Random Copolymer Adsorption at the Polymer Melt/Substrate Interface: Effect of Substrate Type

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ABSTRACT: Using low-energy forward recoil spectrometry (LE-FRES) and dynamic secondary ion mass spectrometry (DSIMS), we measure the interfacial excess, z^*, and the volume fraction profiles of a bromine functionalized polymer chains at the polymer/inorganic substrate interface. Specifically, we investigate a blend of polystyrene (PS) homopolymer and a deuterium-labeled poly-d-(styrene-*ran*-4-bromostyrene) (dPBr$_x$S) random copolymer, where the mole fraction of 4-bromostyrene units in the chain is $x = 0.06$. Our aim is to measure the strength of interaction of bromine functionalized segments of dPBr$_{0.06}$S with silicon oxide, SiO$_x$, and hydrogen-terminated silicon, SiH, surfaces. The results from both LE-FRES and DSIMS show that dPBr$_{0.06}$S segregates at both polymer/SiO$_x$ and polymer/SiH interfaces, demonstrating that that the bromine groups do interact favorably with both surface types. We also use the self-consistent mean-field model (SCMF) to calculate the dPBr$_{0.06}$S concentration profile and z^* at the polymer/substrate interface and to determine the value of the interaction energy between 4-bromostyrene segments and the substrate. The comparison of experimental and SCMF results provides the interaction energy between the brominated polystyrene repeat unit and both substrate types, namely $\epsilon_{\mathrm{dPBr1S}}^{\mathrm{SiO}x} = -0.18kT$ and $\epsilon_{\mathrm{dPBr1S}}^{\mathrm{SiH}} = -0.22kT$. These results show that the interaction of the brominated segment with SiH surface is ca. 20% stronger than that with the SiO$_x$ surface.

Introduction

Many industrial applications of polymeric systems are related to the adhesion of a polymer to an inorganic substrate, which is, in turn, governed by the interactions between polymer molecules and the surface of the substrate. These applications include, for example, adhesives, polymer coatings, colloidal stabilizers, etc. In the case of polymer coatings and adhesives, the strength of adhesion between the polymer and the substrate is the determining factor for the performance and thus the applicability of a particular polymer/substrate system. In most of these applications, the polymer phase is a blend of different polymer species, and thus its adhesion to the substrate depends on the composition of the polymer blend, especially in the interfacial region. Segregation effects at the polymer/substrate interface influence the composition profiles of thin films of polymer blends. The effect of the substrate on polymer segregation is governed by the magnitude of the interaction energy, which arises from the chemical nature of both the substrate and the segments of the segregating polymer molecule. In general, the energy of interaction between a given polymer segment and the substrate is not readily available and is difficult to measure experimentally. As a result, only a few experimental studies measuring the strength of interaction between the polymer and the substrate are available to date.[1−8] These experiments are limited to end-functionalized homopolymers[1−3] and block copolymers.[4−8] In recent studies of end-functionalized homopolymers,[1,2] the interaction energy of a carboxylic acid functional group, COOH, with silicon oxide, SiO$_x$, was found to be an order of magnitude higher than that of butadiene segments.[3] This result is consistent with relatively weak van der Waals interaction between butadiene and SiO$_x$,[9] compared to the chemical reaction between COOH and the SiO$_x$ surface.[1] In the case of block copolymers, the copolymer−substrate interaction is difficult to determine in terms of energy per segment because it requires measuring the number of adsorbing block segments that are in actual contact with the substrate. Qualitatively, the poly(methyl methacrylate) (PMMA) block of the deuterated PS-*b*-PMMA block copolymer was found to have attractive interaction with silicon oxide and aluminum oxide, but not with gold.[4] On the other hand, poly(isoprene) blocks were more strongly attracted to gold than to silicon oxide.[5] Also, poly(2-vinylpiridine) was strongly attracted to SiO$_x$.[6,7] The interaction energy between random copolymers and inorganic substrates is even less researched, and only few qualitative studies are available to date.[10−14]

From a scientific perspective, random copolymers of styrene and 4-bromostyrene, denoted as PBr$_x$S, have proven to be extremely useful as model polymers for a variety of studies. The most important are studies involving systematic variation of the Flory−Huggins segment−segment interaction parameter, χ, in blends of PBr$_x$S and polystyrene, PS. This work is based on the fact that, by varying the mole fraction, x, of the 4-bromostyrene units in the copolymer chain, one can vary the χ parameter between PBr$_x$S and PS.[15−17] In addition, PBr$_x$S can be synthesized easily by bromination of polystyrene.[15] Polystyrene standards with very low polydispersity can be brominated to produce PBr$_x$S copolymers with the same narrow molecular weight distribution as the parent polymer. Although surface and bulk behavior of PBr$_x$S in PS:PBr$_x$S blends has been investigated by many authors, the strength of interaction of PBr$_x$S segments with inorganic substrates is not well understood. It was observed earlier[10,11,18,19] that PBr$_x$S in a dPS:PBr$_x$S blend does not have a preference for silicon oxide surface. This observation was confirmed by Krausch and co-workers,[12] who used secondary ion mass spectrometry (SIMS) and time-of-flight forward

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recoil spectrometry (TOF-FRES) to measure the concentration profile of $PBr_{0.5}S$ in thin films of $dPS:PBr_{0.5}S$ blends. They found no preference of $PBr_{0.5}S$ over dPS not only to the silicon oxide surface but also to the Cr-coated substrate. Interestingly, Krausch and co-workers[12] found that $PBr_{0.5}S$ is strongly attracted to the surface of a silicon wafer with its native oxide stripped (SiH-terminated surface) but made no quantitative estimate of the magnitude of the interaction energy. Similar conclusions were made by Affrossman and co-workers[13] when investigating blends of dPS and PBr_xS at polymer/SiO_x and polymer/SiH interfaces using TOF-FRES. The authors found that PBr_xS segregated preferentially at the polymer/Si−H interface while both dPS and PBr_xS were distributed uniformly in films on SiO_x-covered substrates. Again, no quantitative conclusions were made concerning the magnitude of the interaction energy. Very recently, Dev and co-workers[14] have investigated the distribution of PBr_xS in a blend with PS deposited on gold-coated silicon wafers and found that PS enriches the polymer/gold interface. This finding indicates that the attraction of PBr_xS to gold is weaker than that of the PS.

The first quantitative estimate of the interaction energy between PBr_xS and silicon oxide surface was published recently by Oslanec and co-workers.[20] In these experiments, PS and $PBr_{0.136}S$ were used as matrix polymers in adsorption studies of dPS-*b*-PMMA block copolymer at the polymer/SiO_x interface. The authors used low-energy FRES (LE-FRES) and neutron reflectivity (NR) to measure the volume fraction profile of the dPS-*b*-PMMA at the polymer/SiO_x interface and found that the adsorbed amount decreased as the matrix changed from PS to $PBr_{0.136}S$. This result indicates that the $PBr_{0.136}S$ matrix successfully competes with adsorbing PMMA block for adsorption sites on the substrate and thus, in contrast with previous observations,[10−13,18,19] has an attractive interaction with SiO_x surface. Oslanec and co-workers[20] compared the results from LE-FRES and NR with self-consistent mean-field (SCMF) calculations and estimated the interaction energy between the $PBr_{0.136}S$ matrix and SiO_x substrate to about $-0.01kT$/copolymer segment. For a copolymer having 13.6% (molar) segments brominated this value translates to about $-0.07kT/PBr_1S$ unit. As illustrated here, the nature and the strength of interaction between brominated polystyrene segments and SiO_x substrate are not well understood. In fact, recent studies indicate either neutral or attractive interaction, the discrepancy that clearly needs to be addressed.

In this paper, we use depth profiling methods (LE-FRES and dynamic SIMS, DSIMS) to investigate the behavior of $PS:dPBr_{0.06}S$ blend at the interface with SiO_x and SiH substrates. If the interaction between brominated polystyrene and the substrates is attractive, the $dPBr_{0.06}S$ will enrich the interfacial region. On the other hand, if this interaction is neutral, no enrichment will be visible. To interpret the experimental results, we use a SCMF model that includes the interaction energy between the $dPBr_{0.06}S$ segments and the substrate. The advantage of the SCMF model is that the $dPBr_{0.06}S$/substrate interaction energy is the only fitting parameter in the model; other parameters are given by the system. Using results from SCMF, we show that the interaction between brominated polystyrene segments and both SiO_x and SiH substrates is attractive and that this attraction is stronger for the SiH substrate.

Table 1. Summary of Sample Characteristics

sample ID	technique	substrate	thickness [nm]	annealing
FB1	LE-FRES	SiO_x	207.3	190 °C/3 days
FB2	LE-FRES	SiO_x	207.3	none
FB3	LE-FRES	SiH	206.9	190 °C/3 days
FB4	LE-FRES	SiH	206.9	none
SB5	DSIMS	SiO_x	185.4	190 °C/3 days
SB6	DSIMS	SiO_x	185.4	none
SB7	DSIMS	SiH	184.7	190 °C/3 days
SB8	DSIMS	SiH	184.7	none

Experimental Section

Materials and Sample Preparation. In this study we investigate the adsorption behavior of a polydeuterated (styrene-*ran*-4-bromostyrene) ($dPBr_xS$) random copolymer at an interface between a polymer blend and an inorganic substrate. The polymer blend consists of polystyrene homopolymer matrix and the $dPBr_xS$ copolymer additive. The matrix PS with molecular weight 200 000 g/mol and polydispersity 1.02 was purchased from Polymer Laboratories, Ltd.[21]

The $dPBr_xS$ copolymer was prepared by bromination of a deuterated polystyrene standard purchased from Polymer Laboratories, Ltd.,[21] according to the procedure described in ref 15. The parent polymer had a molecular weight of 203 000 g/mol and polydispersity 1.03. The bromination procedure was carried out such that the resulting polymer contained 6% molar of brominated segments. In this paper we use the notation $dPBr_{0.06}S$ for the brominated copolymer. As pointed out in previous studies,[16,22] the bromination takes place exclusively in the para position of the aromatic ring. In addition, size exclusion chromatography measurements[22] showed that bromination does not alter the number of segments in the polymer chain, nor does it cause any changes in the polydispersity of the polymer. It is also believed[16] that the bromination occurs randomly along the chain because adjacent aromatic rings are separated from each other by three aliphatic carbons and because steric hindrance between para positions on adjacent rings is negligible. Thus, we believe that $dPBr_{0.06}S$ is a random copolymer of brominated and nonbrominated dPS repeat units.

Two types of inorganic substrates were studied: a silicon wafer coated with thin native oxide layer, SiO_x, and a hydrogen-terminated silicon wafer, denoted as SiH. In both cases, the as-received silicon wafers were first etched in 7 vol % HF:water solution (3 min) to remove the original native oxide layer. The HF was found to remove the organics, presumably by removing the oxide layer beneath them. The organic layer on the surface was never thick enough that it passivated the surface and prevented HF from etching through. One-half of the wafers were then placed in an ultraviolet-ozone cleaner for 10 min to grow a ca. 2 nm thick SiO_x film, as measured by ellipsometry. The water contact angle for these surfaces was <15° and thus not reliably measurable. The second half of the wafers were etched in a buffered oxide etch solution (40 wt % NH_4F in water, buffered by HF to pH = 7) for 3 min to produce a SiH functionalized surface. The water contact angle measured on these wafers ranged from about 77° to 82°, indicative of a quite hydrophobic surface.

Polymer films were prepared by spin-casting a toluene solution of $PS:dPBr_{0.06}S$ blend on both SiO_x and SiH substrates. The volume fraction of $dPBr_{0.06}S$ in the blend was $\phi_{dPBr0.06S} = 0.092$. Two sets of samples were prepared: one set for LE-FRES (samples FB1−FB4) and one for DSIMS experiments (samples SB5−SB8). Film thicknesses, as determined by ellipsometry, ranged from 185 nm for samples SB5−SB8 to about 207 nm for samples FB1−FB4. One-half of the samples were annealed in a vacuum oven for 3 days at 190 °C. The annealing time was chosen in a preliminary FRES run where a range of times between 1 h and 4 days were used. Three days was found to be long enough that the samples had sufficient time to reach the equilibrium. The second half of the samples was not annealed so that the $dPBr_{0.06}S$ volume fraction profile before annealing can be established. The summary of sample characteristics is given in Table 1.

The thermodynamics of a polymer blend plays a significant role in adsorption of one of the species from the blend. The degree of bromination of the $dPBr_{0.06}S$ was chosen to be relatively low so that the PS:$dPBr_{0.06}S$ blend would be miscible. The Flory−Huggins interaction parameter between PS and $dPBr_{0.06}S$ segments at the annealing temperature of 190 °C is $\chi_{PS,dPBr0.06S} = 8.5 \times 10^{-4}$.[23,24] The critical χ parameter for this system is $\chi_c = 1.06 \times 10^{-3}$, which means that at 190 °C the blend is miscible at all compositions.

Experimental Techniques. The interfacial excess z^* (z^* is defined as the thickness of a layer at 100% concentration that would contain the same quantity of material as the excess near the interface) of $dPBr_{0.06}S$ in samples FB1−FB4 was determined by LE-FRES using a 1.7 MeV He^+ ion beam at 15° incident and exit angles with respect to the sample surface and a 6 μm thick Mylar stopper foil. Under these conditions, the depth resolution of LE-FRES was 55 nm at the surface and 65 nm at 200 nm beneath the surface. Conventional FRES[25] and LE-FRES[26] have been described in detail elsewhere. The LE-FRES experiments were performed at the Australian Nuclear Science and Technology Organisation (ANSTO), Lucas Heights, Australia, using a 3 MV Van de Graaf accelerator. Because of relatively poor depth resolution, the LE-FRES did not provide the volume fraction profiles of $dPBr_{0.06}S$ in the samples. A technique with much better depth resolution, namely dynamic secondary mass spectrometry (DSIMS),[18,27] was employed to obtain a more detailed distribution of $dPBr_{0.06}S$ in the sample. In the DSIMS experiments a 7.5 keV Cs^+ primary beam was used. The sample was held at −4.5 kV, resulting in Cs^+ impact energy of 12 keV. The primary beam with current ca. 5−6 nA was scanned over a 200 μm × 200 μm rectangular area, forming a sputtered crater in the sample. To avoid crater edge effects, the analysis was performed within an analytical area, 30 μm in diameter in the center of the crater, where H^-, D^-, C^-, and Si^- ions were detected as a function of sputtering time. The sputtering rate was calibrated using samples with known thickness and homogeneous distribution of both H and D in the film. Under these experimental conditions, the depth resolution in the measured profiles was better than 10 nm even at the polymer/substrate interface. The DSIMS experiments were performed at ANSTO, Lucas Heights, Australia, using a Cameca IMS 5F spectrometer.

Self-Consistent Mean-Field Model. To interpret the LE-FRES and DSIMS experiments, a self-consistent mean-field model (SCMF) was used to calculate the volume fraction profiles of $dPBr_{0.06}S$ at the polymer/substrate interface. The SCMF calculations followed the approach described in detail by Shull and Kramer.[28] In brief, this technique involves assuming a segment density profile, calculating a mean field from it and then solving the diffusion equation to recalculate the segment density profile. This process is continued until it converges with a self-consistent mean-field and segment density profile. The input parameters for the SCMF calculations are the segment numbers of both PS and $dPBr_{0.06}S$, the bulk volume fraction of $dPBr_{0.06}S$, the Flory−Huggins segment−segment interaction parameter, $\chi_{PS,dPBr0.06S}$, and the interaction energies between the substrate and polymer segments, namely ϵ_{PS}^{sub} and $\epsilon_{dPBr0.06S}^{sub}$. The values of χ and ϵ enter in the relation between the segment density profile and the mean field. The index "sub" denotes the substrate, which can be either SiO_x or SiH. The $\chi_{PS,dPBr0.06S}$ parameter was calculated for 190 °C from refs 23 and 24: $\chi_{PS,dPBr0.06S} = 8.5 \times 10^{-4}$. In this work we are concerned with the effect of bromination of the interaction of PS with the substrate so without loss of information we can neglect the interaction of PS with both the SiO_x and SiH surfaces by setting $\epsilon_{PS}^{SiOx} = \epsilon_{PS}^{SiH} = 0$. Thus, the only unknown parameter is the interaction energy between the $dPBr_{0.06}S$ and the substrate. Therefore, by systematically varying $\epsilon_{dPBr0.06S}^{sub}$ until the SCMF and experimental volume fraction profiles and z^* values agree, the strength of $dPBr_{0.06}S$ interaction with the substrate can be determined. Such a series of calculations were performed for both SiO_x and SiH surfaces.

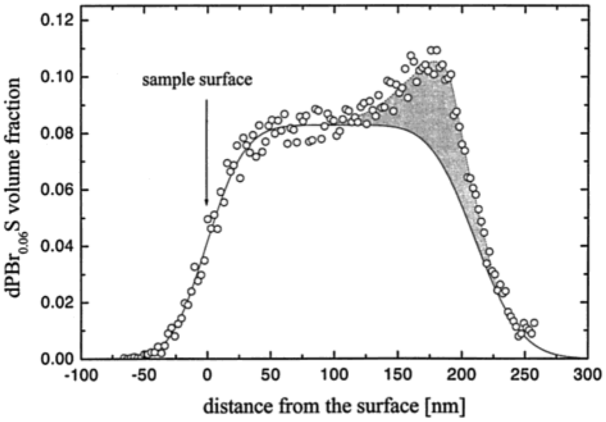

Figure 1. LE-FRES volume fraction profile of $dPBr_{0.06}S$ in a PS:$dPBr_{0.06}S$ blend annealed at 190 °C for 3 days (sample FB3) (open circles). The substrate is a SiH functionalized surface. The volume fraction of $dPBr_{0.06}S$ in the as-cast sample is $\phi_\infty = 0.092$. The shaded area represents the $dPBr_{0.06}S$ interfacial excess, z^*, and the arrow indicates the position of the sample surface. The solid line depicts an expected $dPBr_{0.06}S$ volume fraction profile if no segregation has occurred in the film. The dotted line is a guide to the eye only.

The SCMF model in this paper assumes that the $dPBr_{0.06}S$ chain is represented by a homopolymer chain having each segment identical and corresponding to an averaged segment, which is 6% brominated. This assumption is justified by the fact that the brominated segments are distributed randomly along the chain,[16] and as shown later in the paper, the resulting interaction energy between bromine groups and the substrate is lower than $1kT$. The probability of any individual brominated group atom interacting with the substrate is thus not much greater than that of a PS group in the same location close to the interface, and so the direct effect of bromination on local chain contours is small. The averaged chain is thus liable to give a good estimated of the contacts between the real chain and the substrate. Bromination alters the location of the total brominated chains within the sample as the sum total of brominated interactions is important in this case.

Results

To investigate the interaction between brominated polystyrene and the inorganic substrate, we studied the behavior of $dPBr_{0.06}S$ blended with PS at the polymer/substrate interface, where the substrate was SiO_x in one case and SiH in the other case. Using LE-FRES, we measured the interface excess, z^*, of $dPBr_{0.06}S$ at the polymer/substrate interface for samples before and after annealing at 190 °C for 3 days in a vacuum. Figure 1 shows a $dPBr_{0.06}S$ volume fraction profile of annealed PS:$dPBr_{0.06}S$/SiH sample plotted as open circles (sample FB3). Within the resolution of the LE-FRES technique, the $dPBr_{0.06}S$ is uniformly distributed at the film surface and in the bulk. The $dPBr_{0.06}S$ enrichment at the interface with SiH is, however, clearly visible in Figure 1, where it is denoted by the shaded region. The solid line in Figure 1 represents a $dPBr_{0.06}S$ volume fraction profile as if there had been no interface segregation in the film. The dotted line is only a guide to the eye and was obtained by smoothing the experimental data. Similar results were obtained for samples on SiO_x substrate. In addition, LE-FRES experiments were performed on as-cast reference samples to determine the $dPBr_{0.06}S$ volume fraction profile before the annealing step.

LE-FRES, because of its relatively poor depth resolution (ca. 55 nm at the sample surface), was used only to obtain the z^* values. To get more detailed volume

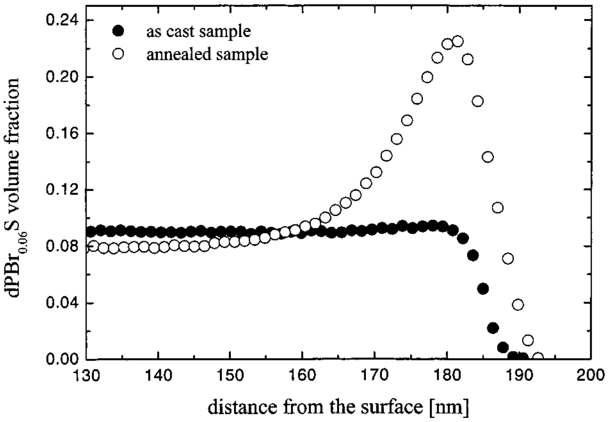

Figure 2. DSIMS volume fraction profiles of dPBr$_{0.06}$S in a PS:dPBr$_{0.06}$S blend in region near the polymer/SiH interface for the as-cast sample (sample SB8) (solid circles) and sample annealed at 190 °C for 3 days (sample SB7) (open circles). The volume fraction of dPBr$_{0.06}$S in the as cast sample is $\phi_\infty = 0.092$.

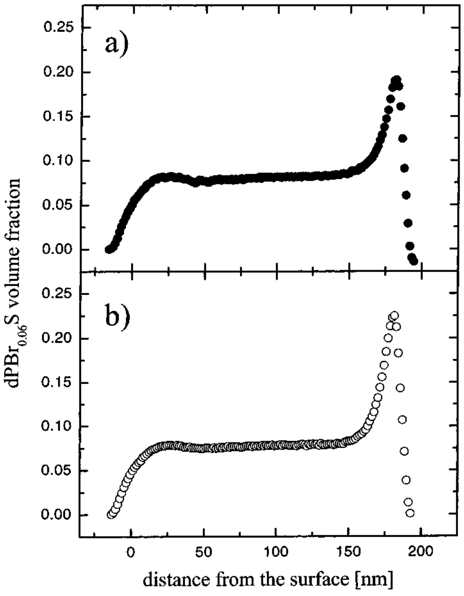

Figure 3. DSIMS volume fraction profiles of dPBr$_{0.06}$S in a PS:dPBr$_{0.06}$S blend for samples annealed at 190 °C for 3 days on (a) SiO$_x$ substrate (sample SB5) (solid circles) and (b) SiH substrate (sample SB7) (open circles). The volume fraction of dPBr$_{0.06}$S in the as-cast samples is $\phi_\infty = 0.092$.

fraction profiles, we have used DSIMS with much better depth resolution (<10 nm). Figure 2 shows the dPBr$_{0.06}$S volume fraction profiles at polymer/SiH interface region measured by DSIMS for as-cast sample (sample SB8) (solid circles) and annealed sample (sample SB7) (open circles). The plot for the as-cast sample shows that the dPSBr$_{0.06}$S is initially distributed uniformly in the interfacial region. Upon annealing, the volume fraction of the brominated polymer increases from its bulk value of about 8% and reaches its maximum of almost 24% at the interface. Such an increase results in a significant interfacial excess of the dPBr$_{0.06}$S, $z^* = 2.15$ nm. The DSIMS volume fraction profiles of dPBr$_{0.06}$S for entire samples are shown in Figure 3a,b. The volume fraction profile in Figure 3a was obtained from sample SB5 (SiO$_x$ substrate), whereas the data in Figure 3b were measured on sample SB7 (SiH substrate). In both cases the samples were annealed at 190 °C for 3 days in a vacuum. Both profiles in Figure 3 show that dPBr$_{0.06}$S is uniformly distributed in the bulk region and that it significantly enriches both the polymer/SiO$_x$ and polymer/SiH interfaces. Quantitatively, however, the z^* at polymer/SiH interface is about 35% higher than that at the polymer/SiO$_x$ interface. The segregation of dPBr$_{0.06}$S at the sample surface is very small in both cases. These results indicate that the brominated segments in dPBr$_{0.06}$S exhibit attractive interaction with both SiO$_x$ and SiH surfaces, although the interaction with SiH surface is measurably stronger. The values of z^* for all annealed samples are summarized in Table 2. Note that the results from LE-FRES are in very good agreement with those from DSIMS.

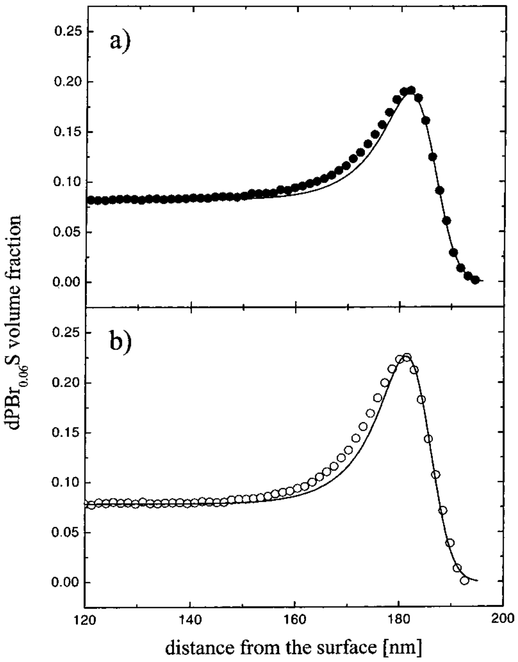

Figure 4. Details of the interface region in DSIMS measured dPBr$_{0.06}$S volume fraction profiles in samples annealed at 190 °C for 3 days on (a) SiO$_x$ substrate (solid circles) and (b) SiH substrate (open circles). The dPBr$_{0.06}$S volume fraction in the as-cast samples is $\phi_\infty = 0.092$. Solid lines in both plots represent the dPBr$_{0.06}$S volume fraction calculated from SCMF model and convoluted with DSIMS depth resolution fwhm = 8 nm, determined from a standard nonannealed sample.

Table 2. Summary of z^* Values from LE-FRES and DSIMS

sample ID	technique	substrate	z^* [nm]
FB1	LE-FRES	SiO$_x$	1.59
FB3	LE-FRES	SiH	1.93
SB5	DSIMS	SiO$_x$	1.59
SB7	DSIMS	SiH	2.15

Figure 4 shows the detail of the interfacial region in samples from Figure 3. Here the dPBr$_{0.06}$S volume fraction profiles are shown as solid circles in Figure 4a (SiO$_x$ substrate) and as open circles in Figure 4b (SiH substrate). Solid lines in both plots represent the dPBr$_{0.06}$S volume fraction profiles calculated from SCMF model and convoluted with DSIMS depth resolution, fwhm = 8 nm. The DSIMS depth resolution was determined by fitting the dPBr$_{0.06}$S volume fraction in a nonannealed reference sample.

Discussion

The degree of bromination in dPBr$_{0.06}$S was chosen sufficiently low ($x = 0.06$) so that the blend of PS and dPBr$_{0.06}$S is miscible at 190 °C at all concentrations. Therefore, the systems do not undergo phase separation, and any changes in concentration distribution in the film are due to interactions with the surface of the substrate. As illustrated in Figures 1 and 2, LE-FRES and DSIMS showed that $dPBr_{0.06}S$ is attracted to both SiO_x and SiH substrates. To test the effect of deuteration, we performed the same experiment with PS:dPS blends where the deuterated polymer was not brominated. We have observed no enrichment of dPS at polymer/SiO_x and polymer/SiH interfaces. Therefore, we believe that the interfacial segregation of $dPBr_{0.06}S$ is driven purely by the presence of bromine groups in the polymer chain. To determine the strength of such an interaction, we have used the SCMF model to calculate the volume fraction profiles and z^* of $dPBr_{0.06}S$ at polymer/substrate interface. As mentioned before, the SCMF model assumes that the $dPBr_{0.06}S$ copolymer is represented by a homopolymer chain with each segment identical and corresponding to an averaged 6% brominated polystyrene segment. The validity of this assumption was justified in the section above on the SCMF model on the grounds that the interaction between the PBrS segments and the wall is significantly less than kT. In the SCMF approach we systematically varied the interaction energy between $dPBr_{0.06}S$ segment and the substrate, $\epsilon^{\rm sub}_{\rm dPBr0.06S}$, for both SiO_x and SiH until a good agreement was reached between experimental and calculated values of z^*. Figure 4 demonstrates the comparison between experimental DSIMS measured volume fraction profiles of $dPBr_{0.06}S$ and those calculated by SCMF. The SCMF profiles were convoluted with DSIMS depth resolution, fwhm = 8 nm. As both parts a and b of Figure 4 show, the experimental and calculated profiles are in a very good agreement. The SCMF profiles, however, slightly underestimate the $dPBr_{0.06}S$ volume fraction further away from the interface. The cause of this small discrepancy is not yet known.

Simmons and Chakraborty[29] have published Monte Carlo simulations of surfaces segregation in a system similar to ours—a random copolymer mixed in a homopolymer. The homopolymer consisted only of A units while the copolymer contained both A and B units. The A units had a repulsive interaction with the surface while the interaction of the B units was attractive. The interaction between the A and the B units was assumed to be repulsive. Most of their work was done assuming much stronger interactions than exist in our system, but one calculation assumed interactions of a similar magnitude to those in the PS, PBrS/silicon system. Qualitatively, their results of both volume fraction of copolymer at the surface and shape of the volume fraction profile (scaled by R_g) were similar to ours. Quantitative comparison would only be possible if the molecular weights and interactions were matched.

The values of $\epsilon^{\rm sub}_{\rm dPBr0.06S}$ were determined for LE-FRES and DSIMS results independently. We are, however, interested in interaction energies of fully brominated segments, $dPBr_1S$, $\epsilon^{\rm sub}_{\rm dPBr1S}$, that are randomly distributed along the chain. Therefore, the values of $\epsilon^{\rm sub}_{\rm dPBr0.06S}$ obtained from the SCMF calculations can be rescaled so that only $dPBr_1S$ segments are responsible for the adsorption behavior of the $dPBr_{0.06}S$ chain. The values of both $\epsilon^{\rm sub}_{\rm dPBr0.06S}$ and $\epsilon^{\rm sub}_{\rm dPBr1S}$ are summarized in Table 3. The negative sign indicates attractive interactions. Table 3 shows that the absolute value of interaction energy between the $dPBr_1S$ segment and the substrate is much lower than thermal energy, about $1kT$. The adsorbed $dPBr_1S$ segments have a high mobility on the substrate surface thanks to their thermal movement and therefore do not act as localized permanent anchoring points on the substrate. This fact also justifies the assumption of the averaged segment we made in the SCMF calculation. Had the interaction energy been higher than $1kT$, the adsorbed brominated segments would have acted at permanent anchors, and the SCMF calculations would have to be changed to account for these localized graft points.

Table 3. Segment/Substrate Interaction Energies Calculated from SCMF Model

sample ID	substrate	$\epsilon^{\rm sub}_{\rm dPBr0.06S}$ [kT]	$\epsilon^{\rm sub}_{\rm dPBr1S}$ [kT]
FB1	SiO_x	−0.011	−0.184
FB3	SiH	−0.013	−0.216
SB5	SiO_x	−0.011	−0.184
SB7	SiH	−0.014	−0.232

The values for interaction energies in Table 3 demonstrate that the $dPBr_1S$ segment is attracted to both SiO_x and SiH substrates and that the interaction with the SiH substrate is stronger by more than 20%. These results are in qualitative agreements with findings of Krausch et al.[12] and Affrossman et al.[13] where the researchers reported strong attraction of brominated polystyrene to the SiH substrate. On the other hand, the interaction between PBr_xS and the SiO_x surface was reported to be neutral.[10−13,18,19] Only Oslanec et al.[20] have reported and quantified the attractive interaction of brominated polystyrene with SiO_x substrate. The interaction energy between $PBr_{0.136}S$ and SiO_x substrate was found to be about $-0.07kT/PBr_1S$, about $^1/_2$ of the value we report in this paper. The discrepancies may be caused by differences in preparation of the silicon oxide film. While many authors used the silicon wafer as received with native oxide layer already on the wafers, we have prepared fresh oxide layers by UV irradiation of HF-etched substrates. This procedure may have resulted in higher concentration of Si−OH groups on the surface and thus increased attraction to brominated polymer segments. For the interaction of PBr_1S and $dPBr_1S$ with SiO_x, we suspect that highly polar and electron-rich −Br groups in the polymer chain will favorably interact with Si−OH groups present on the SiO_x surface by forming hydrogen bonds and via induced dipole−dipole interactions. Such an interaction would explain that the SiH surface attracts the bromine functional group more, simply by providing more hydrogen groups for bromine to interact with. Because it strongly depends on concentration of hydrogen groups on the surface, it is difficult to rigorously quantify strength of $dPBr_1S$/substrate interaction for SiO_x and SiH substrates.

Conclusion

In this paper we have investigated the strength of interaction of bromine functionalized segments of $dPBr_{0.06}S$ with silicon oxide, SiO_x, and hydrogen-terminated silicon, SiH, surfaces. Contrary to previous observations, we found that the bromine groups do interact favorably with both surface types. We also used the SCMF to calculate the $dPBr_{0.06}S$ concentration profile and z^* at the polymer/substrate interface and to determine the strength of $dPBr_1S$−substrate interaction. The comparison of experimental and SCMF results showed that the interaction energy between the $dPBr_1S$ segment and both substrate types is $\epsilon^{\rm SiOx}_{\rm dPBr1S} = -0.184kT$

and $\epsilon^{\mathrm{SiH}}_{\mathrm{dPBr1S}} = -0.224kT$, respectively. The interaction of $\mathrm{dPBr_1S}$ with an SiH surface is ca. 20% stronger than that with the SiO_x surface. We attribute this difference to the difference in surface density of hydrogen functional groups on the substrate surfaces.

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