Surface Modification of Poly(chlorotrifluoroethylene): Introduction of Reactive Carboxylic Acid Functionality

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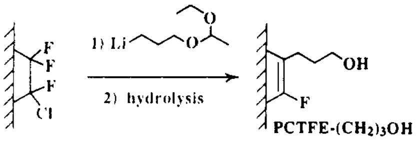
ABSTRACT: The reaction of poly(chlorotrifluoroethylene) (PCTFE) film with trimethyl 4-lithioorthobutyrate in THF/heptane at −78 to −17 °C produces a modified (PCTFE) surface containing orthobutyrate functionality in the outer ~25–~100 Å (PCTFE–$(CH_2)_3C(OCH_3)_3$). Quantitative X-ray photoelectron spectroscopy (XPS) indicates that the modified surface layer contains orthobutyrate groups attached to ~80% of the original PCTFE repeat units; the other ~20% of virgin repeat units has been converted to difluoroolefins. Hydrolysis of the orthobutyrate surface renders carboxylic acids and produces a very hydrophilic polymer film sample (PCTFE–$(CH_2)_3CO_2H$). The advancing water contact angle (θ_A) of PCTFE–$(CH_2)_3CO_2H$ is dependent on pH and is ~56° at low pH and ~30° at high pH. The receding water contact angle (θ_R) is 0° at all pH values. PCTFE–$(CH_2)_3CO_2H$ forms esters in high yields using three standard esterification conditions: The *n*-octyl ester was prepared by acid-catalyzed esterification, through the intermediate acid chloride (prepared with thionyl chloride) and through the intermediate acyl imidazolide (prepared with carbonyldiimidazole). PCTFE–$(CH_2)_3CO_2H$ is reduced to the alcohol, PCTFE–$(CH_2)_4OH$, with borane/THF complex. The surface-chemical transformations reported have been monitored by a combination of XPS, ATR, IR, contact angle, UV–vis, and gravimetric analyses.

Introduction

The chemistry of carboxylic acids, covalently attached to solid polyethylene film (PE–CO_2H) at the solid–solution interface, is rich and versatile and has been studied more extensively[1-11] than any other analogous system. We have been studying the introduction of reactive functionality to chemically resistant polymer film surfaces, specifically poly(chlorotrifluoroethylene) (PCTFE),[12-17] poly(tetrafluoroethylene) (PTFE),[18] poly(vinylidene fluoride) (PVF_2,[17,19-21] poly(tetrafluoroethylene-*co*-hexafluoropropylene) (FEP),[17,22] and poly(ether ether ketone) (PEEK).[23] These polymer choices were made so that film samples could be prepared with reactive surfaces and inert interiors; thus, subsequent chemistry can be effected exclusively at the film surface, permitting the preparation of film samples differing only in their surface chemistry and amenable to surface structure–property correlations. We have focused our attention on the chemistry of alcohol-functionalized surfaces for the particular reasons that (1) we can make them on PCTFE,[13] PTFE,[18] PVF_2,[20] FEP,[22] and PEEK[23,24] and (2) they react with electrophiles in solution in (most often) high yield. In particular, PCTFE–$(CH_2)_3OH$[14] (eq 1), which contains a primary alcohol attached to the polymer chain by a three-methylene spacer, exhibits versatile chemistry. We have reported the synthesis of several carboxylic acid-containing surfaces (on PCTFE,[13,17] PTFE,[18] PVF_2,[17] FEP,[17] and PEEK[23]), but as substrates for surface-chemical studies they are far inferior to the alcohol-functionalized surfaces and PE–CO_2H: they contain either other functionality[13,18,23] or low surface concentrations[17] (submonolayer levels) of carboxylic acids. We studied[25] the esterification of PCTFE–CH_2CO_2H (eq 2) using a wide range of esterification conditions; yields were very low (0–30%). A consistent explanation for the low reactivity is that the carboxylic acid is separated from the polymer backbone by only a single methylene unit.



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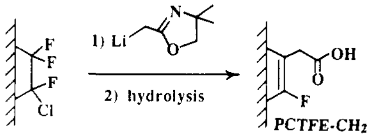

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We report in this paper the synthesis of a reactive, densely functionalized carboxylic acid surface (PCTFE–$(CH_2)_3CO_2H$) that should prove to be a complementary surface to PCTFE–$(CH_2)_3OH$ for surface-chemical studies and with which we can take advantage of the rich chemistry[1-11] of surface carboxylic acids.

Experimental Section

General. PCTFE film (5-mil Allied Aclar 33C) was extracted in refluxing dichloromethane for 2 h and dried (0.05 mm, room temperature, >24 h). Film samples used for gravimetric analysis were dried (0.05 mm, 70 °C) for 3 days. Heptane was distilled under nitrogen from calcium hydride. THF was distilled under nitrogen from sodium benzophenone dianion. Trimethyl 4-bromoorthobutyrate (BrTMOB) was distilled under vacuum (trap-to-trap) from potassium carbonate and stored under nitrogen over potassium carbonate. *tert*-Butyllithium (1.7 M in pentane) was standardized by titration with 4-biphenylmethanol[26] in THF at −78 °C. Potassium chlorate (Alfa) was used as received. Thionyl chloride, 1-octanol, and heptafluorobutyryl chloride were distilled under vacuum (trap-to-trap) and stored under nitrogen. *p*-Toluenesulfonic acid monohydrate was dehydrated by azeotropic distillation of the water with benzene and recrystallized from benzene. Methanol, dichloromethane, THF, and water (house distilled redistilled with a Gilmont still) used as wash solvents were sparged with nitrogen. All reagents, unless otherwise indicated, were obtained from Aldrich. XPS spectra were obtained with a Perkin-Elmer–Physical Electronics 5100 spectrometer using Mg Kα excitation (400 W, 15.0 kV). Spectra were routinely recorded at two takeoff angles, 15° and 75° (measured between the film surface plane and the entrance lens of the detector optics). Atomic composition data were determined using sensitivity factors obtained from samples of known composition: F_{1s}, 1.00; C_{1s}, 0.225; O_{1s}, 0.620; N_{1s}, 0.392; Cl_{2p}, 0.655. Attenuated total reflectance infrared (ATR IR) spectra were recorded using an IBM 38 FTIR at 4-cm^{-1} resolution with a 10 × 5 × 1 mm germanium internal reflection element (45°). UV–vis spectra were acquired with a Perkin-Elmer Lambda 2 optics bench interfaced with an IBM PS/2 using Perkin-Elmer PECSS

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UV–vis software. Spectra were recorded using an unreacted PCTFE sample as the reference. Gravimetric measurements were made with a Cahn 29 electrobalance. Dynamic advancing (θ_A) and receding (θ_R) contact angles were measured with a Ramé-Hart telescopic goniometer and a Gilmont syringe with a flat-tipped 24-gauge needle as probe fluid was added (θ_A) or withdrawn (θ_R) from the drop. Probe fluids were either water purified as described above or buffered solutions[27] that were adjusted to the desired pH using a Fisher 825MP pH meter.

Trimethyl 4-Lithoorthobutyrate (LiTMOB). BrTMOB (3.05 g, 13.4 mmol) was added via syringe to a dry, nitrogen-purged reaction flask containing a glass-coated magnetic stir bar. Heptane (46 mL) was added, and the solution cooled to −78 °C (a small amount of BrTMOB precipitates from the solution at this temperature). A solution of *tert*-butyllithium (1.7 M, 7.8 mL, 13.3 mmol) in heptane (32 mL) (−78 °C) was then added slowly to the BrTMOB solution via cannula. The mixture was stirred at this temperature for 15 min and then placed in a −20 °C bath for 30 min. The resulting white suspension was recooled to −78 °C, and then THF (86 mL, −78 °C) was added to dissolve the precipitate.

Reaction of LiTMOB with PCTFE Film (PCTFE–$(CH_2)_3$-$CO_2H_3)_3$). A nitrogen-purged Schlenk tube containing PCTFE film samples was equilibrated at the desired reaction temperature. Reactions were conducted at −78, −67, −51, −26, and −17 °C. A solution of LiTMOB in heptane/THF (prepared as described above) was equilibrated at the same temperature and then added via cannula to cover the film samples. After 30 min, the reagent solution was removed and the film samples were washed with methanol (1 × 30 mL at the reaction temperature), methanol (3 × 30 mL), H_2O (3 × 30 mL), methanol (3 × 30 mL), and then dichloromethane (3 × 30 mL) and dried (0.05 mm, >24 h). Film samples for gravimetric analysis were dried more extensively (0.05 mm, 70 °C, 3 days).

Oxidation of PCTFE–$(CH_2)_3(OCH_3)_3$. PCTFE–$(CH_2)_3C(OCH_3)_3$ film samples were placed in a solution of 1.0 g of $KClO_3$ in 50 mL of concentrated H_2SO_4 for 2 h. The film samples were then removed, rinsed with distilled water, soaked in distilled water for 2 h, in methanol for 2 h, and in dichloromethane for 1 h, and dried (0.05 mm, 70 °C, 3 days).

Hydrolysis of PCTFE–$(CH_2)_3C(OCH_3)_3$ (PCTFE–$(CH_2)_3$-CO_2H). To a nitrogen-purged, jacketed (for reflux) Schlenk tube containing PCTFE–$(CH_2)_3C(OCH_3)_3$ film samples (prepared at −17 °C) and PTFE boiling chips was added via cannula a solution of CF_3CO_2H/acetone/H_2O (5:20:80 mL). After 24 h at reflux, the solution was removed and the film samples were washed with H_2O (3 × 30 mL), methanol (3 × 30 mL), and then dichloromethane (3 × 30 mL) and dried (0.05 mm, >24 h).

Acid-Catalyzed Esterification of PCTFE–$(CH_2)_3CO_2H$ (PCTFE–$(CH_2)_3CO_2Oct^A$). To a nitrogen-purged jacketed Schlenk tube containing PCTFE–$(CH_2)_3CO_2H$ film samples, PTFE boiling chips, and 1.0 g of *p*-toluenesulfonic acid was added 20 mL of THF followed by 5 mL of 1-octanol. The reaction mixture was then heated to reflux. After 24 h, the solution was removed and the film was washed with THF (5 × 30 mL), H_2O (5 × 30 mL), methanol (3 × 30 mL), and then dichloromethane (3 × 30 mL) and dried (0.05 mm, >24 h).

Esterification of PCTFE–$(CH_2)_3CO_2H$ via the Acid Chloride (PCTFE–$(CH_2)_3CO_2Oct^B$). To a nitrogen-purged Schlenk tube containing PCTFE–$(CH_2)_3CO_2H$ film samples was added 25 mL of THF followed by 3 mL of thionyl chloride. After 24 h at room temperature, the solution was removed and 20 mL of THF was added followed by 5 mL of 1-octanol. The reaction was allowed to proceed for 24 h, and the film was washed with THF (5 × 30 mL), methanol (3 × 30 mL), and then dichloromethane (3 × 30 mL) and dried (0.05 mm, >24 h).

Esterification of PCTFE–$(CH_2)_3CO_2H$ via the Imidazolide (PCTFE–$(CH_2)_3CO_2Oct^C$). To a nitrogen-purged jacketed Schlenk tube containing PCTFE–$(CH_2)_3CO_2H$ film samples was added 1.0 g of carbonyldiimidazole (CDI) in a glove box. THF (25 mL) was then added and the solution brought to reflux. After 24 h, the CDI solution was removed via cannula and 25 mL of THF was added followed by 5 mL of 1-octanol. After 40 h at reflux, the solution was removed and the film samples were washed with THF (5 × 30 mL), methanol (3 × 30 mL), and then dichloromethane (3 × 30 mL) and dried (0.05 mm, >24 h).

Table I
Water Contact Angle Data

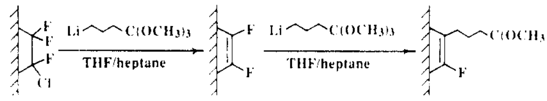
sample	contact angles, deg	
	θ_A	θ_R
PCTFE	104	77
PCTFE–$(CH_2)_3C(OCH_3)_3$ (−78 °C)	76	49
PCTFE–$(CH_2)_3C(OCH_3)_3$ (−67 °C)	77	49
PCTFE–$(CH_2)_3C(OCH_3)_3$ (−51 °C)	78	48
PCTFE–$(CH_2)_3C(OCH_3)_3$ (−26 °C)	76	49
PCTFE–$(CH_2)_3C(OCH_3)_3$ (−17 °C)	73	48
PCTFE–$(CH_2)_3CO_2H$	55	0
PCTFE–$(CH_2)_3CO_2Oct^A$	98	47
PCTFE–$(CH_2)_3CO_2Oct^B$	100	45
PCTFE–$(CH_2)_3CO_2Oct^C$	98	49
PCTFE–$(CH_2)_4OH$	62	22
PCTFE–$(CH_2)_4OCOC_3F_7$	89	47

Reduction of PCTFE–$(CH_2)_3CO_2H$ (PCTFE–$(CH_2)_4OH$). To a nitrogen-purged Schlenk tube containing PCTFE–$(CH_2)_3$-CO_2H film samples was added 25 mL of BH_3·THF (1.0 M in THF). The film samples were allowed to react under nitrogen at room temperature for 24 h and were then washed with THF (5 × 30 mL) and H_2O (5 × 30 mL). The film samples were soaked in a solution of CH_3CO_2H/THF (5:20 mL) for 24 h and washed with THF (5 × 30 mL), H_2O (5 × 30 mL), methanol (3 × 30 mL), and then dichloromethane (3 × 30 mL) and dried (0.05 mm, >24 h).

Reaction of PCTFE–$(CH_2)_4OH$ with Heptafluorobutyryl Chloride. To a nitrogen-purged Schlenk tube containing PCTFE–$(CH_2)_4OH$ film samples was added 25 mL of THF followed by 1.1 mL of heptafluorobutyryl chloride. The film samples were allowed to react for 24 h under nitrogen at room temperature and then were washed with THF (5 × 30 mL) and dichloromethane (3 × 30 mL) and dried (0.05 mm, >24 h).

Results and Discussion

The mechanism and the temperature, solvent, and alkyllithium structure dependencies of the reaction of PCTFE film with lithium reagents have been described in detail elsewhere.[12,13,16] The protected carboxylic acid-containing lithium reagent, trimethyl 4-lithioorthobutyrate (LiTMOB), is conveniently prepared by lithium–halogen exchange between BrTMOB and *tert*-butyllithium in heptane and is soluble in THF/heptane mixtures. PCTFE film reacts with LiTMOB in THF/heptane (50:50) by the reduction–addition–elimination reaction described in eq 3. We wished to control the depth of modification (thickness of the modified layer) and chose to vary reaction temperature to do so.[28] The reaction was run at five different temperatures (−78, −67, −51, −26, and −17 °C) for 30 min. Water contact angle analysis of the reaction product film samples indicated that more hydrophilic surfaces of essentially the same wettability were produced at each temperature. The relatively polar trimethyl orthoester group induced contact angle changes from 104°/77° (θ_A/θ_R) for virgin PCTFE to 73–78°/48–49° (Table I). Figures 1 and 2 show XPS survey and C_{1s} region spectra for PCTFE and PCTFE–$(CH_2)_3C(OCH_3)_3$ prepared at −78 and −17 °C. In agreement with the chemistry described in eq 3, the survey spectra indicate, upon reaction, a decrease in fluorine and chlorine intensity (chlorine is almost completely removed at −17 °C), an increase in carbon intensity, and the introduction of oxygen. The C_{1s} spectra of the −78 and −17 °C reacted samples are shown curve-fitted with four and three peaks, respectively. The highest binding energy peak in the spectrum of the sample



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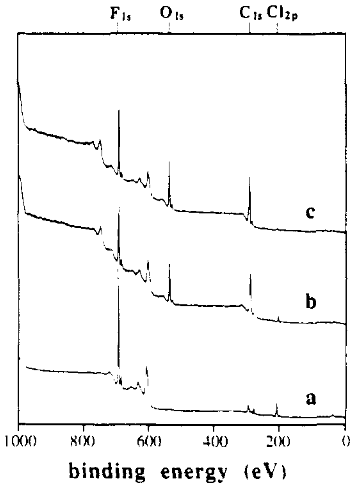


Figure 1. XPS survey spectra (75° takeoff angle) of PCTFE (a), PCTFE–$(CH_2)_3C(OCH_3)_3$ (−78 °C) (b), and PCTFE–$(CH_2)_3C(OCH_3)_3$ (−17 °C) (c).

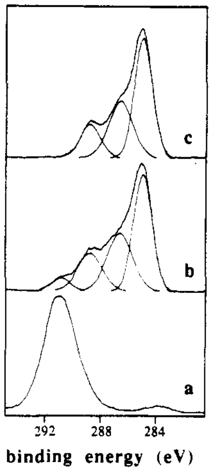


Figure 2. XPS C_{1s} region spectra (75° takeoff angle) of PCTFE (a), PCTFE–$(CH_2)_3C(OCH_3)_3$ (−78 °C) (b), and PCTFE–$(CH_2)_3C(OCH_3)_3$ (−17 °C) (c).

prepared at −78 °C is due to unreacted PCTFE. This peak is not present in the spectrum of the sample prepared at −17 °C. These spectra were recorded at a takeoff angle of 75° (between the film plane and the detector) and represent the composition of the outer ~40 Å (95% of the measured photoelectrons originate in this region).[29] The spectra indicate, assuming that a noncorrosive reaction front proceeds parallel to the film surface, that the reaction depth is less than 40 Å at −78 °C and greater than 40 Å at −17 °C. That there is no virgin PCTFE remaining in the outer 10 Å of samples prepared at all temperatures (indicated by the 15° takeoff angle spectra) supports this assumption. The three peaks in the spectrum of the sample prepared at −17 °C and the analogous peaks from the −78 °C sample are, respectively, in order of decreasing binding energy, due to carbon bonded with three oxygens, carbon bonded to one oxygen or one fluorine, and carbon bonded to only carbon or hydrogen.

Quantitative analysis[30] of the curve-fitted C_{1s} spectrum of the sample prepared at −78 °C indicates that the thickness of the modified layer is ~25 Å. By combined analysis using this XPS-derived value and UV–vis absorbance data (transmission spectra), estimates of modified layer thicknesses for the more deeply modified (higher reaction temperature) film samples can be made. The UV–vis spectra of the PCTFE–$(CH_2)_3C(OCH_3)_3$ film samples exhibit a broad absorbance from 210 to 390 nm with λ_{max} = 245 nm. Using the value of 25 Å for the thickness of the modified layer in the sample prepared at −78 °C, an extinction coefficient of 731 Å/au can be calculated from the absorbance value at 245 nm. Assuming a Beer's law relationship is followed, this allows the calculation of modification depths from absorbance values. The results as a function of reaction temperature are plotted in Figure 3. Similar calculations can be made from ATR IR spectra (see below) using the absorbance at 1740 cm^{-1} (the extinction coefficient is 1196 Å/au). These are also plotted in Figure 3.

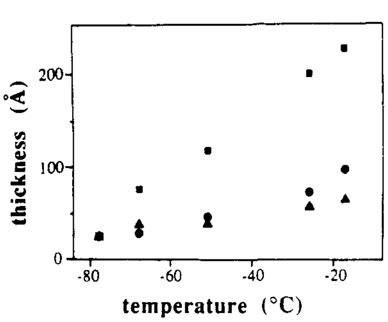


Figure 3. Effect of reaction temperature on depth of modification (modified layer thickness) determined by XPS/UV–vis (▲), XPS/ATR IR (●), and gravimetric analysis (■). See text for details.

Another estimate of reaction depth can be made by oxidatively removing the modified layer with a strong oxidizing agent ($KClO_3/H_2SO_4$).[22] PCTFE is inert to this oxidant. From a measurement of the mass lost upon oxidation, an assumed density (2 g/cm^3, slightly less than that of PCTFE) and the surface area of the film sample an average reaction depth can be calculated. These thickness values are also plotted vs reaction temperature in Figure 3. Differences between these reaction depths are likely due to a number of factors. The XPS/UV–vis and XPS/ATR IR results depend on the validity of a number of assumptions: that the reaction is noncorrosive and gives a sharp interface that is parallel to the film surface (no modified material is present beneath the XPS sampling depth), that the mean free path of C_{1s} electrons is the same in this material as it is in the material in which it was measured,[29] and that Beer's law is valid in this solid. The gravimetric results are likely overestimates: unreacted PCTFE (low molecular weight segments of chains between modified blocks and small less reactive crystallites) is likely removed on oxidation, increasing the mass loss. That the values converge at low temperature and thinner modified layers (all three methods give a reaction depth of 25 Å at −78 °C) implicates the Beer's law assumption and the loss of unreacted PCTFE mass as the important factors giving the differences. Regardless, both methods reveal a reaction temperature-dependent thickness and we are comfortable estimating reaction depths of ~25 Å at −78 °C and ~100 Å at −17 °C.

ATR IR spectra of the more deeply modified samples exhibit lucid infrared absorbances. Figure 4 shows spectra of PCTFE and PCTFE–$(CH_2)_3C(OCH_3)_3$ (−17 °C). The orthoester absorbance[31] at 1740 cm^{-1}, C–H stretching vibrations (2980–2840 cm^{-1}), and C–H bending modes (1460–1360 cm^{-1}) are apparent. Subsequent chemistry with PCTFE–$(CH_2)_3C(OCH_3)_3$ described in this paper was carried out on samples prepared at −17 °C to facilitate infrared analysis.

A more quantitative assessment of the reaction (eq 3) can be made through analysis of XPS atomic composition data (Table II). The predicted stoichiometry for the product of a quantitative conversion is C_9FO_3 (XPS does

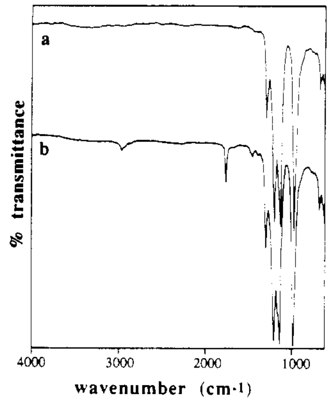


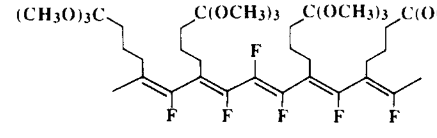
Figure 4. ATR IR spectra of PCTFE (a) and PCTFE–$(CH_2)_3C(OCH_3)_3$ (–17 °C) (b).

Table II
XPS Atomic Composition Data

film sample	takeoff angle, deg	C	F	O	Cl
PCTFE	15	33.6	50.8		15.6
	75	33.4	50.6		16.0
PCTFE–$(CH_2)_3C(OCH_3)_3$ (–78 °C)	15	66.2	17.1	15.6	1.1
	75	65.2	17.1	14.7	3.0
PCTFE–$(CH_2)_3C(OCH_3)_3$ (–67 °C)	15	66.2	15.8	17.2	0.8
	75	67.0	14.9	16.6	1.6
PCTFE–$(CH_2)_3C(OCH_3)_3$ (–51 °C)	15	66.2	16.0	17.0	0.9
	75	66.5	14.9	16.4	2.2
PCTFE–$(CH_2)_3C(OCH_3)_3$ (–26 °C)	15	67.9	12.7	18.7	0.8
	75	68.2	12.3	17.7	1.8
PCTFE–$(CH_2)_3C(OCH_3)_3$ (–17 °C)	15	69.2	10.9	19.5	0.4
	75	69.3	10.8	18.6	1.4
PCTFE–$(CH_2)_3CO_2H$	15	65.6	13.4	19.4	1.6
	75	62.5	15.8	16.7	5.1
PCTFE–$(CH_2)_3CO_2Oct^A$	15	82.8	5.3	11.5	0.5
	75	79.0	7.8	12.1	1.2
PCTFE–$(CH_2)_3CO_2Oct^B$	15	82.4	4.7	12.0	0.9
	75	79.3	6.2	12.7	1.7
PCTFE–$(CH_2)_3CO_2Oct^C$	15	82.8	4.6	10.5	0.5[a]
	75	78.4	6.4	11.8	1.6[a]
PCTFE–$(CH_2)_4OH$	15	72.5	12.3	13.7	1.5
	75	70.4	13.0	12.5	4.1
PCTFE–$(CH_2)_4OCOC_3F_7$	15	54.1	32.1	12.3	1.4
	75	57.3	27.2	12.2	3.4

[a] PCTFE–$(CH_2)_3CO_2Oct^C$ also contains 1.5% and 1.8% nitrogen at 15° and 75° takeoff angles, respectively.

not detect hydrogen). The observed stoichiometries of PCTFE–$(CH_2)_3C(OCH_3)$ prepared at –17 °C are $C_9F_{1.4}O_{2.5}$ (15° takeoff angle) and $C_9F_{1.4}O_{2.4}$ (75° takeoff angle). A small amount of chlorine is also observed and more at the higher takeoff angle. This is due to unreacted PCTFE below the sampling depth of the C_{1s} spectrum (Figure 2c); the mean free path of Cl_{2p} photoelectrons is longer than that of C_{1s} photoelectrons.[30] We ignore the presence of chlorine and use the 15° takeoff angle data to minimize resulting discrepancies in this stoichiometry calculation (chlorine is observed in 0.4% atomic composition). The high fluorine concentration and low oxygen concentrations are inconsistent with a quantitative yield but consistent with a structure consisting of ~80% trimethyl orthobutyrate-functionalized repeat units and ~20% difluoroolefins.



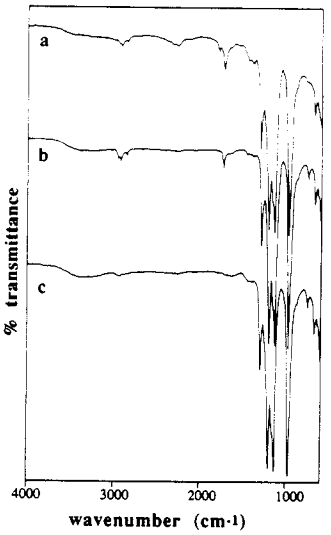
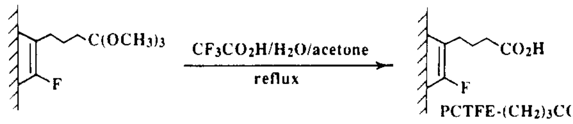


Figure 5. ATR IR spectra of PCTFE–$(CH_2)_3CO_2H$ (a), PCTFE–$(CH_2)_3CO_2Oct^A$ (b), and PCTFE–$(CH_2)_4OH$ (c).

This structure predicts a stoichiometry of $C_{38}F_6O_{12}$, and the observed composition is $C_{38}F_{6.0}O_{10.7}$. This indicates that the first steps of the reaction (eq 3), metal–halogen exchange and elimination of LiF, proceed in quantitative yield to the difluoroolefin and the subsequent addition–elimination reaction proceeds in ~80% yield to render a surface containing four protected carboxylic acids per five PCTFE repeat units. Similar yields are observed in the reaction of PCTFE with lithiopropyl ethyl acetaldehyde acetal.[14]

A range of conditions for hydrolysis were screened; each involved an acid catalyst, water, and an organic solvent to lower interfacial free energy. Refluxing $CF_3CO_2H/H_2O/$acetone (5:80:20 volume ratio) for 24 h proved to completely hydrolyze the orthoester (eq 4). Water contact angles (θ_A/θ_R = 55°/0°) of PCTFE–$(CH_2)_3CO_2H$ indicate a very hydrophilic surface. These values are identical to those of polyethylene carboxylic acid.[1-11] ATR IR (Figure 5a, compare with Figure 4b) indicates the disappearance of the orthoester (1740 cm^{-1}) and the appearance of the carboxylic acid (1710 cm^{-1}). A small absorbance band at 1782 cm^{-1} also appears; we assign this to α-fluoroketone resulting from hydrolysis of the difluoroolefin. Figure 6 (parts a and b) compares the C_{1s} region XPS spectra of PCTFE–$(CH_2)_3C(OCH_3)_3$ and PCTFE–$(CH_2)_3CO_2H$. The middle binding energy region assigned to carbons bound to one oxygen or fluorine (Figure 2) decreases in intensity after hydrolysis as expected. The observed stoichiometries of PCTFE–$(CH_2)_3CO_2H$ (Table II) are $C_{26}O_{7.7}F_{5.3}$ (15° takeoff angle) and $C_{26}O_{6.9}F_{6.6}$ (75° takeoff angle). The theoretical value (based on four $(CH_2)_3CO_2H$ groups per five repeat units) is $C_{26}O_8F_6$.



(4)

The pH dependence of the advancing contact angle for PCTFE–$(CH_2)_3CO_2H$ as well as PCTFE, PCTFE–$(CH_2)_3C(OCH_3)_3$, and PCTFE–$(CH_2)_4OH$ (see below) was measured using buffered pH solutions ranging between pH 1 and 13; the data are displayed in Figure 7. Only the acidic surface exhibits pH-dependent contact angles with θ_A = ~56° at pH <6 and θ_A = ~30° at pH >10. The surface becomes more hydrophilic as PCTFE–$(CH_2)_3CO_2H$ is titrated to PCTFE–$(CH_2)_3CO_2^-$. The data indicate that

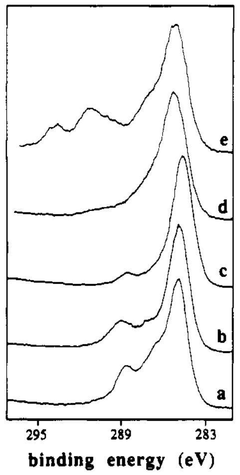


Figure 6. XPS C_{1s} region spectra (75° takeoff angle) of PCTFE–$(CH_2)_3C(OCH_3)_3$ (a), PCTFE–$(CH_2)_3CO_2H$ (b), PCTFE–$(CH_2)_3CO_2Oct^A$ (c), PCTFE–$(CH_2)_4OH$ (d), and PCTFE–$(CH_2)_4OCOC_3F_7$ (e).

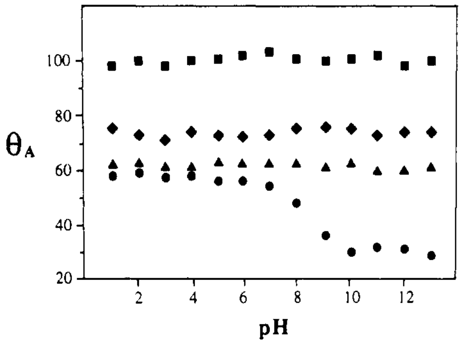


Figure 7. Dependence of θ_A on pH (buffered aqueous solutions): (■) PCTFE; (◆) PCTFE–$(CH_2)_3C(OCH_3)_3$; (●) PCTFE–$(CH_2)_3CO_2H$; (▲) PCTFE–$(CH_2)_4OH$.

the surface carboxylic acids exhibit pK_as ranging from ~6 to ~10. Similar behavior is observed for other carboxylic acid-functionalized surfaces.[3,17] The receding contact angles (θ_R) for PCTFE–$(CH_2)_3CO_2H$ are 0 at all pH values.

The reactivity of PCTFE–$(CH_2)_3CO_2H$ was assessed by esterification reactions using 1-octanol and reduction with BH_3/THF to yield the alcohol (PCTFE–$(CH_2)_4OH$). 1-Octanol was chosen principally for analytical reasons, to induce measurable changes in contact angle, XPS, and ATR IR analyses. The *n*-octyl ester was prepared using three different esterification procedures. Fisher esterification using *p*-toluenesulfonic acid as a catalyst (PCTFE–$(CH_2)_3CO_2Oct^A$), preparation of the acid chloride using thionyl chloride followed by reaction with 1-octanol (PCTFE–$(CH_2)_3CO_2Oct^B$), and preparation of the acyl imidazolide using carbonyldiimidazole followed by reaction with 1-octanol (PCTFE–$(CH_2)_3CO_2Oct^C$) all gave good yields of the octyl ester. Table I gives contact angle data for the three ester surfaces, and these indicate indistinguishable hydrophobic surfaces. XPS and ATR IR spectra of the three esters are essentially identical. Figures 5b and 6c show infrared and C_{1s} region XPS spectra for PCTFE–$(CH_2)_3CO_2Oct^A$. The carbonyl peak has shifted from 1710 to 1736 cm^{-1}, and the intensity of the low binding energy C_{1s} peak has increased. XPS indicates the presence of a small amount of nitrogen in PCTFE–$(CH_2)_3CO_2Oct^C$ (1.5%, 15°; 1.8%, 75°) that is likely due to incomplete esterification. The predicted stoichiometry for PCTFE–$(CH_2)_3CO_2Oct$ is $C_{58}O_8F_6$; observed values based on 15° takeoff angle data (in Table II) are $C_{58}O_8F_{3.7}$ (PCTFE–$(CH_2)_3CO_2Oct^A$), $C_{58}O_{8.4}F_{3.3}$ (PCTFE–$(CH_2)_3CO_2Oct^B$), and $C_{58}O_{7.4}F_{3.2}$ (PCTFE–$(CH_2)_3CO_2Oct^C$). The measured fluorine concentrations are likely low due to the 12-carbon ester groups shielding the polymer chain. Compositions based on 75° takeoff angle data are, respectively, for PCTFE–$(CH_2)_3CO_2Oct^{A,B,C}$ $C_{58}O_{3.9}F_{5.7}$, $C_{58}O_{9.2}F_{4.5}$, and $C_{58}O_{8.7}F_{4.7}$.

Reduction of PCTFE–$(CH_2)_3CO_2H$ to PCTFE–$(CH_2)_4OH$ using 1.0 M BH_3/THF in THF was monitored by following the disappearance of the carbonyl peak in the infrared spectrum. After 12 h of reaction, the carbonyl absorbance is absent and a broad O–H stretching band is observed (Figure 5c). The high binding energy portion of the C_{1s} XPS spectrum is completely removed (Figure 6d). The water contact angles (Table I) are consistent with an alcohol-containing surface; PCTFE–$(CH_2)_3OH$ exhibits $\theta_A/\theta_R = 67°/17°$.[14] The predicted composition for PCTFE–$(CH_2)_4OH$ is $C_{26}O_4F_5$; the observed stoichiometries based on data in Table II are $C_{26}O_{4.9}F_{4.4}$ (15° takeoff angle) and $C_{26}O_{4.6}F_{4.8}$ (75° takeoff angle). PCTFE–$(CH_2)_4OH$ reacts with heptafluorobutyryl chloride to yield the expected ester. Contact angles (Table I) indicate a hydrophobic surface, and the ATR IR spectrum shows an absorbance at 1782 cm^{-1} typical of esters fluorinated at the α-carbon. The C_{1s} XPS spectrum (Figure 6e) shows high binding energy photoelectron peaks due to CF_3, CF_2, and carbonyl carbon.

Summary

PCTFE film reacts with LiTMOB to incorporate protected carboxylic acids in the polymer surface in ~80% of the polymer repeat units. The depth of modification can be controlled by reaction temperature from ~25 to ~100 Å. This surface can be quantitatively hydrolyzed to the carboxylic acid-functionalized surface (PCTFE–$(CH_2)_3CO_2H$) which exhibits low pH-dependent water contact angles and high reactivity.

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References and Notes

(1) Rasmussen, J. R.; Stedronsky, E. R.; Whitesides, G. M. *J. Am. Chem. Soc.* 1977, *99*, 4736.
(2) Rasmussen, J. R.; Bergbreiter, D. E.; Whitesides, G. M. *J. Am. Chem. Soc.* 1977, *99*, 4746.
(3) Holmes-Farley, S. R.; Reamey, R. H.; McCarthy, T. J.; Deutch, J.; Whitesides, G. M. *Langmuir* 1985, *1*, 725.
(4) Holmes-Farley, S. R.; Whitesides, G. M. *Langmuir* 1986, *2*, 266.
(5) Holmes-Farley, S. R.; Whitesides, G. M. *Langmuir* 1987, *3*, 62.
(6) Holmes-Farley, S. R.; Nuzzo, R. G.; McCarthy, T. J.; Whitesides, G. M. *Langmuir* 1987, *3*, 799.
(7) Holmes-Farley, S. R.; Bain, C. D.; Whitesides, G. M. *Langmuir* 1988, *4*, 921.
(8) Wilson, M. D.; Whitesides, G. M. *J. Am. Chem. Soc.* 1988, *110*, 8718.
(9) Whitesides, G. M.; Ferguson, G. S. *Chemtracts* 1988, *1*, 171.
(10) Wilson, M. D.; Ferguson, G. S.; Whitesides, G. M. *J. Am. Chem. Soc.* 1990, *112*, 1244.
(11) Whitesides, G. M.; Laibinis, P. E. *Langmuir* 1988, *4*, 87.
(12) Dias, A. J.; McCarthy, T. J. *Macromolecules* 1985, *18*, 1826.
(13) Dias, A. J.; McCarthy, T. J. *Macromolecules* 1987, *20*, 2068.
(14) Lee, K.-W.; McCarthy, T. J. *Macromolecules* 1988, *21*, 2318.
(15) Lee, K.-W.; McCarthy, T. J. *Macromolecules* 1988, *21*, 3353.
(16) Kolb, B. U.; Patton, P. A.; McCarthy, T. J. *Macromolecules* 1990, *23*, 366.
(17) Shoichet, M. S.; McCarthy, T. J. *Macromolecules* 1991, *24*, 982.
(18) Costello, C. A.; McCarthy, T. J. *Macromolecules* 1987, *20*, 2819.
(19) Dias, A. J.; McCarthy, T. J. *Macromolecules* 1984, *17*, 2529.
(20) Brennan, J. V.; McCarthy, T. J. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* 1987, *29* (2), 338.
(21) Brennan, J. V.; McCarthy, T. J. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* 1989, *30* (2), 152.

(22) Bening, R. C.; McCarthy, T. J. *Macromolecules* **1990**, *23*, 2648.

(23) Franchina, N. L.; McCarthy, T. J. *Macromolecules* **1991**, *24*, 3045.

(24) Five different alcohol-functionalized PEEK surfaces have been prepared (N. L. Franchina, unpublished results).

(25) Dias, A. J. Ph.D. dissertation, University of Massachusetts, 1987.

(26) Juaristi, E.; Martinez-Richa, A.; Garcia-Rivera, A.; Cruz-Sanchez, J. S. *J. Org. Chem.* **1983**, *48*, 2603.

(27) Kolthoff, I. M.; Sandel, E. B.; Meehan, E. J.; Bruckenstein, S. *Quantitative Chemical Analysis*, 4th ed.; MacMillan: Toronto, 1969.

(28) Depth of reaction likely could have alternatively been controlled by varying solvent composition and perhaps by reaction time or LiTMOB concentration.[12,13,16]

(29) These values assume that the mean free path of C_{1s} photoelectrons ejected with Mg Kα radiation is 14 Å. This value was measured in poly(*p*-xylylene): Clark, D. T.; Thomas, H. R. *J. Polym. Sci., Polym. Chem. Ed.* **1977**, *15*, 2843.

(30) Andrade, J. D., Ed. *Surface and Interfacial Aspects of Biomedical Polymers, Vol. 1: Surface Chemistry and Physics*; Plenum: New York, 1985.

(31) Casy, G.; Furber, M.; Richardson, K. A.; Stephenson, G. R.; Taylor, R. J. K. *Tetrahedron* **1986**, *21*, 5849.

Registry No. PCTFE, 9002-83-9; LiTMOB, 139408-80-3; BrTMOB, 55444-67-2; water, 7732-18-5.