuterated PS ($M = 10^6$) with a molecular length comparable to the PS moiety of the long, asymmetric diblock copolymer segregates to both (vacuum/PS and PS/Si) interfaces of the PS host, as was shown also in our earlier studies.[23] The resulting free surface excess $\Gamma \cong 1.4$ nm obtained for 4.8% dPS in the PS host (Figure 4b) is much lower than the corresponding excess $\Gamma \cong 13.7$ nm yielded by 5.3% of analogous PI(10^4)–dPS(10^6) diblock molecule in the same host (Figure 3b). This shows that the isotopic differences between the dPS block and the PS matrix play only a small role in driving long copolymers to the PS/vacuum interface.

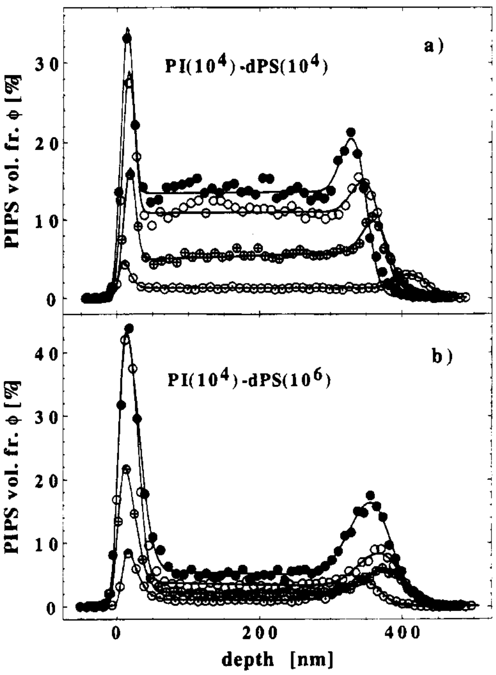

Figure 3. (a) Composition–depth profiles for the short, symmetric PI(10^4)–dPS(10^4) diblock at different bulk volume fractions ϕ_b = 1.4, 5.4, 10.9, and 13.4% in a PS(M=3×10^6) layer mounted on a silicon wafer, following at least 3.2 days at 190 °C (3.5, 3.5, 3.2, and 3.8 days, respectively). (b) Composition–depth profiles for the long, asymmetric PI(10^4)–dPS(10^6) diblock at different bulk volume fractions ϕ_b = 1.1, 2.2, 3.5, and 5.3% in a PS(M=3×10^6) layer mounted on a silicon wafer, following at least 3.5 days at 190 °C (3.8, 3.9, 3.5, and 14.2 days, respectively).

An additional control experiment shows no segregation of this deuterated PS homopolymer to the gold interface of the PS host (Figure 4c), confirming our earlier findings.[23] This time the better depth resolution, obtained thanks to the reversed Au/PS geometry, limits the uncertainty and shows more clearly the absence of any segregation. In contrast, both the short and long copolymers within the PS undergo considerable segregation to the Au/PS interface (Figure 5), demonstrating the exclusive role of the PI moieties in driving the copolymers to these interfaces.

Segregation isotherms $\Gamma(\phi_b)$ were systematically determined at various interfaces. $\Gamma(\phi_b)$ was obtained from the composition–depth profiles, as in eq 2. Since the NRA depth profiling method uses deuterium labeling, the primary observable is the interfacial excess Γ_{dPS} of deuterated PS blocks. This is related to the total excess of block copolymers Γ via $\Gamma_{dPS} = f\Gamma$, with the dPS fraction of the diblock defined as $f = N_{cdPS}/N'_c$; similarly, the volume fraction ϕ_{cdPS} of the dPS block is related to the diblock concentration ϕ as $\phi_{cdPS} = f\phi$. Effective (rather than actual) degrees of polymerization were used (for consistent subsequent discussion in section IV) and are denoted as N_{cdPS} for the dPS block, N'_{PI} for the PI block, and N'_c (=$N_{cdPS} + N'_{PI}$) for the whole copolymer. These were calculated by dividing the total volume of a chain moiety by the volume of a PS chain segment, V_{PS},

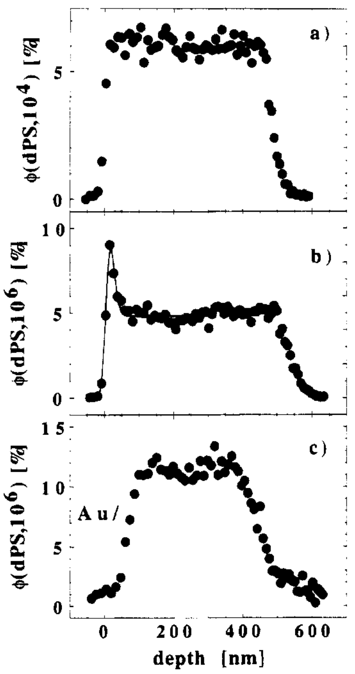

Figure 4. (a) Composition–depth profile for a short deuterated homopolystyrene dPS(10^4) at a volume fraction of 6% in a PS(3×10^6) film annealed for 3 days at 190 °C. (b) Composition–depth profile for a long deuterated homopolystyrene dPS(10^6) at a bulk volume fraction of 4.8% in a PS(3×10^6) film, following 3 days at 190 °C. (c) Composition–depth profile obtained for long deuterated homopolystyrene dPS(10^6) at a volume fraction of 11% in a PS(3×10^6) film spin-cast on a gold layer and mounted with reversed geometry on a silicon wafer, following 1.7 days of annealing at 190 °C. The spectrum was obtained by detecting protons in the backward direction; the depth scale corresponds to polystyrene (note the apparent zero at ca. 75 nm PS depth, corresponding to 15 nm of gold).

which was taken as the reference monomer unit volume. Thus, for example, $N'_{\rm PI} = n_{\rm PI}V_{\rm PI}/V_{\rm PS}$, where $n_{\rm PI}$ is the number of repeat units in the PI block, each of volume $V_{\rm PI}$.

Figures 6a and b present isotherms $\Gamma_{\rm dPS}$ determined for both the short (symmetrical) and long (asymmetrical) PI–dPS diblock copolymers segregating to the vacuum/PS, Au/PS, and Si/PS interfaces of the PS(3×10^6) host over a range of dPS block concentration $\phi^c_{\rm dPS}$. The data points corresponding to the Au/PS interface are somewhat more scattered than the others, possibly reflecting the larger number of stages in the sample preparation (control measurements indicated that the smoothness of the evaporated Au film was very similar to that of the silicon substrate).

For purposes of comparison between the two different diblocks, it is more convenient to present data in terms of the density σ of diblock chains per unit area of the interface, defined as $\sigma = a^2/\Sigma$, where Σ is the mean area per dPS block chain comprising the brush at the interface. σ is related to the interfacial excess Γ as $\sigma = \Gamma a^2/(N'_{\rm c}V_{\rm PS})$. The comparison of segregation isotherms expressed in terms of the interfacial density is presented in Figures 7a and b (which include earlier data on the "intermediate" diblock PI(10^4)–dPS(10^5)). We note at once the main qualitative features: the shorter, symmetric diblocks segregate to an interfacial density that is much higher (by over an order of magnitude) than that of the longer, strongly asymmetric ones for a given volume fraction $\phi_{\rm b}$ of the copolymer; and after an initial rapid rise, the interfacial density of the brushes appears to increase only slowly with $\phi_{\rm b}$.

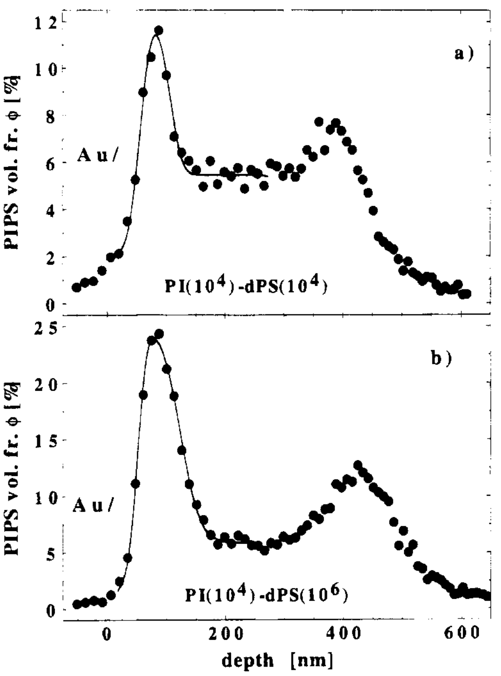

Figure 5. Composition–depth profiles obtained for PI–dPS copolymers in a protonated PS(3×10^6) film spin-cast on a gold layer and mounted with reversed geometry on a silicon wafer, following 3.1 days of annealing at 190 °C. Profile a: short, symmetric PI(10^4)–dPS(10^4) diblock at an initial concentration of 6.3%; profile b: long, asymmetric PI(10^4)–dPS(10^6) copolymer at an initial concentration of 9.9%. Both spectra were obtained by detecting protons in the backward direction; the depth scale corresponds to polystyrene.

IV. Discussion

The qualitative features of our results are readily understood. The PI–dPS diblocks are driven to vacuum/PS, Au/PS, and Si/PS interfaces partly by the unfavorable interactions between the PI segments of the diblock and the PS segments of the host matrix; a further driving force for the PI–dPS segregation is provided by the reduction in interfacial energies resulting from the partial coverage of these interfaces by the PI segments.[24]

A further important qualitative remark concerns the extent of the interfacial coverage by the segregated PI–dPS. Overlap of the dPS moieties occurs at values of the surface coverage $\sigma_{\rm c}({\rm dPS},M{=}10^6) \cong 2\times10^{-4}$ and $\sigma_{\rm c}({\rm dPS},M{=}10^4) \cong 2\times10^{-2}$; this applies to all our isotherms (Figures 7a,b), so that we may assume brush formation (in the sense of overlap) by the interface-segregated PS moieties for the short as well as the long diblocks. At the same time, the coverage necessary for the overlap of the PI moieties is $\sigma_{\rm c}({\rm PI},M{=}10^4) \cong 1.7\times10^{-2}$; thus the PI part of the long (PI(10^4)–dPS(10^6)) diblock can be taken as nonoverlapping over the whole range of σ values studied. In contrast, surface densities obtained for the short (PI(10^4)–dPS(10^4)) copolymer appear slightly higher in the plateau region (Figure 7) than $\sigma_{\rm c}({\rm PI},M{=}10^4)$, indicating the formation of a continuous PI pancake layer at the PS interfaces. These indications are relevant for the modeling of our data below.

There have been a number of quantitative treatments of the structure of layers of polymers attached by one end to a surface and dangling out into a polymer matrix. We consider the present experiments mainly within an approximate mean-field Flory-type model,[25–28] introduced by de Gennes and Leibler. Our data could be also analyzed in terms of the numerical results obtained by

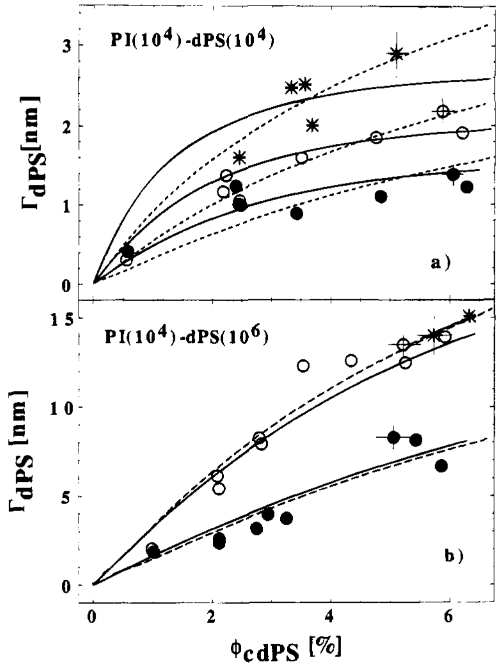

Figure 6. Dependence of the interfacial excess of the deuterated part of the PI−dPS copolymer Γ_{dPS} on its concentration ϕ_{cdPS} at the gold (*), the vacuum (○), and the silicon (●) interfaces of the PS(3×10^6) matrix annealed to equilibrium. Plot a corresponds to the short, symmetric PI(10^4)−dPS(10^4) diblock and plot b to the long, asymmetric PI(10^4)−dPS(10^6) copolymer. Solid curves are based on eqs 7 and 8 of the de Gennes−Leibler theory, using $\beta' = (N'_{\mathrm{PI}}\chi_{\mathrm{PIPS}} - \Delta_i)$ values presented in Table 2. The broken curves were generated based on eq 9 and numerical SCMF results of ref 29, with values of the β parameter as in Table 2.

Shull within the self-consistent mean-field (SCMF) theory.[3,9,29,30] Although the Flory-type model makes a number of simplifying assumptions (such as ignoring the concentration gradient and the distribution of chain ends within the brush layer), its predictions of the main features of the behavior (such as the variation of mean brush height with the size and interfacial densities of the diblocks) anticipate those of more detailed calculations. It has, moreover, the great advantage of transparency, as well as containing the important ingredients of the physics, and we therefore use it as a first framework for our data. The subsequent discussion follows closely the consideration[7] of the PI(10^4)−dPS(10^5) in our earlier study.

Following Leibler[26] (see also refs 5, 25, and 27), we start by writing the free energy of the interfacial film F_{film}:

$$F_{\mathrm{film}} = ng + \gamma A \qquad (3)$$

where γ and A are the interfacial tension and area, respectively. The number of copolymer chains attached at the interface, $n = Aa^2/\sigma = A/\Sigma$, is related to the mean area Σ per chain in the brush. The free energy g of one chain in an interface-attached brush may be expressed as

$$\frac{g}{kT} = \frac{l\Sigma}{V_{\mathrm{PS}}}\left[\frac{1}{P}(1-\Phi)\ln(1-\Phi) + \chi_{\mathrm{hd}}\Phi(1-\Phi)\right] + \ln\frac{NV_{\mathrm{PS}}}{\Sigma a} + \frac{3}{2}\frac{L^2}{Na^2} + \Delta_i(\langle\sigma\rangle) \qquad (4)$$

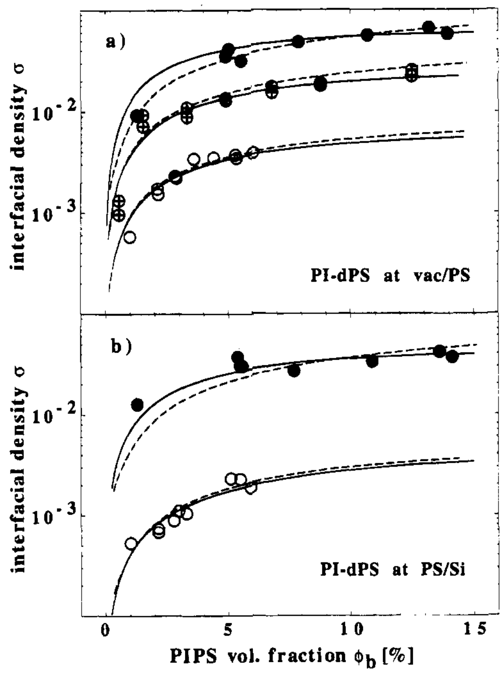

Figure 7. Segregation isotherms, i.e., the interfacial areal densities σ of diblock copolymers corresponding to the Γ_{dPS} data of Figure 6: PI(10^4)−dPS(10^4) (●), PI(10^4)−dPS(10^5)[7] (⊕), and PI(10^4)−dPS(10^6) (○) as functions of the PIPS bulk concentrations ϕ_b for the vacuum and silicon interfaces of the host PS layer annealed to equilibrium. The solid curves are based on eqs 7 and 8 in the text, using $\beta' = (N'_{\mathrm{PI}}\chi_{\mathrm{PIPS}} - \Delta_i)$ values presented in Table 2. The broken curves were generated based on eq 9 and the numerical SCMF results of ref 29, with values of the β parameter as in Table 2. Plot a corresponds to the vacuum/PS interface and plot b to the silicon/PS interface.

Here Φ and N are respectively the volume fraction and degree of polymerization ($N = N_{\mathrm{cdPS}}$) of dPS chains of the brush; L is the brush thickness. The first term on the right-hand side of the equation describes the energy of mixing between the dPS brush and the P-mer PS chains of the host, where χ_{hd} is the interaction parameter between dPS and hPS monomers. The second term on the right-hand side is associated with the 2-D translational freedom of the N-mer at the interface, while the third term represents the increase in the elastic free energy on stretching the chain beyond its unperturbed dimension R_0 ($R_0^2 = Na^2$) to the brush thickness L. The final term Δ_i[6,7] represents the free energy change associated with positioning of the diblock copolymer at the interface. In principle, it could have two (negative) components (neglecting any long-range van der Waals contribution[27])

$$\Delta_i(\langle\sigma\rangle) = \Delta_i^{\mathrm{hd}}(\langle\sigma\rangle) + \Delta_i^{\mathrm{PIPS}}(\langle\sigma\rangle) \qquad (5)$$

These components are associated with the reduction of the interfacial tension when a PS host segment (located at the interface i) is replaced by the dPS segment (Δ_i^{hd}) or the PI unit (Δ_i^{PIPS}) of the PI−dPS copolymer. As long as there is no overlap between PI or dPS moieties at the interface (i.e., at low σ/σ_c values), the Δ_i component can be reasonably assumed as independent of σ.[31] For an interface saturated with the chemical species (i.e., PI or dPS) of the lower interfacial energy ($\sigma/\sigma_c \gg 1$), a new copolymer segregating to the interface would not change the interfacial tension. In this regime the Δ_i component is equal to zero.

The characteristics of the polymeric brush are determined by N, by P, by the brush segment−host segment interaction parameter χ_{hd}, and by the interfacial coverage σ.[28] The two limiting cases correspond to matrices

Table 2. Parameters Obtained from Fitting the Predictions of the de Gennes–Leibler and the SCMF Theories to the Segregation Isotherm Data[a]

interface	$N'_{\mathrm{PI}}-N$	P/N	de Gennes–Leibler theory β'	SCMF theory β	SCMF theory β'_{SCMF} ($e = 0.9$ nm)
vacuum/PS	111–89	312	4.20(7)	2.2(1)	3.4(1)
	114–893[b]	3.6	5.19(4)	2.7(1)	5.1(1)
	114–9551	2.9	5.20(6)	1.5	5.2(1)
Au/PS	111–89	312	4.9(2)	2.8(1)	4.0(1)
	114–9551	2.9	5.30(4)	≈1.5	≈5.2
Si/PS	111–89	312	3.61(8)	1.7(1)	2.9(1)
	114–9551	2.9	4.52(10)	0.7(1)	4.4(1)

[a] e here is the extent normal to each interface to which the anchoring PI moiety is confined. Its value $e = 0.9$ nm was evaluated in our previous work.[7] P is the PS host degree of polymerization. β'_{SCMF} is the value of β corrected for the confinement energy of the PI moieties at the interface.

with very low and very high DP. For $P \ll N$ a large (negative) entropy of mixing, expressed by the first term of eq 4, ensures a high P-mer concentration $(1 - \Phi)$ within the brush, and the brush is referred to as a wet brush. With increasing P, the concentration $(1 - \Phi)$ of P-mer within the brush decreases. Finally, the $P \gg N$, the situation is reached where further increases in P do not change the properties of the brush. In this regime of a "dry" brush, the brush concentration Φ is very high (the matrix chains are expelled) and in the limit $\Phi \rightarrow 1$, the form of free energy g (eq 4) may be simplified to

$$\frac{g}{kT} = \ln N\frac{V_{\mathrm{PS}}}{a^3}\sigma + \frac{3}{2}N\left(\frac{V_{\mathrm{PS}}}{a^3}\sigma\right)^2 + \Delta_{\mathrm{i}}(\langle\sigma\rangle) \tag{6}$$

For the brushes analyzed here, the ratio P/N equals 2.6 and 312 for the long and short PI–dPS copolymers, respectively, i.e., in the dry brush regime. Interfacial coverages σ are also high enough to correspond to the onset of brush stretching. The plateau values of $\sigma N^{1/2}$ are ca. 0.6 for the short copolymer and ca. 0.4 for the long PI–dPS diblock; this compares with previous observation of the onset of stretching for which $\sigma N^{1/2} \cong 0.4$.[32,33] Thus the dry brush limit form of the free energy g (eq 6), is a reasonable approximation.

The basic assumption of the de Gennes–Leibler approach is that the copolymers segregated at the interface are in equilibrium with the free diblocks incorporated (at concentration ϕ_{b}) in the host homopolymer in the bulk of the film. This is expressed by equating the chemical potentials μ_{brush} and μ_{bulk} of the copolymers at the interface and in the bulk. The brush chemical potential (per chain) μ_{brush} is expressed by[26]

$$\begin{aligned}\frac{\mu_{\mathrm{brush}}}{kT} &= g - \Sigma\frac{\partial g}{\partial \Sigma} \\ &= \ln N\frac{V_{\mathrm{PS}}}{a^3}\sigma + \frac{9}{2}N\left(\frac{V_{\mathrm{PS}}}{a^3}\sigma\right)^2 + \Delta_{\mathrm{i}}(\langle\sigma\rangle) + 1\end{aligned} \tag{7}$$

The bulk chemical potential μ_{bulk} is presented in its full form obtained[9,34,35] under the assumption that the interaction parameter between the PI segment and the dPS units can be written as $\chi_{\mathrm{PI-dPS}} = \chi_{\mathrm{PIPS}} + \chi_{\mathrm{hd}}$:

$$\begin{aligned}\frac{\mu_{\mathrm{bulk}}}{kT} = \ln \phi_{\mathrm{b}} + 1 - N'_{\mathrm{c}}\left(\frac{1-\phi_{\mathrm{b}}}{P} + \frac{\phi_{\mathrm{b}}}{N'_{\mathrm{c}}}\right) + \\ \chi_{\mathrm{PIPS}}\left[N'_{\mathrm{PI}}\left(1 - \phi_{\mathrm{b}} + \frac{N}{N'_{\mathrm{c}}}\phi_{\mathrm{b}}\right)^2 + N\left(\frac{N'_{\mathrm{PI}}}{N'_{\mathrm{c}}}\phi_{\mathrm{b}}\right)^2\right] + \\ \chi_{\mathrm{hd}}\left[N'_{\mathrm{PI}}\left(\frac{N}{N'_{\mathrm{c}}}\phi_{\mathrm{b}}\right)^2 + N\left(1 - \frac{N}{N'_{\mathrm{c}}}\phi_{\mathrm{b}}\right)^2\right]\end{aligned} \tag{8}$$

The isotopic term in μ_{bulk} is relevant for the long PI–dPS diblock but would be quite negligible for the short copolymer.

The volume fraction ϕ_{b} of copolymer in the PS host matrix controls the surface coverage σ through its influence on μ_{bulk}, which is pinned to μ_{brush}. With the isotopic interaction parameter χ_{hd} taken as determined directly earlier[36] in dPS/PS blends, we are in a position to calculate the segregation isotherms $\sigma(\phi_{\mathrm{b}})$. These depend in general on two parameters: χ_{PIPS} and Δ_{i}. It turns out[7] that the fitted segregation isotherms are described in practice by the combination $\beta' = (N'_{\mathrm{PI}}\chi_{\mathrm{PIPS}} - \Delta_{\mathrm{i}})$. This combination can be seen simply to represent the sum of the energy gained by the PI moiety by "escaping" from its unfavorable interactions with the PS host together with the interfacial energy reduction gained due to the lower surface tension of PI. The fitted segregation isotherms $\sigma(\phi_{\mathrm{b}})$ are shown in Figures 6 and 7 as continuous lines, and the best-fit β' values are presented in Table 2.

Next we examine our data using SCMF theory.[3,9,29,30] Within this model the copolymer chains can be considered as end-adsorbed N-mers which segregate to the interface of a high molecular weight P-mer. This problem has been treated theoretically (for the neutral wall) by Shull,[29] who obtained numerical solutions to a set of a mean-field equations which govern the statistics of the polymer chains. According to these calculations, the dry brush interfacial excess Γ_{dPS} is a function only of its radius of gyration $R_{\mathrm{g}}(\mathrm{dPS})$ and a normalized brush chemical potential $\langle\mu_{\mathrm{brush}}\rangle$. Neglecting the volume of the adsorbing PI end of the PI–dPS copolymer, we have

$$\begin{aligned}\frac{\langle\mu_{\mathrm{bulk}}\rangle}{kT} = \ln \phi_{\mathrm{b}} + 1 - N'_{\mathrm{c}}\left(\frac{1-\phi_{\mathrm{b}}}{P} + \frac{\phi_{\mathrm{b}}}{N'_{\mathrm{c}}}\right) + \\ \chi_{\mathrm{hd}}N\left(1 - \frac{N}{N'_{\mathrm{c}}}\phi_{\mathrm{b}}\right)^2 + \beta\end{aligned} \tag{9}$$

where the only adjustable parameter is the adsorption parameter β. An important physical difference in the definition of β in the SCMF model is that it includes an energy contribution due to confining the PI moiety to a thin layer. Cast in our symbols, this parameter is given by $\beta_{\mathrm{i}} = N'_{\mathrm{PI}}\chi_{\mathrm{PIPS}} - \Delta_{\mathrm{i}} - 1.1\ \ln(R_{\mathrm{g}}(\mathrm{dPS})/e)$, where i as before refers to the vacuum/PS, Au/PS, or Si/PS interfaces and e is now the layer thickness—adjacent to each interface—to which the anchoring PI moiety is confined.[29] Plotting the normalized surface excess $\Gamma_{\mathrm{dPS}}/R_{\mathrm{g}}(\mathrm{dPS})$ versus the normalized brush chemical potential $\langle\mu_{\mathrm{brush}}\rangle$, we find that all segregation isotherms follow the SCMF master curve. This is shown in Figure 8, where the superimposed data are for the short, symmetric diblocks, the intermediate diblocks (PI(10^4)–dPS(10^5)

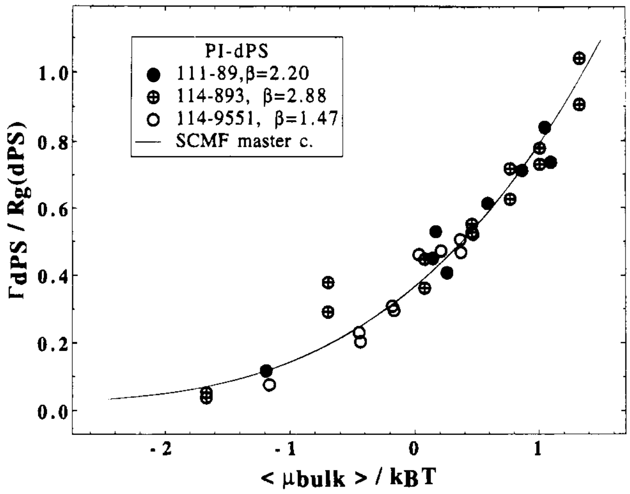

Figure 8. Normalized interfacial segregation $\Gamma_{\rm dPS}/R_{\rm g}$(dPS) for an end-adsorbed chain as a function of the normalized chemical potential $\langle\mu_{\rm bulk}\rangle$ of eq 9. The solid line shows the SCMF master curve;[29] the data points correspond to segregation at the vacuum/PS interface: PI(10^4)–dPS(10^4) copolymer in PS(3×10^6) (●); PI(10^4)–dPS(10^5) diblock in PS(3.3×10^5)[7] (⊕); asymmetrical PI(10^4)–dPS(10^6) copolymer in PS(3×10^6) (○). Data points were adjusted to the SCMF master curve via the adsorption parameters β presented in Table 2.

(from our previous study[7]), and the long diblocks segregating to the vacuum interface of the PS host. β values corresponding to the best fits of the SCMF calculations to experimental isotherms are collected in Table 2. The corresponding fitted segregation isotherms are shown in Figures 6 and 7 as dashed lines. To compare the β' values fitted to the de Gennes–Leibler model with those fitted to the SCMF model, we need to subtract the entropic confinement penalty term from β: this yields $\beta'_{\rm SCMF}$. As seen in Table 2, the values of β' and $\beta'_{\rm SCMF}$ are in reasonable agreement.[37]

It is appropriate at this stage to consider qualitatively why the parameter β', characterizing the adsorption of copolymer to any of the PS interfaces, is systematically larger for longer diblocks than for the shorter ones (see Table 2). This is caused by the very different surface densities of the PI blocks of the long and short copolymers at the PS interface, as indicated schematically in Figure 9. The long (and asymmetric) diblocks at the interface create widely separated, "patchy" PI islands on the otherwise uncovered PS interface ($\sigma < \sigma_{\rm c}$). Therefore any new PI segment of an additional segregating copolymer would further reduce the exposed PS area at the interface, reducing the interfacial tension. This scheme does not apply to short copolymers segregating with high areal densities ($\sigma > \sigma_{\rm c}$) and a continuous PI pancake layer at the interface, as in that case there is little exposed PS left to cover. This is the origin of the larger β' for the asymmetric long diblocks.

V. Summary

Our results indicate that PI–dPS diblocks incorporated in a PS homopolymer segregate to the interfaces formed by the homopolymer with either a solid (silicon or gold) or the air (vacuum) interface. These results are in line with our earlier study.[7] The driving force for the segregation (and resultant brush formation at the interfaces) is the overall free energy gain due to interfacial tension reduction $\Delta_{\rm i}$ (at the interface i) by the PI, together with repulsive PI–PS interactions. This is conveniently expressed by the parameter $\beta' = N'_{\rm PI}\chi_{\rm PIPS} - \Delta_{\rm i}$. While these results are in line with our earlier study on different PI–dPS diblock,[7] they are of particular relevance in that they examine both symmetric and asymmetric diblocks, with brush-forming moieties that differ in length by some 2 orders of magnitude. This provides a basis for understanding in detail the surface segregation behavior in commonly occurring multinodal (e.g., polydispersed) diblock copolymer systems (a study of such a binodal system has recently been completed[38]).

The segregation isotherms in our study could be analyzed in terms of both Flory-type mean-field models and self-consistent field theory. Both enable similar values of β' to be extracted by fitting of the predicted isotherms to the data. β' values for the shorter, symmetric diblocks are lower than those of the much longer, highly asymmetric copolymers; this is probably due to much sparser PI coverage of the interface in the latter case.

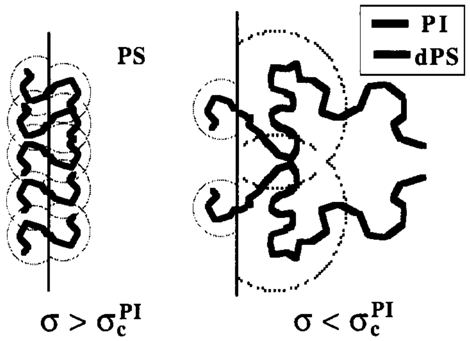

Figure 9. Cartoon to illustrate the origin of different β' values for the symmetric and asymmetric diblocks. The short, symmetric PI(10^4)–dPS(10^4) diblock segregates to the (vacuum) interface of a PS(3×10^6) host at an interfacial areal density σ higher than the coverage $\sigma_{\rm c}^{\rm PI}$ necessary for PI blocks to overlap. The interfacial energy reduction $\Delta_{\rm i}^{\rm PIPS}$ due to positioning an additional PI block of the copolymer at the interface is then lower than for the case where PI moieties do not overlap ($\sigma < \sigma_{\rm c}^{\rm PI}$). This last situation applies for the long, asymmetric PI(10^4)–dPS(10^6) copolymer segregating to the vacuum/PS(3×10^6) interface at low coverages $\sigma < \sigma_{\rm c}^{\rm PI}$, as indicated.

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