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Competitive Adsorption at Homopolymer Interfaces from a Binary Mixture of Diblock Copolymers

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ABSTRACT: Interfacial adsorption from a binary mixture of short and long polystyrene−polyisoprene diblock copolymers (PS−PI or its deuterated analogue dPS−PI) to interfaces of a PS($M = 3 \times 10^6$) homopolymer was studied using nuclear reaction analysis. Short symmetric diblocks dPS($M = 10^4$)−PI($M = 10^4$) (designated dS), or a similar protonated analogue (hS), and a highly asymmetric, long diblock dPS($M = 10^6$)−PI($M = 10^4$) (L) were used in the binary mixtures. We found that the shorter diblocks adsorb preferentially at the interfaces: the isotopic contrast between dS and hS in the mixtures with L enables us to extract detailed information on the surface segregation of the short and long species. Our data are analyzed in terms of a modified Flory-type mean field model due to de Gennes and Leibler. Interfacial segregation from the binary diblock mixture is well predicted by this model with no adjustable parameters, using the adsorption characteristics determined earlier for systems with a single diblock component.

I. Introduction

Polymers attached at solid−liquid, liquid−liquid, or liquid−air interfaces strongly modify the interfacial properties and are important in areas ranging from colloidal stabilization, to coatings and thin-film technology, to tribology. A commonly-used means of attachment is by grafting or end adsorption, in which polymer chains are attached by one end to a surface. For the case when the liquid is a polymer melt, this is often achieved by means of a diblock copolymer of which one block only is strongly adsorbed onto the surface[1−4] or by adsorbing a diblock at the interface between two immiscible melts,[4−7] each of which is preferred by one of the copolymer blocks. The resulting brushlike structure, so-called because the block polymers stretch away from the interface into the homopolymer melts, has been extensively studied experimentally[1−14] as well as theoretically.[15−22]

While the question of brushes formed from polydispersed mixtures at solid−liquid interfaces has been examined for the case of simple liquids,[13,23,24] all studies involving melt matrices have dealt with a single brush component only. Such a brush system is controlled by the molecular weights of the brush and host molecules (and their segment−segment interaction parameter[16]), as well as the grafting density.[15] For a diblock copolymer immersed in a homopolymer and segregating to its interface the grafting density is specified additionally by the copolymer concentration in the homopolymer host and by the change in interfacial energy when the host material is replaced at the interface by copolymer segments. A controlled molecular weight distribution of brush-forming chains offers possibilities for "tailoring" the brush structure, in line with what is expected for brushes at the solid−liquid interface.[25] Finally, an understanding of the influence of the molecular weight distribution on the brush properties is useful since polydispersity is often an unavoidable feature of polymer systems. For these reasons an increasing number of theoretical studies has dealt with this problem.[25−30] Experimentally, brush formation from a bimodal solution of polymeric amphiphiles at solid−liquid interfaces has been studied using surface balance[23,24] and other[13] methods. An interesting observation in these studies was the replacement of long end-attached polystyrene coils by their short analogues when added to the same good solvent host, in contrast to the observed trend for *adsorbed* polymers.[31]

In this work we present the first experimental study on the formation of brushes at the interface of a polymeric host from a binodal mixture of diblocks. The model system, studied in earlier investigations of single-component brushes,[3,4,32] is a polystyrene (PS) homopolymer matrix incorporating polyisoprene (PI)−polystyrene (PS) diblock copolymers as the brush-forming amphiphiles. In this system the PI−PS copolymers segregate to the interfaces of the PS matrix, driven by a combination of unfavorable segmental interactions $\chi_{\rm PIPS}$ of the PI moieties with the PS host, together with the reduction Δ_i in the interfacial energies by the PI moiety at the interface. The strength of this combined interaction at an interface i is conveniently expressed by the adsorption parameter β_i:

$$\beta_i = N_{\rm PI}\chi_{\rm PIPS} - \Delta_i \tag{1}$$

where $N_{\rm PI}$ is the effective degree of polymerization (DP) of the PI block.[33,34] In an earlier study[32] this parameter was determined for segregation from single-component solutions of the copolymers in the polystyrene homopolymer, and its values, which will be useful in the subsequent discussion, are given in Table 1.

Segregation isotherms of the mixture of short and long copolymers were determined (see section III) using nuclear reaction analysis (NRA). While the PS chains of the long copolymers were always deuterated (dPS), the short copolymers investigated (under identical

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Table 1. Net Interaction Parameters β Determined[32] from Segregation Isotherms of dS and of L Incorporated in PS(3 × 10^6)

interface	copolymer	β
vacuum/PS(3 × 10^6)	dS = PI(10^4)–dPS(10^4)	4.20(7)
	L = PI(10^4)–dPS(10^6)	5.20(6)
silicon/PS(3 × 10^6)	dS = PI(10^4)–dPS(10^4)	3.61(8)
	L = PI(10^4)–dPS(10^6)	4.52(10)

Table 2. 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
dS = PI(10^4)–dPS(10^4)[b]	20 000	1.03
	hPI = 10 000	1.03
	dPS = 10 000	
hS = PI(1.3 × 10^4)–PS(1.3 × 10^4)[b]	25 800	1.13
	hPI = 12 900	
	dPS = 12 900	
L = PI(10^4)–dPS(10^6)[b]	1 080 000	1.03
	hPI = 10 300	1.02
	dPS = 1 070 000	

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

conditions) had either protonated or perdeuterated PS blocks. We find, in line with the earlier work on brush formation at solid–liquid interfaces from binodal amphiphile solutions,[23,24] that the shorter diblocks are preferentially attached to the interfaces of the homopolymer matrix. By utilizing the isotopic contrast between the two short diblocks, we are able to separate the contributions from the long and the short copolymers to the overall surface excess of the diblocks. Our results are discussed in section IV in terms of a modified Flory-type mean field mode due to de Gennes and Leibler. The behavior of our two-component diblock system turns out to be well predicted by this model (with no adjustable parameters), using the adsorption parameters β determined in our earlier study.

II. Experimental Section

The monodispersed diblock copolymers of styrene and isoprene used were a long, highly asymmetric chain with a deuterated PS block, PI(10^4)–dPS(10^6), designated L, and two similar short symmetric copolymers: PI(10^4)–dPS(10^4) with a deuterated PS block and its hydrogenated analogue, PI(1.3 × 10^4)–PS(1.3 × 10^4) (see Table 2 for details). The short diblocks are designated S (or hS and dS when there is need to specify the isotopic composition). Monodispersed homopolystyrene PS(M = 3 × 10^6) (Table 2) was used as the matrix material. This homopolymer is identical to that used as the matrix in our earlier investigation of single-component brushes.[32] Polished silicon (Si) wafers purchased from Aurel GmbH, Germany, were used as substrates. The toluene used as spin-casting solvent was analytical grade.

Films of the PS incorporating the PI–PS copolymers were prepared by spin-casting toluene solutions containing appropriate amounts of the different polymers onto the Si wafers (cut to dimensions ca. 1 × 2 cm^2 and degreased in toluene), to thicknesses in the range 380 ± 50 nm.

Samples A–G were made from solutions containing the required volume fractions ϕ^S_0 and ϕ^L_0 of short and long diblocks, as detailed in Table 3, to give binodal mixtures ranging from pure short to pure long copolymer. The intermediate ratios were adjusted so as to fall on a straight line in the ϕ^S_0–ϕ^L_0 plane, as shown in Figure 1. All spin-cast samples were sealed in glass ampules under vacuum ($<10^{-5}$ Torr) and annealed at temperatures of 190 °C (±0.5 deg) for periods up to 3 days.

Table 3. Characteristics of Binary Mixtures, dS/L and hS/L in a PS(3 × 10^6) Matrix[a]

mixture	ϕ^S_0 (%)	ϕ^L_0 (%)	$\phi^{S'}_0$ (%)	$\phi^{L'}_0$ (%)
A	6.3	0	2.8	0
B	5.04	2	2.24	1.99
C	4.2	3.33	1.87	3.3
D	3.4	4.56	1.51	4.51
E	2.1	6.67	0.93	6.59
F	0.63	9.0	0.28	8.89
G	0	10	0	9.88

[a] ϕ^S_0 are the overall volume fractions (in percent) of the short diblocks in the homopolymer matrix (both for dS and hS), while $\phi^{S'}_0$ are the corresponding volume fractions of the short PS blocks alone in these starting mixtures. ϕ^L_0 and $\phi^{L'}_0$ are the analogous volume fractions of the long diblock and of the long PS block. The subscript 0 denotes that these were the overall relative concentrations in the as-cast solution. The copolymer volume fraction and the PS block volume fraction are trivially related via the ratio N_{PS}/N, where N_{PS} and N are the effective degrees of polymerization of each PS block and each copolymer, respectively.

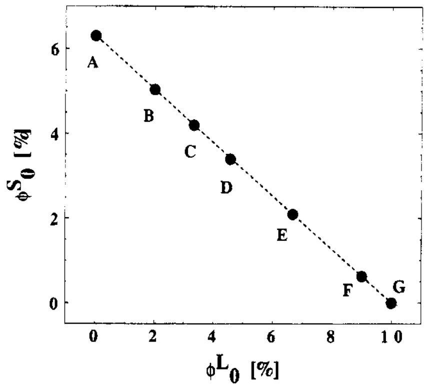

Figure 1. Initial overall compositions of short (S) and long (L) copolymers, in the homopolystyrene matrix (see Table 3), in the as-cast samples.

The composition–depth profile of the deuterated styrene segments of the dPS blocks of the copolymer mixture was determined using nonresonant NRA. The technique has been described in detail earlier.[35–37] Briefly, a beam of ^{3}He ions accelerated to energy $E_{3,0}$ is incident on the polymer film. The nuclear reaction

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

takes place within the sample. From the energy spectrum of the emitted ^{4}He particles and the known energy losses and reaction cross-section, the concentration of the deuterium (^{2}H) atoms (and thus of deuterated sytrene 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 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°) provide 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.

The overall surface excess Γ_{dPS} of the deuterated blocks of the copolymer mixture segregated at any PS surface could be determined from the profile (as shown for example in Figure 4a by hatched areas for vacuum/PS and silicon/PS interfaces),

$$\Gamma_{dPS} = \int_0^{z_b} (\phi_{dPS}(z) - \phi_b)\, dz \qquad (3)$$

where $\phi_{dPS}(z)$ is the overall volume fraction of the dPS segments at depth z and ϕ_b is its value in the bulk of the film, attained at depth z_b. 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 interfacial excess values Γ_{dPS} of the deuterated blocks of copolymer mixture are extracted from the

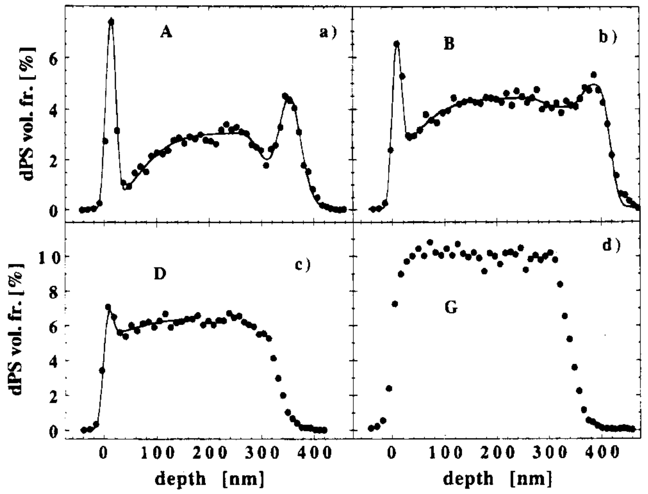

Figure 2. Composition–depth profiles of deuterated PS blocks incorporated in the PS homopolymer at overall concentrations corresponding to A, B, D, and G (Table 3) immediately following spin-casting.

composition–depth profiles. These results are discussed later in terms of an equilibrium model, which is appropriate since all annealings were performed at 190 °C for 3 days. It was shown in our previous studies[32] that, already within 1–2 days of annealing at this temperature, profiles of the segregating long and short PI–dPS copolymers attain their limiting values.

While we are mainly interested in the final equilibrium behavior, the composition–depth profiles following spin-casting but prior to annealing are of interest. Typical unannealed profiles are are shown in Figure 2. As remarked earlier,[32] we find that the shorter copolymers segregate to the PS interface appreciably already during the spin-casting process (Figure 2a with dS alone); in contrast, the mobility of the longer diblocks is low enough so that the solvent evaporates—and the film rendered glassy—before any significant migration to the surface has occurred (Figure 2d, L alone). Mixtures with compositions containing both the short and the long diblocks show surface segregation (during spin-casting) intermediate between the two extremes (Figures 2b,c).

The results we present show that the copolymers with the shorter PS block (S) adsorb preferentially at both the PS/vacuum and the PS/silicon interfaces from a bimodal mixture with L (whose PS block is some 2 orders of magnitude larger). This effect is seen in a striking manner in Figure 3, where a large surface excess arising from a 7% solution of L in the PS matrix $\Gamma_{\mathrm{dPS}} = 12.3$ nm) is halved by the addition of some 2% dS to the matrix (the surface excess becomes $\Gamma_{\mathrm{dPS}} = 6.4$ nm). A similar concentration of dS alone (Figure 3) results in a tiny surface excess, $\Gamma_{\mathrm{dPS}} = 0.4$ nm. Thus the presence of the shorter diblock has a marked inhibiting effect on the adsorption of the longer ones.

To characterize the adsorption more quantitatively, we have employed the "isotope contrast" approach, mentioned in section I, by making use of the fact that our shorter diblock can have either a hydrogenated (hS) or a deuterated (dS) PS block; this makes them either "visible" or "invisible" in the NRA profiles. We have therefore determined the composition–depth profiles for two series of samples (see Figure 4). The first series (series 1; filled circles in Figure 4) consisted of PS layers incorporating binary mixtures of dS and L in the ratios A–G (Table 3). The total measured surface excess of dPS segments for each mixture in this series, $\Gamma^{(1)}{}_{\mathrm{dPS}}$, is simply the sum of the individual surface excess values $\Gamma^{L'}$ and $\Gamma^{dS'}$ of deuterated styrene segments of the long

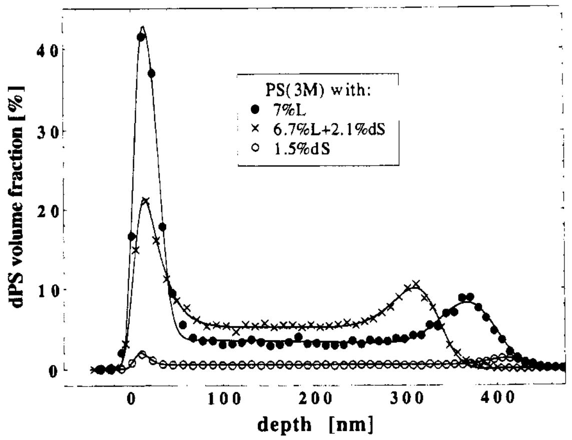

Figure 3. Composition–depth profiles of deuterated PS blocks, from single-component and from binary dS/L mixtures in PS after 3.5 days of annealing at 190 °C. Initial mixtures: (●) 7% L in PS; (×) 6.7% L + 2.1% dS in PS; (○) 1.5% dS in PS.

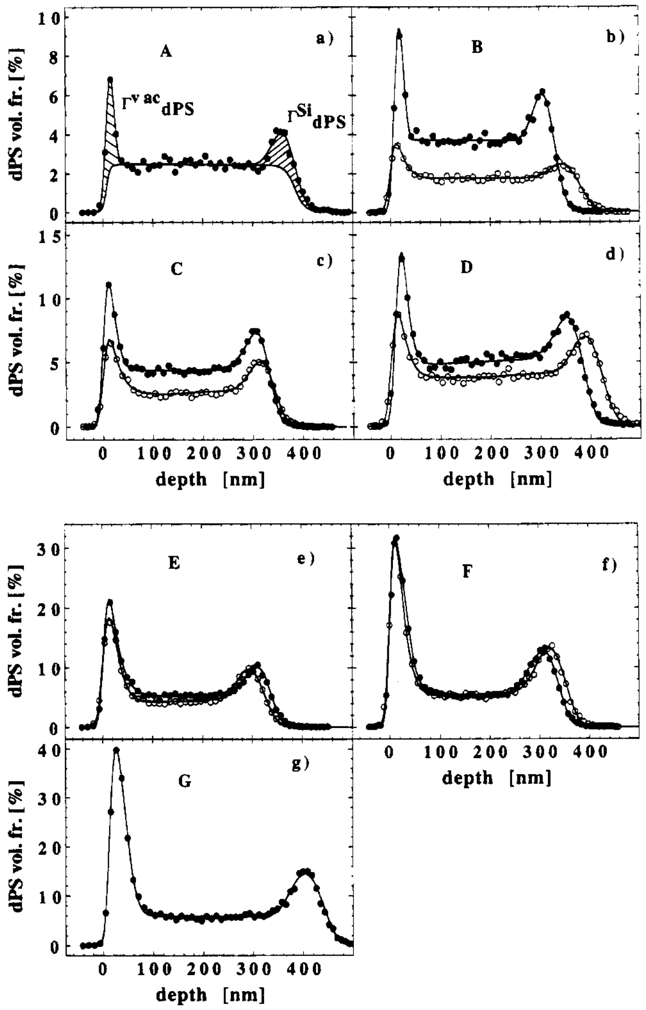

Figure 4. Typical composition–depth profiles of deuterated PS blocks after 3 or more days of annealing at 190 °C, of films prepared with initial overall L/S mixtures in PS at compositions corresponding to A–G (Table 3): (●) dS/L mixtures; (○) hS/L mixtures. The shaded areas in Figure 4a illustrate the surface excess values $\Gamma^{\mathrm{vac}}{}_{\mathrm{dPS}}$ and $\Gamma^{\mathrm{Si}}{}_{\mathrm{dPS}}$ determined as in (3).

and short diblocks, respectively:

$$\Gamma^{(1)}{}_{\mathrm{dPS}} = \Gamma^{\mathrm{L}'} + \Gamma^{\mathrm{dS}'} \qquad (4a)$$

Similarly, the measured overall dPS segmental concentration $\phi^{(1)}{}_{\mathrm{b}}$ in the bulk of the film (i.e. in the plateau region away from the interface peaks) is given by the sum of the concentrations $\phi^{\mathrm{L}'}$ and $\phi^{\mathrm{dS}'}$ in the bulk of the film:

$$\varphi^{(1)}{}_{\mathrm{b}} = \phi^{\mathrm{L}'} + \phi^{\mathrm{dS}'} \qquad (4a')$$

(in eq 4), the prime on $\phi^{\mathrm{L}'}$, $\Gamma^{\mathrm{L}'}$, etc. indicates that these quantities relate to the styrene blocks of the copolymers alone).

A second series (series 2; open circles in Figure 4) was composed of the PS layer incorporating binary mixtures of hS and L, at compositions A–G (Table 3). We expect both the short symmetric diblocks (dS and hS) to behave in closely similar manners at the PS homopolymer interfaces. There are a number of reasons for this. The isotope interaction effect was earlier shown[32] to have a negligible effect on the surface segregation for these short diblocks. Moreover, the small difference in molecular weights between dS and hS leads only to a small modification in the extent to which L is surface-segregated from binary mixtures with either of them (see section IV).[38]

Thus the overall measured surface excess of dPS segments in series 2, $\Gamma^{(2)}$dPS, is simply given by

$$\Gamma^{(2)}{}_{\mathrm{dPS}} = \Gamma^{\mathrm{L}'} \qquad (4b)$$

while the measured overall dPS concentration in the bulk of the film, $\phi^{(2)}{}_{\mathrm{b}}$, is given by

$$\phi^{(2)}{}_{\mathrm{b}} = \phi^{\mathrm{L}'} \qquad (4b')$$

bearing in mind that the corresponding surface excess and bulk concentration due to the hS chains are "invisible" in the NRA profiles. For each mixture, we expect the values of $\Gamma^{\mathrm{L}'}$ in (4a) and (4a′) to be the same, and likewise the values of $\phi^{\mathrm{L}'}$ in (4b) and (4b′) to be the same (within scatter).[38] In this way the "isotope contrast" approach enables us to extract directly, for each of the samples containing the binary mixture, the different surface segregation corresponding to their measured bulk compositions for each component.

Table 4 summarizes the values of $\Gamma^{(1)}{}_{\mathrm{dPS}}$ and $\Gamma^{(2)}{}_{\mathrm{dPS}}$ (for both silicon and vacuum interfaces), as well as $\phi^{(1)}{}_{\mathrm{b}}$ and $\phi^{(2)}{}_{\mathrm{b}}$, obtained from the two series. Representative composition depth profiles from which these data were extracted are shown in Figure 4. Solid circles are for series 1, (L + dS) binary mixtures cast from initial compositions A–G, while the open circles are for the corresponding (L + hS) mixtures. We see at once that both the short and the long components of the diblock mixtures segregate to the two (vacuum/PS and Si/PS) interfaces. We also see (Figure 4, open circles) that the surface excess of L increases rapidly and monotonically as its proportion in the binary mixtures increases, as intuitively expected. This is summarized in Figure 5, where the normalized surface excess of dPS from the L diblocks ($\Gamma^{\mathrm{L}'}/(\Gamma^{\mathrm{S}'} + \Gamma^{\mathrm{L}'})$) is plotted against the relative concentration ($\phi^{\mathrm{L}'}/(\phi^{\mathrm{S}'} + \phi^{\mathrm{L}'})$) of the dL styrene segments in the binary copolymer mixture (in the bulk of the film).

Table 4. Segregated dPS Surface Excess and Equilibrium dPS Volume Fraction from Binary Mixtures L/dS (Series 1, $\Gamma^{(1)}{}_{\mathrm{dPS}}$ and $\phi^{(1)}{}_{\mathrm{b}}$) and L/hS (Series 2, $\Gamma^{(2)}{}_{\mathrm{dPS}}$ and $\phi^{(2)}{}_{\mathrm{b}}$).

interface	samples from mixture	$\phi^{(1)}{}_{\mathrm{b}}$ (%)	$\Gamma^{(1)}{}_{\mathrm{dPS}}$ (nm)	$\phi^{(2)}{}_{\mathrm{b}}$ (%)	$\Gamma^{(2)}{}_{\mathrm{dPS}}$ (nm)
vacuum/PS	A	2.45	1.06	0	0
		2.24	1.38	0	0
		2.18	1.17	0	0
	B	3.71	1.49	1.83	0.58
				1.84	0.63
				1.76	0.71
	C	4.36	2.32	2.81	1.31
				2.52	1.81
				2.76	1.31
	D	4.95	3.44	3.84	2.09
		4.90	3.40	3.46	2.58
		4.85	3.29		
	E	5.20	6.44	4.28	5.88
	F	5.46	10.16	5.29	9.76
	G	5.22	13.51	5.22	13.51
		5.26	12.50	5.26	12.50
		5.92	13.95	5.92	13.95
silicon/PS	A	2.44	1.01	0	0
		2.40	1.24	0	0
		2.48	1.00	0	0
	B	3.64	1.43	1.88	0.64
				1.78	0.41
				1.77	0.63
	C	4.28	2.03	2.92	1.14
				2.72	1.59
	D	5.29	2.42	4.1	2.12
		5.09	2.99		
		5.10	2.71		
	E	5.10	3.44	4.6	3.56
	F	5.19	5.29	5.6	5.49
	G	5.06	8.28	5.06	8.28
		5.44	8.14	5.44	8.14
		5.87	6.69	5.87	6.69

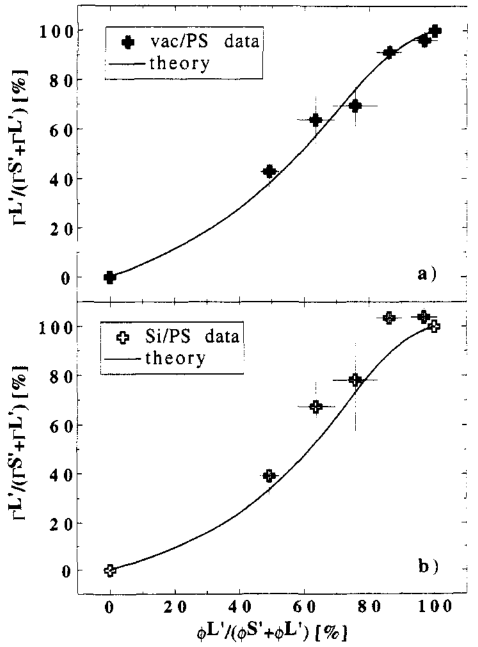

Figure 5. Variation of the normalized surface excess of L styrene blocks with the normalized bulk composition of L styrene blocks in the L/S mixtures: (a) the vacuum/PS interface; (b) at the silicon/PS interface. Solid lines are calculated as described in section IV (note $\Gamma^{(1)}{}_{\mathrm{dPS}} = \Gamma^{\mathrm{S}'} + \Gamma^{\mathrm{L}'}$, (4a), and $\phi^{(1)}{}_{\mathrm{b}} = \phi^{\mathrm{S}'} + \phi^{\mathrm{L}'}$, (4a′)).

The two sets $\phi^{(1)}{}_{\mathrm{b}}$ and $\phi^{(2)}{}_{\mathrm{b}}$ determine directly (via eq 4) the bulk compositions of the PS segments of each component, $\phi^{\mathrm{S}'}$ and $\phi^{\mathrm{L}'}$ (where $\phi^{\mathrm{S}'}$ is the bulk styrene concentration of either dS or hS). From these we can immediately determine the corresponding bulk concentration ϕ^{S} and ϕ^{L} of each diblock as a whole. In Figure

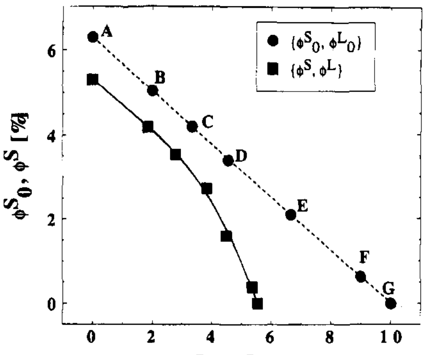

Figure 6. (■) Final equilibrium values of the compositions ϕ^S and ϕ^L in the bulk of the films following annealing. The solid circles (●) show for comparison the compositions $\{\phi^S_0, \phi^L_0\}$ of the starting mixtures A–G (Table 3) from which the samples were spin-cast.

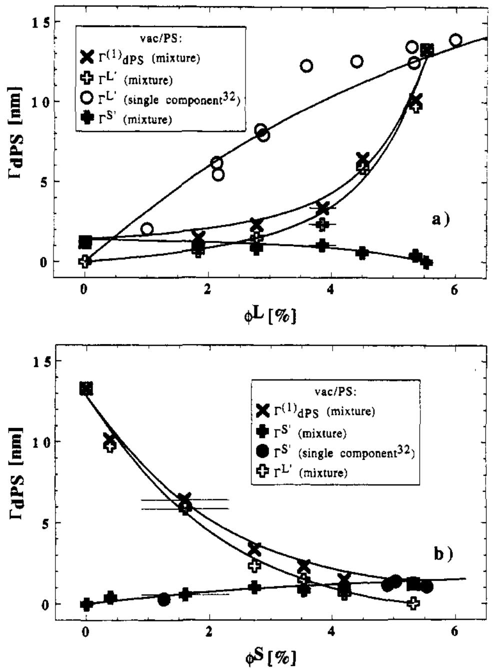

Figure 7. Variation of the equilibrium surface excess at the vacuum/PS interface of S and L styrene blocks ($\Gamma^{S'}$ and $\Gamma^{L'}$) and their sum $\Gamma^{(1)}_{dPS}$ from binary S/L mixtures as a function of ϕ^S and ϕ^L in the bulk of the PS film. Also shown are the surface excess values of S and L from single-component mixtures, taken from oure earlier study.[32] Solid lines were calulated as described in section IV.

6 we show the trajectory $\{\phi^S, \phi^L\}$ of these final bulk composition values in equilibrium with the segregated surface excess of each layer (Figure 4). For comparison, we show the corresponding initial overall compositions $\{\phi^S_0, \phi^L_0\}$ in the mixtures A–G from which the samples were spin cast.

In Figures 7 and 8 we show the way in which the total surface excess $\Gamma^{(1)}_{dPS} = \Gamma^{S'} + \Gamma^{L'}$ of segregated copolymers at the two interfaces varies with the concentration ϕ^L or ϕ^S of each of the components in the bulk of the films, as we traverse the $\{\phi^L, \phi^S\}$ trajectory (Figure 6). In these figures we show also the surface excess of diblocks as a function of bulk concentration for the *single-component* S and L copolymers incorporated in the same homopolymer matrix, taken from our earlier study.[32] We note (Figures 7b and 8b) that for the short diblocks the segregation isotherm is practically the same whether from the single component (●) or from the bimodal mixtures (solid +); this implies that the longer diblock L does little to perturb the S attachment at the homopolymer interfaces. In contrast, Figures 7a and 8a show that the surface segregation of L from its single-component solution in the PS homopolymer (○) is strongly suppressed (open +) by the added short copolymers.

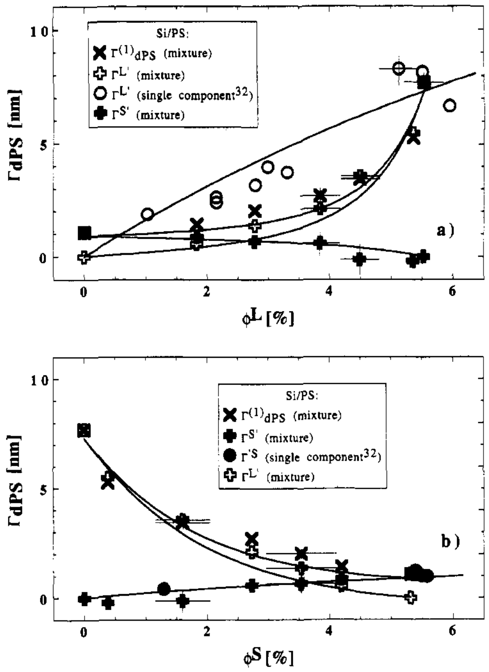

Figure 8. As in Figure 7, but for the Si/PS interface.

The data presented in Figures 6–8 can be combined to construct a 3-dimensional plot where the dependence of the interfacial excess on the concentrations of the short and long copolymers is shown simultaneously. This is done in Figure 9a,b for the vacuum/PS and Si/PS interfaces, respectively. The segregation isotherms plotted at the $\phi^S = 0$ and $\phi^L = 0$ planes correspond to isotherms from the single-component mixtures.[32] The overall surface excess of diblocks (gray circles) is the sum of $\Gamma^{L'}$ and $\Gamma^{S'}$ (open and closed circles), respectively), plotted along the mixing trajectory $\{\phi^S, \phi^L\}$. This highlights the strong dependence of $\Gamma^{L'}$ on ϕ^S, together with the essential independence of $\Gamma^{S'}$ on ϕ^L.

IV. Discussion

The qualitative features of our results are readily summarized: the shorter diblocks attach preferentially to the surface, and their surface excess is hardly perturbed by the presence of the longer diblocks. In contrast the surface excess of the long diblocks is strongly reduced when the short diblocks are added to the host homopolymer matrix. These features are broadly similar to those noted earlier for brush formation from binary mixtures of short and long polymeric amphiphiles (with the same end-anchoring group) in solution.[23,24] While there have been a number of theoretical treatments of brush formation from binary amphiphilic mixtures in good (low molecular weight) solvents,[25,30] the case of a matrix which is itself polymeric presents somewhat different features and has not, to our knowledge, been treated explicity before.[39] In this section we shall attempt a more quantitative analysis of our findings, extending our earlier discussion[32] of

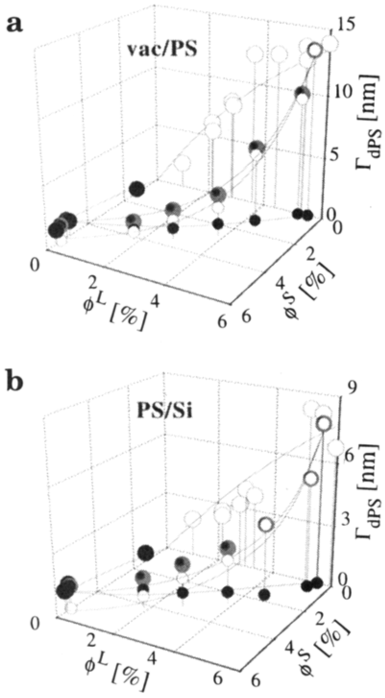

Figure 9. (a) 3-dimensional representation summarizing Figures 6–8, of surface excess values of styrene blocks at the vacuum/PS interface from S/L binary mixtures incorporated in the PS homopolymer. Data from the single-component mixtures, taken from ref 32, shown as large white and large black balls in the $\phi^S = 0$ and $\phi^L = 0$ planes. The smaller black and white balls correspond to $\Gamma^{S'}$ and $\Gamma^{L'}$, while the gray balls are their sum $\Gamma^{(1)}_{dPS}$. Solid lines are calculated (as in Figures 7 and 8). (b) As in Figure 9a, but for the Si/PS interface.

surface segregation from single-component diblocks incorporated in a homopolymer melt.

It is useful to recast our primary experimental output in terms of the interfacial coverage σ, the excess of surface-segregated diblock chains per unit area of interface, defined as $\sigma = (a^2/\Sigma)$, where Σ is the mean area per interface-attached diblock chain and a is a (styrene) statistical segment length. Σ (for the long diblocks, for example), is simply related to the measured surface excess $\Gamma^{L'}$ as $\Sigma^L = N^L_{PS}V_{PS}/\Gamma^{L'}$, where N^L_{PS} is the number of monomer units in the styrene block of the long PI–dPS copolymer and V_{PS} is the volume per styrene monomer. Analogous expressions apply for the short diblocks. Clearly, the surface excess and thus the Σ values depend on the position of the binary mixture along the $\{\phi^S, \phi^L\}$ trajectory. In Figure 10 we have replotted the data of Figure 7a as the variation with ϕ^L of the interfacial densities σ^S and σ^L of the short and long diblocks at the air/vacuum interface. The broken lines are the respective overlap surface densities of the two PS blocks and show that over most of the $\{\phi^S, \phi^L\}$ trajectory these are moderately to strongly overlapped for both the short and the long diblocks.

As noted in the Introduction, the driving force for the surface segregation of the PI–PS diblocks is a combination of unfavorable interactions between the PI segments with the PS host matrix and a reduction in interfacial tension at the ith interface due to the presence of the PI blocks, expressed in the term Δ_i. These are expressed in the adsorption parameter β_i (eq 1 and Table 1). Likewise, the overall free energy of the segregated interfacial layer from the binary mixture, with interfacial densities σ^S and σ^L of the short and long chains, respectively ($\sigma^S + \sigma^L = \sigma$), can be expressed as a combination of the brush energy (see below) and a term expressing the overall interfacial energy reduction. We make the reasonable assumption that the Δ_i component of this parameter may be approximated by the linear average

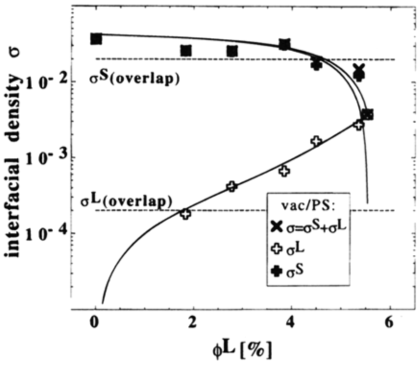

Figure 10. Data of Figure 7a for surface excess values of S and L at the vacuum/PS interface, recast in terms of interfacial densities σ. The broken lines are the overlap interfacial densities (of the styrene blocks) of the two copolymers. Solid lines are calculated (as in Figure 7a).

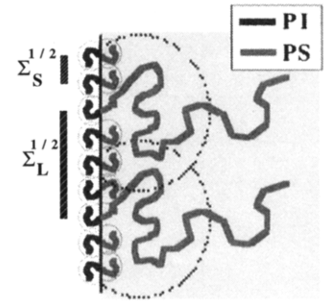

Figure 11. Schematic illustration of the interfacial brush formed from S/L mixtures.

$$\Delta_i(\sigma) = \frac{\sigma^S \Delta^S_{\ i} + \sigma^L \Delta^L_{\ i}}{\sigma^S + \sigma^L} \qquad (5)$$

where the superscripts S or L refer to the values of Δ_i corresponding to segregation from the single-component diblocks in the same homopolymer matrix.[32]

Our subsequent analysis is simplified by the following observation. We expect—and theoretical studies have indicated[26,27,30,25]—that the structure of a brush consisting of both short and long chains can be roughly divided into two regions: the inner layer, adjacent to the interface, which contains segments from both long and short chains, and the outer layer containing segments from the long chains alone. This is illustrated in Figure 11. Since in our binary diblock mixture there is a 100-fold disparity in the sizes of the brush-forming PS blocks, we expect that there will be no interaction between the short and long blocks over most of the trajectory of the latter. At the same time, the interfacial density of the short blocks (in the inner layer) is between 1 and 2 orders of magnitude greater than that of the long blocks over nearly the entire mixing range $\{\phi^S, \phi^L\}$, as indicated in Figure 10. This implies that most of the free energy of the inner layer of the mixed brush is due to the short blocks interacting with themselves. These indications lead us to suggest that any “cross-interactions” between the short and long brushes (consisting of the respective PS blocks) may be neglected: the overall free energy of the mixed brush layer in our system is then approximated by a suitably weighted sum of the free energies of the single-component brushes.

The overall free energy F^{tot}_i associated with a segregated layer at interface i (either vacuum or silicon) from the diblock mixture in a film of area A is then given by the weighted sum of the free energies g per chain in the segregated layer:

$$F^{\mathrm{tot}}_i = n^{\mathrm{S}}g^{\mathrm{S}}(\sigma^{\mathrm{S}}) + n^{\mathrm{L}}g^{\mathrm{L}}(\sigma^{\mathrm{L}}) \tag{6}$$

where supercripts refer to long or short diblocks and the number of long chains (for example) is $n^{\mathrm{L}} = A\sigma^{\mathrm{L}}/a^2 = A/\Sigma^{\mathrm{L}}$ (with analogous expressions for the short diblocks). The interfacial energy terms are implicit in each g.

The form of g, the free energy/chain in surface-segregated brushes at similar relative interfacial densities (of single-component surface layers), has been discussed in our previous papers[3,4,32] mainly using a Flory-type model due to Leibler and de Gennes. The validity of this approach and some comparison to self-consistent mean field results for the same systems was thoroughly considered in those papers. Here we use the same model. Substituting the explicit forms for the chain free energy g into (6), and with the linear approximation (5) for the overall interfacial energy term Δi, we have (for each interface i)

$$F^{\mathrm{tot}}_i = n^{\mathrm{S}}\left\{\ln\left(N^{\mathrm{S}}_{\mathrm{PS}}\frac{V_{\mathrm{PS}}}{a^3}\sigma^{\mathrm{S}}\right) + \frac{3}{2}N^{\mathrm{S}}_{\mathrm{PS}}\left(\frac{V_{\mathrm{PS}}}{a^3}\sigma^{\mathrm{S}}\right)^2 + \Delta^{\mathrm{S}}_i\right\} + n^{\mathrm{L}}\left\{\ln\left(N^{\mathrm{L}}_{\mathrm{PS}}\frac{V_{\mathrm{PS}}}{a^3}\sigma^{\mathrm{L}}\right) + \frac{3}{2}N^{\mathrm{L}}_{\mathrm{PS}}\left(\frac{V_{\mathrm{PS}}}{a^3}\sigma^{\mathrm{L}}\right)^2 + \Delta^{\mathrm{L}}_i\right\} \tag{7}$$

where the interfacial densities σ have their values at the ith interface. $N^{\mathrm{S}}_{\mathrm{PS}}$ and $N^{\mathrm{L}}_{\mathrm{PS}}$ are the DP of the styrene blocks in the short and long diblocks, respectively.[34] The first terms in g^{S} and g^{L} are associated with the 2-dimensional translational freedom of the copolymers at the interface, while the second terms represent the increase in elastic free energy on stretching of the brush-forming PS blocks in each chain beyond their unperturbed dimensions.

The basic assumption of our approach is that the long and the short copolymers segregated at the interface are in equilibrium with the long and short diblocks, respectively, incorporated (at concentrations ϕ^{S} and ϕ^{L}) in the bulk of the host homopolymer film. This is expressed by equating the chemical potentials of the copolymers at the interface ($\mu^{\mathrm{S}}_{\mathrm{brush}}$ and $\mu^{\mathrm{L}}_{\mathrm{brush}}$) with those in the bulk (μ^{S} and μ^{L}):

$$\begin{aligned}\mu^{\mathrm{S}}_{\mathrm{brush}}(\sigma^{\mathrm{S}}) &= \mu^{\mathrm{S}}(\phi^{\mathrm{S}},\phi^{\mathrm{L}})\\ \mu^{\mathrm{L}}_{\mathrm{brush}}(\sigma^{\mathrm{L}}) &= \mu^{\mathrm{L}}(\phi^{\mathrm{S}},\phi^{\mathrm{L}})\end{aligned} \tag{8}$$

The chemical potential per chain in the short brushes is given by

$$\mu^{\mathrm{S}}_{\mathrm{brush}}(\sigma^{\mathrm{S}}) = \left.\frac{\partial F^{\mathrm{tot}}_i}{\partial n^{\mathrm{S}}}\right|_A = g^{\mathrm{S}} + \sigma^{\mathrm{S}}\frac{\partial g^{\mathrm{S}}}{\partial \sigma^{\mathrm{S}}} = \ln N^{\mathrm{S}}_{\mathrm{PS}}\frac{V_{\mathrm{PS}}}{a^3}\sigma^{\mathrm{S}} + 1 + \frac{9}{2}N^{\mathrm{S}}_{\mathrm{PS}}\left(\frac{V_{\mathrm{PS}}}{a^3}\sigma^{\mathrm{S}}\right)^2 + \Delta^{\mathrm{S}}_i \tag{9a}$$

with an analogous expression for the long brushes:

$$\mu^{\mathrm{L}}_{\mathrm{brush}}(\sigma^{\mathrm{L}}) = \left.\frac{\partial F^{\mathrm{tot}}_i}{\partial n^{\mathrm{L}}}\right|_A = g^{\mathrm{L}} + \sigma^{\mathrm{L}}\frac{\partial g^{\mathrm{L}}}{\partial \sigma^{\mathrm{L}}} = \ln N^{\mathrm{L}}_{\mathrm{PS}}\frac{V_{\mathrm{PS}}}{a^3}\sigma^{\mathrm{L}} + 1 + \frac{9}{2}N^{\mathrm{L}}_{\mathrm{PS}}\left(\frac{V_{\mathrm{PS}}}{a^3}\sigma^{\mathrm{L}}\right)^2 + \Delta^{\mathrm{L}}_i \tag{9b}$$

We now evaluate the chemical potentials in the bulk of the film far from the segregated interfacial layers. This region is composed of a concentration ϕ^{S} of the shorter diblocks, with an overall effective DP N^{S},[34] consisting of $N^{\mathrm{S}}_{\mathrm{PI}}$ monomers in the isoprene block and $N^{\mathrm{S}}_{\mathrm{PS}}$ monomers in the styrene block, and a concentration ϕ^{L} of the longer diblock with overall DP N^{L} ($=N^{\mathrm{L}}_{\mathrm{PS}} + N^{\mathrm{L}}_{\mathrm{PI}}$). The volume fraction of the host polystyrene P-mer is ϕ^P. χ_{PIPS} and χ_{hd} are respectively the segmental interaction parameters between isoprene and styrene monomers and between deuterated and protonated monomers. With these parameters, and with the further simplifying assumption that the interaction between PI and dPS segments can be written as the sum of a chemical and an isotopic contribution ($\chi_{\mathrm{PIPS}} + \chi_{\mathrm{hd}}$), the bulk chemical potentials are given by[6,22,40]

$$\frac{\mu^{\mathrm{S}}}{kT} = \ln \phi^{\mathrm{S}} + 1 - N^{\mathrm{S}}\left(\frac{\phi^P}{P} + \frac{\phi^{\mathrm{S}}}{N^{\mathrm{S}}} + \frac{\phi^{\mathrm{L}}}{N^{\mathrm{L}}}\right) + N^{\mathrm{S}}_{\mathrm{PS}}(\chi_{\mathrm{PIPS}}\phi_{\mathrm{PI}}^2 + \chi_{\mathrm{hd}}\phi_{\mathrm{dPS}}^2) + N^{\mathrm{S}}_{\mathrm{PI}}(\chi_{\mathrm{PIPS}}\phi_{\mathrm{PS}}^2 + \chi_{\mathrm{hd}}\phi_{\mathrm{dPS}}^2) \tag{10a}$$

and

$$\frac{\mu^{\mathrm{L}}}{kT} = \ln \phi^{\mathrm{L}} + 1 - N^{\mathrm{L}}\left(\frac{\phi^{\mathrm{P}}}{P} + \frac{\phi^{\mathrm{S}}}{N^{\mathrm{S}}} + \frac{\phi^{\mathrm{L}}}{N^{\mathrm{L}}}\right) + N^{\mathrm{L}}_{\mathrm{PS}}(\chi_{\mathrm{PIPS}}\phi_{\mathrm{PI}}^2 + \chi_{\mathrm{hd}}(\phi_{\mathrm{hPS}} + \phi_{\mathrm{PI}})^2) + N^{\mathrm{L}}_{\mathrm{PI}}(\chi_{\mathrm{PIPS}}\phi_{\mathrm{PS}}^2 + \chi_{\mathrm{hd}}\phi_{\mathrm{dPS}}^2) \tag{10b}$$

Here ϕ_{PS}, ϕ_{dPS}, and ϕ_{PI} are the overall bulk volume fractions of styrene blocks, deuterated styrene blocks, and isoprene blocks, respectively (to be specific we relate (9a) and (10a) to dS).

Subject to our incompressibility assumption, all volume fractions in (10) can be expressed in terms of the bulk copolymer concentrations ϕ^{S} and ϕ^{L}:

$$\begin{gathered}\phi^P = 1 - \phi^{\mathrm{L}} - \phi^{\mathrm{S}} \qquad \phi_{\mathrm{PI}} = \frac{N^{\mathrm{S}}_{\mathrm{PI}}}{N^{\mathrm{S}}}\phi^{\mathrm{S}} + \frac{N^{\mathrm{L}}_{\mathrm{PI}}}{N^{\mathrm{L}}}\phi^{\mathrm{L}}\\ \phi_{\mathrm{dPS}} = \frac{N^{\mathrm{L}}_{\mathrm{PS}}}{N^{\mathrm{L}}}\phi^{\mathrm{L}} \qquad \phi_{\mathrm{hPS}} = \phi^P + \frac{N^{\mathrm{S}}_{\mathrm{PS}}}{N^{\mathrm{S}}}\phi^{\mathrm{S}}\\ \phi_{\mathrm{PS}} = \phi_{\mathrm{hPS}} + \phi_{\mathrm{dPS}}\end{gathered} \tag{11}$$

Thus for any point on the $\{\phi^{\mathrm{S}}, \phi^{\mathrm{L}}\}$ trajectory the bulk chemical potentials of the short and long diblocks may be calculated. Since the chemical potentials $\mu^{\mathrm{S}}_{\mathrm{brush}}(\sigma^{\mathrm{S}})$ and $\mu^{\mathrm{L}}_{\mathrm{brush}}(\sigma^{\mathrm{L}})$ of the segregated layers are pinned to the bulk chemical potentials (eq 8), their values—and thus the interfacial densities σ and surface excess values Γ of the two diblocks—are fully determinable in this model.

For explicit evaluation of the surface segregation isotherms we require three parameters in addition to the known values of χ_{hd}. These are the styrene–

isoprene segmental interaction parameter χ_{PIPS} and the interfacial-energy-reduction values $\Delta^{\mathrm{S}}{}_{i}$ and $\Delta^{\mathrm{L}}{}_{i}$ at the two interfaces i. As noted in the Introduction, these were determined previously in our studies[32] of surface segregation of the S and L diblocks from single-compoent mixtures in the PS homopolymer, where it was shown (as can also be seen from the expressions for μ^{S} and μ^{L}, eq 10) that the relevant parameter is β (eq 1), as tabulated in Table 1. Using these β values and following the approach outlined above, we have calculated the partial segregation isotherms $\Gamma^{\mathrm{S}\prime}(\phi^{\mathrm{S}},\phi^{\mathrm{L}})$ and $\Gamma^{\mathrm{L}\prime}(\phi^{\mathrm{S}},\phi^{\mathrm{L}})$ for the points on the mixing trajectory $\{\phi^{\mathrm{S}}, \phi^{\mathrm{L}}\}$, for both the vacuum/polymer and the polymer/silicon interfaces. These isotherms are shown as solid curves in Figures 5, 7, 8, and 9. We note that using the β values determined from the single-component mixtures of our earlier study—but without using any adjustable parameters at all—yields a good quantitative fit to our data. The main features of our results, namely the essential independence of $\Gamma^{\mathrm{S}\prime}$ on ϕ^{L} together with the strong dependence of $\Gamma^{\mathrm{L}\prime}$ on ϕ^{S}, can also be seen (by inspection) directly from the expressions for the bulk chemical potentials μ^{S} and μ^{L} ((10)) at the large values of $N^{\mathrm{L}}/N^{\mathrm{S}}$ used in our study.

V. Summary

We have determined for the first time the surface segregation from binary mixtures of diblock copolymers (PI–dPS) of very different block sizes incorporated in a homopolymer matrix. Composition–depth profiles using NRA, which is sensitive to the deuterium-labeled part of the chains, were used to extract the surface excess and bulk composition values. We found that the shorter copolymers adsorb preferentially at both the free and solid interfaces. By using similar short copolymers differing in their deuterium labeling, we were able to separate the surface and bulk contributions of the long and short chains (isotope contrast approach). This enabled us to analyze our data in terms of a Flory-type mean field model: the predictions of this model, using adsorption data obtained previously for single-component adsorption but with no adjustable parameters, provide a good quantitative fit to our data.

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