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Surface Segregation Studies of Fluorine-Containing Diblock Copolymers[†]

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ABSTRACT: A diblock copolymer of deuterated styrene and isoprene (dPS−PI) with a small volume fraction of isoprene was chemically modified to incorporate pendant fluorinated side chains ("fingers"). The composition distribution of the diblock copolymers within a high molecular weight polystyrene (PS) homopolymer was determined by forward recoil spectrometry. Surface segregation and interfacial segregation of the modified block copolymers from a polystyrene matrix are observed in as-spun films. Equilibrium segregation was achieved on annealing at 160 °C for several days. The segregation isotherms at the air−polymer interface are shown to be quantitatively described by a self-consistent mean field theory (SCMF), and these permit us to estimate an effective Flory parameter which describes the attraction of the fluorinated segments to the surface and their repulsion from the bulk. The change in the surface tension as a result of the adsorption of the block copolymers at the air−homopolymer interface was evaluated from the predictions of SCMF theory and compared with the changes in the water contact angle observed. Advancing water contact angle data are consistent with the presence of a nonuniform layer of PS, CF_2, and CF_3 segments on the surface of the segregated samples.

Introduction

Fluorocarbon polymers have been widely studied as materials for low surface energy coatings and for nonwetting biological applications.[1−4] Low surface energy polymer coatings are useful in preventing the adherence of marine organisms.[5] In addition, polymers with fluorinated functional groups at the surface can be envisioned to convey other properties such as resistance to corrosive chemicals and organic solvents, flame retardancy, water repellancy, and low coefficient of friction.

Polymers with highly fluorinated side chains in one block of a block copolymer are also likely to be useful in a number of applications if the block copolymer segregates to the surface, driven there by the low surface energy fluorinated block. Such a block copolymer is interface active and falls under the category of interface-active polymers as they are commonly known in the literature. A small amount of such an interface-active polymer can dramatically alter the interfacial energy of a polymer/polymer or a polymer/nonpolymer system. As an example, consider an A−B diblock copolymer in an A polymer matrix with a B block carrying the interface-active component with, for example, fluorinated side chains. The A block will be miscible with the matrix while the B block is likely to segregate to the surface, thereby minimizing the surface energy of the blend. Segregation will be driven both by the unfavorable enthalpic interactions between the fluorinated side chains and the homopolymer and by the decrease in the bare surface energy produced by substituting low surface energy block segments for higher surface energy homopolymer segments. In addition, the blend route offers the possibility of a continued supply of the low surface energy block copolymer from the bulk (by a simple diffusion process) if the surface layer is eroded or abraded.

Block copolymers with fluorinated components in one of the blocks are not only hydrophobic but lipophobic as well. They are likely to be useful in applications such as compatibilizing hydrocarbon−fluorocarbon blends, mold release agents, and in the modification of polymer surface properties in a simple noncorrosive, nondestructive manner. In applications such as those above, block copolymers are thought to form "polymer brushes" at the interface. Polymer brushes are important in the phase behavior of pure block copolymers as well as block copolymer/homopolymer mixtures. Polymer brushes are also involved in the micellization of diblock copolymers where the core of these micelles can be thought of as end-adsorbed block 1 and the corona as the "brush" of block 2.[6] Two limiting cases of brushes are realized theoretically. The "wet brush" is obtained when the concentration of the matrix molecules is high in the brush and is a result of the matrix molecular weight being much lower than that of the brush molecular weight (due to the severe entropic penalty associated with the exclusion of the matrix). With increasing molecular weight of the matrix, the entropy penalty associated by its exclusion from the brush decreases, resulting in brushes with fewer matrix molecules. The brush structure obtained at this limiting case where increasing molecular weight of the matrix has no impact on the brush properties is referred to as the "dry brush" case.

Detailed theoretical and experimental studies of wet polymer brushes at interfaces have been reported before.[7−9] For example, in the surface segregation of an A−B diblock from a homopolymer of A and in the interfacial segregation of an A−B diblock to the polymer A−polymer B interface, it has been shown that the relevant factors are the interaction parameter characterizing the thermodynamic interaction between A and B polymers, the block copolymer asymmetry ratio (N_a/N_b), the molecular weight of the diblock, the molecular weight of the homopolymer, and the free energy of interaction with the surface/interface.[9] Such studies are useful in tailoring the properties of the polymer surfaces and interfaces.

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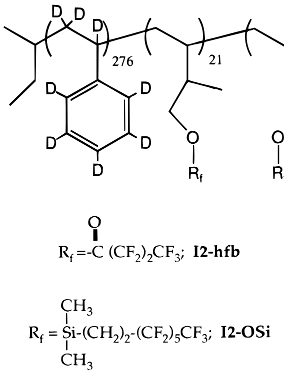

Figure 1. Chemical structure of **I2-OSi** and **I2-hfb**.

Theoretical treatments[7,10] and experimental studies[11−13] of the dry brush case are limited. Recently, Shull[10] has used the self-consistent mean field approach to calculate the properties of end-adsorbed polymer chains or dry polymer brushes of an A−B diblock copolymer from a homopolymer matrix where the molecular weight of the matrix is greater than or equal to that of the molecular weight of the brush ($N_a/N_b \geq 1$) and to describe in detail the properties of dry brushes.[10] In this theory, the brush properties are shown to depend on χ_{ab}, N_a/N_b, and β, where χ_{ab} is the Flory interaction parameter characterizing the thermodynamic interaction between the A and B blocks, N_a and N_b are the respective degrees of polymerization of the A and B blocks, and $kT\beta$ is the net attractive interaction between the adsorbing block and the surface.

We are interested in preparing dry polymer brushes with low surface energy functional groups at the air−polymer interface by the segregation of a block copolymer with a low surface energy block from a homopolymer blend. Toward this end, we have synthesized and chemically modified a block copolymer of isoprene and deuterated styrene, with a small volume fraction of modified isoprene, to incorporate model low surface energy functional groups as shown in Figure 1. Two very simple model reactions involving reaction of hydroxylated isoprene blocks with either acid chlorides or chlorosilanes were carried out. The purpose of these model reactions was to investigate the effect of fluorinated groups on surface behavior in a variety of chemical structures. These studies complement those involving block copolymers modified using hydrosilation reactions previously reported by us.[14] We report here our studies pertaining to the segregation thermodynamics and kinetics of these block copolymers and compare them with some of the predictions of the self-consistent mean field theory of dry polymer brushes. We expect our block copolymers to form dry brushes upon segregation from a homopolystyrene matrix of large molecular weight based on the theoretical predictions of Shull.

Experimental Section

Materials. Tetrahydrofuran (THF; Aldrich Sure Seal) was distilled over purple sodium benzophenone dianion and stored under positive nitrogen pressure. Pyridine (Aldrich) dried over CaH_2 and trap-to-trap distilled under vacuum (∼50 mTorr) was stored under a positive pressure of nitrogen at low temperature (−5 °C). 9-Borobicyclononane (9-BBN; 1 M in THF; Aldrich Sure Seal), 1*H*,1*H*,2*H*,2*H*-perfluorooctyldimethylchlorosilane (PCR), and heptafluorobutyryl chloride (Aldrich) were used as received.

Methods. Transmission infrared spectra were obtained using a Mattson FT-IR from film samples cast on polished NaCl from methylene chloride. Proton NMR spectra were obtained using a Varian XL-200 NMR spectrometer from $CDCl_3$ solutions. Number-average molecular weight (M_n) and polydispersity (MWD) were measured by GPC in THF solvent using a Waters Associates 510 pump, a 410 refractive index detector, and a UV−vis detector (254 nm) calibrated with narrow molecular weight polystyrene standards. Ultrastyragel columns of 500, 10^3, and 10^4 Å pore sizes were used. Dynamic advancing and receding water contact angles were measured with a Ramé-Hart NRL telescopic goniometer equipped with a Gilmont syringe and 24-gauge flat-tipped needle using doubly distilled water. After the samples were annealed above their glass transition temperatures to allow segregation to occur, forward recoil spectrometry (FRES) was carried out at room temperature to determine the total integrated excess of the diblock copolymers at the polymer−vacuum interface and the polymer−silicon oxide/Si interface as previously described.[15−17]

Synthesis of Poly(styrene-*d*$_8$-*b*-isoprene). The unmodified block copolymer (**I2**) was synthesized by the anionic polymerization of styrene-d_8 initiated by *sec*-butyllithium in tetrahydrofuran (THF) at −78 °C followed by the reaction with isoprene (5 h) and terminated with degassed methanol. **I2** has a composition of deuterated polystyrene (dPS) and polyisoprene (PI), with degrees of polymerization of 276 for the dPS block and 31 for the PI block and an overall polydispersity index of 1.04. The ratio of the 1,2:3,4 microstructure in the PI block was determined to be 0.37:0.63 by proton NMR spectroscopy. **I2** exhibits a glass transition at 95 °C (10 °C/min heating rate) and does not lose any mass up to 380 °C (heating rate 25 °C/min under a nitrogen atmosphere) as investigated by thermogravimetric analysis.

Hydroboration/Oxidation of Poly(styrene-*b*-isoprene). Hydroboration followed by oxidation of **I2** was performed using reported procedures.[18,19] One gram (0.98 mmol of vinyl and methylvinyl pendant double bonds) of dry **I2** (M_n = 30 800, MWD = 1.04) was weighed into a 100 mL round-bottomed (RB) flask equipped with a Teflon-coated magnetic stirring bar and fitted with a 14/20 rubber septum. The septum was tied down with Cu wire and the RB flask was purged with nitrogen for 1 h, following which 40 mL of dry THF was transferred in via a cannula under positive nitrogen pressure. 9-BBN (0.5 M, 2.5 mL, 1.25 mmol) in THF was added via cannula under positive nitrogen pressure. The reaction was allowed to proceed with stirring at room temperature for 12 h, following which the RB flask was cooled to −25 °C and 1 mL of anhydrous methanol was injected into the solution to destroy any excess 9-BBN.[18] After 10 min of stirring, 1 mL of 6 N NaOH (6 mmol) was added via a syringe. Following another 15 min, 0.5 mL of 30% H_2O_2 (5 mmol) was added via a syringe (solution turns opaque), and the oxidation was allowed to proceed for 1 h at −25 °C. The solution was then slowly warmed to 40 °C (over 1 h) while stirring vigorously.[19] Subsequently, the solution was cooled to room temperature, filtered, concentrated (final volume 5−8 mL), and precipitated into 100 mL of reagent grade methanol. The hydroxylated polymer (**I2-OH**) was filtered and dried under vacuum (∼0.1 Torr) for 3 days. The IR and proton NMR of **I2**-OH (absence of 885, 912, and 1640 cm^{-1} vinyl peaks in the IR and absence of vinyl protons in the NMR) suggested that the hydroboration followed by oxidation had proceeded essentially to quantitative yields. **I2-OH** exhibits a glass transition at ∼94 °C (10 °C/min heating rate) and does not lose any mass up to 390 °C (heating rate 25 °C/min under a nitrogen atmosphere) as investigated by thermogravimetric analysis.

Attachment of Heptafluorobutyryl "Fingers" by an Esterification Reaction.[20] One gram (0.98 mmol of hydroxyl groups) of **I2-OH** was placed in a 100 mL RB flask equipped with a Teflon-coated magnetic stirring bar and fitted with a 14/20 rubber septum. The septum was tied down with Cu wire and the RB flask was purged with nitrogen for 1 h, following which 50 mL of dry THF was added via a cannula under positive nitrogen pressure. After 10 min, 2 mL of dry pyridine was added to the RB flask via a cannula under positive nitrogen pressure. Following another 20 min, 1 mL of heptafluorobutyryl chloride (6.69 mmol), previously purged with nitrogen for 15 min, was added via a cannula under positive nitrogen pressure. The reaction was allowed to proceed with stirring at room temperature for 24 h, following which 1 mL of anhydrous methanol (24.7 mmol) was added to destroy the excess acid chloride. Subsequently, the solution was filtered, concentrated (final volume 5−6 mL) and precipitated into 100 mL of reagent grade methanol. The polymer with the heptafluorobutyryl "fingers" (**I2-hfb**) was filtered and dried under vacuum (∼0.1 Torr) for 3 days. The transmission IR spectrum of **I2-hfb** indicated that the heptafluorobutyryl "finger" was attached to the hydroxyl groups of **I2-OH** (C=O peak at 1780 cm^{-1} and CF_2 peak at 1230 cm^{-1}) and that the attachment was quantitative (absence of OH peak; peak maximum 3430 cm^{-1}). The results of the proton NMR concurred with the IR result (absence of the hydroxyl proton). The number-average molecular weight and the molecular weight distribution of **I2-hfb** as determined by GPC using narrow molecular weight polystyrene standards were M_n = 32 800 and MWD = 1.05. The molecular weight increase expected based on 100% reaction (hydroboration/oxidation as well as esterification) is 37 500. **I2-hfb** does not lose any mass up to 430 °C (heating rate 25 °C/min under a nitrogen atmosphere) as investigated by thermogravimetric analysis.

Attachment of 1*H*,1*H*,2*H*,2*H*-Perfluorooctyldimethylsilane "Fingers" by a Silane Coupling Reaction.[20] **I2-OH** (0.5 g, 0.49 mmol of hydroxyl groups) was placed in a 100 mL RB flask equipped with a Teflon-coated magnetic stirring bar and fitted with a 14/20 rubber septum. The septum was tied down with Cu wire and the RB flask was purged with nitrogen for 1 h, following which 50 mL of dry THF was added via a cannula under positive nitrogen pressure. After 10 min, 2 mL of dry pyridine was added to the RB flask via a cannula under positive nitrogen pressure. Following another 20 min, 2 mL of 1*H*,1*H*,2*H*,2*H*-perfluorooctyldimethylchlorosilane (6.63 mmol), previously purged with nitrogen for 15 min, was added via a cannula under positive nitrogen pressure. The reaction was allowed to proceed with stirring at room temperature for 24 h, following which 1 mL of anhydrous methanol was added to destroy the excess chlorosilane. Subsequently, the solution was filtered, concentrated (final volume 5−6 mL), and precipitated into 100 mL of reagent grade methanol. The perfluorosilane-coupled polymer (**I2-OSi**) was filtered and dried under vacuum (∼0.1 Torr) for 3 days. The transmission IR spectrum of **I2-OSi** indicated that a large extent of silane coupling had occurred [a large reduction in the area of the OH peak area (peak maximum 3430 cm^{-1}) with respect to the C−D stretch area (peak maximum 2272 cm^{-1})]. Proton NMR suggested that the yield of the silane coupling reaction was 60% (comparing the integrated intensity of the hydroxyl proton with respect to the aliphatic protons). The number-average molecular weight and the molecular weight distribution of **I2-OSi** as determined by GPC (using polystyrene standards) were M_n = 31 600 and MWD = 1.03. For 100% hydroboration/oxidation followed by 60% silane coupling reaction, the molecular weight expected is 38 700. **I2-OSi** loses about 1.5−3.0% of its weight in the temperature range 85−200 °C but does not lose any further mass up to 420 °C as investigated by thermogravimetric analysis (heating rate 25 °C/min under a nitrogen atmosphere).

Results and Discussion

The block copolymers (**I2-hfb** and **I2-OSi**) were blended with a homopolystyrene (PS; degree of polymerization = 1250; narrow-dispersity standard from Pressure Chemical) in different weight fractions ranging from 0.025 to 0.25. Thin-film samples (3000−4000 Å) were spun on a polished Si wafer from 5 wt % solutions of the blend in toluene. Samples were annealed under vacuum at 160 °C for different time periods to facilitate the investigation of the kinetics of segregation. The time taken for the block copolymer distribution to equilibrate varied from 12 h for the 0.025 weight fraction to 168 h for the 0.25 weight fraction. The amount of block copolymer segregated to the air−polymer interface and the silicon/silicon oxide/polymer interface was determined from the volume fraction versus depth profile measured by forward recoil spectrometry (FRES). A typical example of such a profile for the block copolymer **I2-hfb** for an initial bulk volume fraction of 0.05 is shown in Figure 2. The surface excess z^* is defined as $z^* = \int dz\,(\phi(z) - \phi_\infty)$, where z is the depth below the surface and the integral is taken over a region extending to half the thickness of the film. This quantity, represented by the hatched area, and the volume fraction of the block copolymer in the bulk at equilibrium, ϕ_∞, are marked in the figure. Note that segregation of the block copolymer to the interface with the native oxide of silicon also occurs. Since we are interested in the surface properties of the polymer film, we will ignore this interface segregation. Subsequent experiments have shown that this segregation can be completely eliminated by casting the blend film on a "buffer" film of poly(2-vinylpyridine). Since in any case we relate the volume fraction of block copolymer in the bulk that is in equilibrium with the surface excess z^*, the segregation to the silicon interface cannot affect the thermodynamic interpretation of our results.

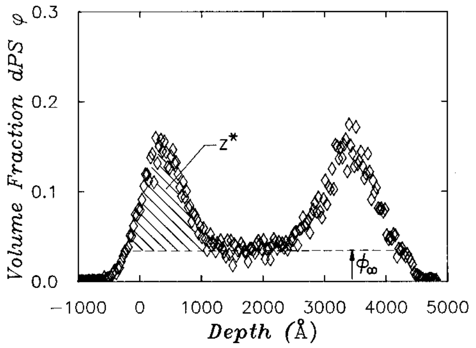

Figure 2. Depth profile of **I2-hfb** (5% initial volume fraction) in PS.

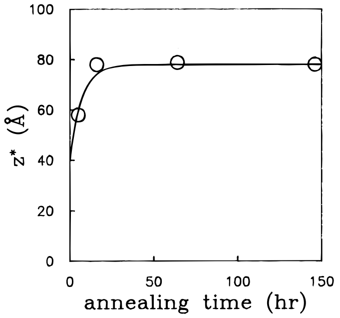

Figure 3. Segregation kinetics (z^* vs annealing time at 160 °C) for **I2-hfb** (5% initial volume fraction) in PS.

The segregation kinetics were determined by measuring z^* versus annealing time. Such plots are shown in Figure 3 and 4 for the block copolymer **I2-hfb** at initial bulk volume fractions of 0.05 and 0.10. The segregation of the block copolymer is relatively rapid at an initial volume fraction of 0.05, with the equilibrium segregated amount being established in ∼50 h. At the higher volume fraction, the time required to establish equilibrium segregation is much longer: about 150 h. The much slower equilibration of the higher volume fraction sample is probably due to the formation of block copolymer micelles in the bulk.[21,22] Formation of micelles can significantly slow the rate of diffusion of block copolymer to interfaces[15] by decreasing the concentration of free block copolymer chains. To ensure that equilibrium was established in doubtful cases, such as the sample annealed for 150 h in Figure 4, we placed a

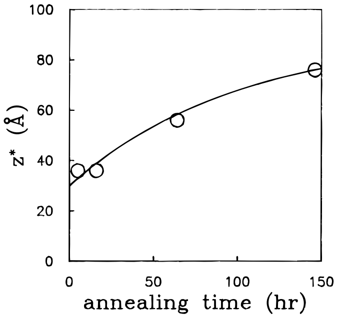

Figure 4. Segregation kinetics (z^* vs annealing time at 160 °C) for **I2-hfb** (10% initial volume fraction) in PS.

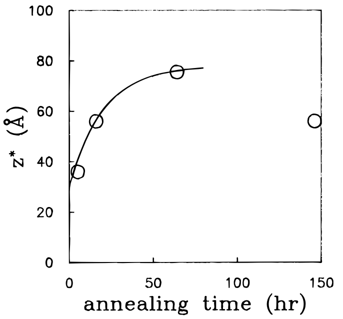

Figure 5. Segregation kinetics (z^* vs annealing time at 160 °C) for **I2-OSi** (10% initial volume fraction) in PS.

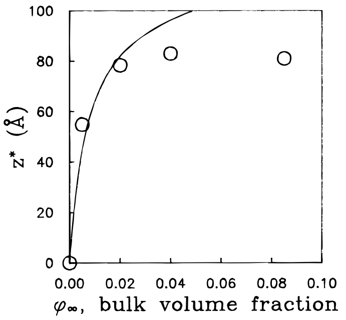

Figure 6. Segregation isotherm for **I2-hfb** at 160 °C.

thin film of PS homopolymer slightly thicker than 1000 Å onto the surface of the segregated sample by picking up the film from the surface of a water bath. The sample was reannealed at 160 °C for a time comparable to the original annealing time. In all cases, the segregated layer was observed to move to the surface of the sample and to decrease somewhat in z^* corresponding to the decrease in ϕ_∞ produced by the extra PS layer.

The kinetics of segregation of the **I2-OSi** block copolymer at an initial bulk volume fraction of 0.10 are shown in Figure 5. At this volume fraction the initial kinetics are considerably more rapid than those of the **I2-hfb** copolymer, perhaps reflecting an increase in the critical micelle concentration for this copolymer for which only 60% of the pendent vinyl groups have reacted with perfluorinated fingers compared to 100% for the **I2-hfb** copolymer. The decrease in z^* at long times however may indicate that **I2-OSi** undergoes some thermal degradation after these long-time annealings. For this polymer therefore we assumed equilibrium was established after 50 h of annealing at 160 °C.

Figures 6 and 7 show the segregation isotherms, namely z^* versus ϕ_∞, for **I2-hfb** and **I2-OSi** at the air–polymer interface. The circles are the data points obtained from experiments. From the experimental data, it is evident that the block copolymer chains segregate to the air–polymer interface such that there is an integrated interfacial block copolymer excess. The segregated block copolymer layers are in equilibrium with the respective block copolymers in the bulk PS matrix phase as evident from the z^* versus time of annealing studies (kinetics data at all the initial block copolymer volume fractions not shown). That is, for each value of ϕ_∞ in the bulk PS phase there is a unique value of z^* for the respective block copolymers at the respective interfaces.[23] Since the degree of polymerization of the block copolymers is much less than that of the homopolymer matrix, these results represent the dry brush case. In both cases, z^* appears to increase linearly with ϕ_∞ in the low-ϕ_∞ regime before reaching a plateau value at high ϕ_∞. At low ϕ_∞, the block copolymer chains that arrive at the air–polymer interface do not face much competition for surface sites and essentially occupy these without stretching. Under these conditions, the adsorption of the block copolymers is controlled by (1) the favorable free energy of interaction of the perfluorinated fingers with the surface given by $k_BT(\chi_{FB-PS} - \chi_{FB-S})N_{FB}$[10] $= k_BT\chi_{eff}N_{FB}$, where N_{FB} is the polymerization index of the isoprene block containing the fluorinated fingers and χ_{FB-S}, χ_{FB-PS}, and χ_{eff} are the Flory interaction parameters characteristic of the interaction between the fluorinated block with the surface, the fluorinated block with the homopolystyrene, and an effective interaction parameter characteristic of the difference; and (2) the entropy loss due to the localization of the block copolymer chains at the surface. Semenov[22] has derived an analytical expression (see eq 1) which predicts a linear dependence of z^* on ϕ_∞, at low ϕ_∞, for the case where adsorption is hindered by the loss of entropy alone (due to localization of the block copolymer chains at the surface of the homopolymer matrix).

$$z^* = (\pi/2)R_g(\chi_{eff}N_{FB})^{-0.5}\exp(\chi_{eff}N_{FB})\phi_\infty \qquad (1)$$

where χ_{eff} is the effective Flory interaction parameter characteristic of the favorable free energy of interaction of the perfluorinated fingers with the surface. The linearity of the z^* vs ϕ_∞ curve, at low ϕ_∞, is thus in accord with both eq 1 and the favorable effective free energy of interaction (χ_{eff}) of the perfluorinated fingers with the surface. The strong adsorption of perfluoro end-functionalized polymers of very low bulk volume fraction (<1%) from the homopolymer matrix to the air–polymer interfaces has been observed by other groups suggesting that the favorable free energy of interaction (χ_{FB-S}) of perfluorinated fingers with the surface is an important term at low ϕ_∞.[24,25] The surface excess increases with different initial slope at low ϕ_∞ and is higher for **I2-hfb**, thereby suggesting that the adsorption isotherm of **I2-hfb** is of higher affinity type when compared to **I2-OSi**.

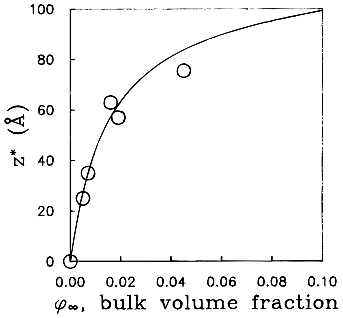

Figure 7. Segregation isotherm for **I2-OSi** at 160 °C.

The surface excess reaches a plateau value at higher ϕ_∞, reflecting the difficulties in packing the copolymer chains. These are due to the stretching of the dry polymer brush, a universal feature of its thermodynamics, which ultimately limits its segregation.[10,11]

In the dry brush regime, the enthalpy gain due to the segregation of the block copolymer is mainly compensated by the entropy loss due to the stretching of the block copolymer and its localization at the surface. The stretching entropy loss of the block copolymer scales approximately as $(z^*/R_g)^2$, where z^* represents the length scale of the stretched block copolymer and R_g, the radius of gyration, represents the dimension of the unstretched polymer (dPS) and is ~50 Å. From the plateau value of z^* (from Figures 6 and 7), we arrive at a (z^*/R_g) value of 1.5 for **I2-OSi** and 1.6 for **I2-hfb**.

An approximate self-consistent mean field theory (SCMF) of Shull,[10] describing the adsorption of dry brushes at the polymer–air interface, was used to fit the adsorption isotherms in Figures 6 and 7 using the effective Flory interaction parameter, χ_{eff} ($\chi_{\text{eff}} = \chi_{\text{FB-PS}} - \chi_{\text{FB-S}}$), as the fitting parameter. The continuous lines in Figures 6 and 7 are those predicted by the theory (SCMF). In the case of the segregation of **I2-hfb** to the air–polymer interface, the measured values of z^* are in agreement with the SCMF theory predictions for $\chi_{\text{eff}}N_{\text{FB}} = 7.5$ (and $\chi_{\text{eff}} = 0.24$) for $\phi_\infty \leq 0.02$ (initial bulk volume fraction ≤ 0.10). In the case of the segregation of **I2-OSi** to the air–polymer interface, the measured values of z^* are in excellent agreement with the SCMF theory predictions for $\chi_{\text{eff}}N_{\text{FB}} = 7.0$ (and $\chi_{\text{eff}} = 0.23$) for $\phi_\infty \leq 0.02$ (initial bulk volume fraction ≤ 0.10). At large ϕ_∞ the experimentally observed values deviate from the theoretical predictions, with the deviation for **I2-hfb** being more prominent at lower ϕ_∞ values than that for **I2-OSi**. This is probably due to the formation of micelles in the bulk. Micelles form at lower values of block copolymer chemical potential if the smaller block (containing the perfluorinated fingers) forms the core.[15] We observe a very good fit up to reasonably high ϕ_∞ values for **I2-OSi**. This is probably due to its μ_{cmc}, the chemical potential at the critical micelle concentration, being higher than that of **I2-hfb**. It is not unreasonable for **I2-OSi** to have a higher μ_{cmc} than **I2-hfb** as 60% of its pendant hydroxyl groups have reacted with perfluorinated fingers compared to 100% for **I2-hfb**. The experimentally observed rapid initial kinetics of segregation for **I2-OSi** compared to **I2-hfb** (see Figures 4 and 5) suggests that this is most likely to be the case.

In addition, we observe that the block copolymer chains segregate to the homopolymer–silicon oxide/Si interface. We find that the integrated interfacial block copolymer excess for **I2-hfb** is greater at the air–polymer interface while that for **I2-OSi** is greater at the silicon oxide/Si–polymer interface. We believe that the greater z^* for **I2-OSi** at the silicon oxide/Si–polymer interface compared to the air–polymer interface is due to the presence of unreacted pendant primary hydroxyl groups on the block copolymer which can adsorb strongly to the oxide surface or couple with silanol groups on the oxide surface.

The SCMF theory predicts many properties of the dry brush, and one such property that we can indirectly measure by experiments (contact angle) is the change in surface tension as a result of segregation. We can fit the surface tension change for given z^*/R_g data, as estimated by SCMF theory,[10] by a third-order polynomial in z^*/R_g, as given in eq 2.

$$\frac{(\gamma_0 - \gamma)V_b}{{R_g}^b k_B T} = 1.38\left(\frac{z^{*b}}{{R_g}^b}\right) - 0.51\left(\frac{z^{*b}}{{R_g}^b}\right)^2 + 0.45\left(\frac{z^{*b}}{{R_g}^b}\right)^3 \quad (2)$$

The changes in surface tension ($-\Delta\gamma = \gamma_0 - \gamma$) as predicted by SCMF theory for the experimental z^*/R_g data were evaluated using eq 2 and are plotted as a function of ϕ_∞ in Figure 8 (the superscript b in eq 2 indicates that the dPS block is used to determine R_g and z^*; i.e., $z^{*b} = [N_{dPS}/(N_{dPS} + N_{FB})]z^*$ and ${R_g}^b = (N_{dPS}/6)^{1/2}a$, where $a = 0.67$ nm is the statistical segment length of dPS; V_b is the volume of the dPS chain. The advancing contact angle is very sensitive to surface energy changes (particularly polarity changes at the very outer few angstroms) as a result of segregation or surface structural rearrangements. The water contact angles of the unannealed and annealed film samples were therefore measured to monitor interfacial energy changes. The advancing water contact angle versus ϕ_∞ are plotted in Figure 9 (**I2-hfb**) and 10 (**I2-OSi**), and the results are in agreement with the trend predicted by SCMF theory. The advancing contact angle saturates at $\phi_\infty \geq 0.02$ for both block copolymers and is in the range 104–105°. (For comparison, the advancing water contact angles of polystyrene, PTFE, and FEB (Du Pont) are 89, 110, and 115°, respectively.[26,27]) This result suggests that changes taking place at the uppermost surface are complete at $\phi_\infty = 0.02$ and that its surface composition is likely to be a mixture of CF_2 and CF_3 groups and polystyrene repeat units and not a monolayer of CF_2 or CF_3. The receding angle for **I2-OSi** after 12 h of annealing is 79–80° while that for **I2-hfb** is 89–90°. The receding contact angles of polystyrene, PTFE, and FEB are 78, 105, and 110°, respectively. Contact angle hysteresis provides information concerning the heterogeneity of surfaces in terms of the distribution of functional groups as well as roughness. The hysteresis that we observe is probably due to the presence of PS segments along with CF_2 and CF_3 functional groups in the dry brush.

One conclusion that can be drawn is that the segregation behavior of the two different block copolymers is very similar. This result may seem surprising in view of the fact that one of the block copolymers is functionalized with $(CF_2)_6F$ groups while the other is functionalized with $(CF_2)_3$ groups. The degree of functionalization however differs, being nearly 100% for the copolymer with $(CF_2)_3F$ groups but only ~60% for the copolymer with $(CF_2)_6F$ groups. The total number of (CF_2) units on the two block copolymer is thus relatively similar, being ~93 for the **I2-hfb** copolymer and ~112 for the **I2-OSi** copolymer.

Summary

We have synthesized model block copolymers with pendant fluorinated functional groups in the shorter block of a poly(styrene-d_8-*b*-isoprene) block copolymer for segregation studies from a polystyrene matrix. We show that these block copolymers segregate to the air–polymer interface from a homopolystyrene matrix. The integrated surface excesses as a function of volume fraction of block copolymer at equilibrium segregation are reported and shown to be well described by the self-consistent mean field theory at small initial volume fractions of the block copolymer or at chemical potentials below micelle formation. Surface tension changes due to the adsorption of the block copolymers at the air–homopolymer interface were evaluated from the surface

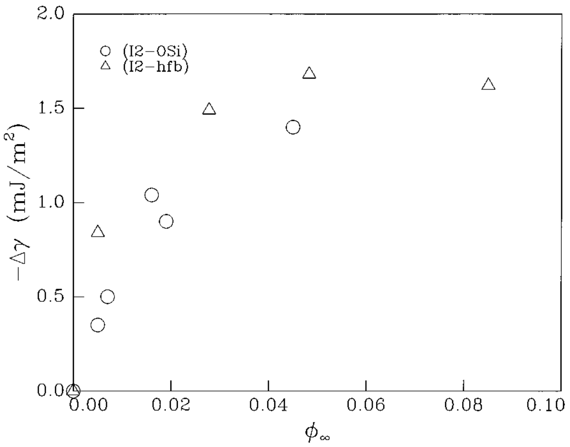

Figure 8. Change in surface tension as a function of equilibrium volume fraction in the bulk: extracted from the segregation isotherms using the SCMF theory of Shull.[10]

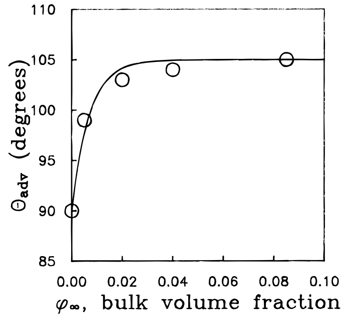

Figure 9. Advancing contact angle for **I2-hfb** as a function of bulk volume fraction.

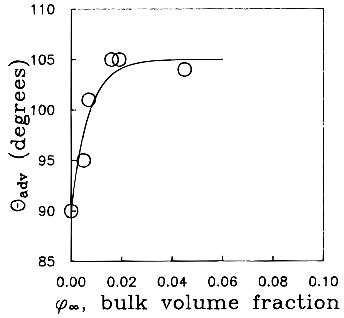

Figure 10. Advancing contact angle for **I2-OSi** as a function of bulk volume fraction.

excess data using the SCMF equation. Water contact angle data are presented to indicate that the composition of the very outer surface is mostly made up of a mixture of PS, CF_2, and CF_3 functional groups.

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