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Surface Segregation in Blends of Polystyrene and Perfluorohexane Double End Capped Polystyrene Studied by Static SIMS, ISS, and XPS

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ABSTRACT: The surface composition of styrene polymers capped at one or both ends by perfluoro groups has been determined by ISS, XPS, and static SIMS. The homopolymers, with M_n 29 000−59 000, have an excess of the perfluoro end groups at the surface that is inversely proportional to the chain length and is commensurate with one or both ends having perfluoro groups. In contrast, double perfluoro end capped homopolymers of M_n ∼9000 have only one of the perfluoro groups at the surface. In blends of perfluoro end capped styrene with hydrogen-terminated styrene, the fluorinated end cap causes the former to segregate to the surface. Nevertheless, the extents of segment segregation of single and double perfluoro end capped polymers of weights 29 000−59 000 are similar. For blends of perfluoro-capped polymer with M_n 9000 in styrene of M_n 30 000, the molecular weight and perfluoro end caps both strongly influence the segment segregation. The concentration of fluorine at the surface of all the blends may be estimated from the homopolymer XPS data and the blend monomer composition determined by static SIMS.

Introduction

The ability of the polar end group of a long-chain molecule to segregate at an interface is well-known,[1] and this phenomenon is important in the anchoring of molecules to solid substrates. The interaction with a substrate will be influenced by the chemical nature of the end groups and leads to significant modification of the properties of the solid surface. Similarly, end groups can “attach” themselves to the polymer−air interface, and produce a modification of the surface, as a consequence of the difference in the surface free energy between the ends and main segments of the chain. The degree to which the end groups fill the surface will be controlled by the surface free energy differences between end group and backbone segments, the relative volumes of these elements, and the competing change in free energy caused by forming a concentration gradient near the surface. In recent work on end-functionalized polystyrenes, Elman et al.[2] incorporated a two-part end group which allowed investigation by neutron reflectivity, from the deuterium content, and by XPS, from oxygen or fluorine elements. End group concentrations could then be obtained both at the surface and within the film. For the fluoro end group, they observed an increased concentration at the surface.

When polymers are mixed to form a blend, the surface free energy can be altered by preferential segregation of one of the blend components. Only slight differences in the polarity of the backbone segments may be sufficient to cause segregation, as exemplified by blends of high molecular weight hydrogenous and deuterated styrenes.[3−5] Addition of a polar end cap to one of the components of a blend provides an additional driving force for the chain segregation and may result in the end-capped molecule being “dragged” to the surface. We have shown that for blends of styrene plus deuterated styrene with a single perfluorohexane end cap there is significant segregation to the air−polymer interface with low molecular weight blends, whereas the hydrogenous and deuterated low molecular weight polymers without the fluorinated end cap do not exhibit appreciable segregation.[6]

In the previous study using single perfluoro end capped polystyrene, the butyl initiator formed one end group, and its ability to surface segregate was difficult to estimate because of its chemical similarity to the main backbone structure, though it has now been shown to be surface active.[2] In this paper the segregation phenomenon is further explored using perfluoro end capped polystyrenes in which both ends are capped. The factors that influence the segregation effects in end-capped polystyrene blends are the backbone isotopic composition, relative molecular weights, and magnitude of the difference in polarity of the end and backbone groups.

This study will use a range of surface analytical techniques to probe the composition to depths from ∼0 to 6 nm, i.e., ion scattering spectroscopy (ISS), static secondary ion mass spectroscopy (static SIMS), and X-ray photoelectron spectroscopy (XPS).

Experimental Section

Polymer Synthesis. Polymers were prepared by anionic polymerization of the hydrogenous or deuterated styrene monomers under high vacuum conditions. Benzene was used as the polymerization solvent, and the dilithium initiator was produced from 1,3-bis(1-phenylethenyl)benzene and *sec*-butyllithium. Termination was achieved by addition of degassed methanol or $R\text{-}(CH_2)_2Si(CH_3)_2Cl$, where R = perfluorohexyl or perfluoromethyl, giving, e.g., $CF_3(CF_2)_5(CH_2)_2(CH_3)_2Si\text{-}[CH_2\text{-}CH(C_6H_5)]_n\text{-}Si(CH_3)_2(CH_2)_2(CF_2)_5CF_3$.

Selected polymers from the previous study[3] were also utilized to provide a comparison with single fluoro end capped macromolecules. The number average molecular weights and

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Table 1. Properties of Homopolymers

			F/C			
	M_n	M_w/M_n	bulk	XPS uniform model	calcd[a] from (F13)-(D29)	XPS monolayer[b] model
single end capped						
(H45)	44 700	1.05				
(D29)	28 300	1.06				
(F13)-(H51)	50 500	1.04	0.003	0.005	0.005	0.045
(F13)-(D29)	28 900	1.06	0.006	0.009	(0.009)	0.082
double end capped						
(H9)	8 900	1.13				
(F13)-(H59)-(F13)	59 000	1.04	0.005	0.014	0.009	0.126
(F13)-(D54)-(F13)	53 800	1.04	0.006	0.015	0.010	0.137
(F13)-(H9)-(F13)	9 400	1.13	0.033	0.042	0.056	0.404
(F3)-(H9)-(F3)	9 200	1.14	0.007	0.007	0.013	0.063

[a] F/C ratio calculated from (F13)-(D29). [b] F/C ratio within top monolayer.

the polydispersity indexes (M_w/M_n) of the polymers used, were obtained from gel permeation chromatography, Table 1.

Polymers are designated according to their termination and backbone isotopic structure, e.g., (F13)-(D54)-(F13) represents the deuterated styrene, M_n 53 800, with perfluorooctyl end caps at both ends.

Blends were prepared by dissolving the polymers in toluene, and films were cast from solution on to silicon wafers cleaned with a sulfuric−peroxide mixture, i.e., retaining the native oxide. The bulk compositions were ~15% (w/w) of the minority component. The film thickness was ~200 nm. Samples were annealed mainly under an argon flow at 130 °C. A few samples, annealed under vacuum, showed no difference in the results.

Surface Analytical Methods. Surface compositions of the blends were obtained by XPS and static SIMS. The former provides quantitative information on the perfluoro end group concentrations in the surface region (~0−6 nm), and the latter quantitative data on the deuterated and hydrogenous styrene surface concentrations to a depth of ~1 nm. Static SIMS analyses were performed using a Vacuum Science Workshop ion gun, operating with a 3 keV argon ion beam at a current of 2×10^{-10} A measured at the gun exit, irradiating an area of ~5 mm^2, and total ion doses were less than 10^{14} cm^{-2}. Spectra were obtained with a Vacuum Generators 12-12 quadrupole. Sample charging was compensated by an electron flood gun operating at 30 eV. The relative concentrations of deuterated and hydrogenous styrene were obtained from the ratio of the $C_7H_7^+$ and $C_7D_7^+$ signals (91 and 98 Da, respectively).[7]

XPS data were obtained with a Vacuum Science Workshop X-ray anode, using aluminium Kα radiation, and 100 mm hemispherical analyzer. The C1s and F1s signals were corrected with Wagner's sensitivity factors adjusted for our instrument to give element concentrations.

ISS probes the outermost atom layer of the film. Measurements were taken with a Kratos WG-541 CMA spectrometer at Louvain-la-Neuve.[8] An ion beam of ^{3}He at 2 keV was rastered over ~4 mm^2 of the sample, and total ion doses were limited to between 15×10^{13} ions cm^{-2} to minimize damage. A VSW electron flood gun, energy 200 eV, was used to compensate charging. The ISS spectra were always analyzed in the same way; after smoothing and background subtraction, elemental peak areas were fitted using a least-squares routine (Gaussian function).

Results

Hompolymers. (a) XPS. Element composition data are presented in Table 1. The bulk F:C ratios are calculated from the molecular weights and end cap structure and the highest ratio used in this study equalled only 3% F. Surface elemental composition data are derived from the XPS results. The analysis of the XPS data depends on the model chosen for the concentration profile, and generally, a uniform distribution of atoms is assumed and the element ratios are then determined simply using XPS sensitivity factors.

$$n_a/n_b = (I_a^\infty I_b)/(I_b^\infty I_a)$$

where n is the atom density, I is the XPS signal intensity, and $^\infty I$ is the signal from the pure material.

Allowing for the errors in measuring the weak fluorine signals, the XPS data from the uniform model showed only modest increases in the F:C ratio compared to the bulk data. However, the fluorinated end caps have been selected because of their known surface activity and the high probability that the perfluoro groups migrate to the surface. Therefore, an alternative model for calculation is proposed which places the measured fluorine groups within a surface monolayer.

The simplest approach for this model is to assume that the fluorinated ends lie flat on the surface. Because the diameter of a polymer molecule of molecular weight 30 000 is ~4 nm, to a first approximation the F atoms in the next layer of polymer will contribute little to the signal. The calculation is then analogous to a partial monolayer of poly(tetrafluoroethylene) (PTFE) on top of the polystyrene.

For fractional monolayer ϕ_a, where ϕ_a is small,[9] on a substrate b,

$$\phi_a = \frac{\lambda_a(E_a)\cos\theta}{a_a}\,\frac{I_a^\infty I_b}{I_b^\infty I_a}$$

where λ_a is the escape depth at kinetic energy E_a, here 2.19 nm, $(a_a)^3$ is the volume of the "molecule", and θ is the takeoff angle (normal to the surface). The values of a_a and a_b are obtained from the densities, 2.2 g cm^{-3} for PTFE and 1.06 g cm^{-3} for polystyrene, and are 0.33 and 0.27 nm for PTFE and polystyrene, respectively, taking units $-(CF_2)-$ and $-(CH)-$, the latter being an average unit for polystyrene.

Selecting (F13)-(D29), the measured value of

$$(I_a^\infty I_b)/(I_b^\infty I_a)$$

is 1/105, which gives $\phi_a = 0.063$ monolayer.

The area of the (CF_2) is $(a_a)^2 = 0.109$ nm^2 and that of (CH) is 0.073 nm^2. Therefore, in the *outermost* surface layer, the ratio of surface

$$\frac{F}{C} = \frac{2(0.063/0.109)}{(0.937/0.073) + (0.063/0.109)} = 0.08$$

compared to the value of 0.01 from the uniform model, indicating a surface excess of fluorine, and this value is the atomic ratio required for comparison of the partial

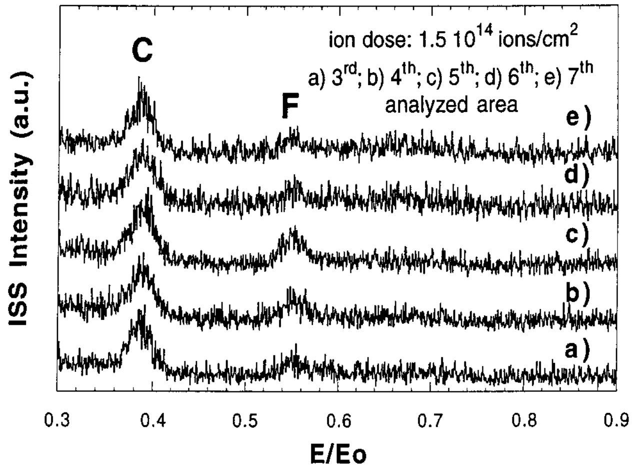

Figure 1. ISS of five different areas of (F13)-(D29). Ion dose, 1.5×10^{14} ions cm^{-2}.

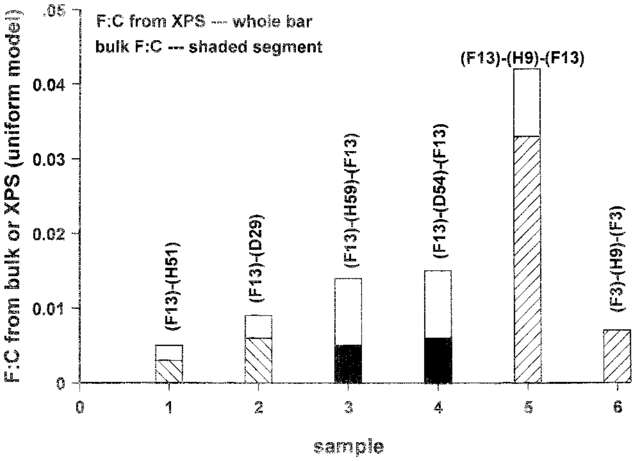

Figure 2. Comparison of bulk (shaded segment) and measured (XPS, uniform model, (whole box) F/C atom ratios.

monolayer model with the ISS data below. Of course, over the total volume probed by XPS, the F/C ratio for the monolayer model would be less than for the uniform model.

(b) ISS. The technique of ISS is extremely surface sensitive. It has the advantage of only probing the outermost atom layer because of the elastic shadowing effect and the high neutralization probability for incident ions penetrating further than the surface. Therefore, in theory, ISS should be able to distinguish between the above uniform and surface partial monolayer models. One polymer was analyzed by ISS to provide further information on the distribution of perfluoro end groups. The polymer chosen for examination, (F13)-(D29), had a single end cap in order that the observed fluorine concentration could be associated with a single molecule: for a double end capped polymer it is possible to have between one and two perfluoro end groups per molecule at the surface. The ion beam dose was reduced to a minimum to prevent damage, but consequently the ISS signals were weak, Figure 1. Only C ($E/E_0 = 0.4045$) and F ($E/E_0 = 0.5688$) atoms can be seen in the case of the analyzed sample, no Si ($E/E_0 = 0.6841$). Observation of the fluorine signal verifies that fluorine is present in the outermost atom layer.

Quantification of the element ratio from ISS depends on the mechanism of the ion scattering,[10] and ISS peak areas are corrected to take into account differences in calculated scattering cross sections, measured channeltron efficiency, and estimated transmission factors, though incomplete knowledge of the polymer surface structure hinders any anticipation of the shadowing effects. Moreover, charge exchange mechanisms (inelastic scattering) make estimation of the $^3He^+$ ion survival probability, after scattering on C or F, difficult. Both aspects limit the quantification of the ISS data.

The corrected ISS F/C ratio (between 0.07 and 0.17, mean 0.11) is higher than the bulk or XPS F/C ratios. Comparison with fully fluorinated structures, PTFE, for which the corrected ISS F/C ratio is 6.15, compared to the stoichiometric value of 2, gives an ISS "sensitivity" factor for F that is 3 times greater than for C. This should roughly account for the unknown inelastic scattering and shadowing effects. Applying this experimental sensitivity factor, the ISS F/C ratio becomes 0.11/3 = 0.04. The XPS F/C ratio varied from 0.01 to 0.08 depending on the model chosen for the concentration profile.

The "calibration" material for the ISS was PTFE, but the local geometry of the perfluoro end cap at the surface of the polystyrenes will not be identical to that of PTFE. Part of the emerging end cap may be slightly subsurface and/or, even if the end cap is fully on the surface, it may be partially shadowed by adjacent polystyrene segments. Consequently, the ISS data probably underestimate the perfluoro groups, and hence, in view of the magnitude of the F/C ratio calculated from ISS [4(XPS uniform value)], it is unlikely that the perfluoro end groups are distributed uniformly through the bulk. Segregation occurs, which results in the perfluoro end caps of the polymer molecules at the surface being detected in an appreciable amount. The XPS partial monolayer model gives an F/C ratio of 0.08, and taking into account the shadowing effects, the ISS value of 0.04 suggests that the partial monolayer model is a better description of the system, though the data are not sufficient to conclude that all the perfluoro end caps in the near-surface region have entirely emerged on to the surface.

Segregation of Perfluoro End Groups from XPS. The XPS data for the homopolymers are given in Table 1, with the F/C ratios derived from the uniform and partial monolayer models. The errors in measuring the low levels of fluorine restrict the accuracy of the F/C ratios to ~10%. Nevertheless, the influence of the various parameters of the system can be readily assessed with the aid of a bar chart which facilitates comparison of the bulk (shaded segment) and XPS (open segments − uniform model) F/C ratios, Figure 2. The polymers are grouped according to end cap and/or weight.

Several points can be inferred, of which the most obvious is that for the single and double C_6F_{13} end capped polymers, the XPS values for the F/C ratio are greater than the bulk ratios, as expected if the perfluoro end caps near the surface migrate to an exposed position.

(F13)-(H59)-(F13) and (F13)-(D54)-(F13), with similar molecular weights, have similar XPS F/C ratios, irrespective of the isotope used for the polymer backbone.

The effect of a molecular weight change on the number of end groups at the surface can be deduced from the data for (F13)-(H51) and (F13)-(D29). Assuming that the fraction of end groups will be inversely proportional to the molecular weight, the F/C ratio for (F13)-(H51) is obtained by multiplying the XPS F/C ratio for (F13)-(D29) by 28.9/50.5, giving 0.005, cf. the measured value of 0.005, Table 1.

Considering the double perfluoro end capped polymers, (F13)-(H59)-(F13) and (F13)-(D54)-(F13), Figure 2 shows that the difference between the bulk and surface F/C ratios is greater than for the single end capped materials of similar molecular weight. In fact, using the same basis for calculation as above, the calculated F/C ratios for the double perfluoro end capped polymers, Table 1, are ~35% less than the measured values, which leads to the conclusion that, if perfluoro groups are placed on both ends of the chain, the probability of a perfluoro chain end reaching the surface is more than doubled. This means that either for the single-ended polymers, the butyl ends were also at the surface in about equal concentration to the perfluoro ends or the double-ended polymers have more chain ends at the surface. The latter view is supported by the data of Elman et al.[2] which show that in a polymer with a butyl group at one end and a perfluoro group at the other the perfluoro end group will dominate the surface.

In contrast, for the low molecular weight double fluoro end capped polymers the bar chart shows relatively less excess fluorine at the surface, and the calculated F/C ratio for (F13)-(H9)-(F13), 0.042 is 31% more than the measured value; i.e., there are fewer chain ends at the surface than expected. Indeed, directly comparing the measured data for double perfluoro end capped polymers (F13)-(H59)-(F13) and (F13)-(H9)-(F13) shows that the F/C ratio changes by 1:3, whereas the molecular weight changes by 6:1; i.e., the relative number of surface chain ends has halved. Even with half the chain ends at the surface, the partial monolayer model suggests that 40% of the surface is covered by CF_2.

The effect of decreasing the fluorine content of the end cap is shown by comparison of (F13)-(H9)-(F13) and (F3)-(H9)-(F3). Adjusting the F/C ratio for (F13)-(H9)-(F13) by 3/13 gives 0.010 compared to the measured value for (F3)-(H9)-(F3) of 0.007. The measured value is slightly less than expected, allowing for experimental error, and is consistent with the CF_3 group being less surface active than the C_6F_{13} group. It is also much less than the value calculated from (F13)-(D29), and in fact is the same as the bulk value, which leads to an interesting question. Is there any surface segregation of the CF_3 groups? Reorientation, locally, of the chains in the surface region could allow the CF_3 groups to lie on the surface. In which case, the partial monolayer model would best define the surface composition. It is difficult to resolve this question using ISS because the fluorine signal from the CF_3 groups is proportionately lower than those from the C_6F_{13} end capped polymers, which were near the limits of detection. As it happens, evidence for the surface segregation of the CF_3 groups will arise from the data for the blends below.

Medium Molecular Weight (29–59K) Blends. Static SIMS. The relative concentrations of deuterated and hydrogenous polymers at the surface of a blend were determined from static SIMS spectra. The effect of capping both, as opposed to one, ends of the polymer with a perfluoro group is shown in Figure 3, where the percentage of the fluorinated component is plotted against the annealing time.

A blend of (F13)-(H51) with (D29) showed segregation of 36% of the perfluoro-capped polymer for the unannealed film, increasing to a plateau of 41% after several days, compared to the solution concentration of 15%.

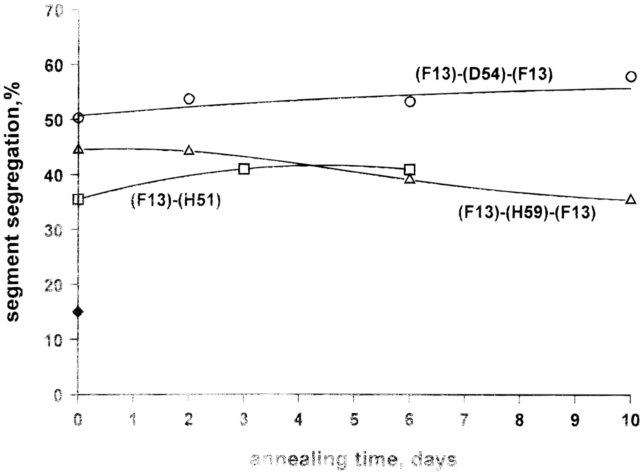

Figure 3. Segment segregation from static SIMS ($C_7H_7^+$ and $C_7D_7^+$ signals): (□) (F13)-(H51) in (D29); (△) (F13)-(H59)-(F13) in (D29); (○) (F13)-(D54)-(F13) in (H45).

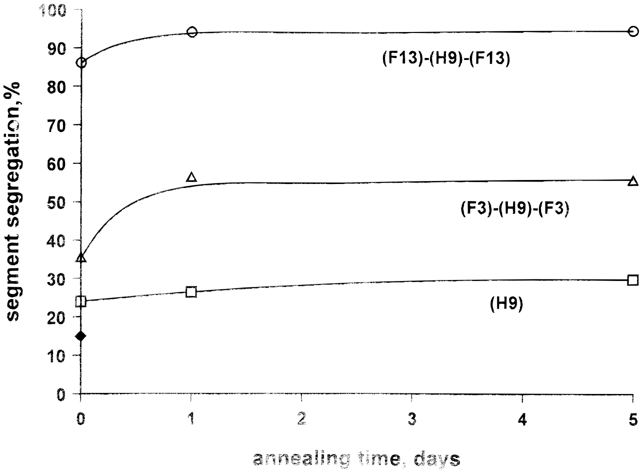

Figure 4. Segment segregation from static SIMS ($C_7H_7^+$ and $C_7D_7^+$ signals): (□) (H9) in (D29); (△) (F3)-(H9)-(F3) in (D29); (○) (F13)-(H9)-(F13) in (D29).

The corresponding blend with double end capped polystyrene, (F13)-(H59)-(F13) and (D29), initially showed a segregation of the perfluoro component of 44%, but this decreased on annealing until after 10 days it reached 35%. It is unlikely that the last result could be caused by contamination of the sample during annealing, as the relative concentration of the hydrogenous polymer decreased.

Reversing the isotopic substitution, a blend of (F13)-(D54)-(F13) with (H45) showed an initial segregation of 50%, rising to near 60% with annealing, Figure 3. A similar blend with a single perfluoro end cap gave a plateau value of 62%.[6] In these cases the deuterio and perfluoro effects are working in the same direction and segregation of the perfluoro component is increased vis à vis the (F)-(H)-(F)/(D) blend.

Low Molecular Weight (9–29K) Blends. (a) Static SIMS. Hydrogenous styrene of M_n ~9000, capped at both ends with H, CF_3, or C_6F_{13}, was mixed with (D29) to form the low molecular weight blends. The surface concentrations of the low molecular weight component, bulk concentration 15% monomer, are shown in Figure 4. The (H9)/(D29) blend has an excess of the hydrogenous styrene at the surface, which after 5 days annealing reaches 30%. The (F3)-(H9)-(F3)/(D29) blend shows an initial segregation of 35%, rising to 55%, while the (F13)-(H9)-(F13)/D(29) blend achieves a segregation of 95%.

Table 2. Segment Segregation from Static SIMS and F/C Ratio from XPS for Blends

blend	Fractn F polymer, static SIMS	F/C		
		bulk	XPS measd[a]	XPS calcd[a,b]
(F13)-(D29)/(H45)	0.62	0.0008	0.006 (0.053)	0.008 (0.051)
(F13)-(H59)-(F13)/(D29)	0.35	0.0008	0.006 (0.050)	0.005 (0.044)
(F13)-(D54)-(F13)/(H45)	0.58	0.001	0.008 (0.076)	0.009 (0.079)
(F13)-(H9)-(F13)/(D29)	0.95	0.005	0.034 (0.332)	0.040 (0.384)
(F3)-(H9)-(F3)/(D29)	0.58	0.001	0.004 (0.034)	0.004 (0.037)

[a] Uniform model (monolayer model). [b] (XPS F/C ratio of the homopolymer) × (static SIMS fraction of F polymer in blend).

(b) XPS. The XPS data, Table 2, confirm the large segregation effects of the perfluoro-capped component in the low molecular weight blends. The fluorine signals from the blends are much greater than calculated from the bulk mixture and approach the perfluoro homopolymer values; e.g., at the highest observed segregation, (F13)-(H9)-(F13)/D(29) blend, the uniform model gives a F/C ratio of 0.034 compared to the homopolymer value of 0.042.

Table 2 also shows the F/C ratio for the blends, calculated from the homopolymer XPS value times the fraction of the perfluoro component detected by SIMS. Except for (F13)-(H9)-(F13)/D(29), the maximum calculated surface coverage of CF_2 groups, from the monolayer model, is only $\sim$0.04 (0.5 × F/C ratio). The fraction of backbone segments hidden by overlying CF_2 groups can be neglected, and the static SIMS data, which are obtained from the $C_7H_7^+$ and $C_7D_7^+$ signals, therefore give a reasonable measure of the surface ratio of polymer segments. For (F13)-(H9)-(F13)/D(29), the coverage of CF_2 groups is 0.17 and the measured segregation of the perfluoro component estimated from static SIMS chain segment concentrations will be less certain. Albeit, within an accuracy of ±10%, the calculated values agree with the measured XPS F/C ratios for the blends over a segregation range of 35–95%.

Generally, the XPS data for the blends suggest that the perfluoro polymers in the mixtures behave similarly to the homopolymers.

Discussion

The ISS results are evidence that when styrene is capped with perfluoro groups, the perfluoro chain ends migrate to the surface and are, at least partially, exposed. Capping both ends of a medium molecular weight styrene with perfluoro groups results in a 2-fold, or more, increase in the fluorine at the surface, compared to the single perfluoro end capped polymer. However, the chain segment segregation of the double perfluoro end capped styrene in the blends is the same or less than the corresponding single perfluoro end capped polymer.

The latter has *n*-butyl groups as the other chain end, but as noted above, the effect of the perfluoro end cap has been shown to be dominant,[2] and consistent with this result, capping the hydrogenous styrene with perfluoro groups increases the surface segregation of the perfluoro end capped polymer markedly over the corresponding H-capped styrene. The perfluoro groups, therefore, “lead” the polymer to the surface, a consequence of their surface activity. No enhanced segregation of the perfluoro end capped polymer would have been observed if the *n*-butyl end cap had a similar surface activity. The inference is that for the double perfluoro end capped medium molecular weight styrene both ends migrate to the surface, whereas for the single perfluoro end capped polymer it is mainly the perfluoro end cap that is at the surface.

This raises the question, why does the double end capped molecule not show greater segment segregation than the single perfluoro end capped molecule? A tentative hypothesis is that attaching both ends of the polymer to the surface will be unfavorable for the configurational entropy contribution to the free energy. Therefore, the advantage of the enhanced surface affinity is cancelled out by the loss of possible configurations.

Effect of Low Molecular Weight. The fine balance of molecular weight, end cap composition, and backbone isotopic structure in determining the segregation effect is shown by the differing behavior of (F13)-(H59)-(F13)/(D29) and (F13)-(D54)-(F13)/(H44) blends with annealing time. Both blends have an excess of perfluoro end capped polymer at the surface immediately after casting. The segregation of the perfluoro-capped polymer in (F13)-(D54)-(F13)/(H44) increased further with annealing time, contrasting with the decrease in perfluoro-capped polymer concentration with time observed for the (F13)-(H59)-(F13)/(D29) blend.

In (F13)-(D54)-(F13)/(H44), the perfluoro groups lead the molecule to the surface, and there is no tendency for the deuterated polymer to be displaced by the hydrogenous styrene. On the other hand, in (F13)-(H59)-(F13)/(D29), the perfluoro groups cause an initial marked segregation which is determined by the properties of the solvent–binary polymer system during evaporation of the solvent. Annealing then allows the deuterated polymer to migrate to the surface of the solid film and partially displace the perfluoro end capped hydrogenous styrene. The diffusion is helped by the relatively low (29K) molecular weight of the deuterated component.

Comparison with the (F13)-(H55)/(D29) blend, which shows a “normal” increase in segregation of the perfluoro polymer with annealing time, shows that capping the molecule at both ends with perfluoro groups can introduce specific features, other than merely increasing the fluorine content. Again, a reduced configurational entropy of the double perfluoro end capped polymer as a consequence of segregation at the surface would account for the experimental observations. For (F13)-(H59)-(F13)/(D29), the surface activity of the end groups is barely sufficient to overcome the balance of configurational plus isotopic factors resulting in part of the segregated perfluoro polymer redispersing in the bulk.

Hariharan et al.[5] pointed out that molecular weight effects become predominant and overshadow the backbone isotopic effect when there is a disparity between the molecular weights of the blend components, thus accounting for the segregation of (H9), which is below the entanglement weight, in (D29). The high surface segregation of (F13)-(H9)-(F13) in (D29) is driven by both a molecular weight effect and the surface activity of the perfluoro groups. It is significant that the XPS data for the double perfluoro end capped polymer suggest that only one chain end is at the surface. The loss of configurational entropy on attaching both ends of the polymer to the surface would be proportionally greater for a small molecule.

The segregation of (F3)-(H9)-(F3) is greater than that of (H9) in (D29), which leads to the conclusion that the CF_3 groups must be surface active, though the F/C ratios for the (F3)-(H9)-(F3) homopolymer, discussed above, from the XPS uniform model and the bulk were the same. On the other hand, the XPS partial monolayer model allows the CF_3 groups of molecules at the surface to segregate locally. This would then explain the increased segregation of (F3)-(H9)-(F3) vis à vis (H9) and provides further justification for the monolayer approach.

Previously,[11] we studied chain-end effects in homopolymers of hydrogenous styrene capped at both ends by deuterated styrene oligomers, (D-H-D), or the reverse triblock copolymer, (H-D-H), where the polymers had molecular weights of ~10 000, similar to the low molecular weight perfluoro capped styrene. The data suggested that a factor in the segregation of chain ends to the surface was the entropic freedom of an end in the surface compared to the bulk. This effect resulted in an increase of the surface end group concentration, compared to the bulk, of 3:1 for H-D-H and 4:1 for D-H-D. The latter value being greater because of the difference in surface activity of the C−H and C−D bonds.

In the present study, there is a major contribution from the surface activity factor. Taking the partial monolayer model as the most probable description of the surface composition, the ratios of surface to bulk end groups are 9:1 for (F3)-(H9)-(F3), and 12:1 for (F13)-(H9)-(F13).

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