Surface Segregation in Blends of Hydrogenous Polystyrene and Perfluorohexane End-Capped Deuterated Polystyrene, Studied by SSIMS and XPS

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ABSTRACT: End capping a polystyrene with perfluorooctyldimethylchlorosilane is shown to strongly influence the surface segregation in blends of deuterated and hydrogenous polystyrenes. The surface composition, determined by static secondary ion mass spectroscopy, of a low molecular weight blend containing 0.14 mole fraction deuterated polystyrene, end capped by proton donation from methanol, was only slightly increased compared to the bulk value, even after annealing for several days at 150 °C. A low molecular weight blend containing the fluoro-end-capped deuteropolymer showed immediate surface segregation, which increased to give ca. 60% deuterated polymer at the surface after annealing. A similar blend, but with the fluoro end cap on the hydrogenous polymer, exhibited a surface enrichment of 41% of the hydrogenous component. Annealing a high molecular weight blend of hydrogenous and deuterated polystyrenes at 155 °C resulted in the gradual segregation of the deuterated component to the surface. A blend of high molecular weight fluoro-end-capped deuterostyrene and hydrogenous styrene showed an increased rate of segregation under the same conditions.

Introduction

The equilibrium thermodynamics of surface segregation in polymer blends has been set out by Schmidt and Binder[1] and elaborated by Carmesin and Noolandi.[2] Jones and Kramer[3] have demonstrated the influence of the various parameters on the near surface depth profile and the surface volume fraction. It is the difference in surface tensions between the components of a polymer mixture which determines the surface volume fraction, whereas the shape of the concentration profile, normal to the surface, is determined by the thermodynamics of the polymer mixture. Some time ago Bates[4] demonstrated that mixtures of high molecular weight hydrogenous and deuterated polystyrene had unfavorable thermodynamics and a positive Flory–Huggins interaction parameter, χ. This effect arises from the differences in zero point energy of H and D atoms leading to C–D bonds being slightly more polar than C–H bonds. Additionally, this difference in polarity influences the surface tensions such that the deuteropolymer has a slightly lower surface tension. Consequently, mixtures of hydrogenous and deuterated polystyrene of high molecular weight approximate to the situation discussed by Schmidt and Binder. Annealed thin films of such mixtures have been investigated by using ion beam analysis[5] and neutron reflectometry,[6] and the results are in broad agreement with the theoretical predictions. However, the balance between the surface free energy and bulk free energy of polymer mixtures is extremely delicate. Placing a $-(CH_2CH{=}CHCH_2)_{3-5}Si(CH_3)_3$ group at one end of the deuteropolystyrene, referred to above, altered this balance so much that the deuteropolymer was now adsorbed at the polymer–silicon substrate interface.[7]

We report here the results of the deliberate capping of one end of the deuteropolystyrene with a fluorinated group in an effort to increase the adsorption of the polymer at the air–polymer interface.

Experimental Section

Polymers. Polymers were prepared by anionic polymerization of the monomers under high-vacuum conditions. Benzene was the polymerization solvent in all cases, and the initiator was *sec*-butyllithium. Portions of the hydrogenous polystyrene (H-PS) and deuteropolystyrene (D-PS) were terminated by addition of degassed methanol. Further portions were terminated by perfluorooctyldimethylchlorosilane, giving (H-PS-F) and (D-PS-F), e.g., $CH_3CH_2CH(CH_3)[CD_2CD(C_6D_6)]_nSi(CH_3)_2(CH_2)_2(CF_2)_5CF_3$.

Table 1 gives the number-average molecular weight of the polymers prepared and their polydispersity indices (M_w/M_n).

Blends were prepared by dissolving H-PS and D-PS-(F) of *similar* molecular weight in toluene, and films were cast from solution onto silicon wafers cleaned with a sulfuric–peroxide mixture, i.e., retaining the native oxide. The bulk compositions were ca. 15% w/w D-PS. The film thickness was ca. 200 nm. Samples were annealed in a vacuum or under an argon flow.

Surface Analytical Methods. The surface compositions of the blends were obtained by X-ray photoelectron spectroscopy (XPS) and by static secondary ion mass spectroscopy (SSIMS). The former provides quantitative information on the perfluoro end-group concentrations at the surface and the latter quantitative data on the D-PS and H-PS surface concentrations.[8]

For SSIMS, samples were irradiated with a Vacuum Science Workshop ion gun, using a 3-keV argon ion beam, with a current of 2×10^{-10} A measured at the gun exit, over an area of ca. 5 mm^2. Spectra were obtained with a Vacuum Generators 12–12 quadrupole. Sample charging was compensated by an electron flood gun at 30 eV.

XPS data were obtained with a Vacuum Science Workshop X-ray anode, using aluminum Kα radiation and a 100-mm hemispherical analyzer.

Results

Low Molecular Weight Blend. SSIMS. The SSIMS spectrum of an unannealed blend of H-PS1 and D-PS1 is shown in Figure 1a. The tropylium ion intensities, $C_7H_7^+$ at 91 and $C_7D_7^+$ at 98, are in theory proportional to the concentrations of H-PS1 and D-PS1, respectively, in the film, after allowance for intrinsic and impurity contribu-

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Table 1

polymer	M_n	M_w/M_n
H-PS1	44 700	1.05
H-PS1-F	50 500	1.04
D-PS1	30 000	1.06
D-PS-F1	30 700	1.06
H-PS2	1 710 000	1.18
D-PS2	816 000	1.69
D-PS-F2	658 000	1.10

tions. The SSIMS spectrum of pure H-PS1 showed no signal at 98, but the pure D-PS1 spectrum showed a contribution at 91 of 0.04 of the $C_7D_7^+$ signal. We have also found previously that all pure deuterostyrenes examined had a significant contribution at 97, which we assigned to a $C_7D_6H^+$ species and which varied in relative intensity from sample to sample.[8] The true measure of the deuterostyrene concentration is thus the sum of the heavy fragment contributions, $C_7D_7^+$ and $C_7D_6H^+$. The 98 and 97 signals originate from the deuterated polymer only, so the ratio of these signals in a blend of a given deuterostyrene with H-PS should remain constant, which was verified experimentally. In this work the 98 signal was adjusted by the fraction of the 97 signal, as found for each pure deuterostyrene. The mole fraction of D-PS1 obtained for the above blend by SSIMS, $I_{98}/(I_{91} + I_{98})$ using the corrected intensities, is 0.165 ± 0.008, compared to the bulk value of 0.140. Since the probe depth of SSIMS is only 0.5–1 nm, the composition of the topmost surface of the unannealed samples shows a slight enhancement of the deuterated component.

Figure 1b shows the SSIMS spectrum of an unannealed blend of H-PS1 and D-PS-F1. The SSIMS mole fraction of D-PS-F1 is 0.363 compared to the bulk value of 0.140. It is evident that the deuterated polymer has preferentially segregated to the surface because of the influence of the perfluoro end cap.

All the polymers are above the critical entanglement molecular weight for polystyrene; hence, annealing may be necessary to achieve equilibrium between bulk and surface free energies. The blends were annealed at 130 or 150 °C for several days. The variation in the mole fraction of D-PS1 in the D-PS1/H-PS1 blend with annealing time is shown in Figure 2a. There is little further segregation even after several days.

In contrast, the D-PS-F1/H-PS1 blend shows a large increase in segregation of the deuterated component on annealing (Figure 2b). The mole fraction of D-PS-F1 reaches a plateau value of ca. 0.62 ± 0.03 after 1 day at 130 °C.

In polymer D-PS-F1, the deuterium and fluorine both act to produce surface segregation. By analyzing a mixture of deuterated polymer and fluoro-end-capped hydrogenous styrene, the relative contributions of the deuterium and fluorine components can be examined. The data for a blend of D-PS1 and H-PS-F1 are shown in Figure 2b. The unannealed sample shows a marked surface segregation of H-PS-F1, which increases slightly to a plateau value of 41% after annealing at 130 °C.

Low Molecular Weight Blend. XPS. The multiple fluorine atoms in the perfluoro end cap facilitate detection of the end groups at the surface using XPS, but the overall fluorine content is small so there will be large errors in the measurement of F:C ratios. The pure D-PS-F1 has a bulk ratio of F:C atoms of 6×10^{-3}, calculated from the molecular weight. The XPS F 1s to C 1s intensities give the ratio of atoms at the surface, and the measured value for D-PS-F1 was $10.9 \pm 1.5 \times 10^{-3}$. XPS probes ca. 4 nm into the bulk. Though the radius of gyration of the polymer is of this order,[9] an XPS signal falls off exponentially with depth; thus, groups in the topmost surface layer of atoms will contribute proportionally more to the signal than those at greater depth. Therefore, the ratio of measured to calculated F:C values of 1.8:1 may be the consequence of segregation of the fluorinated end group to the polymer–air interface.

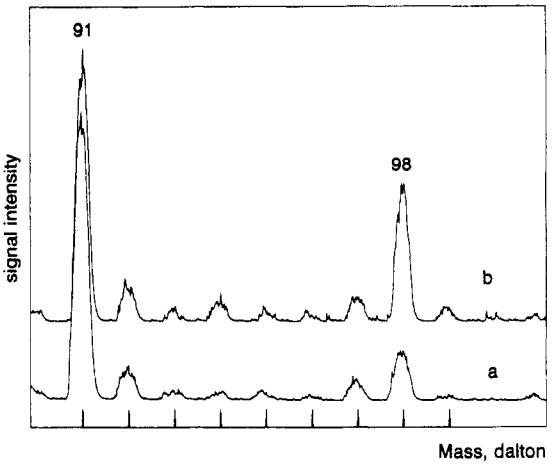

Figure 1. SSIMS spectra: (a) H-PS1/D-PS1 blend; (b) H-PS1/D-PS-F1 blend.

The bulk calculated F:C ratio for the above blend of D-PS-F1 and H-PS1 is 0.9×10^{-3}. The measured values for the unannealed films vary from 1.1 to 2.2×10^{-3}. Annealing produces an increase in the XPS F:C ratio, similar to that observed with the SSIMS $C_7D_7^+$ signal (Figure 2c). The very small F 1s signal from the chain ends in the blend leads to greater errors in calculating the mole fractions than with SSIMS, where the main polymer chain contributes to the intensity. The F:C ratio given by the "plateau" in Figure 2c is ca. 4.5×10^{-3}. The fraction D-PS-F1 at the surface of the annealed films is then

$$4.5 \times 10^{-3}/10.9 \times 10^{-3} = 0.4 \pm 0.15$$

which is less than the SSIMS value, though not significantly in view of the errors in the XPS measurements. The difference in probe depth of the two techniques may also lead to a slightly lower value for the XPS data, because XPS will detect subsurface fluorine.

High Molecular Weight Blends. SSIMS. The fluorine content of the high molecular weight material was too low to be quantified by XPS, so the high molecular weight mixtures were examined only by SSIMS. The SSIMS data for a blend of high molecular weight D-PS2 and H-PS2 gave a value for the mole fraction of deuterostyrene of 0.115, compared to the bulk value of 0.145, i.e., a small decrease in the deuterated component at the surface. A blend of the fluoro-end-capped deuterostyrene, D-PS-F2, and H-PS2 of the same bulk composition gave a surface mole fraction of the deuterostyrene of 0.124. When either of these blends was annealed at 130 °C for up to 7 days, there was no appreciable preferential segregation, in contrast to the behavior of the low molecular weight fluorine containing blend at this temperature.

Increasing the annealing temperature to 155 °C resulted in the deuterocomponent of the D-PS2/H-PS2 blend segregating gradually to the surface (Figure 3), in agreement with the literature reports for high molecular weight mixtures. The blend of D-PS-F2 and H-PS2 also showed preferential segregation of the deuteropolymer, but the effect of the fluoro end cap produced a much enhanced enrichment in a given time (Figure 3).

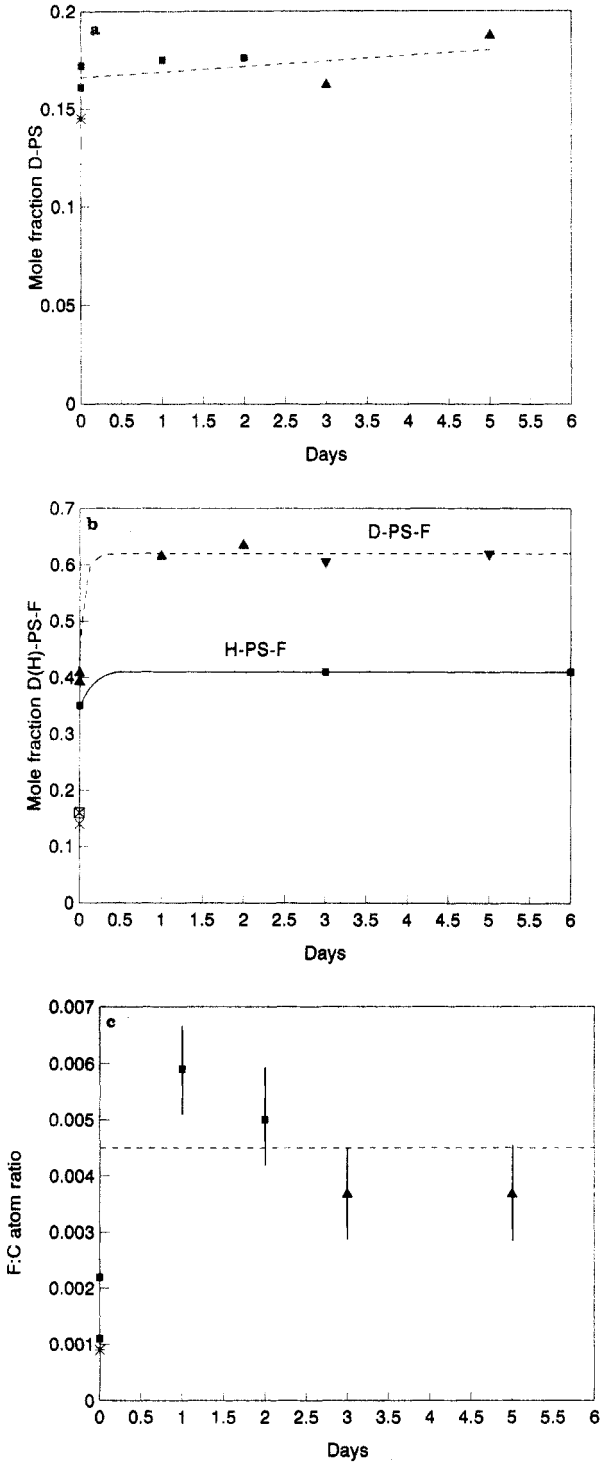

Figure 2. (a) Low MW blend: D-PS1/H-PS1. Mole fraction of D-PS1 from SSIMS versus annealing time. (*) Calculated value. (■) Annealed at 130 °C. (▲) Annealed at 150 °C. (b) Low MW blends: D-PS-F1/H-PS1 and H-PS-F1/D-PS1. Mole fraction of D-PS-F1 or H-PS-F1 from SSIMS versus annealing time. D-PS-F1/H-PS1: calculated value (×); annealed at 130 °C (▲); annealed at 150 °C (▼). H-PS-F1/D-PS1: calculated value (□); annealed at 130 °C (■). (c) Low MW blend: D-PS-F1/H-PS1. F:C atom ratio from XPS versus annealing time. (*) Calculated value. (■) Annealed at 130 °C. (▲) Annealed at 150 °C. (- - -) Plateau value.

The kinetics of the surface segregation are slowed, compared to the low molecular weight mixture, because of the increase in molecular size, but within the time scale of the longest experiment (12 days), the fluorine-containing blend reached a surface enrichment similar to that of the correspondingly low molecular weight mixture.

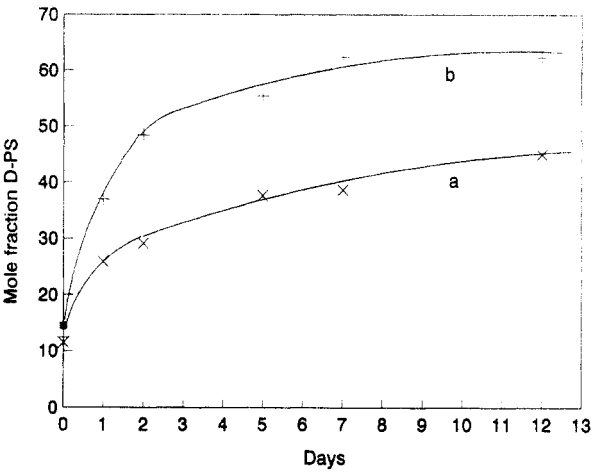

Figure 3. High MW blends. Mole fraction of deuterated polymer from SSIMS versus annealing time at 155 °C. (a) H-PS2/D-PS2; (b) H-PS2/D-PS-F2. (■) Calculated value.

Discussion

The distillation of the detailed theory of the thermodynamics of surface layers and wetting transitions in miscible polymer blends provided by Jones and Kramer[3] enables the calculation of the difference in surface energy ($\Delta\gamma$) of the two components in a mixture, since the surface volume fraction is solely determined by this factor, except where the system is very close to the coexistence boundary of the mixture. From ion beam studies,[6] a value of 0.08 mJ m^{-2} was obtained for D-PS/H-PS mixtures, and for these mixtures a bulk D-PS volume fraction of 0.15 resulted in a surface volume fraction of ca. 0.24 after annealing. For the low molecular weight D-PS-F mixture we observe a mole fraction at the surface of 0.62, considerably greater than that for D-PS with no perfluoro end labeling. Using this value we can calculate that $\Delta\gamma$ for this D-PS-F/H-PS mixture is ca. 0.6–0.9 mJ m^{-2}. The uncertainty in this value arises from the need to use a value for the statistical step length of the polymer. We have used the values for atactic polystyrene, which are between 5 and 8 Å, to calculate the theoretical depth profile, which will be investigated later by neutron reflectometry and ion beam analysis. If the value for $\Delta\gamma$ is used in conjunction with the parameters for the high molecular weight D-PS-F/H-PS blend, and using the simplified equilibrium theory of Jones and Kramer[3] pertinent to polymers of similar molecular weight, then the predicted surface volume fraction is close to 1.0. The maximum observed surface segregation of the D-PS-F in the high molecular weight mixture was only ca. 0.6 mole fraction. The simulation is, however, based on equilibrium calculations, and experimentally the attainment of true equilibrium may be very prolonged at the temperatures employed.

The data for blends of H-PS and D-PS of low molecular weight, (3–4) × 10^4, provide evidence of only slight preferential surface segregation under the above conditions. These results are at first sight contrary to the report of Rei Vilar et al.,[10] who used polymers of similar weight and observed spontaneous segregation of the deuterated component. The film thicknesses were also comparable to our values, but the films were deposited onto gold surfaces, rather than silicon with the native oxide. The choice of substrate may be significant.

Zhao et al.[11] have noted that the segregation behavior of (D-PS)–(H-PS)–(D-PS) triblocks depends on the substrate. The interactions at the substrate–polymer interface must therefore alter the delicate balance of forces sufficiently to cause segregation at that interface, which then

produces an effect at the polymer–air interface of the thin films.

In our system, the addition of the perfluoro end cap provides the small change in interfacial energy which drives the deuteropolystyrene to preferentally segregate to the air–polymer interface. The dominant effect of the relatively small number of fluoro end groups is well illustrated by the surface segregation of the fluoro-end-capped hydrogenous polymer in the low molecular weight blend with deuterated styrene, contrary to the tendency of the deuterated component to be in excess at the surface.

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