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Topography and Surface Composition of Thin Films of Blends of Polystyrene with Brominated Polystyrenes: Effects of Varying the Degree of Bromination and Annealing

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ABSTRACT: A series of thin films of blends of poly(styrene-d_8) and poly(styrene-*co*-*p*-bromo$_x$-styrene), where $1 \geq x \geq 0$, cast on to silicon wafers are examined by atomic force microscopy, X-ray photoelectron spectroscopy, and static secondary ion mass spectrometry. Films deposited on wafers stripped of the native oxide are smooth. The poly(styrene-d_8) component segregates to the polymer−air interface, and the extent of segregation increases with the degree of bromination. An inverse linear correlation is obtained between the extent of segregation and the polymer compatibility, the latter measured by the interfacial width of bilayer films. For films deposited on wafers retaining the oxide, topographical features are observed with dimensions depending on the blend composition and degree of bromination of the polymer. The bromopolymer forms islands that are raised. The most pronounced topography is found with blends containing the fully brominated styrene. Reducing the degree of bromination increases the polymer compatibility thereby suppressing the formation of topographical features. Changes in topography and surface composition are observed when the films are annealed, leading to dewetting of the substrate.

Introduction

The chemical composition profiles of thin films of polymer blends are influenced by segregation effects at both the air−polymer and polymer−substrate interfaces and the effect of the latter interface can be altered by changing the chemical nature of the substrate surface. Recently it has been shown that physical effects, i.e., topography that is not the result of dewetting, may also be observed at the polymer−air interface for very thin films of blends on certain substrates. A blend of poly(styrene-d_8), PdS, and poly(*p*-bromo$_{1.0}$-styrene) on silicon wafers, retaining the native oxide, exhibited a range of features depending on the blend composition.[1] Similar features were reported for thin films of a blend of polystyrene and poly(methyl methacrylate).[2] Subsequently, a detailed study of the polystyrene and poly(methyl methacrylate) system has been made by Walheim et al.,[3] with emphasis on the relationship between the polymer components and the solvent.

In both the above blend systems the polymer components were incompatible. A previous study of interfacial mixing between layers of PdS and poly(styrene-*co*-*p*-bromo$_x$-styrene), PBr$_x$S, showed that the compatibility of the polymers varied with the degree of bromination.[4] The PdS−PBr$_x$S blend system thus presents a means of varying the compatibility of the polymer components in a controlled and monotonic manner. The present investigation explores the relationship between the compatibility of the components and the formation of topographical features in thin cast films of the polymer mixtures. The topography and surface composition of a series of PdS−PBr$_x$S blends with various degrees of bromination, $1 \geq x \geq 0$, and blend composition are examined before and after annealing by atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS), and static secondary ion mass spectrometry (SIMS).

Table 1. Parameters of Polymer Materials

polymer	M_n of PdS or PhS precursors	M_w/M_n	70% (w/w) P(Br$_X$S) blends, bulk fraction P(Br$_X$S)
PdS	157k	1.09	
P(Br$_{0.076}$S)	134k	1.03	0.70
P(Br$_{0.18}$S)	134k	1.03	0.69
P(Br$_{0.33}$S)	138k	1.03	0.67
P(Br$_{0.58}$S)	158k	1.09	0.64
P(Br$_{1.0}$S)	145k	1.04	0.59

Experimental Section

Materials. The poly(bromostyrenes) of different degrees of bromination were obtained by a bromination reaction of the anionically prepared polystyrene; thus all the brominated polymers have the same degree of polymerization. The degree of bromination was obtained from chemical analysis. The initial polystyrene molecular weight and the polydispersities of the polymers are indicated in Table 1, where P(Br$_x$S) designates a statistical copolymer of styrene and *p*-bromostyrene, with *x* denoting the degree of bromination (mol %). A deuterated polystyrene (poly-d_8-styrene, PdS) of the same degree of polymerization was also produced by anionic initiation. The number average molecular weights were obtained by gel permeation chromatography (GPC).

Film Formation and Analysis. The details of film formation, AFM operation, and the conditions for XPS and SIMS analysis are given in the previous publication.[1] Films were formed by dropwise addition of a 1% (w/w) toluene solution of the blend to the substrate spinning at 4000 rpm. The surface compositions of the blends were obtained from the XPS data by comparing the ratio of the Br 3d to C 1s signals for the blend to the ratio for pure brominated polymer, P(Br$_x$S).

The intensities of the SIMS fragments $C_7H_6Br^+$ and $C_7D_7^+$ are related to the surface composition by, fraction P(Br$_x$S) = $[(C_7H_6Br^+)/y]/[(C_7H_6Br^+)/y + C_7D_7^+]$ where $y = 0.39x$. The factor 0.39 compensates for the SIMS fragmentation mecha-

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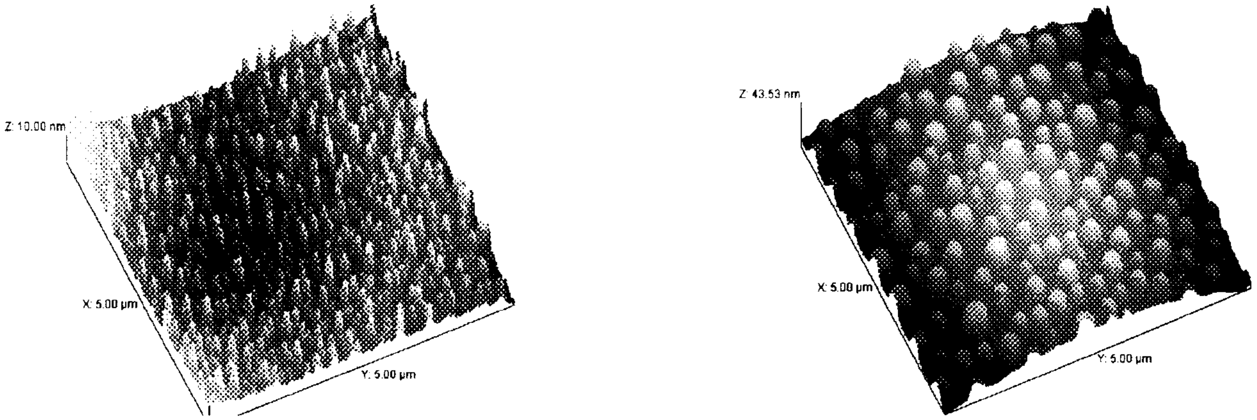
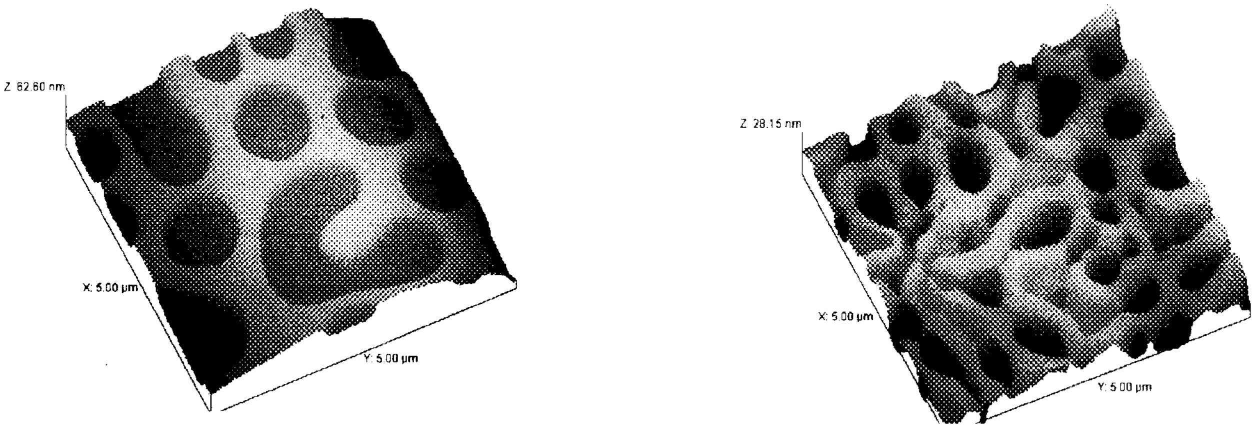
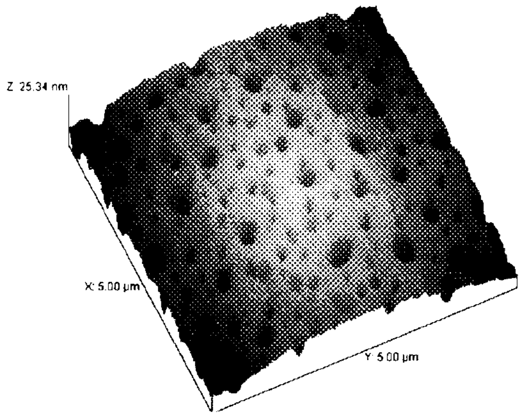


(a) 10%w/w P($Br_{0.58}$ S). **(b)** 30%w/w P($Br_{0.58}$ S).



(c) 60%w/w P($Br_{0.58}$ S). **(d)** 70%w/w P($Br_{0.58}$ S).



(e) 90%w/w P($Br_{0.58}$ S).

Figure 1. Topography of blends of PdS−P($Br_{0.58}$S) on SiO.

nism of the bromopolymers,[1] and the factor x corrects the signal in proportion to the extent of bromination of P(Br_xS).

Film thickness was determined with a Sloan Dektak 11a profilometer.

The use of deuterated polystyrene as a blend component allows it to be distinguished from the hydrogenous styrene comonomer of poly(styrene-*co*-*p*-bromo$_x$-styrene), where $x < 1$, when the film is examined by static SIMS.

Calculation of Blend Composition. AFM images are labeled with the blend composition in percent (w/w). However, XPS data are in terms of the elemental concentrations, which are then converted to monomer concentrations, whereas SIMS data are directly related to monomer concentrations. To allow a direct comparison of the data, the monomer fraction, (Br_XS)/[(Br_XS) + (PdS)], was calculated. Because the degrees of polymerization of the styrene precursors are similar, the monomer fraction is equivalent to the fraction P(Br_XS) polymer.

A specimen calculation is shown for blend composition 50:50% (w/w) PdS:P($Br_{1.0}$S). The molecular weight of PdS monomer (C_8D_8) is 112 and of P($Br_{1.0}$S) monomer (C_8H_7Br) is 183. The monomer ratio of 50:50% (w/w) PdS/P($Br_{1.0}$S) is therefore 0.45:0.27, and thence the P($Br_{1.0}$S) monomer fraction is 0.38.

Since P(Br_XS) is a statistical copolymer of (styrene-h_8) and (Br_XS), when $x \neq 1.0$, a notional monomer molecular weight was calculated for P(Br_XS), e.g., for P($Br_{0.58}$S) notional monomer MW =

$$(MW_{C_8H_7Br} \times 0.58) + (MW_{C_8H_8} \times 0.42) = 149.82$$

which was used in the conversion of % (w/w) to % polymer.

The blend compositions for 70% (w/w) P(Br$_X$S) blends are given in Table 1 in terms of P(Br$_X$S) fraction.

Results

Blends of Poly(styrene-*d*$_8$) and Poly(styrene-*co*-*p*-bromo$_{0.58}$-styrene). AFM. The topography of blends with composition 10−90% (w/w) P(Br$_{0.58}$S) is shown in Figure 1. The features follow the same pattern observed previously[1] with blends of PdS and P(Br$_{1.0}$S); i.e., islands of the bromopolymer are observed at low P(Br$_{0.58}$S) contents and the area of the islands increases as the P(Br$_{0.58}$S) content increases. Eventually, the islands coalesce to form a sheetlike structure with holes. The average dimensions of the topographical features are given in Table 2. In the PdS−P(Br$_{1.0}$S) system[1] the height/depth remained approximately constant, at 13 ± 2 nm, as the blend composition varied. The variation in height/depth for the PdS−P(Br$_{0.58}$S) system is greater, with a value of ca. 16 ± 2 nm in the middle range of composition which decreases at the extremities of the range. However, the film thicknesses of the PdS−P(Br$_{0.58}$S) blends also varied more than those for the previous series of PdS−P(Br$_{1.0}$S) blends, and the feature dimensions were found to vary with film thickness. The lateral dimensions of the features are similar to those found for the P(Br$_{1.0}$S) system.

XPS/SIMS. The surface P(Br$_{0.58}$S) concentrations obtained from the XPS and SIMS data for the series of blends are shown in Figure 2. The XPS P(Br$_{0.58}$S) concentration values are apparently slightly lower at the surface than in the bulk, whereas the P(Br$_{0.58}$S) surface concentrations determined by SIMS agree more closely with the bulk values. Generally, the XPS/SIMS data for a given sample are reproducible to ±5%, indicated by the error bars, but when polymers are mixed, the distribution of impurities and chain lengths may be different from the pure materials. It is difficult to quantify such effects, except that SIMS will be very sensitive to changes in surface concentration because the depths probed by SIMS and XPS are ca. 1 and 5 nm, respectively.

Blends of Poly(styrene-*d*$_8$) and Poly(styrene-*co*-*p*-bromo$_{0.33}$-styrene). AFM. The topographical data for a series of blends of PdS and P(Br$_{0.33}$S) are shown in Figure 3. It is immediately apparent that the features are much diminished compared to the more highly brominated polymer blends. The progression from island to hole structures as the brominated polymer fraction increases is still observed but the average height/depth of the features is now only 3 ± 1 nm.

XPS/SIMS. The XPS data for the range of P(Br$_{0.33}$S) blend compositions, given in Figure 4, show that the composition in the near surface region is dominated by the PdS component. The SIMS data, Figure 4, confirm the large deficiency of P(Br$_{0.33}$S) at the surface and, below 0.8 fraction P(Br$_{0.33}$S), are in good agreement with the XPS results.

Blends of Poly(styrene-*d*$_8$) and Poly(styrene-*co*-*p*-bromo$_{0.18}$-styrene) or Poly(styrene-*co*-*p*-bromo$_{0.076}$-styrene). AFM. No topographical features were observed across the entire blend composition range for either mixture.

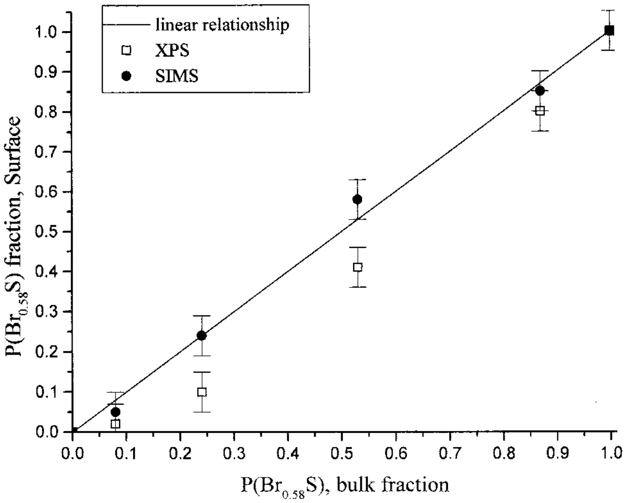


Figure 2. Fraction of P(Br$_{0.58}$S) at the surface compared to the bulk from XPS and SIMS for blends on SiO. The raised features correspond to the bromo-polymer.

Table 2. Variation of the Polymer Film Features with Composition for PdS-P(Br$_{0.58}$S) Blends

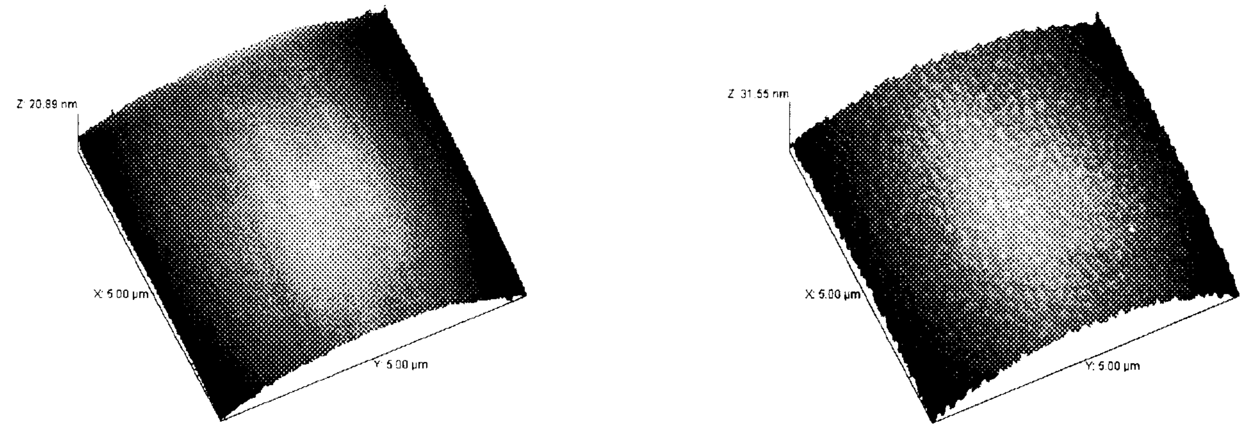
figure	composition of P(Br$_{0.58}$S) in blend (% (w/w))	film thickness (nm)	features	typical height/depth (nm)	typical diameter (nm)
1a	10	51 ± 5	islands	9 ± 2	221 ± 28
1b	30	45 ± 5	islands	18 ± 1	426 ± 39
1c	60	49 ± 5	holes	17 ± 1	1047 ± 235
1d	70	41 ± 3	holes	15 ± 2	678 ± 205
1e	90	38 ± 4	holes	12 ± 1	421 ± 35

Annealed Films. Blend of Poly(styrene-*d*$_8$) and Poly(*p*-Br$_{1.0}$-styrene). The T_g values of PdS and P(Br$_{1.0}$S) are 103 and 142 °C, respectively.[5] The samples were annealed at 150 °C, above the T_g for both components, for various times.

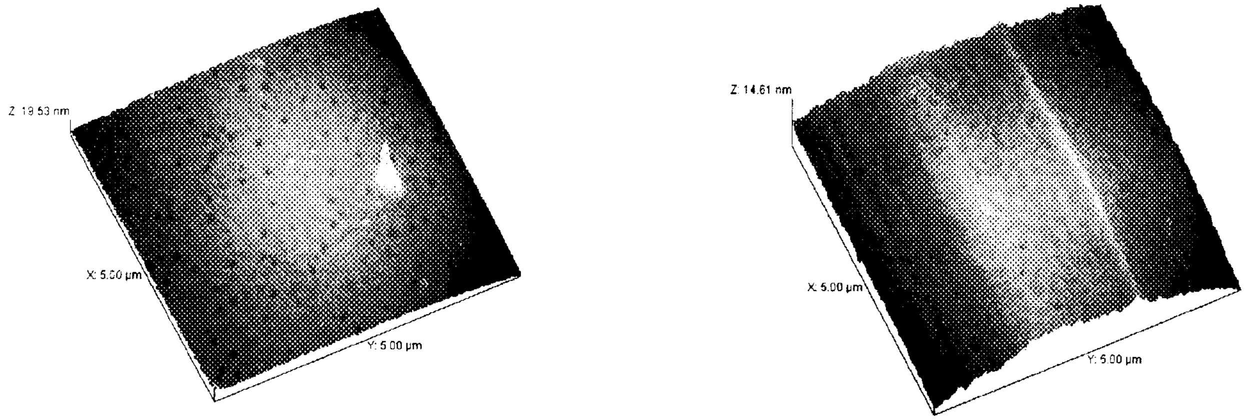
AFM. The initial "sharp" features of the 10% (w/w) P(Br$_{1.0}$S) blend are much reduced after annealing for 2 h, Figure 5a, and totally eliminated after 20 h leaving a smooth surface. On the other hand, the features observed with blends containing >10% (w/w) P(Br$_{1.0}$S) are more persistent. The topography and AFM profiles of a 30 and a 90% (w/w) P(Br$_{1.0}$S) blend after annealing for 1 h are shown in Figures 5b,d and 6a,b, respectively. Annealing causes a migration of material with the result that the "valleys" become deeper, the plateau type features adopt a more rounded profile, and the height of the features increases. Eventually the height of the features exceeds the film thickness, measured with the profilometer, indicating that dewetting is occurring. This is most obvious with the high percent (w/w) P(Br$_{1.0}$S) blends, which show flat regions in the AFM profiles at the expected position of the substrate surface.

Samples were examined over 20 h of annealing at 150 °C, though most of the change occurred within the first hour. Table 3 gives the feature dimensions and the film thickness before and after annealing. The thickness is unchanged by heating at 150 °C for 20 h, within the experimental error of ±10%. The apparent discrepancy between the mean film thickness measured with the surface profilometer and the AFM feature height for the roughened surfaces is assumed to be caused by instrumental differences in the probe tip area and the data evaluation algorithms.

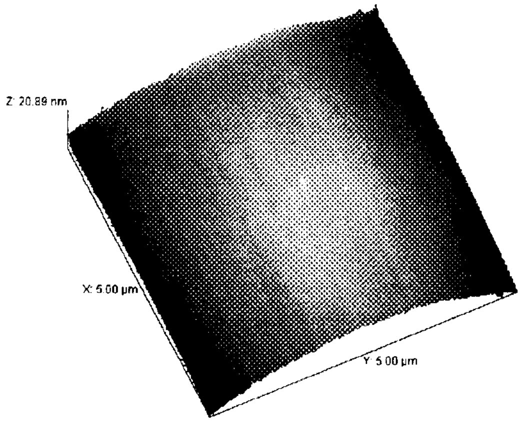
Extended Annealing. Increasing the temperature of annealing of the 30 and 90% (w/w) blends to 160 and



3(a) 10%w/w $P(Br_{0.33}S)$. 3(b) 30%w/w $P(Br_{0.33}S)$.



3(c) 60%w/w $P(Br_{0.33}S)$. 3(d) 70%w/w $P(Br_{0.33}S)$.



3(e) 90%w/w $P(Br_{0.33}S)$.

Figure 3. Topography of blends of PdS–$P(Br_{0.33}S)$ on SiO.

then 170 °C for an extended time gives little further change with a 30% (w/w) $P(Br_{1.0}S)$ blend but causes an agglomeration of features to produce an increased roughness with a 90% (w/w) blend, Figures 5c,e and 6a,b.

XPS/SIMS of Annealed $P(Br_{1.0}S)$ Blends. The surface compositions from XPS and SIMS of the blends after annealing are shown in Figures 7, and 8, respectively. First considering the XPS data, annealing allows the PdS to migrate to the surface region. Increasing the temperature beyond 150 °C does not alter the excess concentration of PdS, which dominates the surface below 0.7 bulk fraction, though at the higher bulk fraction, 0.85 ≡ 90% (w/w), the surface region has ca. equal concentrations of the blend components. In contrast, the SIMS data show that the topmost layer is almost entirely PdS at all blend compositions.

For the 90% (w/w) blend after annealing, when a flat section was observed by AFM at the substrate film interface the corresponding XPS spectrum contained a signal from the silicon substrate, confirming that dewetting of, or very close to, the substrate surface was occurring. When flat sections were observed at the substrate film interface of lower percent (w/w) poly(*p*-

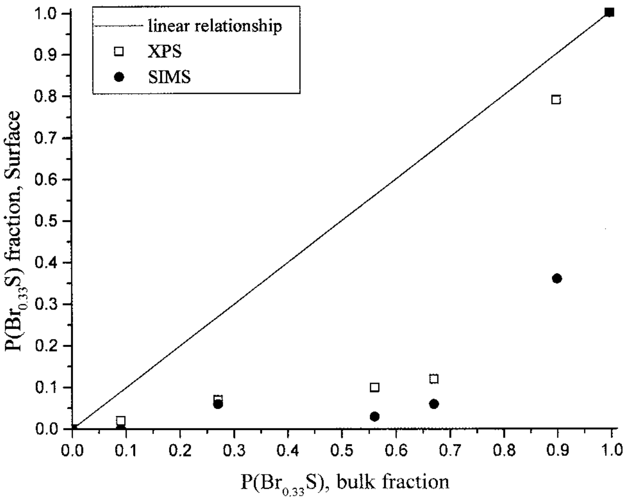


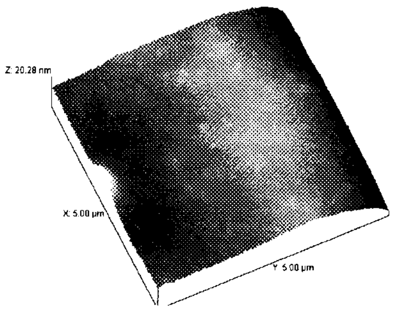
Figure 4. Fraction of P(Br$_{0.33}$S) at the surface compared to the bulk from XPS and SIMS for blends on SiO.

Table 3. Variation of the Polymer Film Features for PdS–P(Br$_{0.58}$S) Blends after Annealing for 20 h at 150 °C

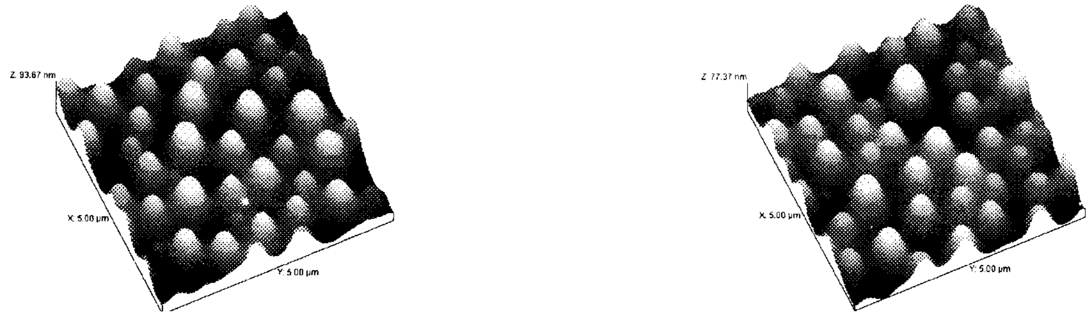
composition of P(Br$_{0.58}$S) in blend (% (w/w))	unannealed film thickness (nm)	typical height/depth (nm)	annealed film thickness (nm)	typical height/depth (nm)
10	51 ± 5	9 ± 2	42 ± 6	6 ± 2
30	45 ± 5	18 ± 1	37 ± 3	29 ± 6
60	49 ± 5	17 ± 1	48 ± 6	65 ± 14
70	41 ± 3	15 ± 2	49 ± 7	70 ± 20
90	38 ± 4	12 ± 1	39 ± 3	70 ± 7

Br$_x$-styrene) blends, no silicon was detected.

Effect of Substrate Modification. Films of PdS–P(Br$_x$S) were also cast on to silicon wafers with the native oxide removed. No topographical features were observed with AFM at any value of x. However, XPS and SIMS showed that PdS segregated to the surface, and a plot of the difference in the surface and bulk concentrations of PdS versus the degree of bromination for 70% (w/w) P(Br$_x$S) blends, i.e., the deviation from the bulk values, is given in Figure 9. Note that the line indicating maximum saturation of the surface with PdS is not horizontal, but slopes down to the right, which is a consequence of the data for the constant percent (w/w) mixtures being plotted in fraction monomer units and the weight of the notional monomer unit increasing with



(a) 10%w/w PBr$_{1.0}$S Annealed @ 150 C/2hrs.



(b) 30%w/w P(Br$_{1.0}$S) Annealed @ 150 C/1hr.

(c) 30%w/w P(Br$_{1.0}$S) Annealed @ 160 C/216hrs then @ 170 C/288hrs.

(d) 90%w/w P(Br$_{1.0}$S) Annealed @ 150 C/1hr.

(e) 90%w/w P(Br$_{1.0}$S) Annealed @ 160 C/216hrs then @ 170 C/288hrs

Figure 5. (a) Topography of 10% (w/w) P(Br$_{1.0}$S) blend on SiO annealed for 2 h at 150 °C. (b) Topography of 30% (w/w) P(Br$_{1.0}$S) blend on SiO annealed for 1 h at 150 °C. (c) Topography of 30% (w/w) P(Br$_{1.0}$S) blend on SiO annealed for 216 h at 160 °C then 288 h at 170 °C. (d) Topography of 90% (w/w) P(Br$_{1.0}$S) blend on SiO annealed for 1 h at 150 °C. (e) Topography of 90% (w/w) P(Br$_{1.0}$S) blend on SiO annealed for 216 h at 160 °C then 288 h at 170 °C.

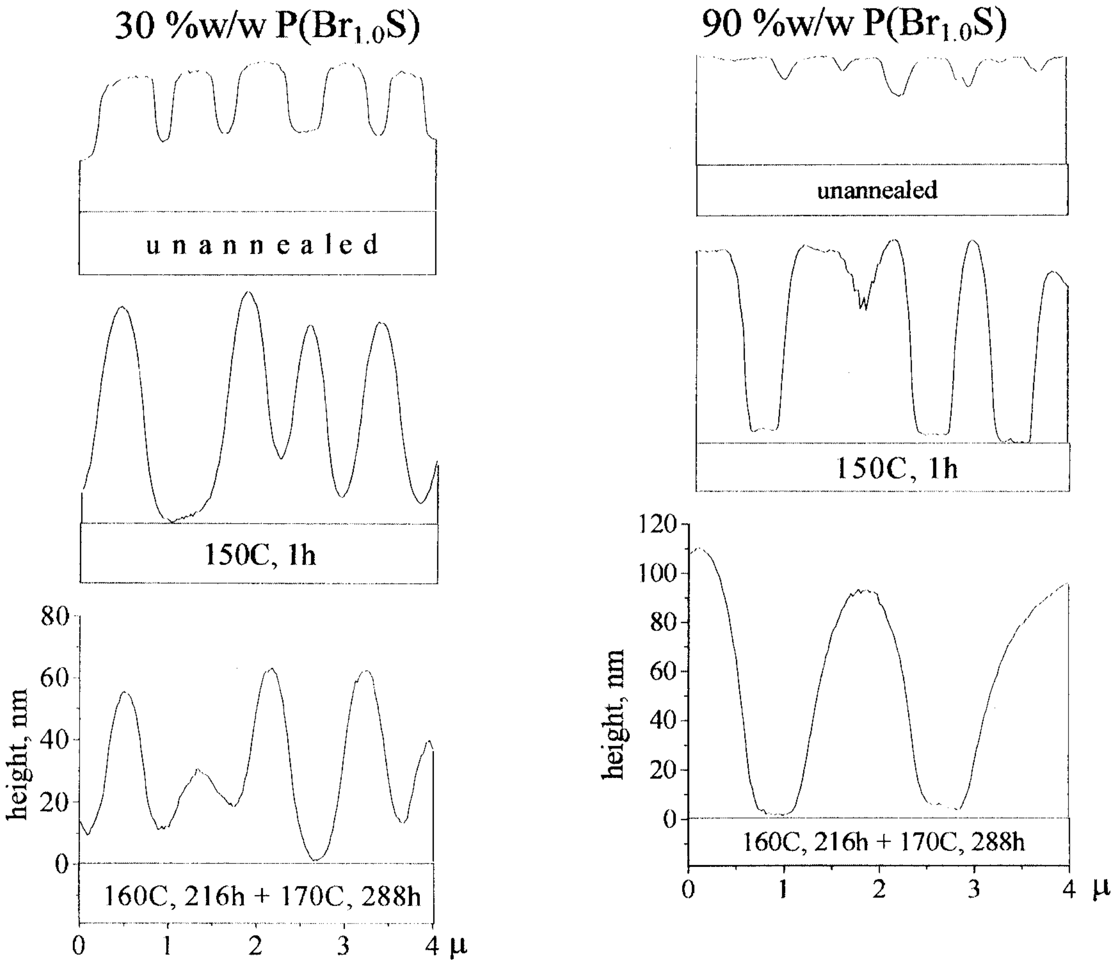


Figure 6. (a) AFM profiles of 30% (w/w) P($Br_{1.0}S$) blend on SiO: unannealed; annealed for 1 h at 150 °C; 216 h at 160 °C; 288 h at 170 °C. (b) AFM profiles of 90% (w/w) P($Br_{1.0}S$) blend on SiO: unannealed; annealed for 1 h at 150 °C; 216 h at 160 °C; 288 h at 170 °C.

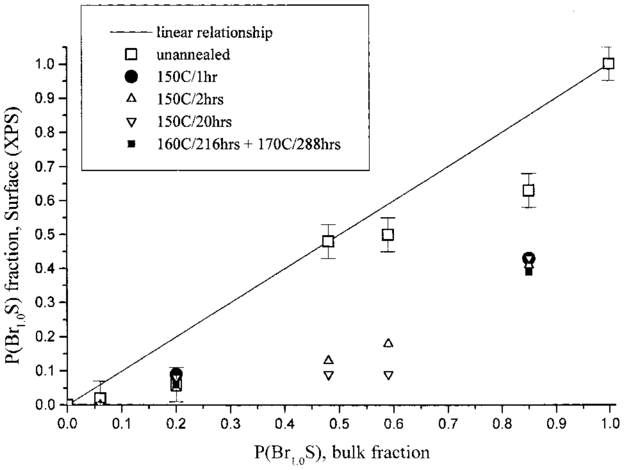


Figure 7. Fraction of P($Br_{1.0}S$) at the surface compared to the bulk from XPS after annealing for blends on SiO.

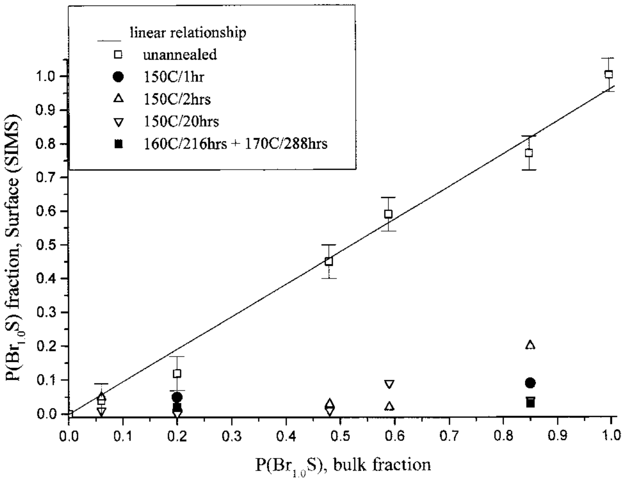


Figure 8. Fraction of P($Br_{1.0}S$) at the surface compared to the bulk from SIMS after annealing for blends on SiO.

degree of bromination.

For all degrees of bromination, annealing the films on silicon with the oxide removed caused the PdS concentration at the surface to increase.

Discussion

Concentration Profiles in Unannealed Films on Silicon Retaining the Oxide. Blends with the highly brominated component P($Br_{0.58}S$) exhibit topography, and examination of the relationship between the surface concentrations and the blend compositions shows that the SIMS data correspond more closely to the bulk values than the corresponding XPS data, Figure 2. The XPS data indicate a small excess of PdS in the near-surface region whereas the SIMS data show that the topmost surface remains the same as the bulk. Similar behavior was observed for the PdS−P($Br_{1.0}S$) blend studied previously,[1] but for blends with the less bromi-

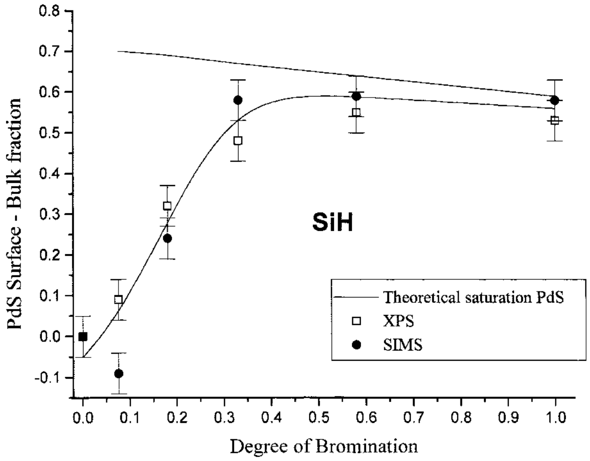


Figure 9. Surface excess of PdS versus degree of bromination for 70% (w/w) PdS−P(Br$_x$S) blends on silicon with the oxide removed.

nated polymers, which have smooth surfaces, the migration of PdS to the surface produces a large segregation, Figure 4. The SIMS results for the blends with highly brominated polymer are contrary to the evident tendency for PdS to cover the surface; i.e., it is the SIMS, rather than the XPS, data that are unexpected. The effect is small, so systematic errors cannot be excluded, but the surface analysis data suggest that when phase separation into distinct blocks takes place, the rapid evaporation of solvent leaves a thin partial layer of frozen solution, or isolated molecules, at the surface.

Annealed Films of P(Br$_{1.0}$S) Blends. The thermodynamically favored surface state is composed mainly of the component with the lower surface energy, PdS. Annealing produces two effects: (a) Diffusion of PdS from the "pure" PdS blocks to the P(Br$_{1.0}$S) blocks causes the features to grow and become rounded. After several hours of annealing the samples with initially marked topography, material has migrated to the extent that dewetting may occur. (b) A PdS-enriched region is formed at the surface producing a discrepancy between SIMS and XPS compositions, Figures 7 and 8. This effect is most marked for high weight percent composition (90% (w/w)) P(Br$_{1.0}$S) blends and is much reduced for weight compositions below 90%, for which the annealed sample surfaces are mainly PdS according to both the SIMS and XPS data. Blends of 90% (w/w) composition consist of sheets of P(Br$_{1.0}$S) with small patches of PdS. Annealing alters the topography by migration of, in this case, a limited amount of PdS. A very thin overlayer of PdS is spread over the P(Br$_{1.0}$S), resulting in a sharp concentration gradient into the bulk and the dewetted areas show a silicon signal with XPS. Blends of lower percent (w/w) P(Br$_{1.0}$S) have correspondingly more PdS, which can form a thicker overlayer on annealing. The XPS and SIMS data then approximately coincide, and enough PdS remains (≥6 nm) on the dewetted areas to mask the XPS silicon signal.

Substrate Effects. Silicon without the Native Oxide. The effect of stripping the native oxide from silicon wafers on the structure of films of polystyrene−poly(*p*-Br-styrene) blends has been investigated by time of flight (TOF) forward recoil spectrometry.[6] The films were thicker, ca. 200 nm, than the ca. 40 nm films used here, but nevertheless the substrate surface influenced the chemical structure of the polymer film. On silicon with the native oxide, both components were distributed throughout the film, whereas for films on silicon without the native oxide, a bilayer structure was obtained, with the poly(*p*-Br-styrene) preferentially at the silicon−polymer interface.

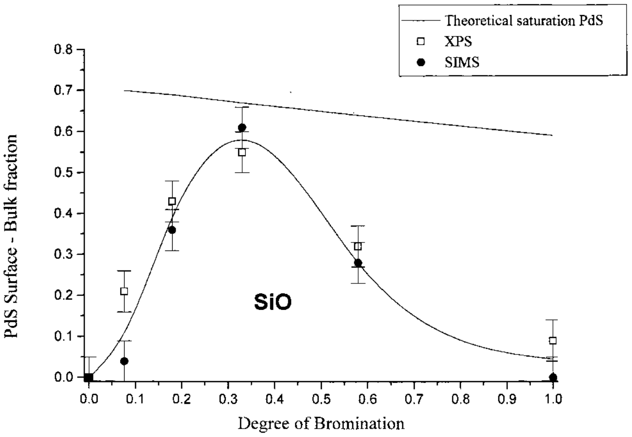


Figure 10. Surface excess of PdS versus degree of bromination for 70% (w/w) PdS−P(Br$_x$S) blends on silicon retaining the oxide.

The data for PdS−P(Br$_x$S) blends with various degrees of bromination on silicon with the native oxide removed, Figure 9, show that when $x > 0.33$ the composition at the polymer−air interface approaches pure PdS, which would be consistent with bilayer formation or strong surface segregation. Marked amounts of P(Br$_x$S) are found in the top layer when $x < 0.33$ and the concentration of P(Br$_x$S) increases as x decreases, until it is similar to the bulk value when $x = 0$. If a bilayer is formed with these very thin films, when $x < 0.33$, and the P(Br$_x$S) is underneath, then the top layer is not pure PdS. The behavior of the system is related, therefore, to the degree of bromination. From neutron scattering experiments with PdS/P(Br$_x$S) bilayers,[4] it has been shown that the compatibility of the blend components, estimated from the thickness of the interface, decreased markedly for $x > 0.33$. Thus, it is reasonable to associate the appearance of P(Br$_x$S) at the air interface with the greater compatibility of the blends at low values of x.

Silicon with the Oxide. Considering the results for the blends on silicon retaining the native oxide, the formation of topographical features in the thin films of the polymer blends depends on the substrate chemistry and the relative properties of the polymers. An increase in the degree of bromination, decrease in polymer compatibility, favors formation of the topography. Therefore, the critical factors that determine the behavior of the system will be the attraction of the polymers to the substrate surface and the degree of compatibility of the blend components. A plot of the difference between surface and bulk concentration of PdS versus the degree of bromination for unannealed 70% (w/w) P(Br$_x$S) blends, on silicon retaining the oxide, is given in Figure 10. At low degrees of bromination the polymers are miscible and no topographical features are apparent, but the lower surface energy component, PdS, segregates to the surface. As the degree of bromination is increased, the excess PdS increases, reaching a maximum near the P(Br$_{0.33}$S) blend, whereupon the topographical features start to become discernible. Further increase in the degree of bromination results in marked topography and reduced excess PdS, in contrast to the blends

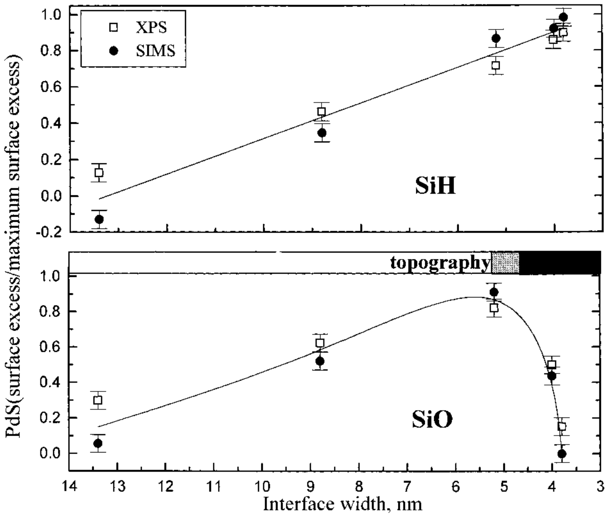


Figure 11. (upper) Surface excess of PdS from XPS versus interfacial width of PdS/P(Br$_x$S) bilayers for 70% (w/w) PdS−P(Br$_x$S) blends on silicon with the oxide removed. (lower) Surface excess of PdS from XPS versus interfacial width of PdS/P(Br$_x$S) bilayers for 70% (w/w) PdS−P(Br$_x$S) blends on silicon retaining the oxide. The extent of topography is indicated by shading.

on silicon with the oxide overlayer removed, where there is no topography at high degrees of bromination and the excess PdS concentration remains a maximum. The topography relates therefore to the compatibility of the polymers.

In the lower bromination region, where the polymers are most miscible, the surface excess of PdS increases as the polymers become more incompatible until the surface is almost completely covered by PdS. At this point the topography develops and thereafter the surface excess of PdS decreases because the phases separate, until almost complete phase separation is achieved with the PdS−P(Br$_{1.0}$S) blend. The measured surface PdS concentration then becomes related to the area of PdS phase exposed.[1]

Relation between Segregation in Blends and Interfacial Width of Bilayers. For 200 nm films of PdS−P(Br$_x$S) blends on silicon with the oxide removed, it has been reported[6] that preferential segregation of P(Br$_x$S) occurs at the substrate interface, which would, therefore, leave a phase enriched in PdS near the air interface. It is not possible to say from the above results whether the unannealed films on silicon without the oxide are separated, wholly or partially, into bilayers, but the top layer is certainly not pure PdS, though it has an excess of PdS compared to the bulk. The extent of segregation has been shown above to relate to the polymer compatibility, and the neutron reflection data[4] for the PdS/P(Br$_x$S) bilayer system give a numerical assessment of the polymer compatibility in terms of the interfacial width. A plot of the extent of surface segregation of PdS, defined as the (surface-bulk)PdS/(maximum possible surface-bulk)PdS, against the interfacial width of the corresponding PdS/PBr$_x$S bilayer is given in Figure 11 for blends of 70% (w/w) PdS−P(Br$_x$S) on a silicon substrate without the oxide. An approximately linear correlation is obtained for the XPS and SIMS data, which shows that the extent of segregation at the featureless polymer−air surface increases inversely proportional to the interfacial width, i.e., proportional to the incompatibility. The deviations of individual points from the line may be ascribed to errors in reproducibility, shown by the error bars, minor differences in purity of the various bromo-polymers, and any concentration gradients near the surface, leading to different SIMS and XPS derived concentrations.

Also as a consequence of the use of a constant percent (w/w) blend, it should be noted that the bulk PdS monomer fraction changes from 0.30 to 0.41 as the degree of bromination increases from 0.076 to 1.00 with a corresponding effect on the (Br$_x$S) monomer weight, but the high segregation of PdS at medium brominations suggests that the effect of increased PdS bulk concentration on the PdS surface segregation will be minimal.

The linear correlation is obtained even though the interfacial width data for the bilayers are equilibrium values obtained after annealing and the extent of segregation of PdS for the unannealed, cast films increases when the films are subsequently heated, confirming that the initially formed films are in a quenched state, i.e., between the frozen solution and equilibrium compositions. Thus, the results lead to the hypothesis that there is a limited ability of chain movement because of solvent removal, but the tendency of the chains to disentangle, or the extent to which they are already entangled in solution, depends on the polymer compatibility. The net result is a movement (segregation) that reflects the equilibrium compatibility. When the films are annealed, further movement can take place, and the thermodynamics of the polymer−air surface becomes the controlling feature, with saturation of the surface by PdS.

A plot of the extent of segregation of PdS against the interfacial width for the blends on silicon with the oxide, Figure 11, shows a similar linear correlation until the interfacial width falls below 5 nm, at which point topography appears and the segregation falls. The linear part of the curve is displaced to slightly higher values of segregation than for the case of silicon without the oxide, opposite to the expected result if P(Br$_{1.0}$S) adsorbs preferentially on silicon with the oxide removed, i.e., the upper layer should consequently be enriched in PdS. The reason for this difference is not known, but the state of the unannealed film will depend on the rate of evaporation of solvent and the effect on that rate of phase separation, which differs in mode for the two substrates.

Conclusion

There is an inverse linear relationship between segregation of PdS to the polymer−air interface of smooth, thin, unannealed films of PdS−P(Br$_x$S) blends on silicon wafers with the oxide removed and the equilibrium interface width of PdS/P(Br$_x$S) bilayers, which is the result of increasing incompatibility of the blend components as the degree of bromination, x, increases.

On silicon retaining the oxide, the films are also smooth and have a similar increase in segregation of PdS as the degree of bromination increases, until $x = 0.33$. Thereafter, the films develop an island type topography, with the lateral dimensions of the islands increasing with the fraction of P(Br$_x$S) in the blend.

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