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Surface Properties and Metathesis Synthesis of Block Copolymers Including Perfluoroalkyl-Ended Polyethylenes

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ABSTRACT: Linear polyethylene with fluoroalkyl end groups has been prepared by ring-opening metathesis polymerization of cyclododecene in the presence of partially fluorinated acyclic olefins (chain transfer agents), followed by reduction of the double bonds in the backbone. Melt surface tensions (γ) were obtained for samples with one or both ends terminated by $F(CF_2)_{10}$ or $F(CF_2)_4$ groups at different molecular weights (MWs) of the hydrocarbon segments down to oligomeric sizes. The polyethylenes with two perfluorinated ends, i.e., $PE(C_{10}F_{21})_2$, were the most effective at lowering γ. At only 10% atomic F in the bulk, values of γ were obtained which were even lower than those for pure poly(tetrafluoroethylene). The surfaces of films of selected fluoroalkyl-terminated polymers were also characterized by advancing and receding contact angle measurements and angle dependent X-ray photoelectron spectroscopy (XPS). Advancing contact angles in hexadecane were as high as 70°, indicating a high surface concentration of perfluorinated species. Comparison with model systems indicate that much of the surface is covered by close-packed CF_3 groups. XPS profiling quantified the ratio of fluorocarbon to hydrocarbon in the surface regions and also indicated a strong surface excess of oriented chain ends. The hexadecane contact angles of fluoroalkyl-ended metathesis polymers [$PE(C_{10}F_{21})_2$] decrease substantially as the molecular weight increases above ca. 40 000. In that range, the bulk concentration of chain ends becomes quite low and surface concentration of fluorocarbon chain ends at the surface is sharply reduced because of configurational entropic reasons. The surface properties of blends of a lower MW $PE(C_{10}F_{21})_2$ copolymer with a PE homopolymer were evaluated and compared to the series of pure $PE(C_{10}F_{21})_2$ copolymers where the high MW limit of the polyethylene center is approached. At similar bulk F levels in the blends and pure copolymer, the surface fluorocarbon content in the blends is significantly enhanced.

Introduction

The surface properties of fluoropolymers are unique in their very low surface energies combined with chemical resistance and good mechanical properties. It is well-known that many materials have a lower surface free energy than a pure perfluorinated substance such as polytetrafluoroethylene (PTFE). These materials are mainly those with a surface dominated by CF_3 groups. Zisman[1] first showed the remarkable low surface free energies (or critical surface tensions) of ordered perfluorinated monolayers with chains terminated by CF_3 groups. The effectiveness of CF_3 compared to $-CF_2-$ in lowering the surface free energy is attributed to the bulky F atom leading to a lower density of attractive centers per unit area at the surface in the case of a CF_3 surface.[2,3] For the same reason the surface free energy of fluorocarbon is much lower than that of hydrocarbon, i.e., the more bulky $-CF_2-$ groups relative to $-CH_2-$ groups leads to a lower density of attractive centers and, thus, a significantly lowered surface free energy of PTFE versus polyethylene (PE).[2]

Side group substituted polymers were developed in order to mimic the ultralow surface energies associated with close packed monolayers, yet they retain the mechanical properties associated with polymers.[4−6] Perfluoroalkyl-terminated polyesters have also been shown to have a high excess of fluoro species at the surface.[7] In some cases, the effectiveness of the side group substituted polymers actually surpassed the monolayer systems.[4,5] Other ultralow surface energy, nonstick perfluoroalkane-substituted systems which form smooth, curable coatings have recently been developed.[8] One common feature of all of these substituted polymers are high advancing and receding contact angles in hexadecane approaching 80°, due to an approximately close-packed surface of CF_3 groups.

In this paper we report on polymers with perfluoroalkyl end groups prepared by metathesis polymerization. Olefin metathesis is a metal-catalyzed reaction which scrambles the alkylidene groups of olefins.[9] When the reaction is carried out on a cyclic olefin, the product is a linear ring-opened polymer with double bonds in the backbone. Acyclic olefins act as chain transfer agents in the metathesis polymerization of cyclic olefins, and they are frequently added as a means of limiting and controlling the molecular weight. Since the alkylidene units of the acyclic olefin become the end groups of the polymer, this is a method of controlling the end groups. In this case acyclic olefins with fluoroalkyl groups were used to cap the polymers. The double bonds can then be reduced to form end-group-modified polyethylenes.

These unique polymers have the melt and solution processability of hydrocarbon polymers, but their low surface energies are more typical of fluoropolymers. As melt additives, they can dramatically lower the surface energy of high molecular weight polyethylene or other polyolefins. This report describes the synthesis of several classes of fluoroalkyl-ended metathesis polymers and the detailed characterization of their surface properties by surface tension, surface energetics, and X-ray photoelectron spectroscopy (XPS).

Experimental Section

Materials. Synthesis of $C_{10}F_{21}(CH_2)_6CH{=}CH(CH_2)_6C_{10}F_{21}$. A solution of $C_{10}F_{21}(CH_2)_6CH{=}CH_2$ (14.97 g, 23.75 mmol) in 50 mL of dry chlorobenzene was warmed to 65 °C in an open flask in a dry-box. A solution of 0.047 g of $W(CHMe_3)(2,6\text{-diisopropylphenyl})(OC(CH_3)(CF_3)_2)_2$ (0.059 mmol) in 1 mL of chlorobenzene was added, and after 2 h a second equal portion of catalyst was added. The solution was stirred in the open flask overnight at 65 °C to allow escape of the ethylene product. The chlorobenzene was removed in vacuo, and the product was distilled on a Kugelrohr apparatus connected to a high vacuum line. A low-boiling fraction collected at 90−

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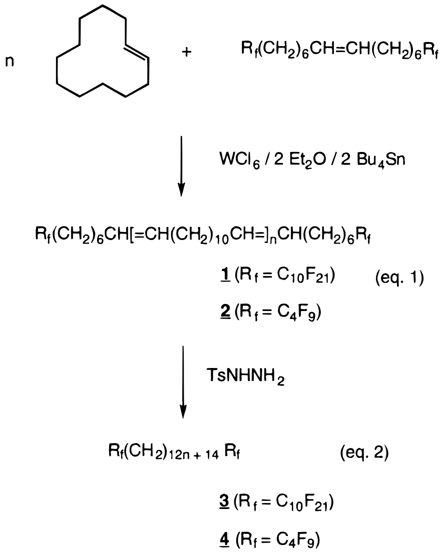
120 °C (3.00 g) showed no olefinic resonances by ^{1}H NMR. The desired product distilled at 180 °C (10.36 g, 71%). It is a white solid with high solubility in 1,1,2-trifluorotrichloroethane (F113), and moderate solubility in THF, $CHCl_3$, and pentane. It is soluble in chlorobenzene at 65 °C. DSC shows a melting endotherm at 104.4 °C (49 J/g).

$C_4F_9(CH_2)_6CH{=}CH(CH_2)_6C_4F_9$ was prepared similarly and distilled on a Kugelrohr apparatus connected to a high vacuum line at 160−180 °C.

Polymerization Conditions. A solution of diethyl ether (0.038 g, 0.52 mmol) in 2 mL of chlorobenzene was added with stirring to a solution of WCl_6 (0.103 g, 0.26 mmol) in chlorobenzene. A reaction mixture consisting of 20 mL of chlorobenzene, cyclododecene (15.0 g, 90.2 mmol), $C_{10}F_{21}(CH_2)_6CH{=}CH(CH_2)_6C_{10}F_{21}$ (2.17 g, 1.76 mmol), and tetrabutyltin (0.180 g, 0.52 mmol) and was heated to 80 °C. The WCl_6/ether solution was added and the mixture became viscous within a few minutes. After 1 h at 80 °C, the hot mixture was poured into a 10-fold excess of stirring methanol to precipitate the polymer and to separate it from cyclic oligomers of cyclododecene that constitute about 10% of the product. The polymer (type **1**, see below) was collected by filtration and then redissolved in minimal hot chlorobenzene and reprecipitated by addition to a 10-fold excess of methanol. The polymer was isolated by filtration and washed on the filter with three portions of 1,1,2-trichlorotrifluoroethane to remove traces of unreacted fluoroolefin and low molecular weight (MW) linear products. The polymer was dried overnight at 50 °C in a vacuum oven (14.9 g). The fluorine content of the 1,1,2-trichlorotrifluoroethane extracts was determined by ^{1}H NMR end group analysis. The bulk of the fluorine, which is contained in the polymer, was calculated by difference, and by combining this information with the isolated yield of polymer, the fluorine content and M_n of the polymer were estimated. Additional methods of determining molecular weight and fluorine content that were used for some samples include elemental fluorine analysis, elemental carbon analysis, ^{1}H NMR integration of end groups (good method for low MW samples), and ^{19}F NMR integration of end groups vs an internal standard. Direct fluorine analysis was not always reliable. One way to access the analyses is to look at the sum of the C, H, and F wt % since these samples contain no other elements. In some cases, the estimated fluorine content obtained from one of the other methods may be closer to the true value than the fluorine elemental analysis.

Synthesis of Fluoroalkyl-Ended Polyethylene via Olefin Metathesis. The cross metathesis of cyclododecene with the acyclic olefins $R_f(CH_2)_6CH{=}CH(CH_2)_6R_f$ ($R_f = C_{10}F_{21}$, C_4F_9) gives fluoroalkyl-ended polymers **1** and **2** (eq 1). They are partially crystalline with a melting point of 73 °C and dissolve at room temperature in chloroform and toluene. By varying the ratio of cyclododecene to acyclic olefin (the *n* value), the molecular weight and fluorine content of the polymers can be controlled.



$C_{10}F_{21}(CH_2)_6CH[{=}CH(CH_2)_{10}CH{=}]_nCH_2$

5

$C_{10}F_{21}(CH_2)_{12n+7}CH_3$

6

Diimide reduction of **1** and **2** gives fluoroalkyl-ended polyethylenes **3** and **4** (eq 2). They are highly crystalline with a melting point of 128 °C. No thermal events attributable to the fluoroalkyl end groups have been observed. The polymers are insoluble at room temperature and show typical polyethylene solubility at higher temperatures.

By using the terminal olefin $C_{10}F_{21}(CH_2)_6CH{=}CH_2$ as the chain transfer agent, analogous fluoroalkyl-ended polymers **5** and **6** with an average of only one $C_{10}F_{21}$ end per chain can be prepared. Because of the nature of the metathesis reaction, these materials are expected to consist of a mixture of linear chains with two fluoroalkyl ends, one fluoroalkyl end and one hydrocarbon end, and two hydrocarbon ends.

Reduction of an Unsaturated Metathesis Polymer. $C_{10}F_{21}(CH_2)_6CH[{=}CH(CH_2)_{10}CH{=}]_nCH(CH_2)_6C_{10}F_{21}$ (**1**, 5.412 g) and *p*-toluenesulfonohydrazide (4.965 g, 2 equiv/olefin) were combined in 270 mL of xylene and refluxed under argon. Additional *p*-toluenesulfonohydrazide (2.483 g, 1 equiv/olefin) was added after 2 and 4 h. The mixture was refluxed overnight and then filtered hot through a fine-fritted glass filter. The insoluble material collected on the filter was washed with 4 × 25 mL of hot xylene. Methanol (500 mL) was added to the combined cooled filtrates to complete the precipitation of the polymer. The off-white solid polymer **3** was collected by filtration, washed on the filter with methanol, and dried at high vacuum at 55 °C (5.111 g, 94%). ^{1}H NMR (toluene-d_8, 95 °C) showed no detectable olefinic resonances. If reduced polyethylene products were not washed thoroughly on the filter with MeOH, they sometimes contained small amounts of the byproduct $MeC_6H_4SO_2SC_6H_4Me$. This compound has been reported as a byproduct of *p*-toluenesulfonohydrazide reduction of polybutadiene.[10]

Molecular Weight Characterization. Several of the fluoroalkyl-ended polymers have been characterized by gel permeation chromatography (GPC) vs polystyrene standards. The MW values determined by GPC are systematically higher than the MWs determined by fluorine analysis. All the MWs reported in the body of this paper are based on fluorine analysis. GPC shows that most of the samples have relatively narrow, monomodal molecular weight distributions. This confirms that the workup procedure is effective in removing cyclic oligomers and unreacted fluoroolefin (see Experimental Section for details). Most of the polymers have $M_w/M_n < 2$, indicating that the polymerization is under kinetic control and that there is not enough secondary metathesis of the double bonds in the polymer backbone to reach thermodynamic equilibrium.

Film Preparation. Films of low molecular weight polymers were prepared by pressing samples between glass slides above the melting point. The glass slides could then be easily separated, generally fracturing the polymer film for most samples with MW< ca. 10 000 because of the low cohesive strength of the material. The films were studied before and after remelting. Remelting for several seconds at 140 °C with the top surface exposed to air allows one to "equilibrate" the melt/air interface, and this state should be retained during quenching to a solid. Samples were tested to ensure that longer equilibration times did not change the results. Before equilibration, the surfaces were generally depleted of fluoro species as compared to after equilibration. Films of higher molecular weight polymers were prepared by pressing between Kapton sheets in a press at 140 °C, solidifying by cooling to 20 °C, and then removing the Kapton. In this case the materials remain intact and do not cohesively fracture, leaving a smooth surface. A section of the film is then heated to $T >$ 140 °C on a glass slide in air for several minutes to generate an "equilibrium" surface. Before heating, the surface originally in contact with Kapton (or glass) is depleted in fluorine[11] due to the polar nature of Kapton (or glass). The rate at which one can approach equilibrium in the melt depends on the mobility and concentration of fluoro species (i.e., diffusivity and diffusion length). Mobility is influenced by MW and temperature.

Blends of the fluoroalkyl-terminated polyethylenes with a linear high MW polyethylene homopolymer (Hoechst Hostalen GF 7740 F2) were prepared on a small scale by codissolution in dichlorobenzene at 150 °C, followed by precipitation into cold methanol, filtration, and vacuum drying at 100 °C. Larger samples were prepared by melt blending in a Brabender mixer.

Methods. Advancing and receding contact angles of test liquids on polymer films were obtained using the sessile drop technique and a Rame' Hart contact angle goniometer by injecting (advancing) or withdrawing (receding) liquid from a drop on a horizontal surface.

The molten polymer surface tension apparatus has been described earlier.[12] All values of surface tension (γ) were measured by determining the apparent wetting mass using the micro-Wilhelmy technique with an electronic balance and a bare glass fiber as a surface tension probe. Fibers were used as vertical Wilhelmy probes leading to rapid equilibration of the molten polymer meniscus because of the small dimensions of the wetting menisci.[12]

Angle-dependent XPS (X-ray photoelectron spectroscopy or ESCA) can be used to characterize the outer 20−100 Å.[13] Variable take-off angle XPS data were taken with the VG ESCALab Mk II using Mg Kα radiation. An aperture limiting the solid angle of acceptance of the analyzer to ±3.5° was used. Data sets (consisting of the C1s and F1s regions of the spectra) were taken at 90°, 30°, 20°, 90° (repeat), and finally 45°. (Angles are electron take-off angles measured from the surface plane.) Care was taken to minimize the total X-ray exposure of the samples during data acquisition. The second 90° data set was used to monitor any changes in the surface during X-ray exposure. In all cases the loss of F was less than 11% and usually 0% within experimental error.

The XPS signal intensities were used to obtain "apparent" surface compositions as atomic percentages of the detected species, i.e., ignoring hydrogen, in the standard way using normal sensitivity factors. In some cases, there was sufficient signal in the fluorocarbon region of the C1s spectrum to allow the areas of peaks due to CF_2 and CF_3 to be quantified. The CF2 and CF3 signals were not cleanly resolved at the 50 eV pass energy used, so the two components were fit with Gaussian peaks of 1.9 eV full-width at half-maximum fixed at the CF2 and CF3 positions. With the hydrocarbon C1s peak fixed at 284.6 eV, CF2 was set to 291.4 and CF3 to 293.2 eV, consistent with the literature.[14] Uncertainties in choosing a baseline, peak positions, and areas make the CF2 and CF3 quantifications only approximate, but the use of consistent procedures in fitting ensures that correct trends are observed.

In samples of low F content, only a total fluorocarbon (CF_2 + CF_3) signal could be extracted from the C1s spectrum. Otherwise, only total C and F elemental compositions were obtained. The F1s binding energy in all cases indicated that the F was bound to carbon.

The variable take-off angle data were compared to models of surface layers over a bulk composition using a computer program based on the standard model for XPS[13] and were fit to layer models using a nonlinear least squares fitting program in order to obtain an objective estimate of the surface depth profile. Fits are not unique and their accuracies are not easily assessed, but they do serve to supply a quantitative feel for conclusions derived from examination of the data. Electron attenuation lengths (λ) were taken to be 3.5 nm for C1s and 2.4 nm for F1s. This corresponds to an $E^{0.7}$ dependence of the attenuation length on electron kinetic energy (E). An $E^{0.5}$ dependence was also tried but had no effect on the conclusions from the modeling.

Results

Surface Tension. The melt surface tensions of selected homopolymers, copolymers, and oligomers are shown in Figure 1. High MW in homopolymers relative to oligomers leads to higher surface tensions because of higher melt density in the bulk[15,16] as can be seen in the comparison of PTFE and a perfluorinated oligomer of PTFE [$CF_3(CF_2)_{18}CF_3$] (i.e., Figure 1). This is a general feature of most homopolymers.[15] For copolymers, the effect is more subtle. There is a bulk density effect for oligomers which generally becomes less important at moderate MWs (i.e., MW > 3000 g/mol), similar to the case of homopolymers and oligomers.[15] Another more important factor is the composition of the copolymer. If the percent fluorocarbon in the fluoroalkane-terminated polymers decreases, either because of a smaller fluoroalkane group or because of a larger degree of polymerization of the polyethylene center, then the surface composition will begin to change because of dilution of the overall fluorinated end group concentration and/or reduction in surface activity.

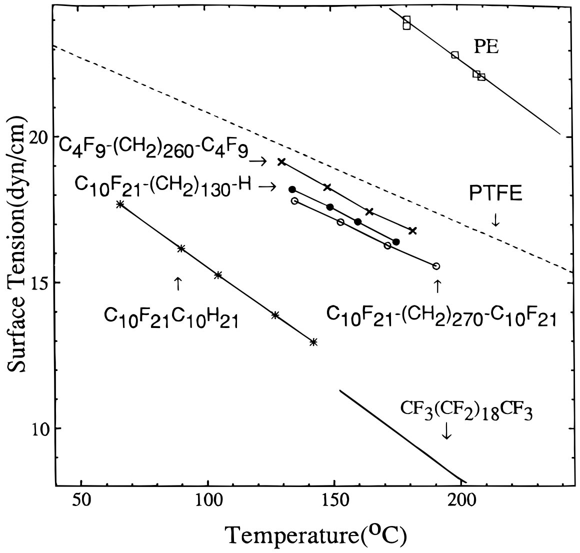


Figure 1. Melt surface tensions of the indicated copolymers and homopolymers.

In one case where the bulk melt densities are similar because of similar degrees of polymerization, it is seen that the two oligomers, $CF_3(CF_2)_{18}CF_3$ and $C_{10}F_{21}C_{10}H_{21}$ have comparable surface tensions if one considers a similar temperature range. On the basis of this comparison we conclude that the surface is dominated by the perfluorinated chain ends and γ does not seem to be influenced significantly by the hydrocarbon half of the molecule. This indicates that there is substantial surface orientation of the perfluorinated end toward the surface in $C_{10}F_{21}C_{10}H_{21}$, explaining why the values of γ are similar for these two oligomers. Data for three higher MW polyethylene-based copolymers are also given in Figure 1, showing that the values of γ are much lower than those for the polyethylene homopolymer of comparable MW. In fact, γ for these three copolymers are lower than those for a pure perfluorinated polymer, PTFE.[1] This is an example of the remarkable and well-known ultralow surface free energy properties of the CF_3 group.[1−3] An example is shown in Table 1, where it is seen that a model monolayer surface of close packed CF_3 groups is significantly lower in surface free energy than pure PTFE in the solid state. The values of γ for the higher MW copolymers in Figure 1 are higher than those of the $C_{10}F_{21}$-$C_{10}H_{21}$ oligomer mainly because of the bulk density effect discussed above.

The surface tensions of some of the higher MW copolymers are ranked in the order C_4F_9- $(CH_2)_{260}$ -C_4F_9 > $C_{10}F_{21}$–$(CH_2)_{130}$-CH_3 > $C_{10}F_{21}$-$(CH_2)_{270}$-$C_{10}F_{21}$ (Figure 1). The small differences seen between the three are due to small differences in the degree of surface excess of the fluoro species. It will be shown below that the

Table 1. Advancing and Receding Contact Angles (in deg) of Selected Perfluoroalkyl-Terminated Polymers

polymer type	%F[c]	θ_{adv} (θ_{rec}), deg water	hexadecane
5, PCD($C_{10}F_{21}$)[a]	8.2	120 (94)	76 (39)
1, PCD($C_{10}F_{21}$)$_2$	7.81	126 (108)	77 (33)
6, PE($C_{10}F_{21}$)[b]	7.76	130 (99)	66 (19)
3, PE($C_{10}F_{21}$)$_2$	9.47	127 (99)	71 (33)
monolayer,[d] (CF_3)	83	130 (125)	78 (74)
PE, [$(CH_2)_n$]	0	95 (91)	0 (0)
PTFE, [$(CF_2)_n$]	76	109 (100)	46 (42)

[a] PCD = polycyclododecene. [b] PE = polyethylene. [c] Weight percent F in the bulk is calculated from the chemical structure. [d] Perfluorolauric acid monolayer on platinum surface. This is essentially a close-packed CF_3 surface. See ref 17.

surface concentration of the perfluorinated groups in the -C_4F_9 terminated materials are somewhat reduced in their solid state surface properties.

Melt surface tensions were also obtained for unsaturated copolymers of type **1** (data not shown) and the data are reasonably consistent with those for the saturated copolymers (type **3**) discussed above.

Surface Energetics. Contact angles are a sensitive probe of surface composition.[17] Advancing contact angles tend to be sensitive to the low-energy species at the surface, even if they are a minor fraction of the total surface species. Hexadecane advancing contact angles are a particularly sensitive method for detecting fluorocarbon on a surface. This is because the advancing contact angle of hexadecane on hydrocarbon (polyethylene, PE) is zero (i.e., complete wetting), whereas the advancing contact angle of hexadecane on PTFE is 46° and for a surface composed of close-packed CF_3 groups it is 78° (Table 1, bottom)! Receding contact angles are sensitive to the higher energy component of the surface.[2,3,17] Many of the copolymers show a large difference between advancing and receding contact angles which is attributed to the heterogeneity of the surfaces. Both physical heterogeneity, such as surface roughness, or chemical heterogeneity, specifically a mixed surface of fluorocarbon and hydrocarbon domains or patches, could contribute. Films of most of these polymers have some surface roughness due to crystallinity during melt equilibration and subsequent cooling (see the Experimental Section), but much evidence suggest that it is a minor effect in these thin films. Most results, especially those for higher MW copolymers or blends with high MW PE where the surface remains smooth, indicate that the high hysteresis seen in hexadecane contact angles (Table 1) is due to surface chemical heterogeneity and not roughness. Surface rearrangement of fluorocarbon groups in the hexadecane environment could also explain the relatively low receding hexadecane angles of the copolymers (Table 1), but we do not feel that this is likely because of the reduced mobility due to crystallinity. Also, data showing very high hysteresis are obtained for partially annealed films, inconsistant with surface rearrangement.

Advancing and receding contact angles in H_2O and hexadecane are given in Table 1 (entries 1−4) for four of the copolymers with comparable MWs and fluorine weight fractions less than 10%. The advancing angles (θ_{adv}) in hexadecane are found to be all greater than that for a pure perfluorinated polymer, PTFE (Table 1). The high contact angles are consistent with a CF_3 rich surface. The hysteresis between advancing and receding hexadecane angles indicates that the surface is chemically heterogeneous and contains both fluoro- and hydrocarbon domains, presumably on a submicron length scale because we do not see any drop size dependence of θ. CF_3rich surfaces are known to have lower surface energies (thus, higher hexadecane contact angles) than a CF_2 (PTFE) surface.[1−3] In general, the surface fluorocarbon content as determined by contact angles seems to be relatively independent of unsaturation in the hydrocarbon chain whether or not one or both ends are terminated by $C_{10}F_{21}$ (Table 1). This is also consistent with the melt surface tension results discussed above.

Table 2. Studies of Equilibrated and Nonequilibrated Copolymer Surfaces by Contact Angle and XPS Profiling[a,b] [sample type 3, PE($C_{10}F_{21}$)$_2$, MW = 6.4*k*, 12.4 bulk wt % F]

angle, deg	atomic percentages F	HC	FC
Freshly Cleaved Surface, Not Annealed, θ_{adv} = 10°, θ_{rec} = 0° in Hexadecane			
90	21.6	72.3	6.0
90 repeat	21.8	72.1	6.2
45	24.7	69.2	6.1
30	24.6	69.0	6.4
20	24.6	67.6	7.7
Equilibrium Surface, Annealed at 140 °C, for 30 s, θ_{adv} = 65°, θ_{rec} = 16° in Hexadecane			
90	34.6	55.6	9.8
90 repeat	35.2	55.4	9.3
45	39.4	50.0	10.6
30	42.5	44.8	12.7
20	44.3	40.4	15.3

[a] Atomic percentages determined by XPS are given. [b] All atomic percentages were directly determined by fitting XPS C1s and F1s regions(see experimental).

The properties of nonequilibrated interfaces can be investigated by examining freshly cleaved surfaces before and after melt annealing (see the Experimental Section). A study of a freshly cleaved surface is expected to probe a surface composition similar to that found in the bulk copolymer, assuming that room temperature aging effects are small; i.e., the fluorocarbon near the surface does not have sufficient mobility to reorient and to position the CF_3 group at the outer surface. This would cause the fluorocarbon species to have less of an effect in reducing the surface energy. This fractured system also provides a nice control for the surface profiling methods, especially the XPS technique discussed below.

The MW = 6.4K sample of PE($C_{10}F_{21}$)$_2$ in Table 2 is 87.6% hydrocarbon and only 12.4% fluorocarbon in the bulk. For the freshly cleaved film surface, the low hexadecane contact angles of 10° and 0° (θ_{adv} and θ_{rec}) of the "unannealed" surface show that it is almost completely wettable, indicating a low surface concentration of fluorocarbon roughly representative of the bulk value. Note that the volume fractions fluorocarbon in the tables are almost identical to the wt % F because of the higher density of the F atom. Thus we call this sample PE($C_{10}F_{21}$)$_2$ (12.4% F). It is seen that melt annealing to equilibrate the surface gives rise to a surface fluorine enrichment as evidenced by a large increase in the hexadecane contact angles to 65° and 16° (θ_{adv} and θ_{rec}) (Table 2). This suggests a significantly higher fluorocarbon surface coverage compared to the bulk concentration which will be quantified below by XPS. Since the advancing angle is greater than that for pure PTFE (Table 1), there must be patches of CF_3-containing groups at the surface. The XPS data discussed later are also consistent with an orientation of

Table 3. Advancing Contact Angles (in deg) vs Molecular Weight

			θ_{adv}	
type	M_n	%F[a]	water	hexadecane
1, PCD($C_{10}F_{21}$)$_2$	6600	12.1	124	74
	10000	7.81	126	77
	40000	2.01	119	61
	140000	0.56	104	25
3, PE($C_{10}F_{21}$)$_2$	6400	12.4	131	65
	8400	9.47	127	71
	40000	1.99	124	40
	160000	0.49	114	20
6, PE($C_{10}F_{21}$)	3300	12.15	127	61
	5100	7.76	130	66

[a] Weight percent F in the bulk is calculated from elemental analysis.

Table 4. Advancing Contact Angles vs Fluoroalkyl End Group

			θ_{adv}	
type	M_n	%F[a]	water	hexadecane
1, PCD($C_{10}F_{21}$)$_2$	10000	7.81	126	77
2, PCD(C_4F_9)$_2$	5100	6.72	113	$\leq$10
3, PE($C_{10}F_{21}$)$_2$	8400	9.47	127	71
4, PE(C_4F_9)$_2$	5100	6.71	123	43

[a] Weight percent F in the bulk is calculated from elemental analysis.

Table 5. Hexadecane Contact Angles at 22 °C for Blends of PE($C_{10}F_{21}$)$_2$ (12.4% F) with High MW PE

	%F[a]	θ_{adv}	θ_{rec}
100% PE($C_{10}F_{21}$)$_2$	12.4	67	23
100% PE	0	0	0
2% PE($C_{10}F_{21}$)$_2$ + 98% PE homopolymer			
0 s[b]	0.25	0	0
100 s, 200 °C[b]	0.25	45	0

[a] Weight percent F in the bulk is calculated from elemental analysis. [b] Blend surfaces that were freshly prepared by pressing against a polar surface initially show a depletion of fluoro species for thermodynamic reasons. Melt annealing with the melt surface exposed to air facilitates fluorocarbon migration to the surface.

the perfluorinated chain ends normal to the surface with the CF_3 pointing outward.

The effect of molecular weight on contact angles for the $C_{10}F_{21}$-terminated triblock copolymers of types **1** and **3** is illustrated in Table 3. The molecular weights are calculated from the chemical structure determined by fluorine analyses, using the assumption that molecular weights are determined entirely by chain transfer to the acyclic fluorine-containing olefin. At higher MWs, the bulk fluorine content drops. Up to MWs of approximately 10 000, the surface is quite dense in fluorocarbon, as can be seen by hexadecane advancing contact angles of about 70°. As MW increases, the chain end density in the bulk apparently is not high enough to allow saturation of the surface. This is expected because of the entropic penalty for distorting the chains near the surface, in order to position chain ends at the surface.

The effect of fluorocarbon end group size on contact angles is illustrated in Table 4. Contact angles of polymer types **1** ($C_{10}F_{21}$ ends) and **2** (C_4F_9 ends) with about the same fluorine content show that **1** has a fluorine-rich surface, while **2** has a hydrocarbon-like surface. It appears that $C_{10}F_{21}$ ends are better than C_4F_9 ends at driving the surface excess and/or orientation of the chain ends that leads to high hexadecane contact angles. Microphase separation of fluoroalkyl end groups from hydrocarbon polymer may play a role in determining the surface properties and explain the effect of end group size. Microphase separation (liquid crystalline phases) is known to occur in the solid state in small molecular analogs of polymers of type **3**,[18,19] although the idealized ordered monolayers may be different from the random bulk behavior expected here. $C_{10}F_{21}$ linked to PE would be expected to be borderline compatible in the melt on the basis of the fact that perfluorohexane is compatible with hexane, but perfluoroheptane is not compatible with heptane. The covalent bond between fluoro- and hydrocarbon blocks in the copolymer is a driving force for improved compatibility compared to physical mixtures of the separate materials. C_4F_9-terminated PE is almost certainly a homogeneous system in the melt. For both of these, phase separation of the PE chain center due to crystallization would lead to strong segregation of the perfluorinated groups in the cooled sample. There is also a possibility of crystallization of the $C_{10}F_{21}$ groups,[18,19] but no evidence of this was seen in thermal analysis of chain-end-modified copolymers studied here, possibly because of the dilute concentration of chain ends. The surface of semicrystalline films is known to be amorphous,[17] so if segregation of perfluorinated groups did occur during PE crystallization, a significant excess of perfluorinated groups may be driven to the surface because of this. This would explain some of the differences between noncrystalline unsaturated materials of type **2** and saturated materials of type **4**, both with C_4F_9 ends (Table 4), where it is shown that there is a much higher surface fluorocarbon content for the crystalline **4** as compared to the amorphous material **2**.

Blends. When small amounts of PE($C_{10}F_{21}$)$_2$ and related materials are blended with polyethylene, there is a dramatic change in surface properties (Table 5). By comparing the contact angle data, it is clear that a blend at a very low level of a rather low MW copolymer gives rise to surface properties significantly different than pure polyethylene. The high contact angle hysteresis in the annealed blend (Table 5) is due to patchy and incomplete fluoropolymer coverage at the surface.

The blend series also gives useful insight as to the most effective way to modify the surface at a constant bulk fluorine level. We have found that the blend gives rise to a much higher surface fluorocarbon content than a pure copolymer, where the fluorocarbon level is lowered due to incorporation of a larger polyethylene chain center into the copolymer. For example, this comparison can be seen in Table 3 where the M_n = 40 000 copolymer of type **3** (PE($C_{10}F_{21}$)$_2$, (1.99% F)) is characterized by an θ_{adv} in hexadecane of 40°. It has a bulk F content of about 2% while the blend in Table 5, at a bulk F level of only 0.24%, has a slightly higher contact angle of 45°, showing that the blend system is significantly more effective at modifying the surface. As was discussed earlier, as the polyethylene center becomes larger in the pure copolymer, entropic penalties of distorting chains in order to position chain ends at surfaces are probably the explanation for the poorer performance of the pure copolymer system as compared to the blends.

XPS Surface Profiling. A list of samples studied by XPS along with hexadecane contact angle measurements and calculated surface free energies at 22 °C are given in Table 6. The surface free energies were calculated using advancing water and methylene iodide contact angles and the empirical harmonic mean equation.[17] The samples are all of comparable molecular

Table 6. Structures and Properties of Samples Studied by XPS Including Advancing and Receding Contact Angle Data at 25 °C[a]

				water		hexadecane		
type	structure	M_n	%F	θ_{adv}	θ_{rec}	θ_{adv}	θ_{rec}	γ, mN/M[b]
3	PE($C_{10}F_{21}$)$_2$	6400	12.4	131	93	65	16	9
3[c]	PE($C_{10}F_{21}$)$_2$	6400	12.4	134	73	10	0	27
1	PCD($C_{10}F_{21}$)$_2$[d]	6600	12	124	90	74	22	10
2	PCD(C_4F_9)$_2$[d]	5100	6.7	113	90	~10	0	27
4	PE(C_4F_9)$_2$	5100	6.7	123	92	43	10	12

[a] Film surfaces were melt equilibrated except the indicated PE($C_{10}F_{21}$)$_2$ sample. [b] Solid surface free energies at 22 °C calculated using H_2O and methylene iodide contact angles and the harmonic mean equation. [c] Both PE($C_{10}F_{21}$)$_2$ entries in the table are the same polymer but this surface was not melt equilibrated (see the text). [d] PCD = polycyclododecene.

Table 7. XPS Data: Apparent Atomic Percentage of Compositions of Distinct Elements and Carbon Species[a]

Sample: PE($C_{10}F_{21}$)$_2$ (12.4% F)

angle	F	C	HC	CF_2	CF_3	CF_3/CF_2
90	34.3	65.7	56.5	7.2	2.0	0.28
90 repeat	34.3	65.7	57.2	6.6	2.0	0.30
45	37.7	62.3	52.4	8.1	1.9	0.23
30	41.8	58.2	45.4	9.3	3.5	0.38
20	44.1	55.9	42.0	10.1	3.9	0.39

Sample: PCD($C_{10}F_{21}$)$_2$ (12.1% F)

angle	F	C	HC	CF_2	CF_3	CF_3/CF_2
90	45.9	54.1	40.6	10.8	2.7	0.25
90 repeat	44.6	55.4	42.7	10.5	2.2	0.21
45	50.7	49.3	33.5	12.8	3.0	0.23
30	55.1	44.9	25.6	14.8	4.5	0.30
20	58.1	41.9	21.0	15.9	5.0	0.31

Sample: PCD(C_4F_9)$_2$ (6.7% F)

angle	F	C
90	16.7	83.3
90 repeat	14.8	85.2
45	17.1	82.9
30	21.7	78.3
20	23.5	76.5

Sample: PE(C_4F_9)$_2$ (6.7% F)

angle	F	HC	FC
90	16.0	81.6	2.3
90 repeat	15.4	82.5	2.1
45	18.3	78.8	3.0
30	20.6	75.0	4.4
20	21.9	73.9	4.2

[a] All atomic percentages were directly determined by fitting XPS C1s and F1s regions, so FC is not always equal to *F*/2 as it should be theoretically (see the Experimental Section).

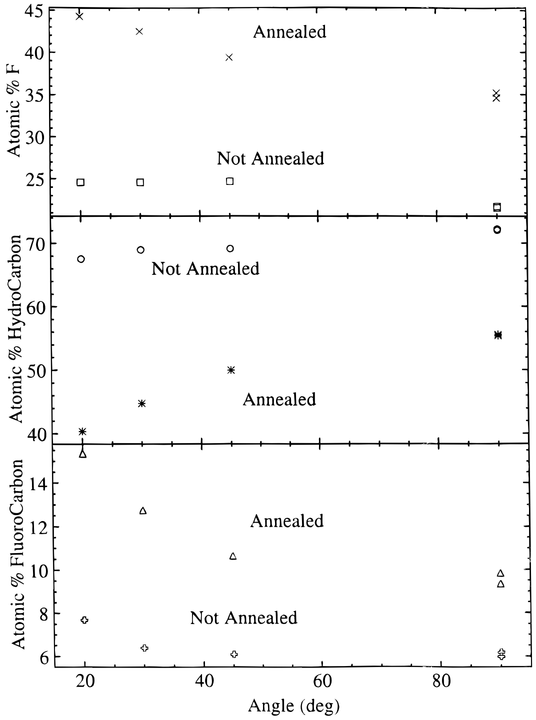


Figure 2. Atomic percents determined by XPS vs angle for annealed and unannealed samples of PE($C_{10}F_{21}$) (12.4% F). The data were taken from Table 2. (see text)

weights and have both ends terminated by either $C_{10}F_{21}$ or C_4F_9. The extent of fluoroalkyl coverage of the outer few angstroms of the surface can be qualitatively accessed by the hexadecane contact angles. The $C_{10}F_{21}$-terminated materials are the most effective at lowering the surface free energy, and all of these have lower surface energies than pure PTFE, which is about 24 mN/m.[17]

XPS data are summarized in terms of atomic compositions for several samples in Table 7. Typical angular dependent data from Table 2 are plotted in Figure 2, showing a strong angular dependence for the annealed sample. The "unannealed" sample will be discussed below. A simple, qualitative interpretation of the results is that the data taken at near-grazing emission give an approximate composition of the "outermost" surface. The depth probed is on the order of $\lambda \sin \theta$, or about 1 nm for 20°. Using this interpretation, the 20° emission analyses in Table 7 indicate that sample PCD($C_{10}F_{21}$)$_2$ (12.1% F in the bulk) has a high fluorocarbon (FC) fraction throughout this ~1 nm layer of FC/*C* = ~70%, where FC + HC = *C*, the total amount of carbon. This is about 10 times the bulk fluorocarbon content. PE($C_{10}F_{21}$)$_2$ (12.4% F) has less but still substantial fluorocarbon (FC/*C* = ~40%) at 20°, and samples PCD(C_4F_9)$_2$ (6.7% F) and PE(C_4F_9)$_2$ (6.7% F) only somewhat less fluorocarbon (FC/*C* = ~16%), but still well above their bulk concentrations. The XPS values of F can also be directly compared with those for the bulk compositions in Table 7, also illustrating the large excesses of fluorine at the surface. Thus, the XPS data can distinguish the $C_{10}F_{21}$-capped materials (40−70% FC/*C* at 20°) from the C_4F_9 materials (~16% FC/*C* at 20°). Note that in atomic percents, FC + HC = total carbon, *C*. Also, atomic percent FC can be inferred to be equal to 0.5 × atomic percent F, because most of the fluorine containing species are CF_2 groups. In cases where the C1s spectrum can be directly analyzed to give atomic percent FC, and F1s spectra analyzed to give atomic percent F, there is some experimental imprecision which makes the above relationships only approximately correct when comparing experimental data.

The fluorocarbon contents of the surface regions measured with XPS reflect both the composition at the outermost surface and the depth of surface segregation. The angular dependence of the XPS signals can indicate the depth of the surface segregation. The ratio of the

Table 8. Ratio of Apparent F (in Atomic %) at Grazing to Normal Emission

entry	sample[a]	F(20°)/F(90°)
1	$\mathrm{PE(C_{10}F_{21})_2}$ (12.4% F)	1.29, 1.28
2[b]	$\mathrm{PE(C_{10}F_{21})_2}$ (12.4% F)[b]	1.14
3	$\mathrm{PCD(C_4F_9)_2}$ (6.7% F)	1.41
4	$\mathrm{PE(C_4F_9)_2}$ (6.7% F)	1.37
5	$\mathrm{PCD(C_{10}F_{21})_2}$ (12.1% F)	1.27
	Model Calculation[c]	
	$\mathrm{C_{10}F_{21}}$	1.50
	$\mathrm{C_4F_9}$	1.86

[a] See Table 6 for contact angle data. [b] This sample is the only one in the table that was not annealed, giving rise to a nonequilibrium, low fluorine coverage surface (see the text). [c] See ref 20 for a description of the model used here.

Table 9. Single Layer Fits of XPS Data Assuming Fixed Bulk Composition, $\mathrm{C_{10}F_{21}}$-Terminated Materials[a]

entry[a]	5	1[b]	1[b]	2[c]
thickness (nm)	2.4	1.5	2.2	3.0
composition (atomic %)[d]				
F	66	57	51	26
C	34	43	49	74

[a] See Table 8 for sample compositions corresponding to the entry numbers given here. The nominal bulk compositions are 12.5 atomic % F and 87.6 atomic % C. [b] These are repeat runs on different portions of the same material. [c] This sample was fractured and not melt equilibrated leading to a lower surface fluorocarbon content (see the text). [d] FC = F/2 (see the text).

F signals between 20° and 90°, F(20°/F(90°), are compared in Table 8 with predicted ratios based on a model[20] where a single layer of the perfluorinated group at the surface is oriented normal to the surface. Note that the ratio F(20°)/F(90°) does not depend on the composition itself, only the depth dependence of the composition. If the thickness of the segregated layer were infinite, the ratio F(20°)/F(90°) would be 1. For the $\mathrm{C_{10}F_{21}}$ caps, the predicted ratio is 1.50, but experiment gives 1.27–1.29. For the $\mathrm{C_4F_9}$ caps, the predicted ratio is 1.86, with measured values of 1.37 and 1.41 (Table 8). The emission angle dependencies indicate that the depths of the fluorocarbon-enriched surface layers exceed the length of a single fluoroalkyl unit oriented normal to the surface.

To obtain a better estimate of the depth and extent of surface segregation, the XPS data can be fit to model depth profiles using nonlinear least-squares methods. The validity of the fits depend on the quality of the data and the validity of the model used. The simplest model depth profile is a single layer of arbitrary thickness and composition over a bulk of the nominal sample composition. The results of such fits in Table 9 are in agreement with the previous conclusions and give estimates of the surface compositions and segregation depths. Entry 5, $\mathrm{PCD(C_{10}F_{21})_2}$ (12.1% bulk atomic F), has a 2.4 nm layer of essentially pure fluorocarbon material (Table 9). We state this based on FC + HC = C = 34%. Since FC = F/2 = 33%, where F is from Table 9, we can see that essentially all the carbon is FC, e.g., FC/C ~ 1.0.

Similarly, the two measurements of entry 1, $\mathrm{PE(C_{10}F_{21})_2}$ (12.4% F) in Table 9, suggest a thinner surface layer with about FC/C = 60 ± 10%, e.g., HC/C = 40%. The unannealed $\mathrm{PE(C_{10}F_{21})_2}$ (12.4% F) (entry 2) is suggested to have a thick surface layer of only twice the bulk fluorocarbon content, e.g., 26% F or FC/C = 18%. The XPS profiling data in Table 10 for $\mathrm{C_4F_9}$-terminated materials also give results in agreement with the conclusions derived above. Data from both materials in Table 10 are fit with the same composition profile, indicating a thin layer with lower F content, but with F content still substantially higher than that in the bulk.

Table 10. Single Layer Fits over Constrained Bulk Composition, $\mathrm{C_4F_9}$-Terminated Materials[a]

entry[a]	3	4
thickness (nm)	1.3	1.4
composition (atomic %)[b]		
F	29	28
C	71	72

[a] See Table 8 for sample compositions corresponding to the entry numbers given here. The nominal bulk compositions for these two samples are 6.3 atomic % F and 93.7 atomic % C. [b] FC = F/2 (see the text).

To briefly summarize the findings in Tables 9 and 10 for the two different chain termination groups, quantitative analysis of the XPS surface composition data for the $\mathrm{C_{10}F_{21}}$-capped materials shows that the surface of $\mathrm{PCD(C_{10}F_{21})_2}$ (12.1% F) is nearly pure fluorocarbon and $\mathrm{PE(C_{10}F_{21})_2}$ (12.4% F) has FC/C = 60%, both with a segregation layer of ca. 2 nm. The surfaces of the $\mathrm{C_4F_9}$-capped materials have FC/C = 20% with a sharper segregation layer of 1.3 nm.

The XPS data also clearly distinguish the annealed and unannealed $\mathrm{PE(C_{10}F_{21})_2}$ (12.4% F) copolymer (Tables 2, 8, and 9 and Figure 2). The higher F level in the unannealed sample at a grazing XPS angle of 20°, as well as the change in composition with angle, show that a slight segregation of F has occurred even without annealing. The low hexadecane contact angles (Table 6) indicate a predominantly hydrocarbon surface for the unannealed sample, consistent with the XPS data.

Discussion

Because of the high fluorocarbon content of the surfaces of samples $\mathrm{PCD(C_{10}F_{21})_2}$ (12.1% F) and $\mathrm{PE(C_{10}F_{21})_2}$ (12.4% F) in Table 7, there is sufficient signal to curve fit the C1s lines to give the amounts of carbon associated with $\mathrm{CF_3}$, $\mathrm{CF_2}$, and hydrocarbon. This allows evaluation of the depth distribution of these carbon species as well. Because the central hydrocarbon portion of the chains will be excluded from the surface, it is expected that the $\mathrm{CF_3}$ ends of the fluorocarbon segments will tend to lie at the surface. The data are in agreement with this expectation, although the structural detail is poor because the intramolecular distances are so short with respect to the electron mean free path used to measure them.

The $\mathrm{CF_3/CF_2}$ ratio increases from 0.29 to 0.39 for $\mathrm{PE(C_{10}F_{21})_2}$ (12.4% F) and from 0.23 to 0.31 for $\mathrm{PCD(C_{10}F_{21})_2}$ (12.1% F) with decreasing angle (Table 7). This shows that in both samples the $\mathrm{CF_3}$ groups are closer to the surface than the $\mathrm{CF_2}$ groups, in some average way. In a randomly oriented $\mathrm{C_{10}F_{21}}$ group, the $\mathrm{CF_3/CF_2}$ ratio measured with XPS should be independent of angle and equal to 0.11. The higher ratios measured and the dependency on emission angle both indicate that the $\mathrm{CF_3}$ groups lie closer to the surface than the $\mathrm{CF_2}$. The data are consistent with perfect fluoroalkyl chain orientation, but do not exclude a high degree of misorientation. It should be recalled that the outermost surface layer does contain a finite fraction of hydrocarbon material, with $\mathrm{PE(C_{10}F_{21})_2}$ (12.4% F) being more rich in hydrocarbon than $\mathrm{PCD(C_{10}F_{21})_2}$ (12.1% F) (Table 9). The presence of a small amount of hydrocarbon is consistent with the substantial contact angle hysteresis in hexadecane (Table 6) for these two.

Hydrogenation of **2** to **4** [i.e., to PE(C_4F_9)$_2$] results in increased contact angles that are consistent with a partially fluorinated surface. In contrast to the contact angle data, XPS of samples of **2** and **4** are similar. Modeling of the angle-dependent XPS data suggest that both samples have a partially fluorinated surface with about half of the fluorine level expected for a pure C_4F_9 surface. One possible explanation of the difference between the contact angle data and XPS of **2** is that because of its low crystallinity, it may have enough mobility to allow rearrangement of the surface under hexadecane to give a hydrocarbon-like interface with a low contact angle. The higher crystallinity of **3** and **4** and the larger fluoroalkyl ends of **1** may prevent this rearrangement. Microphase separation of fluoroalkyl end groups during crystallization of the hydrocarbon polymer probably plays a role in determining the surface properties and may explain the effect of end group size. Microphase separation is much more likely to occur with $C_{10}F_{21}$ end groups than with C_4F_9 ends, especially in the solid state where crystallization of PE would drive phase separation. Microphase separation (liquid crystalline phases) is known to occur in small molecular analogs of **3**.[18,19]

On the basis of the contact angle and XPS data, we propose that the surfaces are chemically heterogeneous, consisting of some regions that are mostly hydrocarbon, and other regions that are ordered aggregates of fluoroalkyl end groups arranged with the CF_3 ends pointing outward. A structure of this type has recently been directly observed by atomic force microscopy on an LB film of arachidic acid mixed with a partially fluorinated carboxylic acid.[21]

Although not as low in surface free energy as certain high fluorine level side group polymers,[4−6] the perfluoroalkane-terminated polyolefins become quite low in surface energy due to the high level of chain end segregation to the surface. In one of the cases where we can compare surface free energy as a function of bulk fluorine weight fraction, perfluoroalkane-terminated PE at a level of 12 wt % F has about the same surface properties as side-group-substituted styrene-based copolymers with 36 wt % F.[6] Several recent studies have probed the extent of segregation of perfluorinated chain ends to the vacuum/polymer surface,[7,11,22,23] including detailed XPS studies of fluorine excesses in partially fluorinated systems.[22−24] The segregation was driven by the strong enthalpic attraction of the low-energy species to the surface.[11]

Conclusions

Linear polyethylene (PE) with fluoroalkyl end groups has been prepared by ring-opening metathesis polymerization of cyclododecene in the presence of partially fluorinated acyclic olefins (chain transfer agents), followed by reduction of the double bonds in the backbone. Melt surface tension data were obtained for polyethylenes with one or both ends terminated by F(CF_2)$_{10}$ or F(CF_2)$_4$ groups. Surface characterization of fluoroalkyl-functionalized polymers consisted of melt surface tension, contact angles, and XPS (X-ray photoelectron spectroscopy). Copolymers typically have very high hexadecane contact angles, consistent with CF_3rich surfaces. XPS profiling measurements confirm the fluorine-rich nature of the surfaces. Modeling of the angle dependent XPS data of a copolymer of type **1** at only 12 wt % F in the bulk shows that the surface is enriched in fluorocarbon by a factor of 6−10 over that in the bulk. A sample of **3** with the same wt % F also shows fluorine enrichment at the surface, although modeling of this sample indicates that the fluorocarbon coverage is closer to 60%. In both **1** and **3**, separate carbon signals were resolved for the CH_2, CF_2, and CF_3 groups, and the angle dependence shows that the CF_3 groups are closer to the surface on average than the CF_2 groups. Comparison of hexadecane contact angles of **1** ($C_{10}F_{21}$ ends) and **2** (C_4F_9 ends) with the same total fluorine content demonstrates that $C_{10}F_{21}$ ends are significantly better than C_4F_9 ends at driving the surface excess and/or orientation of the chain ends that leads to high fluorocarbon surface coverage detected by surface energetics and XPS.

The hexadecane contact angles of fluoroalkyl-ended metathesis polymers [PE($C_{10}F_{21}$)$_2$] decrease substantially as the molecular weight increases above ca. 40 000. In that range, the bulk concentration of chain ends becomes quite low and the surface concentration of fluorocarbon chain ends at the surface is sharply reduced due to configurational entropic restrictions. The surface properties of blends of a lower MW PE($C_{10}F_{21}$)$_2$ copolymer with a PE homopolymer were evaluated and compared to the series of pure PE($C_{10}F_{21}$)$_2$ copolymers where the high MW limit of the polyethylene center is approached. At similar bulk F levels in the blends and pure copolymer, the relative surface fluorocarbon content in the blends is significantly enhanced.

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References and Notes

(1) Zisman, W. A. In *Advances in Chemistry Series 43*; Gould, R. F., Ed.; American Chemical Society; Washington, DC, 1964; p 1.
(2) Johnson, R. E.; Dettre, R. H. *Surf. Colloid Sci.* **1969**, *2*, 132.
(3) Johnson, R. E.; Dettre, R. H. In *Wettability*; Berg, J. C., Ed.; Marcel Dekker, New York, 1993; p 1.
(4) Johnson, R. E.; Dettre, R. H.; Brandreth, D. A. *J. Colloid Interface Sci.* **1977**, *62*, 205.
(5) Johnson, R. E.; Dettre, R. H. *Polym. Prep. (ACS Division of Polym. Chem.)*, **1987** *28(2)*, 48.
(6) Höpken, J.; Möller, M. *Macromolecules* **1992**, *25*, 1461.
(7) Albert, B.; Jerome, R.; Teyssie, P. *Makromol. Chem.* **1984**, *185*, 579.
(8) Schimdt, D. L.; Coburn, C. E.; DeKoven, B. M.; Potter, G. E.; Meyers, G. F.; Fischer, D. A. *Nature* **1994,** *368*, 39.
(9) Ivin, K. J. *Olefin Metathesis*; Academic Press: New York, 1983.
(10) Edwards, H. G. M.; Johnson, A. F.; Lewis, I. R.; Maitland, D. J.; Webb, N. *J. Mol. Struct.* **1992**, *268*, 363−372.
(11) Elman, J. F.; Johs, B. D.; Long, T. E.; Koberstein, J. T. *Macromolecules* **1994**, *27*, 5341.
(12) Sauer, B. B.; DiPaolo, N. V. *J. Colloid Interface Sci.* **1991**, *144*, 527.
(13) Hazell, L. B.; Brown, I. S.; Freisinger, F. *Surf. Interface Anal.* **1986**, *8*, 25−31. Fadley, C. S. *Prog. Surf. Sci.* **1984,** *16*, 275−388.
(14) Dilks, A. *Electron Spectroscopy, Theory, Techniques and Applications*; Vol. 4.; Brundle, C. R.; Baker, A. D., Eds.; Academic Press: London, 1984; p 277.
(15) Dee, G. T.; Sauer, B. B. *J. Colloid Interface Sci.* **1992**, *152*, 85.
(16) Sauer, B. B.; Dee, G. T. *Macromolecules* **1994**, *27*, 6112.
(17) Wu, S. In *Polymer Interface and Adhesion*; Marcel Dekker: New York: **1982**.
(18) Rabolt, J. F.; Russell, T. P.; Twieg, R. J. *Macromolecules* **1984**, *17*, 2786.

(19) Höpken, J.; Möller, M. *Macromolecules* **1992**, *25*, 2482.

(20) Calculations[13] were done for single layers intended to represent pure $C_{10}F_{21}$ and C_4F_9 layers over uniform bulk material with the specified composition. For the $C_{10}F_{21}$ calculation, 1.67 nm of 32 atomic % C, 68 atomic % F over a bulk of 87.6 atomic % C, 12.5 atomic % F was used. For the shorter segment, C_4F_9, 0.7 nm of 31 atomic % C, 69 atomic % F over a bulk of 93.7 atomic % C, 6.3 atomic % F was used. Equal atomic densities in both layers was assumed. The relative thicknesses were chosen to give the correct relative numbers of atoms in the two fluoroalkyl units.

(21) Overney, R.; Meyer, E.; Frommer, J.; Brodbeck, D.; Howard, L.; Guntherodt, H.; Fujihira, M.; Takano, H.; Gotoh, Y. *Nature*, **1992,** *359*, 133.

(22) McLain, S. J.; Sauer, B. B.; Firment, L. E. *Am. Chem. Soc. Polym. Prepr.* **1993,** *34 (2)*, 666.

(23) Hunt, M. O. Jr.; Belu, A. M.; Linton, R. W.; DeSimone, J. M. *Macromolecules* **1993**, *26*, 4854.

(24) Kassis, C. M.; Steehler, J. K.; Betts, D. E.; Guan, Z.; Romack, T. J.; DeSimone, J. M.; Linton, R. W. *Macromolecules* **1996**, *29*, 3247.

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