Surface Segregation of Fluoroalkyl Side Group of Fluorinated Block Copolymers

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X-ray photoelectron spectroscopy (XPS) revealed surface segregation of the fluoroalkyl side groups of poly[styrene-block-4-(perfluorooctylpropyroxy)styrene] (PS-PF). The surface was fully covered by the fluoroalkyl side groups orienting toward the surface unless the block fraction of the PF block is extremely low, i.e. 0.09. When the block fraction is 0.25, the surface domain of the fluorinated alkyl side groups, however, has an approximate thickness of 1.5 nm, which is comparable to a monolayer of fluoroalkyls. As the block fraction goes beyond 0.3, the surface domain becomes much thicker than a monolayer of fluoroalkyls and resembles the structure of a surface lamella. The block fraction strongly affects on the surface coverage of fluoroalkyl side groups and their orientation.
Key words: XPS, Surface, Fluorinated, Segregation

INTRODUCTION

Fluorinated polymers are typical low surface energy materials, which can be used for industrial applications, such as coatings and non-wetting biological applications. [1-4] Block copolymers with fluorinated blocks enrich the fluorinated block concentration near the surface because of their low surface energy in addition to the capability of forming ordered structures in bulk. It has been experimentally revealed that fluorinated blocks of fluorinated block copolymers segregate to the surface, and the surface concentration of fluorinated blocks are much higher than the average concentration. [5, 6] Fluorinated block copolymers with fluorinated side groups develop two dimensional liquid crystal structures of a monolayer of fluorinated side group at the surface.[7, 8]

Fluorinated polymers with fluorinated side groups potentially have the more hydrophobic surface than that of widely used main chain fluorinated polymers such as Teflon. This is due to the lower surface tension of CF_3 groups than that of CF_2 groups constructing the main chain fluorinated polymers. If the fluoroalkyl side groups are not packed tightly, the surface concentration of CF_3 should be low and decrease as the surface reconstruction when exposed to polar environment such

as water. Thus, the hydrophobicity and its stability are strongly influenced by surface structures of fluoroalkyl side groups.

Fluorinated polymers can be used to improve the surface hydrophobicity; however, it is difficult to process those polymers. They do not dissolve in most of ordinary organic solvents and are incompatible with almost all of the other polymers. Adding a fluoropolymer as an additive to improve the surface property can have a significant effect on the surface property, but substantially reduce the mechanical property. In that respect, block copolymers with fluorinated blocks are expected to improve the surface property without sacrificing bulk properties. Although there have been a continuous effort to improve the stability of fluoroalkyl side groups of fluorinated block copolymers by replacing the more stable fluoroalkyl side groups that resist reconstruction upon contact with water, the effect of block fraction has been poorly understood. We report the segregation behavior of fluoroalkyl side groups of PS-PF block copolymers and its dependence on the block fraction.

EXPERIMENT

poly[styrene-block-4-(perfluorooctylpropyloxy)styr

ene] (PS-PF) block copolymers were obtained by anionic polymerization of poly(styrene-block-4-hydroxystyrene) (PS-PSOH) followed by The Williamson reaction to introduce 1-bromo-3-perfluorooctylpropane into PSOH. [9, 10] The chemical structure of PS-PF is shown in Figure 1 and a list of PS-PF used in this study is in table I.
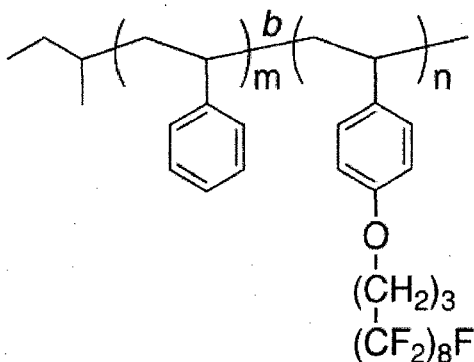

Figure 1 Chemical structure of PS-PF.

Table I: Characteristics of PS-PF block copolymers

Code	M_n/kg mol^{-1}	f_{PF}
PSF75-09	75	0.09
PSF27-25	27	0.25
PSF34-28	34	0.28
PSF94-28	94	0.28
PSF92-37	92	0.37

The specimens for X-ray photoelectron spectrometry (XPS) were prepared by spin-casting of a toluene solution of PS-PF on a silicon substrate of which surface was covered with a native silicon oxide layer. The specimens were annealed at 180 °C in vacuum at the pressure less than 10^{-3} Pa for 24 hours.

Spectra were acquired on a PHI Quantum 2000 spectrometer equipped with a hemispherical capacitor analyzer using monochromated X-ray from Al Kα. Elemental survey scans from 0 to 1000 eV were acquired with a pass energy of 100.5 eV, while high-resolution scans of the C 1s, F 1s, and O 1s regions were acquired with a pass energy of 35.8 eV at a take-off angle, θ, which is the angles between the surface and the direction toward the analyzer. θ of 10, 15, 20, 25, 30, 35, 40, 45, 55, 65, and 85 were chosen for the angular dependence measurements.

RESULTS

Binding energies of C1s regions are assigned as follows: The chemical shifts of C1s of CF_3, CF_2, carbons adjacent to CF_2 and oxygen, and hydrocarbon (reference) are 293.9, 291.6, 286.0 and 284.8, respectively. An example, PSF92-37, of the atomic fractions of CF_2 and CF_3 are plotted in Figure 2. As θ increases, the fractions decrease monotonically. This is a clear indication of an enrichment of fluorine at the surface since, at lower number of θ, a photoelectron

ejected without inelastic scattering process is limited and the information depth is small. For the other block copolymers except PSF75-09 have the same trend. We were not able to apply this analysis for PSF75-09 due to its low small fluorinated carbon peaks relative to π-π* shake-up peaks. In addition, CF_3 has stronger dependence on takeoff angle than CF_2, which is suggestive of enrichment of CF_3 and of oriented
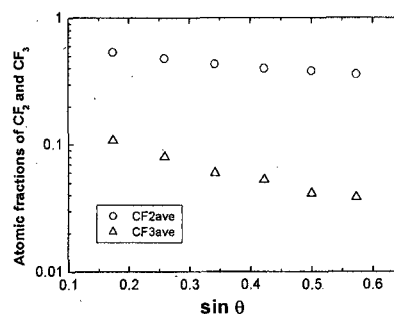

Figure 2 Atomic fractions of CF_2 and CF_3 as a function of sine of takeoff angles of PSF92-37.

fluorinated side groups toward the surface. The fluoroalkyl side groups are enriched near the surface and the CH_3 side group ends are pointing up to the surface. However, we need to obtain more quantitative pictures by analyzing the takeoff angle dependence and converting to a real space depth profile for a detailed analysis of the surface structure.

In order to analyze the surface structure in detail we employed the intensity ratio of F 1s and C 1s instead of the ratio used in Figure 2 since the CF_x peak has an interference with a π-π* shake-up peak and hence we found the ratio of F1s and C1s more reliable. The intensity ratios of F1s and C1s are plotted in an inset of Figure 3. The lines are the fit of equation (1) using a model real space depth profile in the Figure.
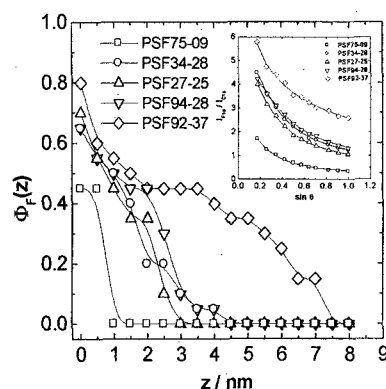

Figure 3 Real space depth profiles of PS-PF block copolymers extracted from the angular dependence of intensity ratio of F1s and C1s shown in the inset.

$$\frac{I_{F1s}}{I_{C1s}} = \frac{I^0_{F1s}/I^0_{C1s}}{\lambda_{F1s}/\lambda_{C1s}} \frac{\int_0^\infty \Phi_{F1s}(z)e^{-\frac{z}{\lambda_{F1s}}}dz}{\int_0^\infty \Phi_{C1s}(z)e^{-\frac{z}{\lambda_{C1s}}}dz} \tag{1}$$

I_i, I^0_i, Φ_i and λ_i are an intensity, a sensitivity factor, an atomic fraction and an inelastic mean free path of an element i, respectively. The inelastic mean free path was calculated by the equation proposed by Ashley[11]. The model was adjusted until the best fit was achieved. The fit is excellent for all the PS-PF block copolymers and the same depth profiles are reproduced from different initial guesses of the depth profiles.

PSF75-09 shows an extremely thin layer of the fluorinated domain. The thickness of this layer is even thinner than the length of C8 fluoroalkyl chains. Therefore, it is suggestive of a fluoroalkyl side groups segregating to the surface and lying parallel to the surface. This is in contrast to the structures previously found in the reference[7,8], in which a C8 fluoroalkyl side group tends to stand perpendicular to the surface or to tilt slightly from the surface normal. It is surprising that the asymmetry of the block has such a strong influence on the surface structure of side groups.

PSF34-28, PSF27-25 and PSF94-28 have almost the same surface domain thickness irrespective of the molecular weight. It should be emphasized that the depth profiles of PSF94-28 and PSF27-25 are not significantly different in contrast to the fact that the Mw of PSF94-28 is three times larger than PSF27-25. This molecular weight independence is strong evidence that the PF block is not orienting perpendicular to the surface. An each block of a general diblock copolymer tends to orient perpendicular to the interface dividing the domains. This is clearly not the case. The surface domain of those PS-PF block copolymers clearly lacks the character of a surface lamella.

PSF92-37, however, shows a significantly different depth profile. The thickness of the domain is well above the length of C8 fluoroalkyl chains, suggesting that the surface domain is not a monolayer of C8 fluoroalkyls but a surface lamella, in which PF block orient perpendicular to the PS/PF interface and hence to the surface. Note that the top most surface is still similar to PSF34-28, PSF27-25 and PSF94-28 block copolymers, in which fluoroalkyl side group are orienting perpendicular to the surface. Therefore, the structure of PF backbone is quite different in PSF92-37 whereas the top surface structure is the same.

DISCUSSION

We propose three different regimes of the surface structure depending on the asymmetry as schematically shown in Figure 4. When the asymmetry is very strong, e.g. the block fraction of PF of 0.09, the PS block would have to be highly stretched if the surface was fully covered by the PF block. In such a case, there is a possibility that the system chose not to cover the surface completely with the PF block but to cover the surface partially to reduce the elastic energy of the PS block. In such a case, the surface may be partially covered with the fluoroalkyl side group lying parallel to the surface. As f increases, the fluoroalkyl side group saturates and begins to pack and orient perpendicular to the surface.

In this case, the surface is packed by CF_3 group instead of CF_2 group, resulting in a lower surface energy. The backbone supporting the monolayer lies parallel to the surface resembling the surface structure of graft copolymers with mesogenic side group.[12] As f further increases, the degree of segregation of the PS-PF becomes strong and the surface lamella becomes stable.
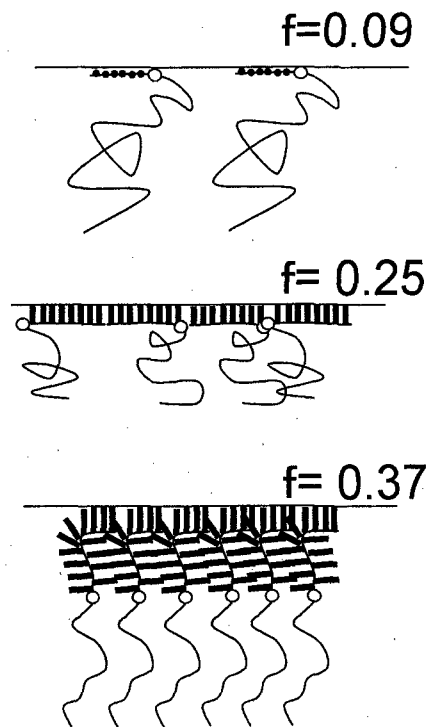

Figure 4 Schematic pictures of possible chain conformations depending on a block fraction of PF, f.
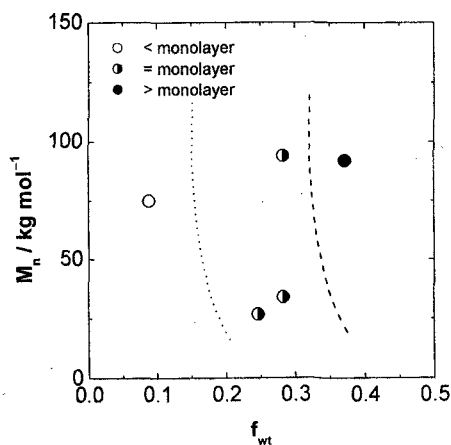

Figure 5 A schematic phase diagram of surface domain of PS-PF block copolymers. Dotted and broken lines are guides for the eye.

In the surface lamella, the backbone of PF prefer the orientation perpendicular to the surface; however, the surface still requires CF_3 group reside in the top most

region to reduce the surface energy.

We summarize the observed surface structures in a Mn-f map in Figure 5. In bulk a phase diagram of diblock copolymer has been theoretically calculated and supported by a plenty of experiments.[13]   At the surface, only lamellar structure can be employed geometrically and the lamella is more stable than that in bulk due to lack of possibility of the other structures and preferential segregation of one component. Therefore, there may be a transition to a surface lamellar at the fraction indicated by the broken line in Figure 5. While a graft copolymer likes to lie parallel to the surface, a block copolymer prefers to stand perpendicular to the surface.   The fluorinated "block-graft" copolymers in this study clearly indicate two aspects of characters of block and graft architectures. The two characters crossover at the broken line and the domain thickness suddenly increases.

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