Surface Structure and Dynamics of Block and Graft Copolymers Having Fluorinated Poly(ethylene oxide) Chain Ends

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ABSTRACT: The surface compositions of poly(styrene-*b*-ethylene oxide) and poly(styrene-*g*-ethylene oxide) films were found to be largely determined by the nature of the poly(ethylene oxide) (PEO) chain ends. Angle-dependent X-ray photoelectron spectroscopy revealed that polystyrene (PS) dominated the surfaces of the copolymers having PEO chain ends terminated by hydroxyl groups (SEO). Also, the PEO content decreased with decreasing sampling depth. In contrast, the surface regions of the corresponding copolymers having fluorinated PEO chain ends (fSEO) were dominated by PEO, and the PEO content increased with decreasing sampling depth. The fluorine content of fSEO also increased with decreasing sampling depth, indicating that the fluorinated chain ends were segregated at the outermost surface. The studied fSEO block copolymer seemed to have a higher surface concentration of fluorinated chain ends than the fSEO graft copolymers. Although it is likely that the fSEO surfaces were fully covered by fluorinated chain ends, the advancing water contact angles on fSEO films were markedly lower than on the corresponding SEO films. Moreover, low contact angles were retained even after prolonged annealing of the fSEO films in a vacuum. The surface behavior of fSEO may be explained by the presence of flexible, fluorinated PEO chain ends, providing a highly dynamic surface. When fSEO films are immersed in water, the surfaces can rapidly restructure and expose PEO.

Introduction

The molecular compositions of surfaces in systems containing small amounts of block and graft copolymers are normally dramatically different from the bulk compositions. The reason for this difference is the ability of these copolymers to segregate at surfaces where they minimize the interfacial tension, γ. Provided that such a system is close to equilibrium, the surface free energies of the individual polymer segments of an A−B copolymer will determine whether it is the A or the B segment that will dominate the surface region. Addition of small amounts of A−B block and graft copolymers have been extensively investigated as a method to modify surfaces of polymer (A) materials, e.g., to obtain surfaces having low friction, improved adhesion, increased wettability, or decreased biofouling and protein adsorption.[1] In these systems, the A segments of the copolymer act as anchoring chains, extending into the polymer (A) matrix and securing the copolymer to the surface. The B segments function as the surface modifying chains, facing out into the surrounding medium, thereby providing the desired surface properties.

In many applications the orientation of block and graft copolymers at surfaces is of great importance because the desired properties may be critically linked to a particular surface structure. It is perhaps especially difficult to obtain the proper surface structure in instances when the anchoring chain (A) has a lower value of γ than the surface modifying polymer chain (B). An important case is when copolymers are utilized for preparing surfaces resistant to protein adsorption. One successful method to produce protein-resistant surfaces is to use copolymers with poly(ethylene oxide) (PEO) segments connected to a hydrophobic and water-insoluble polymer segment. Surfaces covered with PEO are thought to have a high degree of protein resistance because the high water content of the PEO layer produces a low value of γ at the polymer−water surface.[2−4] Also, a steric exclusion mechanism involving rapid chain mobility and surface dynamics of hydrated PEO segments has been proposed.[5] To optimize the effect of such a surface, the mobility of the PEO chains should be maximized and the surface should also be completely covered by PEO. However, when a biomedical material is coated with a PEO block or graft copolymer, the surface will most probably be dominated by the hydrophobic polymer block. Some degree of reorientation at the surface can be expected when the surface is exposed to, for example, blood or a protein solution. This process will, however, be slow if the mobility of the hydrophobic polymer is low, i.e., if it has a high glass transition temperature.

Early X-ray photoelectron spectroscopy (XPS) studies by Thomas and O'Malley on PS−PEO block copolymers showed that the outermost surfaces of these polymers were dominated by the PS blocks.[6,7] In the present paper the surface properties of PS−PEO block and graft copolymers having fluorinated PEO chain ends (fSEO) are described and compared with the surface properties of the corresponding copolymers having PEO chain ends terminated by hydroxyl groups (SEO). fSEO copolymers were prepared by esterification of the terminal hydroxyl groups of the SEO copolymers using heptafluorobutyric anhydride. It was expected that PS would dominate the surfaces of SEO. After functionalization of the PEO chain ends with heptafluorobutyric groups, enrichment of fluorinated groups at the polymer−air surface was expected. Because of the connectivity between the fluorinated groups and PEO, the fSEO copolymers were also anticipated to have a higher surface concentration of PEO than the corresponding SEO copolymers. Angle-dependent XPS and water contact angle measurements

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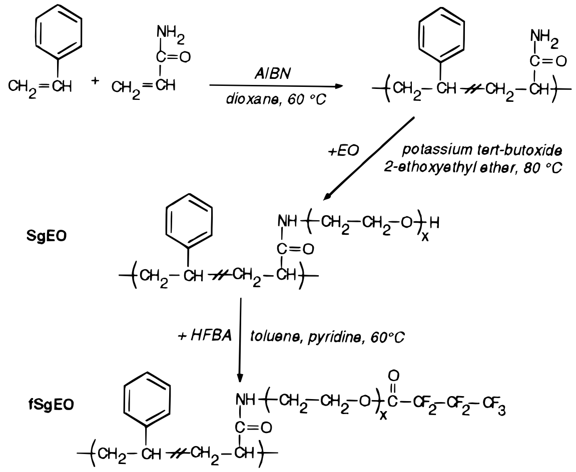
Scheme 1. Preparation Route of the fSgEO Copolymers, where the Styrene and Grafted Units in the Backbone Copolymer Were Distributed Statistically



were used to study the surface structure and dynamics of the copolymers.

Experimental Section

Materials. All solvents and chemicals were used without further purification. The SEO block copolymer (SbEO) was supplied by Polymer Source Inc. It was prepared by conventional sequential anionic polymerization of styrene and ethylene oxide in THF using cumylpotassium as initiator. The copolymer was analyzed by gel permeation chromatography (GPC) and ^{1}H NMR and was found to be free from impurities and to have the specified composition.

Two SEO graft copolymers (SgEO) were prepared according to the first part of the preparation route shown in Scheme 1. Styrene−acrylamide copolymers were synthesized by free radical copolymerization of styrene and small amounts of acrylamide, 1 and 10 mol % for SgEO-1 and SgEO-2, respectively. The copolymerization was performed in dioxane at 60 °C using 2,2′-azobisisobutyronitrile (AIBN) as initiator. The copolymers were purified and dissolved in 2-ethoxyethyl ether in a steel reactor. The reactor was degassed, and a solution of potassium *tert*-butoxide was injected through a septum by means of a syringe. A steel vessel containing ethylene oxide (EO) was connected to the reactor, and EO was transferred to the reactor gradually by self-distillation at ambient temperature. The grafting reaction was allowed to continue under isobaric (∼1.5 bar absolute pressure) conditions at 80 °C until all of the EO had been consumed.

The SgEO copolymers were precipitated from the reaction mixture in cold hexane, and after drying, the precipitates were successively leached with distilled water to remove salt and homoPEO. The copolymers were characterized by a combination of elemental analysis, ^{1}H NMR, and GPC. Further details of the preparation and characterization of these copolymers have been reported in a previous paper.[8]

The PEO chain ends of the SbEO and SgEO copolymers were fluorinated by reacting the terminal hydroxyl groups with heptafluorobutyric anhydride (HFBA). A mixture of toluene (p.a. grade, Romil Ltd.) containing a catalytic amount of dry pyridine (p.a. grade, Romil Ltd.) was used as reaction medium. The copolymers were dried under vacuum and then dissolved in the reaction medium (5% w/v) in a three-necked glass flask equipped with an argon inlet/outlet, a rubber septum, and a magnetic stirrer. After degassing, the reactor was brought to 60 °C, and an amount of HFBA (p.a. grade, Fluka AG) corresponding to 2 molar equiv of the hydroxyl groups was injected. The fluorination was allowed to continue for 12 h under argon.

The fluorinated block and graft copolymers, designated fSbEO and fSgEO, respectively, were precipitated from the reaction mixtures in diethyl ether cooled by dry ice. The precipitates were successively washed with a large excess of cold fresh diethyl ether to remove HFBA species. Finally, the purity of the fSEO copolymers was checked by GPC. The degree of fluorination, i.e., the percentage of fluorinated PEO chain ends, was determined by triplicate elemental analyses. The structural characteristics of the fSbEO and fSgEO copolymers are shown in Tables 1 and 2, respectively.

Table 1. Molecular Data of fSbEO

$\bar{M}_n$ of PS Block	$\bar{M}_n$ of PEO Block	$\bar{M}_w/\bar{M}_n$	PEO content (wt %)	degree of fluorination (%)
29800	8400	1.03	22	88

Table 2. Molecular Data of fSgEO

sample designation	$\bar{M}_n$ of PS backbone	$\bar{M}_n$ of PEO grafts	PEO content (wt %)	degree of fluorination (%)
fSgEO-1	10000	2500	55	87
fSgEO-2	80000	5000	29	94

The melting points of the SEO copolymers were determined with a Perkin-Elmer Pyris 1 differential scanning calorimeter (DSC). The samples, contained in aluminum pans, were first annealed at 100 °C for 5 min. After the samples were cooled down to 0 °C and retained at this temperature for 5 min, the samples were reheated to 100 °C. The temperature scan rate was 10 °C/min, and the melting points were evaluated from the last scan.

Copolymer films were cast from dilute chloroform solutions (2.5% w/v) onto glass wafers. The volume of deposited solution was chosen to obtain film thicknesses of approximately 50 μm. All films were annealed at 100 °C for 1 h under argon atmosphere prior to analysis. Polymers containing HFB groups have been reported to be thermally stable up to 430 °C under nitrogen atmosphere.[9] No signs of degradation were observed by XPS after annealing the samples in the present investigation.

XPS. Angle-dependent XPS analysis (ADXPS) was performed with a SpecsLab Sage 100 instrument. Spectra were acquired from a 1 × 2 mm^2 sample region illuminated by an Mg X-ray source operating at 100 W. The chamber pressure was $<10^{-7}$ mbar during analysis, and electron flooding was not used to offset charging. Survey scans were performed on each sample to ensure that no foreign elements were present. High-resolution scans of the C_{1s}, O_{1s}, and F_{1s} regions were acquired with a pass energy of 16 eV. Data were collected at 30, 45, and 90° takeoff angles (TOA) between the sample and the analyzer. No sample degradation, e.g. fluorine depletion, was detected after using the above conditions.

Atomic surface compositions were determined after including the appropriate instrumental sensitivity factors. The spectra were corrected to align the C−C component of the C_{1s} region to 285.0 eV. Peaks in the C_{1s} region were resolved into contributions of different chemical components corresponding to segments and functional groups of the polymers by use of a curve fitting program. Peak positions were allowed to vary during the fitting procedure. Peaks from O−C and F−C were found at 534 and 689 eV, respectively, and peaks in the C_{1s} region from C−O, C−F_2, and C−F_3 were found at 286.5, 293.0, and 295.7 eV, respectively. Because of their low concentrations, the curve fitting program was unable to resolve peaks for the C=O and the O=C components, which are normally observed at 289 and 533 eV, respectively.

The molar monomer unit surface concentrations were evaluated from information in the C_{1s} regions of the spectra. The monomer concentrations of heptafluorobutyryl (HFB), ethylene oxide (EO), and styrene (S) were calculated by first integrating the resolved peak areas associated with C−C, C−O, C−F_2, and C−F_3, designated A_1, A_2, A_3, and A_4, respectively. Finally, the molar monomer concentrations were calculated as follows:

$$\% \text{ HFB} = \frac{(A_3 + A_4)/3}{A_1/8 + A_2/2 + (A_3 + A_4)/3} \quad (1)$$

$$\% \text{ EO} = \frac{(A_2)/2}{A_1/8 + A_2/2 + (A_3 + A_4)/3} \quad (2)$$

$$\% \text{ S} = \frac{(A_1)/8}{A_1/8 + A_2/2 + (A_3 + A_4)/3} \quad (3)$$

Because of their low concentrations, contributions from the carbonyl groups in HFB and from the acrylamide units in the graft copolymers were neglected.

Contact Angle Measurements. The films were placed in different environments, i.e., water at 21 °C, air at 21 °C, and vacuum at 100 °C, to study surface dynamics. After immersion, and prior to measurements, excess water was removed by centrifugation of the films. Water contact angle measurements were carried out with a Leitz sessile drop contact angle meter. A 5 μL droplet of Milli-Q water was deposited on the film surface by means of a microsyringe, and the advancing contact angle, θ_a, was measured. At least four measurements of θ_a were made at different positions on each film. The standard deviation was in all cases below 3°.

Results and Discussion

The surface behavior of block and graft copolymers is dependent on parameters such as chemical structure, composition of each polymer segment, glass transition temperature, melting temperature, and surface energy.[1] For the SEO and fSEO copolymers, the first two parameters were controlled by the structural characteristics given in Tables 1 and 2. The calculated PEO chain end concentrations for SbEO, SgEO-1, and SgEO-2 were 26, 220, and 58 μmol/g, respectively. It was found by elemental analysis that between 87 and 94% of PEO chain ends were fluorinated in the fSEO copolymers, and no further efforts were made to optimize the reaction conditions to reach higher degrees of fluorination. The PS segments of the copolymers can be expected to have a glass transition temperature close to that of PS, i.e., approximately 100 °C. The melting point of the PEO side chains depends on their chain lengths and were found by DSC to be 42, 41, and 58 °C for SgEO-1, SgEO-2, and SbEO, respectively. PS has γ equal to 41 mJ/m^2. Fluorinated polymers are known for their low values of γ, e.g. poly(tetrafluoroethylene) (PTFE) and poly(hexafluoropropylene) have γ equal to 23 and 17 mJ/m^2, respectively.[10] A surface closely packed with HFB groups should have a γ close to that of completely fluorinated polymers, i.e., less than 23 mJ/m^2. While the γ of dry PEO is 44 mJ/m^2, a fully hydrated PEO surface can be expected to have a γ approaching that of water, i.e., approximately 73 mJ/m^2.[10]

XPS. Angle-dependent XPS (ADXPS) was used to quantify the surface composition of the different copolymers. The sampling depth was varied by collecting data at takeoff angles (TOA) between the sample surface and the analyzer of 90, 45, and 30°. Consequently, the sampling depth was directly proportional to sin(TOA), and the sampling depth at 30° TOA was thus half that at 90° TOA. Survey scans of SbEO and fSbEO are shown in Figure 1, while Figure 2 shows the surface atomic concentrations of the copolymer films. The surface concentration of O was much higher for all the fSEO copolymers, as compared to the corresponding SEO copolymers. Furthermore, when the sampling depth was decreased, the concentration of O decreased for the SEO copolymers, while it increased for the fSEO copolymers.

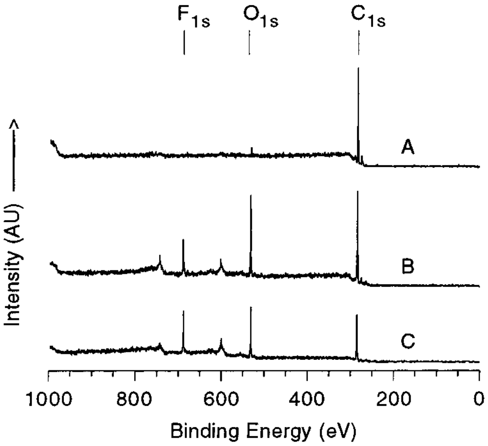


Figure 1. XPS survey scans for (A) SbEO, 90° TOA, (B) fSbEO, 90° TOA, and (C) fSbEO, 30° TOA.

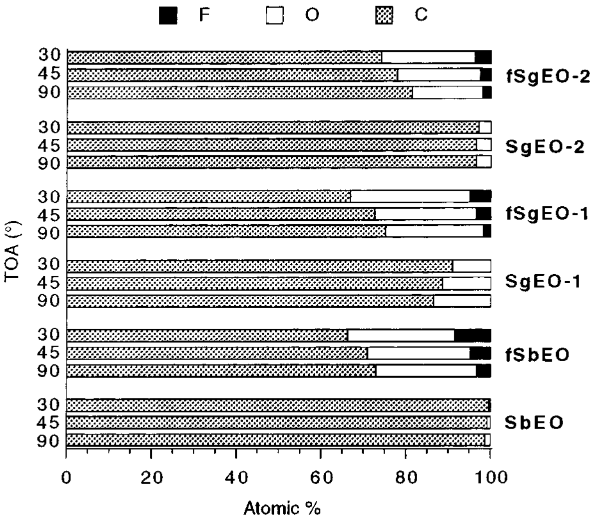


Figure 2. Surface atomic % at different TOA:s for SEO and fSEO copolymers.

Figure 3 shows the resolved C_{1s} regions of SgEO-1 and fSgEO-1. The C_{1s} regions of the SEO copolymers showed contributions from C−O elements at 286.5 eV and C−C elements at 285.0 eV, arising from EO and S monomer units, respectively. Also seen were $\pi-\pi^*$ shake-up satellite peaks from the PS phenyl groups at 291 eV. The C_{1s} region of SgEO-1 was dominated by the C−C signal, with only a small contribution of C−O, and showed that the surface region mainly contained PS. This was as expected because PS was the most hydrophobic component in the SEO copolymers. In addition to signals from C−O and C−C elements, the C_{1s} regions of the fSEO copolymers also contained signals from $C-F_2$ and $C-F_3$ elements at 293.0 and 295.7 eV, respectively, arising from the HFB units. In contrast to what was observed with the SEO samples, the surface regions of fSEO were dominated by PEO. This was indicated by a large signal from C−O elements, as compared to the C−C signal, in the spectrum shown in Figure 3B. The observations made in the C_{1s} region of the spectra were thus in agreement with results obtained when comparing the signals from the different atomic species.

The monomer unit concentrations at the different sampling depths were evaluated from information ob-

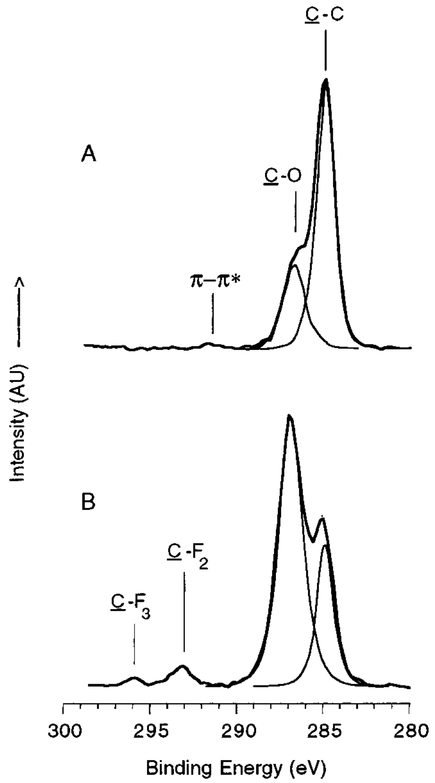


Figure 3. Raw and curve-fit data of the C_{1s} region of SgEO-1 (A) and fSgEO-1 (B) collected at 45° TOA.

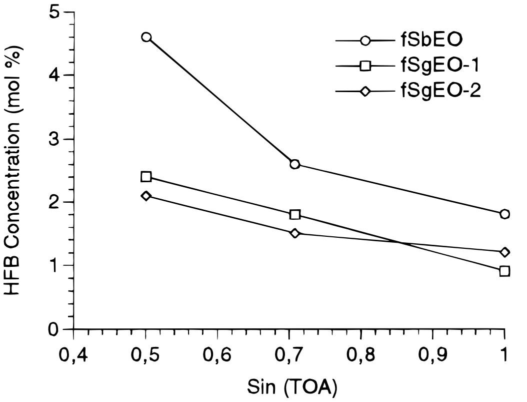


Figure 4. Percent HFB units vs sin(TOA) for the fSEO copolymers as determined from data in the C_{1s} region.

tained in the C_{1s} regions of the spectra. Figure 4 shows the surface concentration of HFB units as a function of sin(TOA). As expected, the concentration of HFB units increased with decreasing sampling depth for all the fSEO copolymers. The concentration was slightly above 2 mol % for the fSgEO copolymers at 30° TOA, while fSbEO had a concentration approximately twice as high. The calculated HFB bulk concentrations were 0.2, 1.3, and 0.4 mol % for fSbEO, fSgEO-1, and fSgEO-2, respectively. When the sampling depth was decreased by a factor 2, from 90 to 30° TOA, the HFB concentration roughly doubled for all the fSEO copolymers. This indicated that the HFB units were preferentially located at the top few angstroms of the surface. The low value of γ of the HFB units made it likely that the surfaces of the fluorinated copolymers were covered by these units. The observed concentrations approximately corresponded to 4.4, 2.1, and 1.9 Å thick HFB layers for fSbEO, fSgEO-1, and fSgEO-2, respectively. These values were obtained under the assumption that the maximum sampling depth was ~40 Å at 30° TOA and that the surfaces of the fSEO copolymers were covered by layers of HFB groups, density ~ 2 g/cm^3, with underlying zones of pure PEO, density ~ 1.1 g/cm^3. Although conformational entropy considerations favor the surface segregation of chain ends as such, the effective reduction in the value of γ can be considered to be the strongest driving force for the surface segregation of HFB groups. However, the surface segregation of HFB groups can be expected to be limited by unfavorable stretching of the anchored chains beyond their random flight conformation when the packing density of HFB units increases at the surface. It may be that there were severe conformational restrictions when chain ends of branched fSgEO were packed at the surface, thereby limiting the HFB surface concentration. There might have been less conformational restrictions when chain ends of linear fSbEO copolymers were packed at the surface, thereby allowing a higher HFB surface concentration.

de Gennes has argued that the extent of chain end segregation to a surface is controlled by the difference in γ between an infinite polymer chain and the end groups.[11] Especially if the difference in γ between the polymer chain segments and the chain ends is comparable to the thermal energy, all chains closer than two times the radius of gyration, R_g, from the surface will tend to localize their ends at the surface.[11] This implies that A–B block copolymers in which the size of the B block is only a very small fraction of the total block copolymer size will also segregate at surfaces when blended into polymer A. It is required that the B block has a strong affinity to the surface. If a segregation at the polymer-air surface is desired, the B block should have a low value of γ. Recent investigations have shown that homopolymers with fluorinated chain ends have a preferential segregation to the polymer–air surface. PS terminated by fluorinated end groups have been investigated by neutron reflectivity,[12,13] XPS,[13–15] ion scattering spectroscopy,[15] and secondary ion mass spectroscopy.[14,15] In all cases, the fluorinated end groups were found to be strongly surface segregated. By contrast, a surface depletion of chain ends with high values of γ have been observed for PS having terminal carboxylic acid groups.[13] Su et al. have studied surfaces of PEO end-capped with perfluorodecanoyl groups.[16] They found by XPS that the surfaces contained a large excess of fluorocarbon groups, occupying the outermost ~5 Å of the polymer–air interface. The zone immediately beneath the highly fluorinated surface region was found to be depleted of fluorine. The molecular weight of PEO was found to only have a slight effect on the surface fluorine contents. Further, the advancing contact angle, θ_a, of hexadecane on surfaces of fluorinated PEO was found to be closer to that of PTFE than to that of a surface covered by $-CF_3$ groups. From these results, the authors concluded that the fluorocarbon groups were lying reasonably close-packed at the surface, exposing mainly $-CF_2-$ units.

Figures 5 and 6 show the concentrations of EO and S units, respectively. Common for all the copolymers was that the surface concentration of EO was higher for the fSEO copolymers, as compared to the corresponding SEO copolymers. Furthermore, the EO concentration decreased with decreasing sampling depth for all the SEO copolymers. In contrast, the EO concentrations

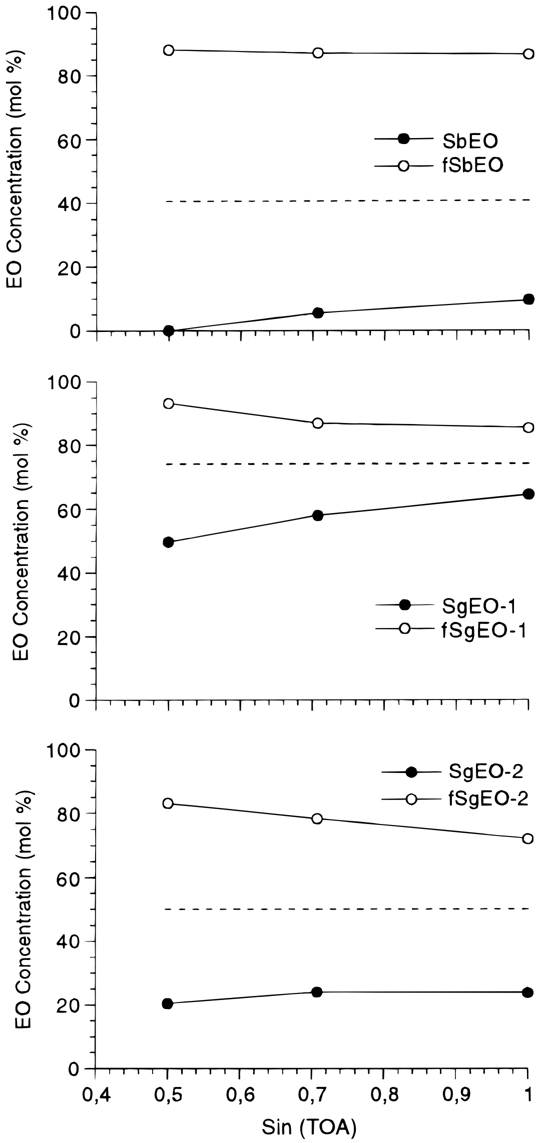


Figure 5. Percent EO units vs sin(TOA) as determined from data in the C_{1s} region. The dashed lines indicate bulk concentrations.

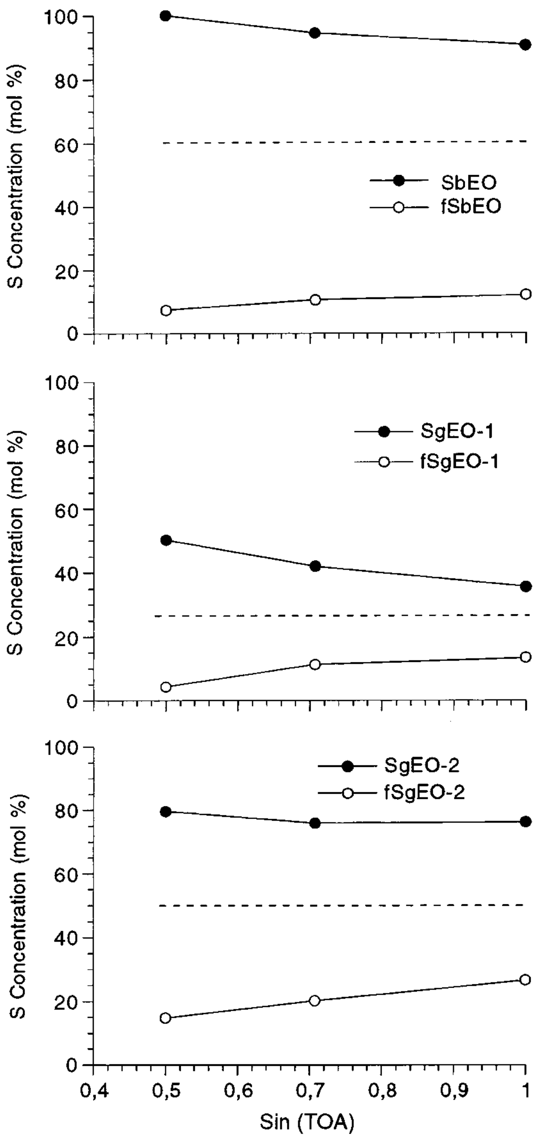


Figure 6. Percent S units vs sin(TOA) as determined from data in the C_{1s} region. The dashed lines indicate bulk concentrations.

increased with decreasing sampling depth for the fSEO copolymers, however only slightly for fSbEO. These general observations are in agreement with those made in Figure 2. As is seen in Figure 5, the EO concentrations of SgEO-2 differed more from the bulk concentration than SgEO-1. This observation was consistent with the molecular structure of the SgEO copolymers, i.e., the higher segmental molecular weights of the SgEO-2 segments allowed for a higher degree of surface segregation of the polymer segments, as compared to SgEO-1. The PEO side chains grafted on the PS backbones of SgEO-1 and SgEO-2 were spaced by PS segments having weight average molecular weights of 3600 and 19000, respectively. By using

$$\frac{R_g}{(\bar{M}_w)^{0.5}} = 0.275\ \text{Å} \qquad (4)$$

for glassy PS, the radius of gyration, R_g, of these segments were estimated to be 17 and 38 Å, respectively.[17] On the basis of an estimated inelastic mean free path of a C_{1s} photoelectron of 27 Å originating from organic materials,[18] 30, 45, and 90° TOA correspond to sampling depths down to 41, 57, and 81 Å, respectively. Thus, the maximum sampling depth at 30° TOA was comparable with the chain dimensions of SgEO-2 but was approximately twice as large as the chain dimensions of SgEO-1.

SbEO contained 40 mol % PEO. As can be seen in Figure 5, the EO concentration of SbEO detected at 30° TOA was 40% lower than the bulk concentration, while the corresponding EO concentration of fSbEO was 49% higher than the bulk concentration. Of the studied copolymers, SbEO had the largest chain dimensions and also showed the largest difference in EO surface concentration before and after fluorination. The PS block of SbEO had a weight average molecular weight of 30 700, which corresponded to an R_g of 48 Å. Thus, the R_g of the PS block was slightly higher than the sampling depth at 30° TOA, and consequently the space of analysis at this TOA may be completely occupied by PS blocks. It should however be mentioned that eq 4 only gives estimated values of R_g. The reason for this is that unfavorable stretching of the PS segments, beyond the random flight confirmation normally displayed by glassy

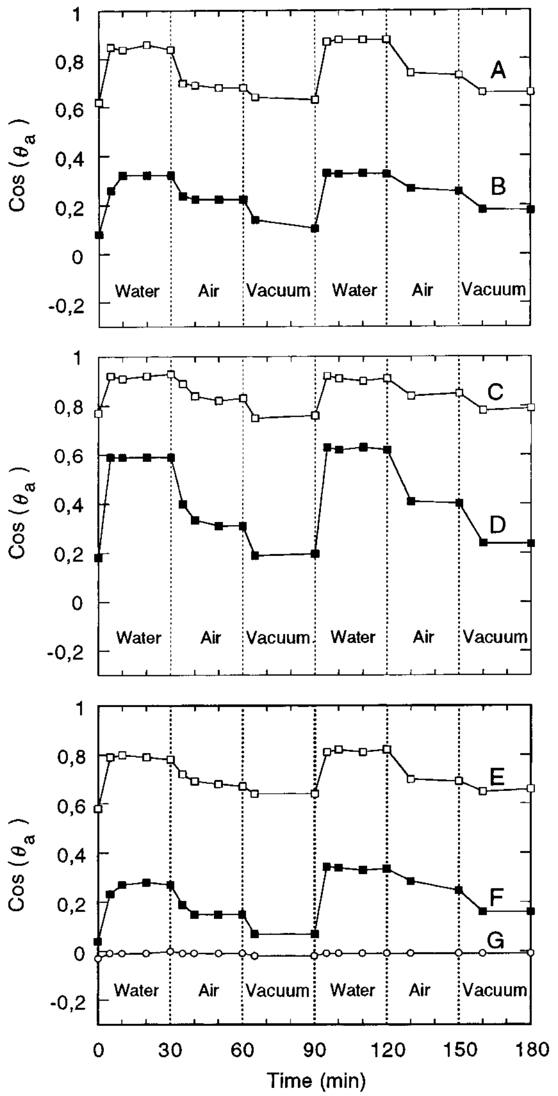


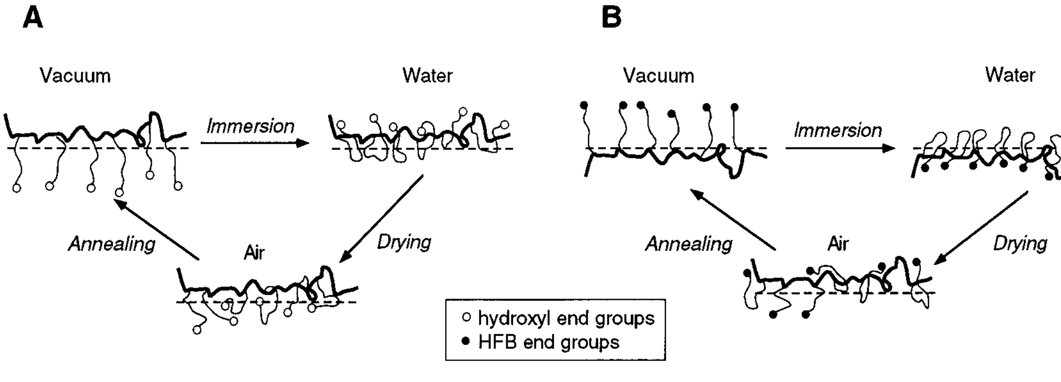
Figure 7. cos(θ_a) measured on fSbEO (A), SbEO (B), fSgEO-1 (C), SgEO-1 (D), fSgEO-2 (E), SgEO-2 (F), and PS (G) surfaces after exposing the annealed films to water at 21 °C, air at 21 °C, and vacuum at 100 °C (annealing).

PS, may occur as a consequence of constraints at the surface. At 30° TOA, the curve fitting program was unable to resolve a peak for the *C*-O component of SbEO. Although a small oxygen peak indicated that some EO units were present in the surface region, the S concentration was essentially 100%, as seen in Figure 6.

Contact Angle Measurements. Most polymer surfaces are dynamic with segments rotating and diffusing in varying degrees depending on the temperature and polymer structure. Chain segments at polymer surfaces normally have a higher degree of mobility as compared to segments in the bulk. The orientation and mobility of the surface segments are further affected by the nature of the surrounding medium. Minimization of γ between the polymer and the surrounding medium is the thermodynamic driving force for reorientations at the surface. Many studies of surface dynamics have been performed on block and graft copolymers.[1] The surface dynamics of the copolymers in the present study were investigated by water contact angle measurements. Contact angles are controlled by the outermost few angstroms of polymer materials and are thus strongly affected by the orientation and mobility of the segments and functional groups present at the surface. The copolymer films were exposed to different media, and the ability of the copolymers to restructure was studied by advancing water contact angle measurements. The annealed films were first immersed in water for 30 min, then dried under air at ambient temperature for 30 min, followed by annealing again at 100 °C under vacuum for 30 min. This cycle was repeated once more for each sample.

Figure 7 shows the variation of cos(θ_a) of the copolymers and PS during the time of the two cycles. The results obtained with the SEO copolymers, plotted with filled markers, are considered first. The initial θ_a's of the annealed SEO samples were only slightly lower than that of PS. Notably, the θ_a of SgEO-1 was lower than for the other two copolymers. When the films were immersed in water, the θ_a's decreased sharply to reach plateau values. The θ_a's of SbEO and SgEO-2 decreased to approximately the same level, while the θ_a of SgEO-1 decreased to a significantly lower level. It seems likely that the decrease in θ_a during water immersion was a result of reorientation of PEO segments to the outermost surface layer in combination with swelling of this layer. When dried under air, the θ_a's increased again to reach another plateau value. After annealing in a vacuum, the initial θ_a's measured before immersion were essentially reestablished. The values of the θ_a decreased again after immersion during the second cycle, but to a level slightly lower than that reached during the first cycle. After drying under air, and after annealing, the θ_a's were lower than corresponding θ_a's measured during the first cycle. It may be that some change in the surface structure had been introduced during the cycles.

Scheme 2. Graphic Representation of the Molecular Restructuring of SgEO (A) and fSgEO (B) Copolymers at the Surface When Exposed to Different Environments, Where the Thick and Thin Lines Represent PS and PEO Chains, Respectively, the Dashed Lines Indicate Film Surfaces, and the Circles Indicate End Groups



The surface dynamics of the fSEO copolymers was similar to that of the corresponding SEO copolymers, as seen in Figure 7. However, an important observation was that the surfaces of the fSEO copolymers all had markedly lower θ_a's than the corresponding SEO copolymer. Fluorinated groups located at the outermost surface normally give high values of θ_a, e.g. PTFE has a θ_a of 108°.[10] Surfaces reasonable close-packed with HFB groups should similarly have high values of θ_a. This implies a reorientation of the fSEO copolymers at surface when the films were exposed to water. Furthermore, this reorientation was occurring faster than the time scale of the contact angle measurement. The rapid reorientation of the HFB groups to yield a hydrophilic surface was consistent with the presumably high mobility of the HFB groups, and the high concentration of PEO segments in the surface region.

Scheme 2, which is based on the experimental information obtained in this study, shows a graphic representation of the dynamics of the copolymers. Surface regions of annealed SEO copolymers are dominated by PS segments. When a SEO surface is immersed in water, there is some degree of reorientation of PEO segments to the outermost surface, where hydration and swelling take place. However, this process is probably limited by the low mobility of the PS segments. After drying under air, the PEO segments are partly dehydrated and oriented toward the bulk. During annealing, the last water residues are removed, and it is likely that enough mobility is induced in the surface region for the PS segments to diffuse to the outermost surface again. On the other hand, surfaces of annealed fSEO copolymers have HFB groups segregated at the outermost surface, and the region immediately below is dominated by PEO. When such a sample is immersed in water, the highly mobile HFB chain ends rapidly diffuse from the surface, away from the water. PEO is now facing the water and, as a consequence of the connectivity between PEO and HFB, may form loops at the surface. After drying under air, the PEO is partly dehydrated and oriented toward the bulk. During annealing, the mobility in the surface region is probably high enough for the copolymer to rearrange back to a configuration with HFB groups segregated at the outermost surface.

Conclusions

After modification of the SEO copolymer structure by attaching HFB groups at the PEO chain ends, the molecular orientation in the surface region was "inverted" as compared to the unmodified copolymer. The surface region of the unmodified copolymers was dominated by PS, while the surface region of the modified copolymers was dominated by PEO, with fluorinated groups segregated at the outermost few angstoms. This finding implies it is possible to control the surface composition, within the limits defined by the surface compositions of the completely chain end fluorinated and the nonfluorinated copolymer, by changing the degree of chain end fluorination. Although the SgEO copolymers in this study had a higher bulk concentration of fluorinated chain ends than the SbEO copolymer, they had lower surface concentrations of fluorinated chain ends. However, the data are too limited to arrive at a general conclusion.

It is likely that the surfaces of the fSEO films appeared hydrophilic because of a highly dynamic behavior involving reorientation of the fluorinated chain ends. Hydrophobic recovery, which is often observed with hydrophilic surfaces in contact with air, was prevented because the structure with the HFB groups at the surface was thermodynamically stable under air and vacuum. Low values of θ_a were thus retained even after prolonged annealing. Because of their higher PEO concentrations, fSEO surfaces may be more resistant to protein adsorption than SEO surfaces. It is probable that the PEO chains of fSEO copolymers form loops at the polymer−water surface, while the PEO chains of SEO may stretch out into the surrounding water. This difference in conformation may, together with the PEO surface concentration, have a large influence on the protein resistance.

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