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Adsorption of End-Functionalized Poly(ethylene oxide)s to the Poly(ethylene oxide)−Air Interface

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ABSTRACT: Samples with one or both ends of monodisperse poly(ethylene oxide) (PEO) functionalized with perfluorodecanoyl groups (PEO^F or PEO^{2F}) were synthesized and blends of these end-capped PEOs with PEOs of the same molecular weight (M_n ~2000 to ~16 000 K) were prepared as cast films. As-cast and annealed samples were analyzed by X-ray photoelectron spectroscopy (XPS) and contact angle analysis. XPS analysis was also performed on samples at elevated temperatures (melts). Due to the lower surface energy of the fluorocarbon end groups, the modified PEOs preferentially adsorb to the free polymer surface. The surface concentration of the perfluoroalkyl end groups was measured by XPS which indicates that perfluoroalkyl chain ends adsorb to the polymer surface in a reasonably close-packed fashion (at all molecular weights) and leave a zone depleted of fluorine immediately beneath the highly fluorinated surface region. The dependence of adsorption on temperature was investigated for one sample and adsorption appears to be slightly favored at lower temperatures. PEO^{2F} samples are found to have a slightly higher surface affinity than PEO^F of the same molecular weight. There is only a slight effect of molecular weight on surface fluorine content, indicating a "stretched brush" conformation for the higher molecular weight samples.

Introduction

The surface composition and interfacial properties of multicomponent organic polymers can be significantly different from those of the bulk. Polymer surfaces can reconstruct in response to environmental changes to minimize (or lower) interfacial free energy by segregating their low surface energy components at the interface. This phenomenon has been observed in homopolymers, modified homopolymers, copolymers, and polymer blends and has been reviewed previously.[1−3] Monodisperse end-functionalized polymers and block copolymers have proven to be useful model systems to study surface segregation; element and/or isotope labels that are sensitive to appropriate analytical techniques can be conveniently incorporated into well-controlled polymer structures. Several groups have recently shown that perfluoroalkyl groups which are incorporated into polystyrene are surface-active.[4−9] X-ray photoelectron spectroscopy and contact angle and other techniques indicate a surface excess (over the bulk) of fluorine due to the adsorption (surface segregation) of the low surface energy fluorocarbon at the polymer−air interface. Similar results using poly(dimethylsiloxane) as the surface-active component have been described.[10]

In this paper we report the results of surface analyses of blends of perfluorodecanoyl-modified poly(ethylene oxide)s (surface-active polymers) with unmodified (alcohol-terminated) poly(ethylene oxide)s (matrix polymers) of the same molecular weight. Samples with perfluorodecanoyl groups at one chain end of poly(ethylene oxide) (PEO^F) and at both PEO termini (PEO^{2F}) were studied as well as the effects of PEO molecular weight and temperature. The driving force for chain end segregation at (adsorption to) the polymer−air interface is the reduction of surface free energy: PEO exhibits a surface tension of 43 dyn/cm[11] and a perfluoroalkyl surface should exhibit a surface tension less than 20 dyn/cm (the surface tension of poly(tetrafluoroethylene) is 18.5 dyn/cm[11]). Accompanying and opposing the adsorption of perfluorodecanoyl groups is the unfavorable entropic contribution associated with PEO chain stretching that must occur to concentrate perfluorodecanoyl groups at the surface. The surface excess of perfluorodecanoyl groups should be determined by a balance between the opposing forces of surface energy reduction (enthalpic) and chain stretching (entropic). The entropic contribution should be molecular weight dependent and we expect, *a priori*, to be able to control the fluorine content with the surface-active polymer molecular weight. The entropic contribution should also depend on temperature, and one surface-active polymer was studied in this regard.

Experimental Section

General Information. Poly(ethylene oxide) diol samples were purchased from American Polymer Standards Corp. and Polysciences. Monohydroxyl poly(ethylene oxide) samples were purchased from Polymer Laboratories. Chloroform, methanol, and hexane (Fisher HPLC grades) were used as received. Benzene (Fisher HPLC grade) was distilled from CaH_2; THF (Aldrich, anhydrous) was distilled from the sodium benzophenone dianion.

X-ray photoelectron spectra were collected using a Perkin-Elmer Physical Electronics 5100 spectrometer equipped with a specimen heater controller using Mg Kα (200 W, 15 kV) (achromatic) excitation. Spectra were acquired at both 15 and 75 takeoff angles (between the sample plane and detector); samples were exposed to X-rays for less than 10 min using pass energies of 89.45 and 39.75 eV for survey and C_{1s} region spectra, respectively. X-ray damage (loss of fluorine intensity) was not observed under these conditions, but was with longer acquisitions at higher X-ray power. Atomic sensitivity factors were determined using samples of known composition: F_{1s}, 1.000; C_{1s}, 0.250; O_{1s}, 0.660. Contact angle measurements were made with a Ramé-Hart telescopic goniometer using a Gilmont syringe with a 24-gauge flat-tipped needle. Hexadecane was used as the probe fluid. Dynamic advancing (θ_A) and receding angles (θ_R) were recorded while hexadecane was added to and withdrawn from the drop, respectively. Infrared spectra were recorded on a Perkin-Elmer System 2000 FT IR; ^1H NMR spectra were recorded at 200 MHz using a Bruker AC 200 spectrometer. Microanalyses (C, H, F) were performed by the University of Massachusetts Microanalysis Laboratory.

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Table 1. Surface-Active Polymers

sample	M_n	M_n/M_w	reacn yield (%)	conversion (%) anal.	IR	NMR
$^{3K}PEO^{2F}$	3100	1.06	45	95	95	92
$^{8K}PEO^{2F}$	7720	1.04	33	94	94	84
$^{15K}PEO^{2F}$	15260	1.18	53	92	94	79
$^{2K}PEO^{F}$	1900	1.05	58	53	58	49
$^{16K}PEO^{F}$	16350	1.02	60	90	87	61

Perfluorodecanoyl Chloride. Under a nitrogen purge, 25 g (~0.048 mol) of nonadecafluorodecanoic acid (Aldrich) and 31.4 g (~0.144 mol) of phosphorus pentachloride (Aldrich) were placed in a round bottom flask equipped with a Teflon-coated magnetic stir bar and a reflux condenser. The flask was cooled to ~0 °C in an ice bath, ~250 mL of benzene was added by cannula, and the solution was stirred for ~1 h. The ice bath was replaced with an oil bath, the solution was heated gently to a slow reflux and allowed to reflux overnight under nitrogen. The flask was cooled to room temperature; the acid chloride precipitated. The supernatant was removed by cannula and the acid chloride was redissolved in fresh benzene with gentle heating. Recrystallization was repeated until the crystals were white and the supernatant was clear. The residual benzene was removed by freeze-drying. The perfluorodecanoyl chloride (yield 55%) was stored refrigerated under nitrogen.

PEO Derivatizations. Samples (1.0 g) of monohydroxy or dihydroxy PEO were dissolved under nitrogen in ~30 mL of dry THF with gentle heating in a round bottom flask equipped with a Teflon-coated magnetic stir bar and a reflux condenser. A ~2-fold excess of perfluorodecanoyl chloride was added via syringe. The solution was stirred overnight at 50−60 °C, after which the solution was allowed to cool to room temperature. The polymer was precipitated in ~200 mL of hexane which had been cooled to ~0 °C using an ice bath. The polymer was collected by filtration and redissolved in ~15 mL of chloroform; then the polymer solution was passed through a basic alumina (Aldrich, activated Brockmann I, standard grade) column (1 × 8 cm). The column was washed with 100 mL of chloroform/methanol (4/1 v/v), and the solvent was removed by freeze-drying. The polymer was dissolved in ~30 mL of THF, precipitated in ~200 mL of cold hexane, collected by filtration, and dried under vacuum. Table 1 presents the characteristics, yields, and conversions for the end-functionalized PEOs prepared and used in this study.

Blend Sample Preparation. The polymer blend samples were prepared by dissolving various ratios of modified and unmodified PEO samples in chloroform (~4 weight % solutions) and casting solutions on silicon wafers. The volume of polymer solution used was chosen to yield films with thicknesses of ~8 μm.

Results and Discussion

Surface-Active Polymer Synthesis. Five samples of reasonably monodisperse poly(ethylene oxide) (PEO) of varying molecular weights were obtained from commercial suppliers and used without further purification. Three of the samples contain an alcohol functionality at both chain ends and two are monofunctional (methoxy groups at one end and alcohols at the other terminus). The molecular weight and polydispersity data (provided by the suppliers) for these samples are shown in Table 1. Each of these samples was modified by reaction with perfluorodecanoyl chloride to yield perfluorodecanoyl-terminated PEOs (surface-active polymers) (eq 1). The samples are named using abbreviations where the superscript preceding PEO indicates the molecular weight and the superscript following PEO indicates the end-group functionality. Examples are $^{3K}PEO^{2F}$ which describes a $M_n = 3000$ PEO containing perfluorodecanoyl groups at both chain ends and $^{16K}PEO^{F}$ which describes a $M_n = 16\ 000$ PEO containing one perfluorodecanoyl end group. Samples were purified by chromatography using basic alumina; this procedure removes perfluorodecanoic acid that is present in unpurified samples. Figure 1 shows carbonyl regions of infrared spectra of the surface-active polymers; the insert shows spectra of ^{16K}PEO and $^{16K}PEO^{F}$ before chromatography and purified $^{16K}PEO^{F}$. The absence of bands at 1729 (free acid) and 1693 cm^{-1} (acid dimer) in the purified sample indicates that no perfluorodecanoic acid is present and supports our contention that all fluorine in the sample is attached to polymer chain ends. The absence of perfluorodecanoic acid in all samples was confirmed by infrared spectroscopy. Table 1 reports yields of esterification reactions and conversion data (percent of alcohols that react to form perfluorodecanoates) that were measured by elemental analysis, infrared spectroscopy, and proton NMR. The NMR data were obtained by ratioing the integration values of the peaks at δ 4.5 ($-CH_2OC(O)C_9F_{19}$) and δ 3.7 ($-CH_2CH_2O-$). The IR data were obtained by ratioing the absorbance values of the carbonyl (1781 cm^{-1}) and CH_2 stretching bands (2884 cm^{-1}) and assuming that the ratio of the bands in the spectrum of $^{3K}PEO^{2F}$ indicates a 95% yield (analytical data). The NMR data are not uniformly consistent with the IR and elemental analysis data, and we suspect that the NMR data are compromised by ratioing very small to very large integration data. The reaction yields and end-group conversions for these polymer modifications were not optimized, as the samples were used to prepare blends with unmodified PEOs. The compositions of blends of surface-active polymer and matrix polymer (unmodified PEO) were determined using the elemental analysis conversion data, and we assume that the unconverted PEO in the surface-active polymer samples is identical to that in the matrix polymer. The PEO^{2F} samples contain a small amount (less than 10%) of monofunctional (PEO^{F}) polymer.

$$PEO-(OH)_{1\text{ or }2} \xrightarrow{C_9F_{19}COCl} PEO-(OC(O)C_9F_{19})_{1\text{ or }2} \quad (1)$$

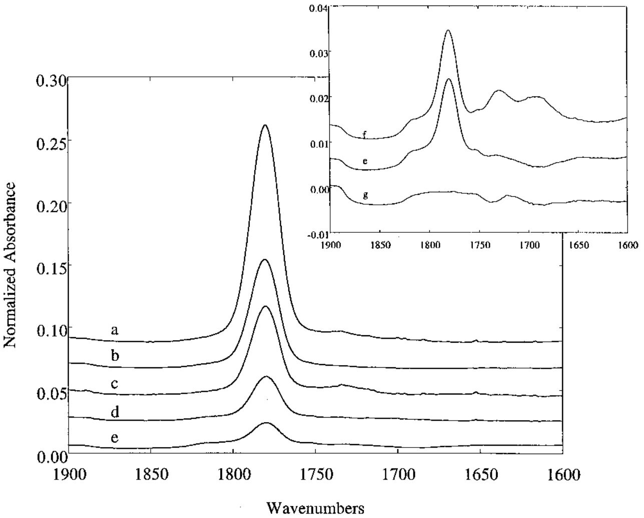

Figure 1. Carbonyl regions of infrared spectra of surface-active polymers: (a) $^{3K}PEO^{2F}$; (b) $^{2K}PEO^{F}$; and (c) $^{8K}PEO^{2F}$; (d) $^{15K}PEO^{2F}$; (e) $^{16K}PEO^{F}$. The insert contains spectra of (f) $^{16K}PEO^{F}$ before purification, (e) purified $^{16K}PEO^{F}$, and (g) ^{16K}PEO.

Much of the data that we discuss below involves variable takeoff angle X-ray photoelectron spectroscopy (XPS). Spectra were recorded at two takeoff angles: 15 and 75° (between the plane of the film and the entrance lens of the detector optics). Figures 2 and 3 show survey

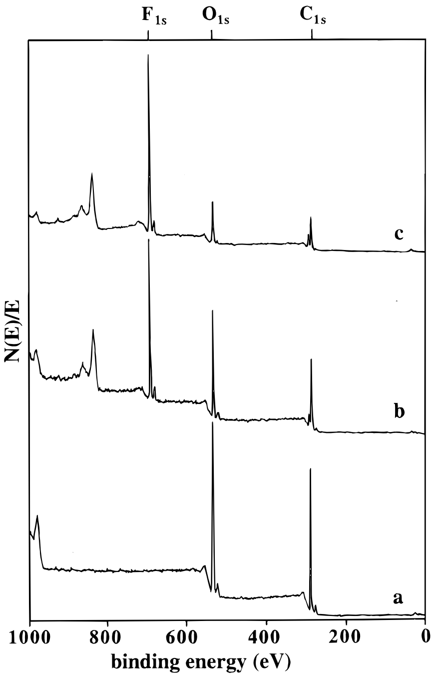

Figure 2. XPS survey spectra for (a) ^{3K}PEO (75° takeoff angle), (b) ^{3K}PEO^{2F} (75° takeoff angle), and (c) ^{3K}PEO^{2F} (15° takeoff angle).

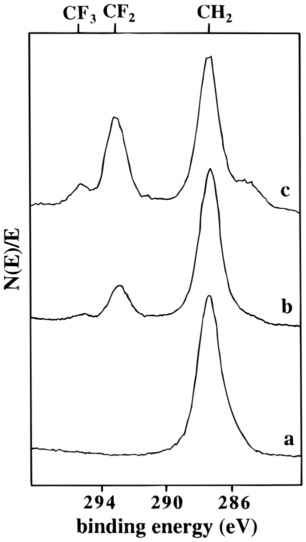

Figure 3. XPS C_{1s} region spectra for: a, ^{3K}PEO (75° takeoff angle); b, ^{3K}PEO^{2F} (75° takeoff angle); c, ^{3K}PEO^{2F} (15° takeoff angle).

and C_{1s} region spectra, respectively, for ^{3K}PEO (75° takeoff angle) and ^{3K}PEO^{2F} (15 and 75° data) samples (cast on silicon wafers as described below). Spectra for ^{3K}PEO (and all other PEO samples) show no takeoff angle dependence. The spectra for ^{3K}PEO^{2F} exhibit pronounced takeoff angle dependence. XPS atomic composition data for ^{3K}PEO^{2F} are as follows (15°) C 44.5, O 13.8, F 41.7; (75°) C 49.9, O 20.1, F 30.0. Equation 2[12] describes the attenuation of photoelectron intensity

$$I = I_o e^{-t/\lambda \sin\phi} \tag{2}$$

in solids as a function of sampling depth (t), takeoff angle (ϕ), and electron mean free path (λ), where I_o is the number of photoelectrons that originate at depth t and I is the number of photoelectrons emitted from the solid that have not been inelastically scattered. This expression indicates that the 15° takeoff angle spectra are representative of the composition of the outermost ~11 Å of the film sample (95% of the C_{1s} photoelectrons detected originate in this region[13]). The 75° takeoff angle spectra represent the composition of the outermost ~40 Å (95% of the measured C_{1s} photoelectrons are ejected from this region[13]), and because the sensitivity of XPS decreases exponentially with depth, 54% of the signal in the 75° spectrum is due to electrons originating in the outermost 11 Å. Spectra of all surface-active polymers (see below) exhibit a pronounced takeoff angle dependence (the atomic concentration of fluorine detected at 75° is about half that detected at 15°), indicating that the fluorine is confined to the outer few angstroms of the film sample and that there is a >~35 Å thick zone beneath the fluorine-rich layer that is depleted of fluorine.

Room Temperature Adsorption Isotherms. Blends of PEO^{2F} polymers and matrix polymers (unmodified PEOs with the same degree of polymerization as the surface-active polymers) were prepared by dissolving the desired ratio of polymers in chloroform (~4 weight % solutions) and casting films on silicon wafers. The total mass of polymer used was chosen to yield films with thicknesses of ~8 μm. Blends were prepared with composition ranges varying from 0.005% to 100% surface-active polymer. The polymer film samples (blends of all compositions) crystallize as the solvent evaporates, and we note (qualitatively) that the surface-active polymer affects crystallization behavior. As the concentration of surface-active polymer increases, the number of spherulites decreases and their size increases.

XPS spectra were obtained of blends in the forms of both as-cast films and film samples that were cast from solution, annealed in a vacuum oven at 75 °C (above the T_m of both components) and cooled to room temperature. XPS indicates that the surface composition of as-cast films does not change after annealing. Figure 4 shows plots of fluorine atomic concentration (15 and 75° takeoff angle data) vs the concentration of ^{3K}PEO^{2F}, ^{8K}PEO^{2F}, and ^{15K}PEO^{2F} in blends with PEO of the same molecular weight as the surface-active polymer. The takeoff angle dependent data indicate that the perfluorodecanoate groups concentrate in the outer few angstroms and leave a fluorine-depleted subsurface zone, as in the case of neat surface-active polymers. This stratification behavior is observed in blends of all surface-active polymers at all compositions.

The plots in Figure 4 resemble typical high-affinity adsorption isotherms[14] that are seen for monodisperse polymers adsorbing from solution to a solution−solid interface: high adsorption is observed at low concentrations and a plateau is reached indicating saturation of the surface. We view the surface reconstruction of these blends that occurs during casting and/or annealing as polymer adsorptions from PEO or the PEO/chloroform solution to the polymer−air interface. In these cases the driving force for adsorption is the lowering of surface free energy that occurs when perfluorodecanoate groups concentrate at the free surface. As all perfluorodecanoate groups are attached at PEO chain ends, the adsorbed polymer structure is that of chains end-grafted to the free surface. Because of concern that the crystallization that occurs affects the adsorbed polymer structure and the surface composition, surface analysis was performed on blends above T_m (below).

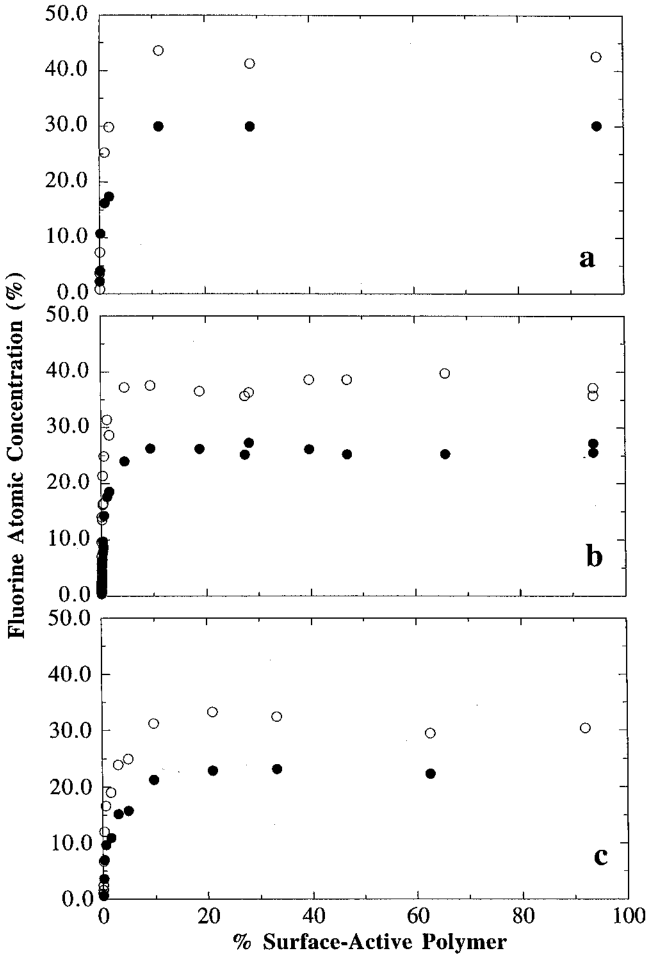

Figure 4. Plots of XPS fluorine atomic concentration vs. the concentration of $^{3K}\text{PEO}^{2F}$ (a), $^{8K}\text{PEO}^{2F}$ (b), and $^{15K}\text{PEO}^{2F}$ (c), in blends with PEO of the same molecular weight as the surface-active polymer (data obtained at room temperature). The open (○) and closed (●) circles are data recorded at 15 and 75° takeoff angles, respectively.

Contact angle analysis was performed on as-cast and annealed samples of $^{8K}\text{PEO}^{2F}$ and gave further insight into the surface structure. A film sample prepared by casting from chloroform solution exhibited a hexadecane advancing contact angle (θ_A) of 46°. After annealing at 75 °C for 2 h and cooling to room temperature, θ_A remained essentially unchanged (46.5°). Receding contact angles (θ_R) for the as-cast and annealed $^{8K}\text{PEO}^{2F}$ samples were 27 and 28°, respectively. ^{8K}PEO exhibits contact angles of $\theta_A/\theta_R = 10°/0°$. The θ_A values compare with literature values[15] of 45° for poly(tetrafluoroethylene) (PTFE) and 72° for a monolayer containing $-CF_3$ groups at the surface. A sample of PTFE in our laboratory exhibited hexadecane contact angles of $\theta_A/\theta_R = 42°/9°$. These data indicate that the surface of $^{8K}\text{PEO}^{2F}$ (as assessed by the hexadecane probe fluid) is similar to that of PTFE, with perfluoroalkyl groups lying reasonably close-packed at the surface, exposing primarily CF_2 functionality. A model of this view is shown in Figure 5.

XPS data for $^{8K}\text{PEO}^{2F}$ support the validity of this model; the 15° takeoff angle data indicate that the composition of the outermost 11 Å is $C_{43}F_{41}O_{16}$. We can calculate the composition predicted by the model in Figure 5 using the structure of the polymer and reasonable assumptions. If we assume that the outermost 5 Å of the sample is perfluoroalkyl groups (this is a reasonable analysis of the XPS data and the approximate diameter of the cross-section of a perfluoroalkyl chain in an all trans configuration), that the density of this layer is 2 g/cm^3, and that both end groups are adsorbed to the surface, the surface area occupied by a $^{8K}\text{PEO}^{2F}$ chain is 156 Å^2 (a single chain's "footprint"). Assuming a density of 1.1 g/cm^3 for PEO, 14 $-CH_2CH_2O-$ repeat units reside in the 6 Å beneath this footprint that are assessed by XPS. The composition of the outermost 11 Å predicted by this analysis is $C_{46}F_{38}O_{17}$, which is very close to the observed composition. This analysis also indicates that the PEO chain must be stretched in a brush conformation that extends ~75 Å. This is calculated by assuming a density of 1.1 g/cm^3 for PEO, a 156 Å^2 footprint, and a chain of 175 repeat units (M_n = 7700). The brush conformation accounts for the fluorine-depleted zone observed by XPS.

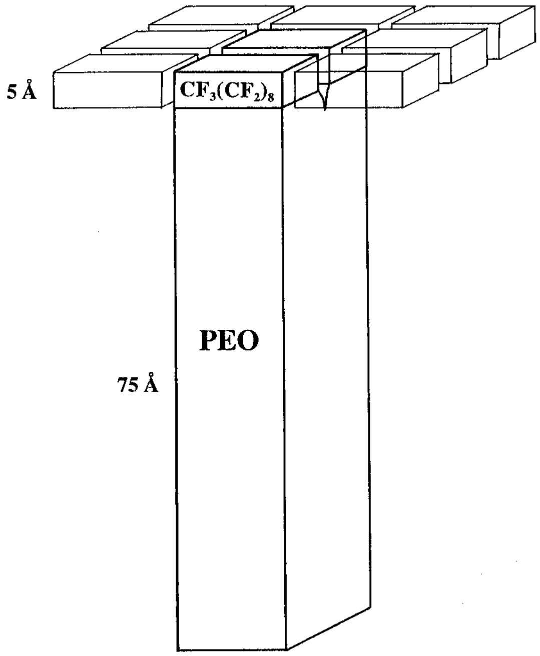

Figure 5. Graphic description of a $^{8K}\text{PEO}^{2F}$ chain adsorbed to the polymer–air interface. The PEO chain must stretch to accommodate the geometric restriction imposed by reasonably close-packed perfluoroalkyl groups at the surface.

Adsorption Isotherms of Blends in the Melt. Because of our concern that the crystallization of samples may affect the structure and composition of the blend surfaces, adsorption isotherm data were acquired using XPS at 90 °C with a heated sample stage. DSC analysis indicates that all PEO, PEO^F, and PEO^{2F} samples have melting transitions below 70 °C. The thermal stability of polymer samples was assessed by thermal gravimetric analysis and infrared spectroscopy. No mass loss or changes in infrared spectra were observed after heating samples at 110 °C or lower temperatures. Mass losses and changes in the infrared spectra are observed at higher temperatures. For example, $^{16K}\text{PEO}^F$ begins to lose mass (under nitrogen) at ~150 °C when the temperature is raised 10 °C/min and loses ~3% of its mass when held at 240 °C for 2 h. Additional carbonyl bands (1722 and 1753 cm^{-1}, likely due to oxidation of the PEO backbone) emerged in the infrared spectrum when $^{16K}\text{PEO}^F$ was heated at 130 °C for 1 h on a KBr crystal. The ester carbonyl band at 1780 cm^{-1} remains unchanged.

Plots of XPS fluorine concentration vs surface-active polymer concentration (adsorption isotherms) for PEO^{2F} samples are shown in Figure 6. Analogous data for PEO^F samples are shown in Figure 7. These data were

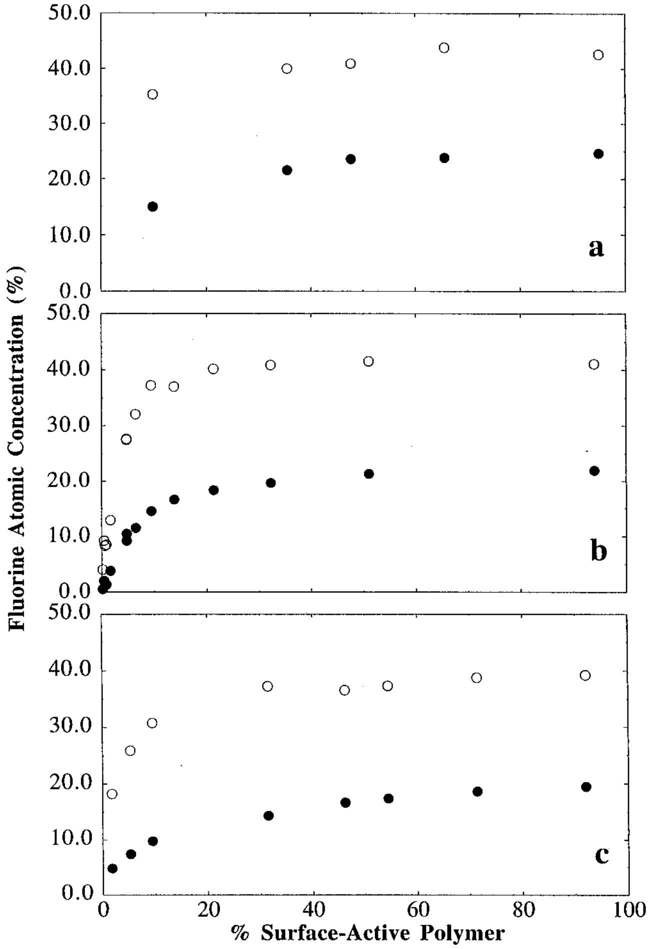

Figure 6. Plots of XPS fluorine atomic concentration vs surface-active polymer concentration (adsorption isotherms) for PEO^{2F} samples: (a) ^{3K}PEO^{2F}; (b) ^{8K}PEO^{2F}; (c) ^{15K}PEO^{2F}. The open (○) and closed (●) circles are data recorded at 15 and 75° takeoff angles, respectively.

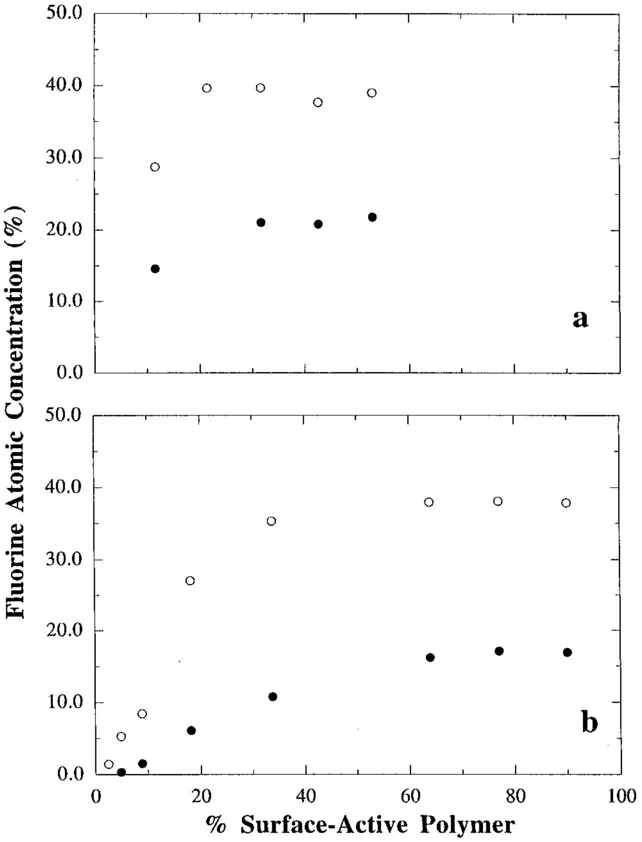

Figure 7. Plots of XPS fluorine atomic concentration vs. surface-active polymer concentration (adsorption isotherms) for PEO^{F} samples: (a) ^{2K}PEO^{F}, (b) ^{16K}PEO^{F}. The open (○) and closed (●) circles are data recorded at 15 and 75° takeoff angles, respectively.

Table 2. Plateau Values for Fluorine Atomic Concentration of Blends (90 °C Adsorption Isotherms)

sample	surface concn (%) 15^{a}	surface concn (%) 75^{a}	bulk concn^{b} (%)	surface excess^{c}
^{3K}PEO^{2F}	42	24	2.3	19
^{8K}PEO^{2F}	41	20	1.2	36
^{15K}PEO^{2F}	38	18	0.7	57
^{2K}PEO^{F}	39	21	2.0	19
^{16K}PEO^{F}	37	17	0.4	95

[a] Takeoff angle. [b] Determined at the lower limit of the plateau concentration. [c] Ratio of 15° takeoff angle fluorine concentration to bulk fluorine concentration.

obtained after allowing the blend specimens to equilibrate at 90 °C in the XPS analysis chamber for 45 min to 12 h. Equilibration times were chosen on the basis of kinetics experiments performed on samples of different surface-active polymer concentrations. Concentrated samples (>10% surface-active polymer) equilibrated in less than 30 min. Dilute samples (<2% surface-active polymer) equilibrated after 7–10 h at 90 °C. Concentrated samples (>10%) were annealed for 45 min, dilute samples (<5%) were annealed for 12 h, and intermediate concentration samples (5–10%) were annealed for 2 h. The adsorption isotherms are similar to those obtained at room temperature, reaching similar surface compositions at the plateau values, but plateau surface-active polymer concentrations are higher (~20%). We have no explanation for the higher affinity isotherms observed at room temperature. A pronounced takeoff angle dependence (more pronounced than room temperature data, discussed above) is observed in all systems. We ascribe the less pronounced takeoff angle dependence observed in spectra acquired at room temperature to sample roughness, due to the crystallization.

The fluorine content data for blend samples in the plateau region are summarized in Table 2. The atomic concentration of the bulk of the polymer samples, determined at the lower limit of the plateau concentration is included in this table. The data indicate that all of the end-functionalized polymers are extremely surface-active in PEO and that the surfaces of all of the blends above the plateau concentration are essentially fluoropolymer-like. The surface composition (and structure) is only slightly dependent on molecular weight and only slightly dependent on whether the surface-active polymer contains one (PEO^{F} samples) or two (PEO^{2F} samples) perfluorodecanoate groups. There is clearly a slightly greater fluorine content in the surface regions of PEO^{2F} samples, but the differences are not great enough to unambiguously determine whether PEO^{2F} samples adsorb with one (as tails) or two (as loops) perfluorodecanoate groups at the polymer–air interface.

These data also indicate that the PEO chains in all of the surface-active polymers stretch to accommodate a reasonably close-packed arrangement of perfluoroalkyl groups at the surface. The degree of stretching (brush extension) is essentially linear in molecular weight, e.g. the ^{16K}PEO^{F} chains extend ~8 times as far as the ^{2K}PEO^{F} chains. Figure 8 graphically depicts the conformation of these surface-active polymers at the polymer-air interface. The rectangles in the figure are

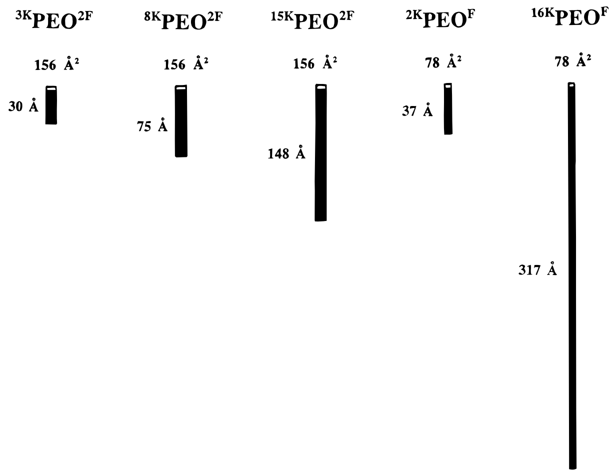

Figure 8. Stretching required of PEO chains in surface-active polymers to adsorb to the polymer–air interface. The rectangles are drawn assuming that both chain ends adsorb in PEO^{2F} samples.

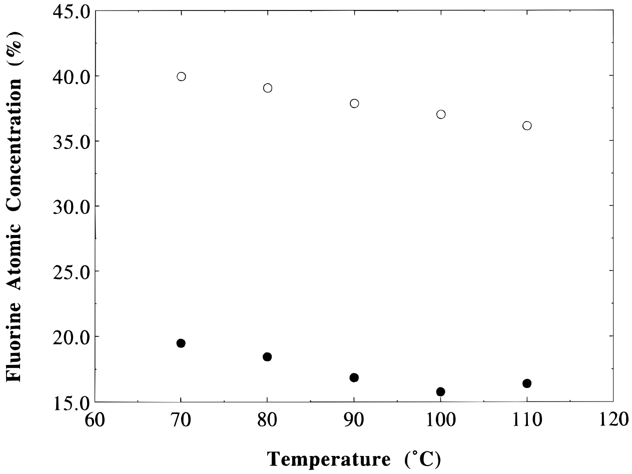

Figure 9. Plots of XPS fluorine atomic concentration vs. temperature for ^{16K}PEO^{F}. The open (○) and closed (●) circles are data recorded at 15 and 75° takeoff angles, respectively.

2-dimensional representations (cross sections) of chain conformations drawn to indicate the extent of stretching required to accommodate the perfluoroalkyl groups at the surface in a close-packed fashion. The assumptions made are discussed above in the text concerning Figure 5. The rectangles for PEO^{2F} samples are drawn by assuming that both chain end perfluoroalkyl groups adsorb with a 156 Å^2 footprint.

Temperature Dependence of Adsorption. In the Introduction we state that we expected to be able to control the surface fluorine content with PEO molecular weight due to the molecular weight-dependent entropic contribution (chain stretching) to the adsorption free energy. The data in Table 2 indicate that, for these molecular weights, the surface fluorine concentration is not controlled by molecular weight. For the samples studied, the PEO chains extend as far as neccessary to accommodate a close-packed arrangement of perfluoroalkyl groups. The enthalpic gain due to lowering surface free energy dominates in all cases studied. In an attempt to demonstrate an entropic component to the adsorption, a variable temperature XPS analysis of ^{16K}PEO^{F} (the sample most entropically taxed by chain stretching) was carried out. Figure 9 shows the surface fluorine content (both 15 and 75° takeoff angle data) as a function of temperature from 70 to 110 °C for the neat surface-active polymer. The temperature range studied is limited by the crystallization that occurs at temperatures lower than 70 °C and the thermal degradation that occurs at temperatures above 110 °C (discussed above). The data show a small, but statistically significant, dependence of the surface fluorine content on temperature, indicating the existence of an entropic contribution to the adsorption free energy.

Summary

Surface analyses indicate that perfluoroalkyl end-functionalized PEOs are extremely surface-active molecules in blends with unfunctionalized PEOs. They adsorb to the polymer–air interface, exhibiting high-affinity concentration isotherms to yield structures that contain essentially only fluorocarbon in the outermost ~5 Å and regions beneath this layer that are depleted of fluorine. The enthalpic gain due to the lowering of surface free energy dominates the entropic loss due to stretching of the PEO chain. The composition of the surface region (fluorine content) is only weakly a function of molecular weight and depends only weakly on whether one or two perfluoroalkyl groups are attached to the polymer. This indicates that the conformations of adsorbed chains are brushlike with the degree of brush extension (chain stretching) roughly linear in molecular weight. Adsorption is favored at lower temperatures, but only slightly—again indicating the dominance of enthalpy in this system.

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References and Notes

(1) See: Cross, E. M.; McCarthy, T. J. *Macromolecules* **1990**, *23*, 3916 and references cited therein.
(2) Koberstein, J. T. In *Encyclopedia of Polymer Science and Engineering*, 2nd ed.; Mark, H. F., Bikales, N. M., Overberger, C. G., Menges, G., Kroschwitz, J. I., Eds.; John Wiley and Sons: New York, 1989; Vol. 8, p 237.
(3) Andrade, J. D.; Gregonis, D. E.; Smith, L. M. In *Surface and Interfacial Aspects of Biomedical Polymers*; Andrade, J. D., Ed.; Plenum: New York, 1986; Vol. 1, Chapters 2 and 7.
(4) Iyengar, D. R.; Perutz, S. M.; Dai, C.-A.; Ober, C. K.; Kramer, E. J. *Macromolecules* **1996**, *29*, 1229.
(5) Schaub, T. F.; Kellogg, G. J.; Mayes, A. M.; Kulasekere, R.; Ankner, J. F.; Kaiser, H. *Macromolecules* **1996**, *29*, 3982.
(6) Affrossman, S.; Bertrand, P.; Hartshorne, M.; Kiff, T.; Leonard, D.; Pethrick, R. A.; Richards, R. W. *Macromolecules* **1996**, *29*, 5432.
(7) Affrossman, S.; Hartshorne, M.; Kiff, T.; Pethrick, R. A.; Richards, R. W. *Macromolecules* **1994**, *27*, 1588.
(8) Elman, J. F.; Johs, B. D.; Long, T. E.; Koberstein, J. T. *Macromolecules* **1994**, *27*, 5341.
(9) Hunt, M. O., Jr.; Belu, A. M.: Linton, R. W.; DeSimone, J. M. *Macromolecules* **1993**, *26*, 4854.
(10) Chen, X.; Gardella, J. A. Jr. *Macromolecules* **1994**, *27*, 3363.
(11) Wu, S. In *Polymer Handbook*, 3rd ed.; Brandrup, J., Immergut, E. H., Eds.; John Wiley and Sons: New York, 1989; p VI 411.
(12) Andrade, J. D. *Surface and Interfacial Aspects of Biomedical Polymers, Surface Chemistry and Physics;* Plenum Press: New York, 1985; Vol. 1, p 176.
(13) These calculations use the value of 14 Å for the mean free path of C_{1s} photoelectrons excited with Mg Kα irradiation. This value was measured in poly(*p*-xylylene): Clark, D. T.; Thomas, H. R. *J. Polym. Sci., Polym. Chem. Ed.* **1977**, *15*, 2843.
(14) Fleer, G. J.; Cohen Stuart, M. A.; Scheutjens, J. M. H. M; Cosgrove, T.; Vincent, B. *Polymers at Interfaces;* Chapman & Hall: London, 1993; p 29.
(15) Zisman, W. A. *Adv. Chem. Ser.* **1964**, *43*, 1.

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