Diblock Copolymers Attached to Homopolymer Surfaces and Interfaces

Andrzej Budkowski,[†,‡] Jacob Klein,[*,†] Ullrich Steiner,[†] and Lewis J. Fetters[§]

Department of Materials and Interfaces, Weizmann Institute of Science, Rehovot 76100, Israel, and Corporate Research Laboratories, Exxon Research and Engineering Company, Annandale, New Jersey 08801

Received November 18, 1992; Revised Manuscript Received February 2, 1993

ABSTRACT: Nuclear reaction analysis (NRA) was used to study the segregation of an asymmetric diblock copolymer, consisting of polyisoprene (PI, molecular weight $M = 10^4$)/deuterated polystyrene (dPS, $M = 10^5$) blocks, to the interfaces formed by polystyrene (PS) homopolymer with various phases. PS/vacuum, PS/silicon, and PS/PI homopolymer interfaces were investigated for different M values of the PS matrix ($M = 1.7 \times 10^3$–330×10^3), and segregation isotherms were established as a function of temperature and of diblock concentration within the PS homopolymer. In all cases the diblocks attach to the interfaces by their PI moieties alone, to form brushlike structures of end-attached PS tails. The high spatial resolution of the NRA technique enabled studies of the brush conformation as a function of the attachment density at the PS/vacuum surface and was used to characterize the extent of penetration of the PS matrix chains into the diblock brushes. Detailed analysis of the brush conformation and of the segregation isotherms, mainly in terms of a Flory-type mean field model based on those due to de Gennes and to Leibler, provided a consistent description of our data; it enabled the extraction of the PI/PS segmental interaction parameter χ_{PIPS}, yielding values in accord with scattering studies, and of the attachment energies of the PI diblock moiety to the PS/air and PS/silicon interfaces. The values of χ_{PIPS} extracted from our data using this Flory-type model were found to increase at lower M values of the PS matrix, in qualitative accord with previous results.

I. Introduction

Polymers attached at surfaces or at interfaces can profoundly modify surface interactions and related behavior, an effect deriving from their large size and their flexibility. Thus polymers at the solid–liquid interface can modify fluid flow or lubrication properties at these surfaces,[1] while polymers attached at solid–air or at solid–solid interfaces can control friction and wear properties,[2] adhesion,[3,4] and load transfer characteristics.[5] Chains attached densely by one end only (for example, via a polar head-group or by a covalent bond) at an otherwise nonadsorbing interface form so-called polymer brushes; in the context of understanding steric stabilization of colloidal dispersions,[6,7] the properties and structure of such brushes at the solid–liquid interface, and in particular the way in which they modify long-ranged interactions between the surfaces immersed in a liquid, have been intensively studied.[8–11] A–B block copolymers in which one of the blocks (of polymer A say) selectively attaches to a surface or at an interface between two phases while the other (polymer B) dangles out to form a brushlike layer provide a simple means for the realization of polymeric brushes. In particular, such A–B diblocks are intuitively attractive as modifiers of interfacial properties between incompatible A and B polymers, where one expects a natural segregation of the diblocks at the A/B interface, with each block dangling into its respective homopolymer. Brushlike layers formed by such diblocks at the phase boundary can reduce the interfacial tension between A and B.[12] This in turn can significantly modify the mechanical properties of adhesive joints between them[3] and the rheological properties, stability, and domain size in phase-separated A/B mixtures. Brush layers at solid/polymer interfaces can also lead to stabilization of thin polymeric films against rupture and breakup.[13,14] A number of theoretical models have dealt specifically with the case of brush layers in polymer melt matrices, either grafted on a surface or formed by A–B diblock copolymers at A/B interfaces. These include scaling approaches,[15,16] simple Flory-type models of the brush layers,[16,17] and more detailed self-consistent mean field calculations[18,19] (generally requiring numerical evaluation).

In contrast to the case of polymeric brushes at solid–liquid interfaces there have been relatively few direct experimental studies of polymeric brushes formed by diblock copolymers in melt matrices, whether at a polymer/air[20] or polymer/solid interface[21] or at the interface between two incompatible polymers.[22–25] Brown and co-workers[22] deposited a layer of an A–B diblock copolymer at the interface between an A and a C polymer, where C and B were compatible (i.e., the segmental interaction parameter $\chi_{\mathrm{BC}} < 0$); using secondary ion mass spectrometry for deuterium depth profiling, they demonstrated the enthalpic swelling of the B moieties of the diblock in the C homopolymer. Shull, Kramer, and co-workers[23,24] and Green and Russell[21,25] studied the segregation of A–B diblock copolymers to the interface between incompatible A and B homopolymers (and between A and a solid substrate), where a thin film of A homopolymer incorporating the A–B diblock was laid on top of a B homopolymer film which was spin-cast onto a silicon wafer. The A–B copolymers were polystyrene (PS)–poly(2-vinylpyridine) (PVP) and PS–poly(methyl methacrylate), respectively, in the two studies. These investigations utilized elastic ion beam scattering methods to determine the excess of diblocks attached to the A/B interfaces as a function of diblock concentration in the bulk of the A homopolymer and as a function of the molecular weight of the A homopolymer. Formation of polymeric micelles can occur readily in diblock/homopolymer mixtures above the critical micelle concentration (cmc), and such micelles were in clear evidence in the PS–PVP case,[23,24] where they segregated strongly both at the A/B and at the A/air interfaces, leading to interesting interfacial structures combining both brushes and micelles.[26]

[†] Weizmann Institute of Science.

[‡] On leave of absence from Jagellonian University of Cracow, Cracow, Poland.

[§] Exxon Research and Engineering Co.

0024-9297/93/2226-2470$04.00/0

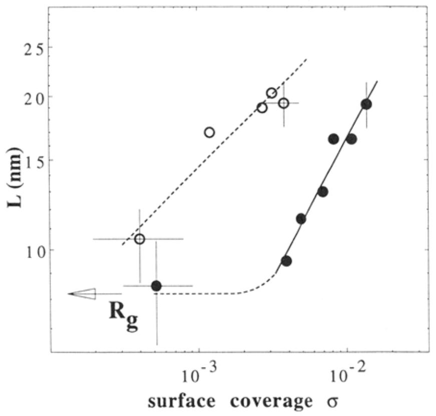

Figure 1. Variation of the mean brush height L with surface coverage (expressed in terms of areal density) σ of the PI–PS diblocks at the air interface of polystyrene films of degree of polymerization P (taken from ref 20): (○) $P = 88$; (●) $P = 3173$. The broken line is the relation $L \sim \sigma^{1/3}$, while the solid curve is a guide to the eye: its linear portion corresponds to $L \sim \sigma^{0.54}$.

In a recent study[20] related to the present report, we used a depth-profiling technique based on nuclear reaction analysis (NRA) to determine the structure of a polyisoprene (PI)–PS diblock copolymer (PI–PS) segregating to form a PS brush at the air interface of PS films of varying molecular weight. The high spatial resolution of the NRA method[20,27–29]—comparable with the unperturbed dimensions of the PS diblock moiety (of molecular weight $M = 10^5$)—enabled the mean PS brush heights $L(\sigma)$ to be determined as a function of the density σ of diblock chains at the interface, as described in detail in ref 20; here $\sigma = a^2/s^2$ is the areal density of the end-tethered PS chains, where a (=0.66 nm for polystyrene) and s are the segment size and the mean spacing of the copolymers at the interface, respectively. Both Flory-type[16,17] and self-consistent mean-field[18] models give similar predictions for the variation of the brush height L with σ; these depend on the density of the diblocks at the interface and on the relative degrees of polymerization N and P of the brush-forming chains and of the matrix chains, respectively. In the regime $N > P > N^{1/2}$ the P-mer matrix chains may penetrate the brush (the so-called "wet-brush" regime), and in this case the brush thickness is predicted to vary as

$$L = \text{const} \times NaP^{-1/3}\sigma^{1/3} \qquad \text{(wet-brush regime)} \qquad (1)$$

At high values of the surface coverage by the tethered N-mer, progressive exclusion of the P-mer matrix chains from within the brush layer occurs (leading to the so-called "dry-brush" regime), while at high values of P ($P \geq N$) essentially complete exclusion of the P-mers from within the brush is predicted. In this dry-brush regime the brush height becomes independent of P and is then a function of the surface coverage alone: $L \sim \sigma$. The variation of brush height with areal density of the PI–PS diblocks was determined at the air interface of two of the homopolystyrenes used in the present study and is reproduced in Figure 1. For the PS matrix with $M = 9.2 \times 10^3$ there is some scatter in the data (open circles), but it is consistent with the wet-brush behavior, shown as the broken line, predicted by eq 1, as is also expected in this case for which $N > P > N^{1/2}$. For the PS matrix with $M = 3.3 \times 10^5$ (solid circles) the brush height in the region $\sigma \geq 3 \times 10^{-3}$ varies as $L \sim \sigma^{\alpha}$ (solid line in Figure 1) where the exponent $\alpha = 0.54$. The value of the exponent is smaller than that expected for a dry brush ($L \sim \sigma$), indicating that despite the fact that $P > N$, the behavior is still in transition to the limiting dry-brush behavior. (We also note that both sets of data approach the value $L \approx R_g$, the radius of gyration of the PS moiety of the diblock, at the lowest σ values studied, as expected for isolated chains.) We shall find these indications useful when examining our data in the light of theoretical models.

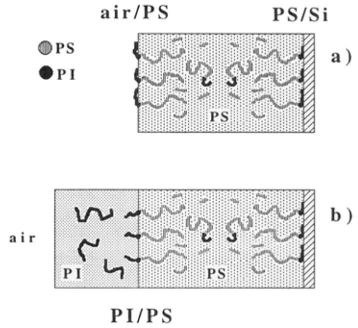

Figure 2. Schematic illustration of the different interfaces in the present study.

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

polymer	M_w[a]	M_w/M_n[b]
PS(16)	1700	1.06
PS(88)	9200	1.03
PS(495)	51500	1.04
PS(962)	100000	1.06
PS(3173)	330000	1.04
dPS(929)	104000	1.02
dPS(17411)	1950000	1.14
PI(5182)	374000	1.05
PI–PS	PI = 10300[b]	1.03
	dPS = 100000	1.03

[a] Via low-angle laser light scattering. [b] Via size exclusion chromatography.

In the present study we extend our investigation of the segregation of PI–PS diblocks from PS homopolymer matrices in which they are incorporated to interfaces of these matrices with air (or vacuum) (henceforth PS/air), with a silicon substrate (PS/Si), and with a PI homopolymer (PS/PI). The respective geometries are shown schematically in Figure 2. In section II we describe the experimental approach and materials used; in section III we present results of control experiments, typical profiles of the PI–PS brushes at the various interfaces, and of the segregation isotherms as a function of PS host-matrix molecular weight and the bulk concentration of the PI–PS diblocks in the homopolystyrene host. In section IV we consider our data mainly in terms of the Flory-type models,[16,17] with some modifications due to the particular conditions of our experiments.

II. Experimental Section

The copolymer used was a monodisperse, highly asymmetric polyisoprene–deuterated polystyrene diblock (PI–PS, with the respective blocks having M values of ca. 10^4 and 10^5). Monodisperse homopolystyrene samples covering a range of (weight average) molecular weights $M = 1.7 \times 10^3$–3.3×10^5 (with corresponding degrees of polymerization $P = 16$–3173) and designated PS(P) were used as the matrix polymers, while a monodisperse homopolyisoprene sample ($M \simeq 4 \times 10^5$) was used for the PS/PI interfacial segregation measurements. In addition, perdeuterated homopolystyrene samples (dPS(P)) were used in control measurements. All molecular characteristics are given in Table I. Polished silicon (Si) wafers were purchased from Aurel GmbH, Germany, and from Intel Electronics, Israel, and degreased in toluene (but not otherwise pretreated) prior to use. All solvents used were analytical grade.

Films of the PS incorporating different PI–PS concentrations were prepared by spin-casting a toluene solution containing the

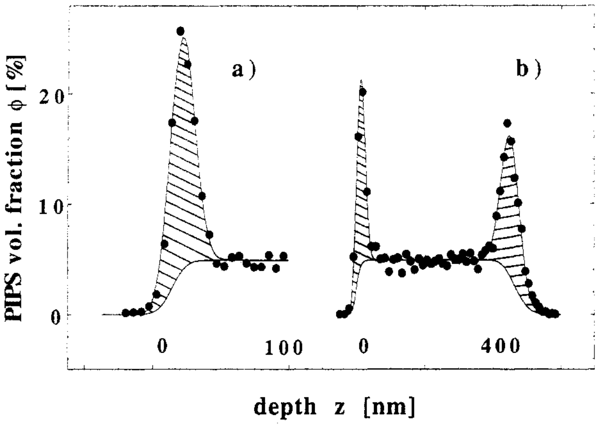

Figure 3. Composition–depth profiles of the (deuterated) PS moiety of the PI–PS diblock, illustrating the resolution/depth range trade-off using NRA in the present study. The profiles are for the PI–PS diblocks at volume fraction $\phi_b = 4.9\%$ in a layer of PS(3173) mounted on a silicon wafer, following 1 day of annealing at 180 °C. Profile a: incident ^{3}He energy $E_{3,0} = 700$ keV; profile b: $E_{3,0} = 1.2$ MeV. The shaded areas are the surface excess values Γ as defined in eq 2; the air interface is at $z = 0$, while the Si interface is at $z \approx 470$ nm.

appropriate homopolymer/diblock ratios onto the Si wafers (cut to dimensions ca. 1×2 cm^2) to thicknesses in the range 400–600 nm. Where segregation to the PS/PI interface was studied, a layer of the PI (thickness in the range 100–200 nm) was spin-cast onto freshly cleaved mica, floated off on distilled water, and mounted on the precast PS film on the Si wafer to form a bilayer. Samples were sealed in glass ampules under vacuum ($<10^{-5}$ Torr) and annealed at temperatures in the range 130–187 °C (±0.5 °C) for periods up to several days. Control experiments were carried out to examine the questions of equilibrium and of the possibility of micellar formation, as will be described in the following section.

The composition–depth profile of the deuterated styrene segments of the PS block of the copolymer was determined using nonresonant NRA. The technique has been described in detail earlier.[27-30] Briefly, a beam of ^{3}He ions accelerated to energy $E_{3,0}$ is incident on the polymer film. The nuclear reaction

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

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 styrene segments) is directly obtained as a function of depth. The depth range as well as the depth resolution of this method depends strongly on $E_{3,0}$. The reaction cross-section has a broad maximum around 700 keV; beams of higher incident energies probe a greater depth into the sample but have a lower resolution at the sample surface, and incident energies in our experiments were optimized as appropriate in the various configurations. Values in the range $E_{3,0} = 700$ keV to 1.2 MeV were utilized. The resolution δ at the sample surface for $E_{3,0} = 700$ keV is some 8 nm half-width at half-maximum (hwhm), but the depth range is limited to some 300 nm by the counting statistics. For $E_{3,0} = 1.2$ MeV a depth of ca. 1000 nm may be probed, which enables segregation of the diblock to be studied also at the PS/Si and at the PS/PI interfaces. The resolution in this case is some 12 nm hwhm at the sample surface and deteriorates due to straggling to some 40 nm hwhm at a depth of 600 nm. While the lower resolutions preclude any estimate of the brush height, the overall excess of copolymer segregated at the deeper interfaces is readily evaluated, as seen in Figure 3: this shows clearly both the higher resolution at the sample surface at $E_{3,0} = 700$ keV and the excess of diblock chains Γ at both PS/air and PS/Si interfaces (hatched areas in Figure 2b) determined from the profile taken at $E_{3,0} = 1.2$ MeV, 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 absolute values of the volume fractions are derived from the known overall amount of the deuterated polystyrene segments in the cast films.

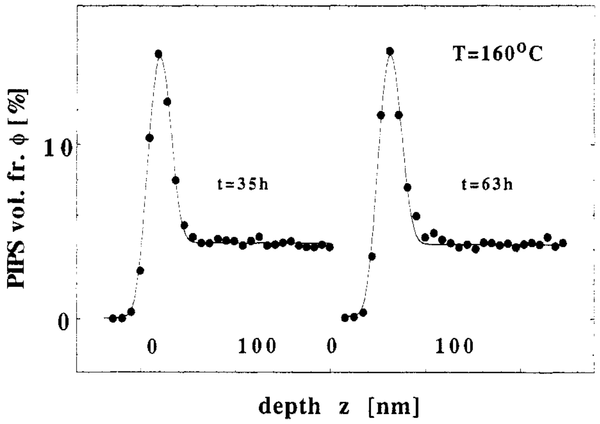

Figure 4. Composition–depth profiles for the PI–PS diblock in a PS(495) host matrix film, following 35 and 63 h of annealing at 160 °C, showing that little change occurs subsequent to the shorter annealing time.

III. Results

The primary output of our experiments is the NRA composition–depth profiles, from which brush conformation and interfacial excess Γ of the segregated copolymers are extracted. These results are discussed in terms of equilibrium models, and care was taken to ensure that the profiles attained their limiting values. The annealing times necessary depended on the temperatures; 1 day was ample at 180 °C, with somewhat longer times being required at the lower temperatures used. Figure 4 illustrates this for the case of the diblock segregating to the polymer/air interface at 160 °C, where no change in profile shape is observed after 35 h of annealing.

It was shown earlier that the PI–PS chains incorporated in the PS homopolymer segregate to the air interface and attach to it by their PI moieties, due to the lower surface energies associated with the PI segments at the polymer surface. The same is true also at the PS/Si interface, as seen in Figure 5. Panels a and b of Figure 5 show the composition–depth profiles of a dPS(930) homopolymer (close in size to the dPS moiety of the copolymer) and of the PI–PS diblock incorporated in a polystyrene film on silicon following annealing. Following 1–3 days at 180 °C, the dPS chains remain uniformly distributed in the PS matrix while the diblock has clearly segregated to both the PS/air and the PS/Si interfaces, showing unambiguously that it is the PI moiety and not the isotopic differences that drives the copolymer to these interfaces.[31] The question of micelle formation, which occurs above the cmc and which was prominent in earlier studies,[23,26] was carefully examined in the conditions of our experiments. Segregation of the diblocks to the interfaces was observed to occur from the lowest PI–PS concentrations in the PS matrix ($\phi_b = 0.6\%$) and to increase monotonically up to the highest concentrations studied ($\phi_b = 15\%$)[32] as indicated in Figure 6a and in segregation isotherms later in this section. The possibility that micelles form and, while screening the interface-active PI moiety in their core, are attracted to the interfaces by the isotope effect due to their dPS coronas was investigated by incorporating a high molecular weight dPS homopolymer in the PS matrix. At concentrations of up to 15% of dPS(17411) in PS(3173)—the longest PS matrix in our study—no trace was observed of interface excess of the deuterated polystyrene over annealing times at which the PI–PS had already segregated to equilibrium, as shown in Figure 6b. These

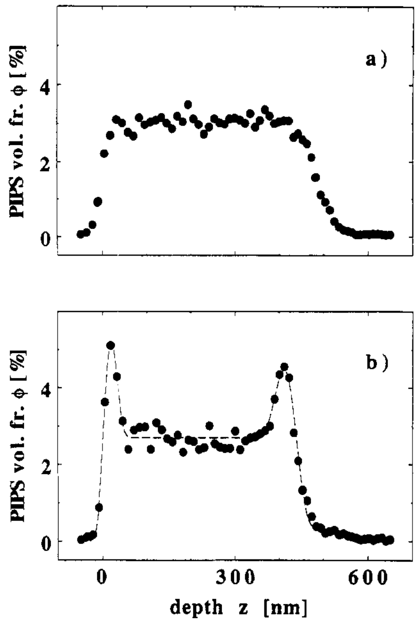

Figure 5. (a) Composition–depth profile for a perdeuterated homopolystyrene sample (dPS(929)) at volume fraction $\phi_b = 3\%$ in a PS(88) film, annealed for 3 days at 180 °C. (b) Composition–depth profile for the PI–PS diblock at volume fraction $\phi_b = 2.7\%$ in a PS(88) film, annealed for 1 day at 180 °C. Clear peaks corresponding to surface excess of the copolymer are seen at the PS/air ($z = 0$) and at the PS/Si ($z \approx 430$ nm) interfaces.

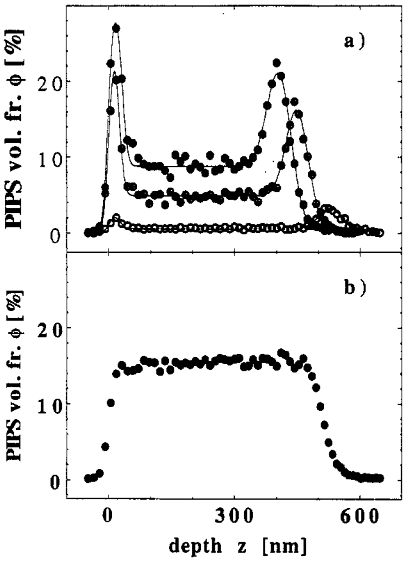

Figure 6. (a) Composition–depth profiles for the PI–PS diblock at different bulk volume fractions $\phi_b = 0.6\%$, 4.9%, and 8.8% in a PS(3173) mounted on a silicon wafer, following 1 day of annealing at 180 °C in all three cases. (b) Composition–depth profile for a high molecular weight perdeuterated homopolystyrene sample (dPS(17411)) incorporated at $\phi_b = 15.3\%$ in a PS(3173) film mounted on a silicon wafer and annealed for 5 days at 175 °C.

observations together strongly indicate that micelle formation is not contributing to interface segregation in our experiments.[33]

In the Introduction we recalled that at the highest spatial resolutions—for $E_{3,0} = 700$ keV—we were able to estimate the mean thickness $L(\sigma)$ of the brush formed by the PS block of the copolymer at the polymer/air interface as a function of the area σ per diblock chain.[20] Figure 7 shows the $L(\sigma)$ variation at the PS/air interface also for the PS(495) matrix; the data are intermediate between the solid curves a and b which summarize the variation, seen in Figure 1, for the PS(88) and PS(3173) homopolymers. The behavior of PI–PS diblock in the PS(495) matrix is closer to that of the wet-brush regime, an observation we shall take account of in the following section. We note that we were unable to extract $L(\sigma)$ data for the PS(16) matrix as the surface excess in this case was too low for a satisfactory analysis.

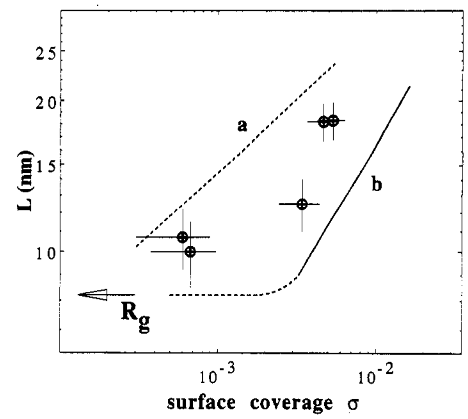

Figure 7. Variation of the mean brush height L with surface coverage (expressed in terms of areal density) σ of the PI–PS diblocks at the air interface of a PS(495) film cast on a silicon wafer and annealed to equilibrium (19 days) at 130 °C. The continuous curves a and b correspond to the diblock brushes in PS(88) and PS(3173), respectively, taken from Figure 1.

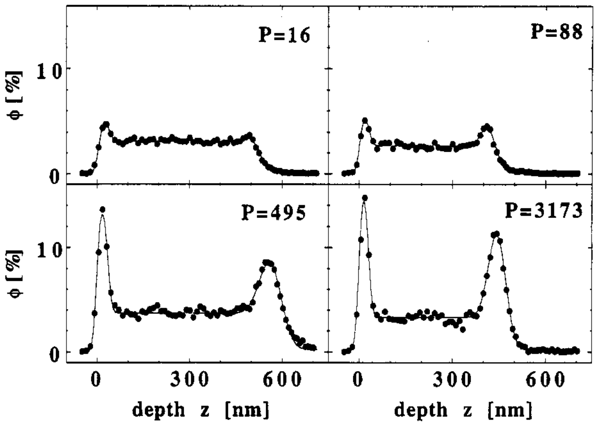

Figure 8. Composition–depth profiles of PI–PS copolymer at volume fractions ϕ_b in the range 3.2 ± 0.5% in the different PS(P) homopolystyrene films cast on silicon, following annealing to equilibrium (annealing times and temperatures were 2 days at 125 °C, 1 day at 180 °C, 19 days at 130 °C, and 1 day at 180 °C in increasing order of P). Clear surface excess peaks are seen at the air and silicon interfaces in all cases, with Γ increasing with P.

Segregation isotherms were determined for the PI–PS chains at the various interfaces, deriving Γ from the composition–depth profiles at different bulk concentrations ϕ_b of the copolymer, as in eq 2. In practice it turns out to be more convenient to plot the variation with ϕ_b of σ rather than Γ; the two are related as $\sigma = \Gamma/(N_c a)$, where N_c (=1040) is the copolymer degree of polymerization (implicit in this relation is the near-equality of the statistical length of the PS segments and of the mean segment length of the diblock as a whole). Some qualitative observations are in order. For a given homopolystyrene matrix PS(P) the surface excess increases, as expected, with the bulk volume fraction ϕ_b of the diblock; this is seen clearly in Figure 6a for $P = 3173$. We also remark that for a given ϕ_b the surface excess increases with P, as seen in Figure 8, where there is a steady increase of Γ at both the PS/air and PS/Si interfaces for $\phi_b = 3.2 \pm 0.5\%$ as the homopolystyrene degree of polymerization P varies from 16 to 3173. The latter effect indicates that the

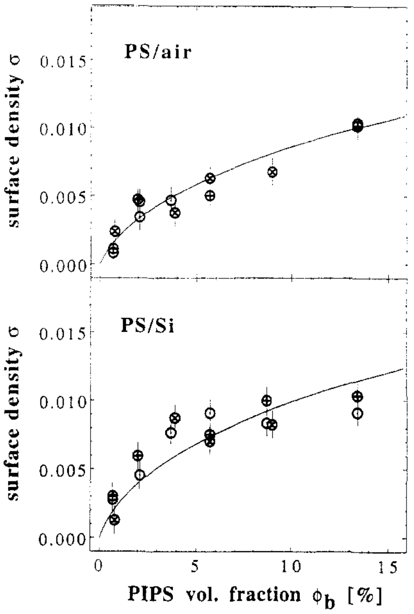

Figure 9. Segregation isotherms $\phi_b(\sigma)$ of the PI–PS diblocks at the air and silicon interfaces of a PS(495) film annealed to equilibrium at different temperatures: (⊙) 19 days at 130 °C; (⊕) 19 days at 150 °C; (⊗) 27.5 h at 187 °C. The solid curves are based on eq 6a ("wet brush") with best-fit $(\chi_{PIPS} - \Delta_i/N_{cPI})$ values of 0.0408 and 0.0427 for the PS/air and PS/Si interfaces, respectively (see text and Table II).

homopolystyrene molecular weights used in our study are traversing the regime of matrix molecule sizes *P* where the copolymer brush behavior is approaching the "dry" (*P* independent) limit.[16,17]

Figure 9 shows the $\phi_b(\sigma)$ isotherms at the PS/air and PS/Si interfaces at 130, 150, and 187 °C for PI–PS in PS(495). Within the scatter there is little difference in the surface excess at the three temperatures. We anticipate what follows and note that this insensitivity to temperature reflects the small temperature variation of the styrene/isoprene segmental interaction parameter[34] and also the similarity in temperature variation of the surface tensions of PI and PS homopolymers.[12] The solid curves in these and in subsequent experimental plots are the calculated isotherms discussed in section IV.

The *segregation isotherms for the copolymer* at the PS/air and PS/Si interfaces are shown in Figure 10 for the various PS(*P*) matrices. As above, the solid (and broken) curves are the calculated ones. Figure 11 shows NRA profiles at the PI/PS interface created, as described above, between a homopolyisoprene layer and a homopolystyrene film (mounted on silicon) incorporating the PI–PS diblock. As for the other interfaces, here, too, the interfacial excess increases with ϕ_b. The corresponding isotherm is shown in Figure 12. We note that due to poorer resolution resulting from the presence of the overlaid PI layer, surface excess values at the PS/PI interface could not be adequately determined for $\phi_b < 2\%$. Finally, the data appearing in Figures 10 and 12 is tabulated in Table II, in terms of the adsorbance Γ defined in eq 2, recalling always that the surface density is related to the adsorbance as $\sigma = \Gamma/(N_c a)$. In the following section we consider these results in terms of recent theoretical approaches.

IV. Discussion

The qualitative features of our results are readily understood. In the absence of micelle formation, as indicated by the control measurements, the PI–PS diblocks are driven to the PS/air, PS/PI, and PS/Si interfaces by the unfavorable interactions between the PI segments of the diblock and the PS segments of the host matrix. In addition, at the PS/air and PS/Si interfaces there is a further driving force for the PI–PS segregation due to the reduction in interfacial energies resulting from the partial coverage of these interfaces by the PI segments of the diblock; this is seen by comparison of the surface tensions of the pure polymers. While we do not have the value of the surface tension of pure PI, we may compare the surface tension γ_{PIB} of pure poly(isobutene)—which is expected to be similar to that of PI—with the surface tension γ_{PS} of pure PS; at 180 °C we have (from the review by Wu[12])

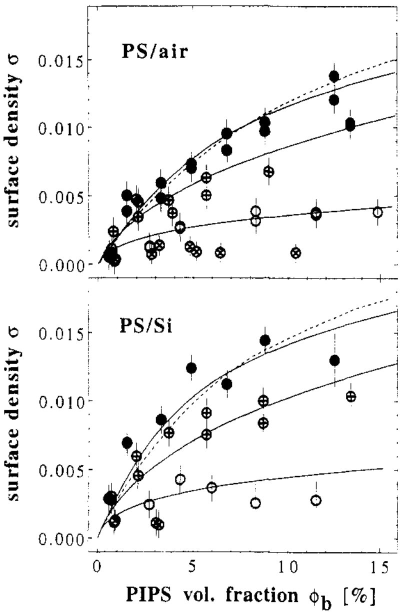

Figure 10. Segregation isotherms $\phi_b(\sigma)$ of the PI–PS diblocks at the air and silicon interfaces in different PS(*P*) matrices cast on silicon and annealed to equilibrium: (⊗) *P* = 16; (○) *P* = 88; (⊕) *P* = 495; (●) *P* = 3173. The solid curves are based on eq 6a ("wet brush") for *P* = 88 and 495, using $(\chi_{PIPS} - \Delta_i/N_{cPI})$ values of 0.0512 and 0.0553 at the PS/air and PS/Si interfaces, respectively, for PS(88) and $(\chi_{PIPS} - \Delta_i/N_{cPI})$ values of 0.0408 and 0.0427 at the PS/air and PS/Si interfaces, respectively, for PS(495) (see Table II). The solid curve for the PS(3173) data is based on eq 6b ("dry brush"), using $(\chi_{PIPS} - \Delta_i/N_{cPI})$ values of 0.0374 and 0.0406 at the PS/air and PS/Si interfaces, respectively. The broken curves running through the PS(3173) data were generated using the appropriate equation from ref 19 (see text), using values of the parameter β = 2.96 and 3.35 for the PS/air and PS/Si interfaces, respectively.

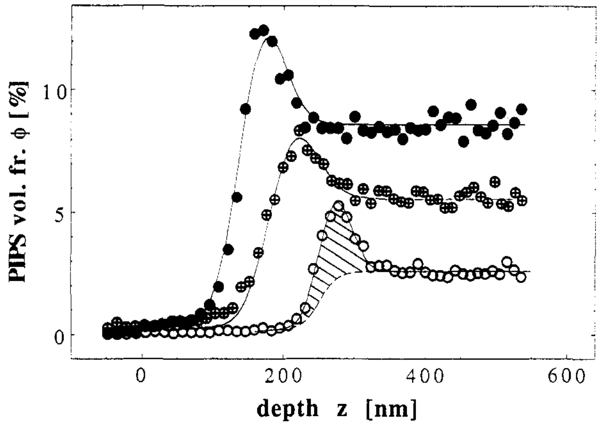

Figure 11. Composition–depth profiles for PI–PS diblocks at the interface between a homopolystyrene film PS(962) and a homopolyisoprene film PI(5182) for volume fractions ϕ_b = 2.7%, 5.6%, and 8.6% of the copolymer in the polystyrene. Samples were annealed for 4 days at 175 °C. The polyisoprene/air interface is at z = 0; the shaded area at the PI/PS interface shown for one of the profiles is the interfacial excess Γ of the diblock.

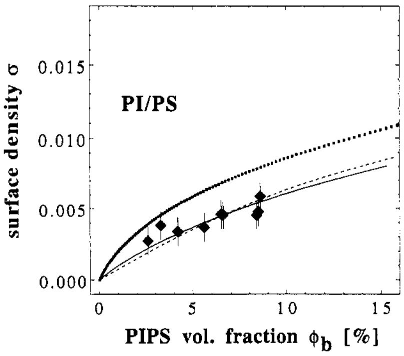

Figure 12. Segregation isotherms $\phi_b(\sigma)$ of the PI–PS diblocks at the PI/PS interface as in Figure 11. The bilayers were annealed at temperatures of 175–180 °C up to 6.5 days. The solid and broken curves are based on eqs 6a ("wet brush") and 6b ("dry brush"), using ($\chi_{PIPS} - \Delta_i/N_{cPI}$) values of 0.0329 and 0.0359, respectively. The dotted curve is the best fit to the data from the segregation isotherm of the PI–PS diblock at the PS(495)/air interface, taken from Figure 10 (or Figure 9).

Table II. Adsorbance Γ of the PI–PS Diblock Copolymers at the PS(*P*)/Air, PS(*P*)/Si, and PS/PI Interfaces

(i) PS(*P*)/Air (Corresponding to Figure 10a)

P = 88		*P* = 495		*P* = 3173	
ϕ_b (%)	Γ (nm)	ϕ_b (%)	Γ (nm)	ϕ_b (%)	Γ (nm)
0.85	0.28	0.7	0.58, 0.78	0.6	0.36, 0.50
2.7	0.9	0.8	1.66	1.5	2.70, 3.51
4.3	1.90, 1.82	2.0	3.30	3.3	3.35, 4.14
8.3	2.20, 2.69	2.1	2.39, 3.18	4.9	4.88, 5.11
11.5	2.52, 2.64	3.7	3.26	6.8	5.79, 6.64
14.9	2.66	3.9	2.61	8.8	6.75, 7.20
		5.7	3.50, 4.39	12.5	8.34, 9.61
		9.0	4.71		
		13.4	7.05, 7.17		

(ii) PS(*P*)/Si (Corresponding to Figure 10b)

P = 88		*P* = 495		*P* = 3173	
ϕ_b (%)	Γ (nm)	ϕ_b (%)	Γ (nm)	ϕ_b (%)	Γ (nm)
0.85	0.79	0.7	1.93, 2.10	0.6	1.98
2.7	1.69	0.8	0.89	1.5	4.83
4.3	2.97	2.0	4.16	3.3	6.00
6.0	2.55	2.1	3.17	4.9	8.61
8.3	1.78	3.7	5.34	6.8	7.90
11.5	1.94	5.7	5.25, 6.35	8.8	10.03
		8.7	5.83, 6.96	12.5	9.05
		13.4	7.20		

(iii) PS(962)/PI (Corresponding to Figure 12)

ϕ_b (%)	Γ (nm)	ϕ_b (%)	Γ (nm)
2.6	1.89	8.4	3.12
3.3	2.65	8.5	3.31
4.2	2.35	8.6	4.08
5.6	2.55		
6.5	3.20		
6.6	3.17		

$\Delta\gamma = \gamma_{PS} - \gamma_{PIB} \approx 6$ dyn/cm. It is this additional reduction in energy (related to $\Delta\gamma$), arising from the presence at the surface of PI segments, which is responsible for the somewhat larger surface excess of the diblock at the PS/air surface relative to the PS/PI interface; a similar consideration applies to the larger surface excess observed also at the PS/Si interface. A further important qualitative remark concerns the extent of interfacial coverage by the segregated PI–PS. Overlap of the PS moieties occurs at values of the surface coverage $\sigma > 10^{-3}$; this applies to all our isotherms with the exception of the $P = 16$ data, so that (except for this shortest PS matrix) we may assume brush formation by the interface-segregated PS moieties of the diblock. At the same time, the coverage necessary for overlap of the much shorter PI moieties is $\sigma \approx 10^{-2}$; so that the PI part of the diblock can be taken as nonoverlapping in all cases over the range of σ values studied. These indications will be 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 (brushes), including diblock copolymers where one of the blocks is selectively adsorbed at the surface, and of the related problem of A–B diblock copolymers attached at an A/B interface. We consider the present experiments mainly in terms of a mean field Flory-type model introduced by de Gennes[16] and by Leibler.[17] This approach is less detailed than self-consistent mean field (SCMF) models[18,19,35] but captures the main features of the physics of the segregated copolymers; in addition, even though it makes a number of assumptions (such as ignoring concentration gradients within the brush layer) which are a simplification compared with the SCMF results, its predictions of the main features of the behavior (such as the variation of mean brush height with the size and surface densities of the diblocks) agree with those of more detailed calculations. It has, moreover, the advantage of transparency, and we use it as a first framework for our data.

Following de Gennes and Leibler, we start by writing down the free energy g of one chain in an interface-attached brush:

$$\frac{g}{kT} = \frac{L\Sigma}{a^3}\frac{1}{P}(1-\phi)\ln(1-\phi) + \ln(N\sigma) + \frac{3}{2}\frac{L^2}{Na^2} + \Delta_i \qquad (3)$$

where $\Sigma = s^2$ is the mean area per chain comprising the brush and N is the degree of polymerization (DP) of the chain. The first term on the right-hand side of the equation describes the entropy of mixing between the brush and the P-mer chains of the host matrix; it assumes interpenetration of the host chains into the brush (wet-brush regime). The form of this term is strictly valid (even within the Flory-type treatment) only for $P \leq N$. The second term is associated with the 2-D translational freedom of the (N-mer) chains at the interface, while the third term represents the increase in elastic free energy attendant on stretching the chains beyond their unperturbed dimensions ($R_0^2 = Na^2$). The final term, Δ_i (earlier introduced in ref 21), represents the free energy change associated with the presence of the attaching group (i.e., the PI moiety of the diblock) at the interface i (i = PS/air, PS/Si, PS/PI). Its origin for the air and silicon surface is due to the reduction in interfacial energies noted above (and its value may be reasonably assumed independent of Γ as long as there is no overlap between the PI moieties at the interface, as is the case throughout our study), while for the PS/PI interface we expect $\Delta_i \approx 0$. This is because the presence of the PI moieites of the diblocks at the PS/PI interface does not lead to a change in the extent of PS/PI interaction at the interface (except for the small reduction—of order σ—associated with the covalent bond joining the two blocks), while their configuration as they dangle into the PI homopolymer is unperturbed (and thus costs no energy). This is equivalent to having the PI homopolymer act as a "neutral" surface, to which the PI–PS diblocks are driven only by the unfavorable interactions of their PI moieties with the PS homopolymer matrix.[31] In general, the picture in these experiments is one where the copolymer is attached to the interface by the PI block, so that N in eq 3 refers to the PS moiety of the copolymer. We shall later use N_{cPI} (=147) for the DP of the PI moiety of the diblock, so that $N_c = N + N_{cPI}$.

Earlier detailed examination of eq 3 for the case of overlapping chains revealed two main regimes. For $PN^{-3/2} < \sigma < P_{-}^{1/2}$ the brush is expected to be appreciably penetrated by the matrix P chains (ϕ low, wet-brush regime), and minimization of g with respect to the brush height yields the $L(\sigma)$ relation of eq 1. The corresponding free energy is now (in the low-ϕ limit) given by

$$g/kT = (3^{4/3})(2^{-5/3})\sigma^{2/3}NP^{-2/3} - (N/P) + \ln (N\sigma) + \Delta_i \qquad \text{(wet brush)} \quad (3a)$$

At higher surface coverages ($\sigma > P^{-1/2}$) progressive expulsion of the host matrix coils from the brush is expected, leading to the dry-brush regime. The brush height now becomes independent of the matrix molecular weight and varies linearly with σ, as noted in the Introduction and discussed in greater detail in our earlier report. The corresponding free energy per brush chain has the form given in eq 3 less the first entropy of mixing term,

$$\frac{g}{kT} = \ln (N\sigma) + \frac{3}{2}N\sigma^2 + \Delta_i \qquad \text{(dry brush)} \qquad (3b)$$

The data of Figures 1 and 7 give us an indication of which regime the PI–PS diblock brushes in the different PS matrices fall into, guiding us when we come to evaluate the associated segregation isotherms.

The basic assumption is that the copolymers segregated at the interfaces 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 evaluating the chemical potentials μ_{brush} and μ_{bulk} of the copolymers at the interface and in the bulk, respectively (normalized per chain), and equating them, where[17]

$$\mu_{\text{brush}} = g - \Sigma\frac{\partial g}{\partial \Sigma} \qquad (4)$$

and

$$\frac{\mu_{\text{bulk}}}{kT} \cong \ln \phi_b + 1 - N_c/P + \chi_{\text{PIPS}}N_{\text{cPI}} \qquad (5)$$

where χ_{PIPS} is the PI/PS segmental interaction parameter. Equation 5 is the low-ϕ_b limit of the expression used by Shull and Kramer.[35,36] We use it to describe μ_{bulk} not only in single PS films but also in the PS side of the PS/PI bilayer, where we make the assumption that PI homopolymer chains do not penetrate into the PS side of the bilayer and that the PI–PS chains are confined to the polystyrene layer; these assumptions derive from the large unfavorable (χ_{PIPS} related) energies associated with their violation.

The volume fraction ϕ_b of copolymer in the PS host matrix controls the surface coverage σ through its influence on μ_{bulk}. The segregation isotherm $\phi_b(\sigma)$ is evaluated for the *wet-brush* regime, setting $\mu_{\text{brush}} = \mu_{\text{bulk}}$ using eqs 3a, 4, and 5, giving

$$\phi_b(\sigma) = \exp\{KN(\sigma/P)^{2/3} + \ln (N\sigma) - \chi_{\text{PIPS}}N_{\text{cPI}} + N_{\text{cPI}}/P + \Delta_i\} \qquad (6a)$$

where the constant $K = 5 \times (3^{1/3})(2^{-4/3}) = 2.27$. For the dry-brush regime we equate the chemical potentials using eqs 3b, 4, and 5, giving

$$\phi_b(\sigma) = \exp\{{}^9/_2N\sigma^2 + \ln (N\sigma) - \chi_{\text{PIPS}}N_{\text{cPI}} + N_c/P + \Delta_i\} \qquad (6b)$$

We recall that in the conditions of our experiments the density of the PI moieties of the diblock within the PI homopolymer side of the PS/PI interface is well below overlap, so that the PI moieties do not form a brush; for such a case the PS brush created at this interface can be treated using the above equations setting $\Delta_i = 0$.

Table III. Parameters Obtained from Fitting Equations 6 to the Segregation Isotherm Data

interface	P	dPS brush fit	$\chi_{\text{PIPS}} - \Delta_i/N_{\text{cPI}}$	Δ_i	χ_{PIPS}
PI/PS	962	dry	0.0359(2)	0	0.0359
		wet	0.0329(2)		0.0329
Si/PS	3173	dry	0.0406(3)	−1.07(3)	0.0333
	495	wet	0.0427(2)		0.0354
	88	wet	0.0553(2)		0.0480
air/PS	3173	dry	0.0374(1)	−0.62(3)	0.0332
	495	wet	0.0408(4)		0.0366
	88	wet	0.0512(2)		0.0470

We are now in a position to examine the segregation isotherms $\phi_b(\sigma)$ presented in Figures 9, 10, and 12. As indicated in Figures 1 and 7, we shall use the wet-brush expression for $P = 88$ and 495 and the dry-brush expression for $P = 3173$, where the approach to dry-brush behavior is suggested; for the case of $P = 962$ we attempt both expressions (the isotherm for $P = 16$, where the data are limited and where the scatter is comparable with the signal, will not be examined quantitatively in terms of the brush model). We fit the predicted isotherms to the experimental data; the unknowns in eqs 6 are χ_{PIPS} and Δ_i, which are adjusted—in the combination ($\chi_{\text{PIPS}} - \Delta_i/N_{\text{cPI}}$)—to yield the best fit.

Table III summarizes the values of the combinations ($\chi_{\text{PIPS}} - \Delta_i/N_{\text{cPI}}$) which best fit eqs 6, to the experimental isotherms. The fits themselves are shown as the solid lines running through the data in Figures 9, 10, and 12. We remark on a number of features: for the PS/PI interface, for which $P = 962$, both the dry and wet expressions, shown as broken and solid curves, respectively, in Figure 12, give rather good fits; at this interface the value of $\Delta_i \approx 0$, as discussed, so that the fit yields directly the value of the segmental interaction parameter χ_{PIPS}.[37] In principle, using this value, we should be able to extract the Δ_i's from the values of ($\chi_{\text{PIPS}} - \Delta_i/N_{\text{cPI}}$) tabulated for the other interaces. We note, however, a small but systematic increase in the magnitude of the quantity ($\chi_{\text{PIPS}} - \Delta_i/N_{\text{cPI}}$) at each interface as P decreases. If we assume that the energy Δ_i associated with the adsorption of the PI moiety of the diblock to air and silicon interfaces is essentially unchanged as P changes,[38] this suggests that the magnitude of the segment–segment interaction parameter χ_{PIPS} may be a decreasing function of P.[39] This observation is consistent with the results of the small-angle X-ray scattering (SAXS) study by Tanaka and Hashimoto,[34] where a marked increase in χ_{PIPS} (deduced via the random phase approximation from the scattering data on blends on PI–PS diblocks in homopolystyrene matrices with different P) was observed at decreasing P. While the SAXS-derived data do not yield a systematic dependence of χ_{PIPS} on P, our observations have prompted us to examine such a dependence at the simplest level. The procedure is described in the Appendix, while the resulting $\chi_{\text{PIPS}}(P)$ and Δ_i values are summarized in Table III. Two comments are in order: while detailed comparisons cannot be made because different compositions and moelcular weights of the PS matrices were used in the two studies, the absolute values of the PS/PI segmental interaction parameter χ_{PIPS} deduced from our segregation isotherms are comparable with the values measured by SAXS, and the differences in χ_{PIPS} as a function of P are also comparable with those noted in the SAXS studies.[34,39] We remark also on the values of Δ at the air and silicon interfaces deduced from the segregation isotherms. These are due to adsorption of the PI moiety segments at these interfaces, and their negative value is in line with our earlier comments concerning the reduction in the homopolystyrene surface energies. The absolute values of the net adsorption energies per PI monomer, at some $(\Delta_i/N_{cPI})kT \approx 0.01kT$, are low but are in the range expected for the competitive adsorption between two such similar species.[6] Finally, we return to the observation that the surface excess depends only weakly on the temperature (Figure 9): this reflects the weak temperature dependence measured by SAXS for the χ_{PIPS} as well as the small T dependence of the difference in PS and PI surface energies (reflected in Δ) noted earlier.

We have not examined our data in detail using SCMF calculations, but for the case of the $P = 3173$ isotherm (closest to a dry-brush regime) we may apply results obtained by Shull.[19] In his model of a brush composed of N-mers in a chemically-identical P-mer melt, where $P > N$, the (dry) brush characteristics are fully defined in terms of P, N, and ϕ_b (the concentration of N-mers in the P-mer bulk matrix), together with an adsorption parameter β. Cast in our symbols, this parameter is given by $\beta_i = N_{cPI}\chi_{PIPS} - \Delta_i + 1.1 \ln (e/R_{gc})$, where R_{gc} is the radius of gyration of the diblock (=8.7nm) and i as before refers to the PS/air or PS/Si interface. e here is the extent normal to each interface to which the anchoring PI moiety is confined.[40] Best fits of the SCMF calculations to the PS-(3173) isotherms at the air and Si interfaces (broken curves, Figure 10) were obtained for β values 2.96 and 3.35, respectively. The difference between them, $\delta\beta = 0.39$, is quite close to the difference $\delta\Delta = 0.45$ obtained from the Flory-type approach (Table II). Inserting values of the other known parameters into the expression for β, we find the value of the parameter e to be ca. 0.9 nm, a physically reasonable value for the surface-adsorbed PI moieties. This admittedly limited comparison suggests that within the range of parameters considered the Flory-type approach and the SCMF picture of the segregated layers are comparable.

In summary, we have shown that PI–PS diblocks incorporated in P-mer homopolystyrene matrices can be useful model polymeric amphiphiles for investigating segregation of copolymers to interfaces. We find that the diblocks segregate at the surfaces of the host matrix with air (or vacuum) and with the solid silicon support, as well as at the interface with a PI homopolymer. Within the range of our experimental parameters, we find no evidence for micelle formation. The copolymers are driven to the interfaces by a combination of unfavorable segmental interactions of the PI moieties with the PS host, together with a reduction in surface energies due to the presence of PI segments at the air and silicon surfaces. The brushes formed by the polystyrene N-mer moieties at the interfaces can be classified as "wet" or "dry" depending on their interpenetration by the host chains, and our results indicate that even for $P > N$ the brushes do not exhibit completely "dry" behavior. Using these indications, we employ a Flory-type mean field model (due to de Gennes and to Leibler) to analzye our data and to evaluate both the PS/PI segmental interaction parameter χ_{PIPS} and the surface adsorption characteristics of the PI moieties. The values of χ_{PIPS} extracted are consistent with earlier data based on small-angle X-ray scattering. A limited comparison indicates also that self-consistent mean field calculations are compatible with our data.

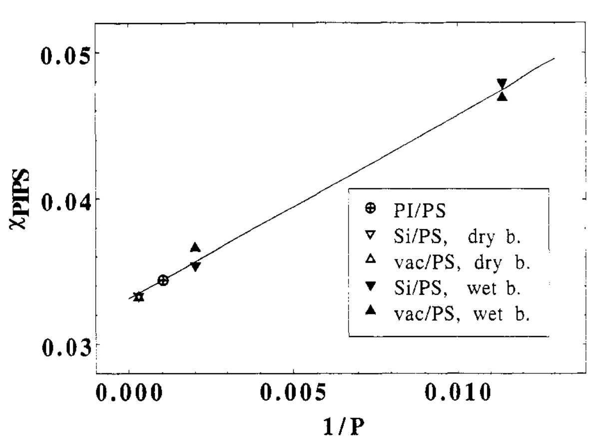

Figure 13. Procedure used to deduce the P dependence of the PI/PS interaction parameter from the best-fit values of $(\chi_{PIPS} - \Delta_i/N_{cPI})$ listed in Table II for the three interfaces. The value of χ_{PIPS} for $P = 962$ (⊗) is the mean of the "wet" and "dry" brush fits to the isotherm at the PS/PI interface (Figure 12 and Table II), while the other six data points are obtained by adjusting the $(\chi_{PIPS} - \Delta_i/N_{cPI})$ parameters as described in the Appendix. The straight line is the relation $\chi_{PIPS} = 0.0331 + (1.27/P)$.

Acknowledgment. We thank L. Leibler for a useful discussion and the German–Israel Foundation (GIF), the U.S.–Israel Binational Science Foundation (BSF), and the Minerva Foundation for financial support of this work.

Appendix: Derivation of a *P* Dependence of the PI/PS Segmental Interaction Parameter

The procedure we adopted is as follows: at each P value the difference between the best-fit values of $(\chi_{PIPS} - \Delta_i/N_{cPI})$ at the PS/Si and at the PS/air interfaces (as listed in Table III) is evaluated, to yield a mean value $(\delta\Delta/N_{cPI}) = 0.0031$. Adding this mean difference to the value of $(\chi_{PIPS} - \Delta_i/N_{cPI})$ at the air interface yields a single set of values of $(\chi_{PIPS} - \Delta_i/N_{cPI})$ as a function of P, where by construction i now corresponds to the PS/Si interface and which is fitted by an empirical dependence

$$\chi_{PIPS} - \Delta_i/N_{cPI} = A_i + B/P \qquad \text{(A1)}$$

(where $A_i \equiv A_{PS/Si} = 0.0404$ and $B = 1.27$). At the PS/PI interface we expect $\Delta_i \approx 0$, so that $\chi_{PIPS}(962) = 0.0344(7)$, the latter value being the mean χ_{PIPS} derived from the "wet" and the "dry" fits to the isotherm at the PI/PS interface (Figure 12 and Table III). Substituting in eq A1 for $P = 962$ we deduce the values of $\Delta_{PS/Si}$ and hence $\Delta_{PS/air}$ which appear in Table III. By adding $(\Delta_{PS/Si}/N_{cPI})$ to the set of $(\chi_{PIPS} - \Delta_i/N_{cPI})$ values constructed earlier to deduce (A1), the relation $\chi_{PIPS}(P) = 0.0331 + B/P$, shown in Figure 13, is finally obtained.

References and Notes

(1) Klein, J.; Perahia, D.; Warburg, S. *Nature* **1991**, *352*, 143.
(2) Bowden, F. P.; Tabor, D. *The Friction* and *Lubrication of Solids*; Clarendon Press: Oxford, 1964.
(3) Brown, H. R. *Macromolecules* **1989**, *22*, 2859.
(4) Lee, L. H., Ed. *Fundamentals of Adhesion*; Plenum: New York, 1991.
(5) Drzal, L. T. *Adv. Polym. Sci.* **1985**, *75*, 1.
(6) Napper, D. H. *Steric Stabilisation of Colloidal Dispersions*; Academic: London, 1983.
(7) Pincus, P. In *Lectures on Thermodynamics and Statistical Mechanics*; Gonzales, A. E., Varea, C., Eds.; World Scientific: Singapore, 1989; p 74.
(8) Klein, J. In *Molecular Conformation and Dynamics of Macromolecules in Condensed Systems*; Nagasawa, M., Ed.; Elsevier: Amsterdam, 1988; p 333.
(9) Halperin, A.; Tirrell, M.; Lodge, T. *Adv. Polym. Sci.* **1991**, *100*, 31.
(10) Taunton, H. J.; Toprakcioglu, C.; Fetters, L. J.; Klein, J. *Macromolecules* **1990**, *23*, 571.
(11) Auroy, P.; Mir, Y.; Auvray, L. *Phys. Rev. Lett.* **1992**, *69*, 93.

(12) Wu, S. In *Polymer Blends*; Paul, D. R., Newman, S., Eds.; Academic Press: New York, 1978.

(13) Safran, S. A.; Klein, J. *J. Phys. II*, in press.

(14) Yerushalmi-Rozen, R.; Klein, J.; Fetters, L. J., submitted.

(15) Alexander, S. *J. Phys. (Paris)* **1977**, *38*, 983.

(16) de Gennes, P.-G. *Macromolecules* **1980**, *13*, 1069.

(17) Leibler, L. *Makromol. Chem., Macromol. Symp.* **1988**, *16*, 1.

(18) Zhulina, E. B.; Borisov, O. V.; Brombacher, L. *Macromolecules* **1991**, *24*, 4679.

(19) Shull, K. R. *J. Chem. Phys.* **1991**, *94*, 5723.

(20) Budkowski, A.; Steiner, U.; Klein, J.; Fetters, L. J. *Europhys. Lett.* **1992**, *18*, 499.

(21) Green, P. F.; Russell, T. P. *Macromolecules* **1992**, *25*, 783.

(22) Brown, H. R.; Char, K.; Deline, V. R. *Macromolecules* **1990**, *23*, 3383.

(23) Shull, K. R.; Kramer, E. J.; Hadziioannou, G.; Tang, W. *Macromolecules* **1990**, *23*, 4780.

(24) Dai, K. H.; Kramer, E. J.; Shull, K. R. *Macromolecules* **1992**, *25*, 220.

(25) Green, P. F.; Russell, T. P. *Macromolecules* **1991**, *24*, 2931.

(26) Shull, K. R.; Winey, K. I.; Thomas, E. L.; Kramer, E. J. *Macromolecules* **1991**, *24*, 2748.

(27) Chaturvedi, U. K.; Steiner, U.; Zak, O.; Krausch, G.; Schatz, G.; Klein, J. *Appl. Phys. Lett.* **1990**, *56*, 1228.

(28) Steiner, U.; Chaturvedi, U. K.; Zak, O.; Krausch, G.; Schatz, G.; Klein, J. *Makromol. Chem.* **1991**, *45*, 283.

(29) Chaturvedi, U. K.; Steiner, U.; Zak, O.; Krausch, G.; Klein, J. *Phys. Rev. Lett.* **1989**, *63*, 616.

(30) Klein, J. *Science* **1990**, *250*, 640.

(31) In this discussion we shall ignore the effect of the isotopic interaction parameter $\chi_{h/d}$, whose magnitude at ca. 10^{-4} (see, e.g.: Budkowski et al. *Europhys. Lett.* **1992**, *18*, 705) is some 2 orders smaller than that due to the PI/PS segmental interactions.[34]

(32) Calculations based on the Leibler model indicate a cmc at $\phi_b = 12\%$ for the PI–PS diblock in the PS(3163) matrix; we note however that previous estimates based on this model have been lower than the experimentally determined cmc in similar diblock/homopolymer blends (for example, the (isobutene/styrene diblock copolymer)/homopolystyrene system; see: Kinning, D. J.; Thomas, E. L.; Fetters, L. J. *Macromolecules* **1991**, *24*, 3893).

(33) We note also that electron microscopy of thin (ca. 50 nm), grid-mounted films of PS(3173) containing 15% by weight of the PI–PS diblocks that had been annealed as above and stained with OsO_4 as described in previous studies[26] revealed no evidence of micelle formation.

(34) Tanaka, H.; Hashimoto, T. *Macromolecules* **1991**, *24*, 5398.

(35) Shull, K. R.; Kramer, E. J. *Macromolecules* **1990**, *23*, 4769.

(36) Sanchez, I. C. In *Encyclopedia of Polymer Science and Technology*; Wiley: New York, 1987; p 1.

(37) For comparison, the experimentally determined $\phi_b(\sigma)$ isotherm at the PS/Si interface taken from Figure 10 for $P = 495$, summarized as a dotted line in Figure 12, shows a significantly larger surface excess corresponding to the effect of $\Delta_i < 0$ at that interface.

(38) There may be possible small γ_{PS} changes with P, as discussed in the review by Wu.[12]

(39) An analogous observation was made by Dai et al.[24] on the increase, at smaller P, of the interaction parameter $\chi_{PS/PVP}$, extracted using the Leibler model from segregation isotherms of PS–PVP diblocks at a PS(P)/PVP interface; this was attributed to shortcomings in the model when compared to SCMF calculations, from which a *constant* $\chi_{PS/PVP}$ could be shown to be consistent with the same data.

(40) β is related to the free energy reduction due to the presence of the adsorbing moiety at the interface; the first two terms on the right-hand side of the relation defining β are a contribution due to the unfavorable interactions of segments of the PI moiety with the PS matrix and one related to the reduction in surface tension, while the third term is the change in the free energy due to confinement of the adsorbing moiety.