Convenient Syntheses of Carboxylic Acid Functionalized Fluoropolymer Surfaces[1]

Molly S. Shoichet and Thomas J. McCarthy*

Polymer Science and Engineering Department, University of Massachusetts, Amherst, Massachusetts 01003

Received May 15, 1990; Revised Manuscript Received August 2, 1990
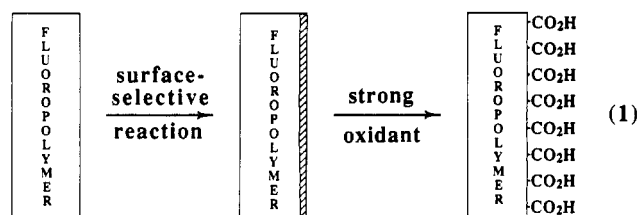
ABSTRACT: Carboxylic acid groups have been introduced to the surfaces of poly(vinylidene fluoride) (PVF₂), poly(tetrafluoroethylene-*co*-hexafluoropropylene) (FEP), and poly(chlorotrifluoroethylene) (PCTFE) film by two-step chemical surface modifications. In each case a surface-selective reaction was run to introduce a thin layer (several tens of angstroms) of modified fluoropolymer: PVF₂ was dehydrofluorinated with aqueous sodium hydroxide and phase-transfer catalysis, FEP was reduced with sodium naphthalide, and PCTFE was reduced/alkylated with *n*-butyllithium. The modified layers, susceptible to oxidation, were removed with strong oxidant (potassium chlorate/sulfuric acid) to yield fluoropolymer functionalized with carboxylic acid groups at the sites where virgin and modified polymer were covalently attached. The presence of carboxylic acid groups was indicated by contact angle (wettability) behavior and chemical reaction.

Introduction

We are presently studying the adsorption from solution of selectively (density, location, and functional group identity) functionalized linear polymers to solid polymer film samples that are specifically surface–functionalized to interact with groups on the dissolved polymer.[2] Since amine-containing polymers (polystyrenes, poly(amino acids), and proteins) are one class of soluble polymers of interest, we have a need for solid polymer substrates containing surface acid functionality.

We are developing[3–7] the surface chemistry of several fluoropolymers with the objective of preparing substrates for the study of surface structure–property and structure–reactivity relationships. These materials have a variety of advantages as substrates; these have been described in detail.[3] Some of the advantages, in particular the chemical inertness, nonswellability, and spectroscopic uniqueness (particularly their high binding energy C₁ₛ photoelectron lines), also make them attractive substrates for polymer adsorption; we envision an ideal substrate for amine-containing polymer adsorption to be a fluoropolymer containing a "monolayer" or submonolayer coverage of covalently attached carboxylic acids. We have reported the synthesis of two carboxylic acid functionalized fluoropolymer surfaces; however, they are inconvenient to prepare and their structures are not ideal. Poly(chlorotrifluoroethylene) (PCTFE) is carboxylic acid functionalized by reaction with 2-(lithiomethyl)-4,4-dimethyloxazoline and subsequent hydrolysis;[3] the hydrolysis is complicated and does not always proceed to completion; thus, the surface contains oxazoline as well as carboxylic acid functionality. Carboxylic acid groups are introduced to PTFE by reduction with dipotassium benzoin dianion, radical addition of maleic anhydride, and subsequent hydrolysis.[5] This structure is complex because the initial reduction reaction is corrosive and the resulting product is heterogeneous and quite thick.

We report in this manuscript two-step chemical modifications designed to introduce a submonolayer coverage of carboxylic acids confined to the surface (at the solvent-polymer interface) of poly(vinylidene fluoride) (PVF₂), poly(tetrafluoroethylene-*co*-hexafluoropropylene) (FEP), and PCTFE. Our strategy is depicted generically in eq 1. The fluoropolymer is modified by a surface-selective reaction under conditions chosen to convert a thin surface layer (several tens of angstroms) to an oxidation-sensitive product. The modified product is then completely removed by oxidation; the fluoropolymers are inert to these

$$
\begin{array}{ccc}
\boxed{\text{FLUOROPOLYMER}} & \xrightarrow[\text{reaction}]{\text{surface-selective}} & \boxed{\text{FLUOROPOLYMER}} \\
\end{array} \xrightarrow[\text{oxidant}]{\text{strong}} \boxed{\text{FLUOROPOLYMER}}\begin{smallmatrix} -CO_2H \\ -CO_2H \\ -CO_2H \\ -CO_2H \\ -CO_2H \\ -CO_2H \\ -CO_2H \\ -CO_2H \end{smallmatrix} \quad (1)
$$

oxidation conditions. At sites where virgin polymer and the modified layer were covalently attached (partially modified chains), carboxylic acids are produced as chain termini.

Introduction of carboxylic acid groups to polymer surfaces by oxidation with strong oxidants is well-known for polyethylene[8] and polypropylene[9] and, in principle, is applicable to any oxidation-sensitive polymer; however, these reactions continue corrosively to pit the polymer and produce carboxylic acids over a range of depths. The systems reported here are unique because the oxidation stops when virgin polymer is reached and the topography of the surface is controlled and can be controlled by the sharpness/diffuseness of the modified polymer–virgin polymer interface.

Experimental Section

Materials. Fluoropolymer film samples (PVF₂, 5 mil, Pennwalt Kynar obtained from Westlake Plastics; FEP, 5 mil, obtained from Du Pont; PCTFE, 5 mil, Allied Aclar 33C) were extracted in refluxing dichloromethane for 30 min, dried (50 °C, 0.05 mm) to constant mass, and stored under vacuum. THF was distilled from sodium benzophenone dianion; pyridine and heptane were distilled from calcium hydride. Ethanol (absolute) was distilled from magnesium/CCl₄; house distilled water was redistilled with a Gilmont still. Dichloromethane and methanol (Fisher HPLC) were sparged with nitrogen prior to use. Tetrabutylammonium bromide, borane–THF complex (1.0 M in THF), trichloroacetyl chloride, *n*-butyllithium (all from Aldrich), and potassium chlorate (Alfa) were used as received; *n*-butyllithium was standardized with diphenylacetone *p*-tosylhydrazone.[10] Thallous ethoxide was filtered just prior to use.

Methods. All reactions were carried out under nitrogen and solutions degassed by sparging with nitrogen unless otherwise noted. Contact angle measurements were obtained with a Ramé-Hart telescopic goniometer and a Gilmont syringe with a 25-gauge flat-tipped needle. Water was used as a probe fluid and purified as described above. Buffered pH solutions were prepared by a published procedure[11] and adjusted to the desired pH by using a Fisher 825MP pH meter. Dynamic angles were deter-

© 1991 American Chemical Society

mined by measuring the tangent of the drop at the intersection of the air–drop–surface while adding (advancing contact angle, θ_A) and withdrawing (receding contact angle, θ_R) solution to and from the drop. The values reported are averages of at least five measurements taken at different locations on the film sample. X-ray photoelectron spectra (XPS) were recorded by a Perkin Elmer-Physical Electronics 5100 spectrometer using Mg Kα excitation (300 W). The pressure in the analysis chamber was $\sim 10^{-8}$ mm during data acquisition. Samples were analyzed at a takeoff angle of 15° (from the surface) at a pass energy of 71.55 eV. Attenuated total reflectance infrared (ATR IR) spectra were obtained under nitrogen by an IBM 32 FTIR and a germanium (45°) internal reflection element. UV–vis spectra were recorded with a Perkin-Elmer Lambda 3A spectrophotometer with a virgin film sample in the reference beam. Gravimetric analysis was performed by a Cahn 29 electrobalance containing a polonium source. Scanning electron micrographs were recorded on a JEOL 60 SEM at magnifications of 20 000× and 100 000×.

Dehydrofluorination of PVF$_2$ (PVF$_2$-CH=CF-).[12,13] Sodium hydroxide solution (20 mL, 8 M) was introduced to a Schlenk tube containing a PVF$_2$ film sample, and the tube was equilibrated to 40 °C. An aqueous solution of tetrabutylammonium bromide (3 mL, 0.03 M), which had been equilibrated to 40 °C, was added via cannula. After 3 min, the solution was removed and the film sample washed with water (10 × 20 mL), methanol (5 × 20 mL), and then dichloromethane (3 × 20 mL) and dried (>48 h, 50 °C, 0.05 mm).

Reduction of FEP (FEP-C).[6] THF (5 mL) was introduced via cannula to a Schlenk tube containing an FEP film sample, and the tube was equilibrated at –78 °C. A THF solution of sodium naphthalide (15 mL, 0.12 M) was equilibrated to –78 °C and added to the Schlenk tube. After 60 min, the solution was removed and the film sample washed with THF (5 × 20 mL), water (5 × 20 mL), and then THF (2 × 20 mL) and dried (>24 h, 50 °C, 0.05 mm).

Reaction of PCTFE with n-Butyllithium (PCTFE-Bu). Heptane (15 mL) and n-butyllithium (3 mmol) were equilibrated at –78 °C; THF (15 mL, –78 °C) was added. This solution was well mixed and added to a Schlenk tube containing a PCTFE film sample that had been equilibrated at –78 °C. After 60 min, the solution was removed and the film was rinsed with methanol (–78 °C, 20 mL), methanol (room temperature, 4 × 20 mL), water (5 × 20 mL), and then dichloromethane (5 × 20 mL) and dried (>24 h, 0.05 mm).

Oxidation of Modified Film Samples (PVF$_2$-CO$_2$H, FEP-CO$_2$H, PCTFE-CO$_2$H). A modified film sample was allowed to react with a solution of 0.5 g of potassium chlorate in 25 mL of sulfuric acid for 2 h at room temperature in an open vessel. After this time, the solution was removed and the film sample was washed with water (10 × 20 mL), methanol (5 × 20 mL), and then dichloromethane (3 × 20 mL) and dried (>24 h, 50 °C, 0.05 mm).

Labeling of Surface Carboxylic Acids with Thallium (PVF$_2$-CO$_2$Tl, FEP-CO$_2$Tl, PCTFE-CO$_2$Tl).[14] A film sample was exposed to neat thallous ethoxide at room temperature in a nitrogen-purged glovebag for 30 s. The film sample was washed with ethanol (3 × 20 mL) and dried (>24 h, 50 °C, 0.05 mm).

Reduction of Surface Carboxylic Acids (PVF$_2$-CH$_2$OH, FEP-CH$_2$OH, PCTFE-CH$_2$OH). A solution of borane in THF (20 mL, 1.0 M) was added via cannula to a Schlenk tube that contained an oxidized film sample. After 1 h at room temperature, the solution was removed and the film was rinsed with THF (5 × 20 mL), water (5 × 20 mL), and then methanol (5 × 20 mL) and dried (>24 h, 50 °C, 0.05 mm).

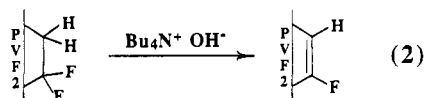**Reaction of Surface Alcohols with Trichloroacetyl Chloride (PVF$_2$-CH$_2$OC(O)CCl$_3$, FEP-CH$_2$OC(O)CCl$_3$, PCTFE-CH$_2$OC(O)CCl$_3$).** THF (19 mL), 0.5 mL of trichloroacetyl chloride, and then 1 mL of pyridine were added to a Schlenk tube containing a film sample. After 12 h at room temperature, the solution was removed and the film sample washed with THF (3 × 20 mL), methanol (6 × 20 mL), and then dichloromethane (3 × 20 mL) and dried (>24 h, 50 °C, 0.05 mm).

Results and Discussion

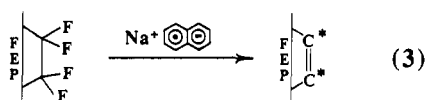The strategy described in eq 1 is based on the development of methods for introducing covalently attached surface layers of oxidation-sensitive modified polymer on the fluoropolymer film substrates. We have developed these methods for PVF$_2$[7,12,13], FEP,[6] and PCTFE[2–4] with, among others, the objectives of controlling both the thickness of the modified layer and the diffuseness (sharpness) of the modified polymer–virgin polymer interface.[15] The ability to control these variables will allow control of the topography (roughness) of the carboxylic acid surface: a modified layer of uniform $\sim$20-Å thickness would render, upon oxidation, a surface that closely replicates the topography of the virgin fluoropolymer film; a diffuse interface, with modified polymer extending deep into the film and virgin polymer remaining in the outer few angstroms would give a surface that is much rougher than the original surface. We discuss, in this regard, the modification chemistry of each fluoropolymer:

PVF$_2$ is modified by reaction with bases.[7,12,13] When PVF$_2$ is immersed in aqueous sodium hydroxide at room temperature, there is no reaction, but when a small amount of tetrabutylammonium ion is included in the solution, a rapid dehydrofluorination occurs (eq 2). A sharp interface

$$\underset{\substack{\text{P}\\\text{V}\\\text{F}\\\text{2}}}{\left|\right.}\begin{array}{c}\text{H}\\\text{H}\\\text{F}\\\text{F}\end{array} \xrightarrow{\text{Bu}_4\text{N}^+\ \text{OH}^-} \underset{\substack{\text{P}\\\text{V}\\\text{F}\\\text{2}}}{\left|\right.}\begin{array}{c}\text{H}\\\text{F}\end{array} \qquad (2)$$

exists between the polymer and the solution (there is no "wetting"), and hydroxide (in the absence of tetrabutylammonium) in solution cannot access the surface. Tetrabutylammonium serves as a phase-transfer catalyst or "wetting agent" and transports hydroxide across the sharp aqueous–organic interface where it effects the dehydrofluorination. The modified polymer does not interact with the solution (there is no "swelling"), and when the accessible polymer repeat units have been dehydrofluorinated, the reaction stops; we refer to this as "autoinhibition". PVF$_2$-CH=CF- prepared under these conditions has a uniform surface layer of less than 10-Å thickness. Increasing the reaction temperature influences the outcome: at 40 °C an autoinhibitive reaction occurs to a depth of $\sim$40 Å; at 80 °C a deeper reaction, which does not display autoinhibition, proceeds, giving a more diffuse PVF$_2$-PVF$_2$-CH=CF- interface. Dehydrofluorination of PVF$_2$ with other bases in organic solvents proceeds very differently. Using 1,8-diazabicyclo[5.4.0]-undec-7-ene (DBU) in heptane[7] produces a deeply (this depends on reaction temperature) modified surface, but significant amounts of unreacted PVF$_2$ remain in the outer 40 Å (as assessed by XPS); thus, the PVF$_2$-PVF$_2$-CH=CF- interface is diffuse (rough).

FEP is modified with single-electron-reducing agents;[6,16] we have studied sodium naphthalide and dipotassium benzoin dianion. The product (indicated by C* in eq 3) is an

$$\underset{\substack{\text{F}\\\text{E}\\\text{P}}}{\left|\right.}\begin{array}{c}\text{F}\\\text{F}\\\text{F}\\\text{F}\end{array} \xrightarrow{\text{Na}^+\ \text{naphthalide}} \underset{\substack{\text{F}\\\text{E}\\\text{P}}}{\left|\right.}\begin{array}{c}\text{C*}\\\text{C*}\end{array} \qquad (3)$$

oxidation-sensitive complex carbonaceous material, which we abbreviate FEP-C. We do not understand the reaction well in terms of the relative importance of diffusion of reducing agent into the product and reduction by electrons transported through the electronically conducting[17,18] product to virgin polymer; at and above room temperature, the reaction is rapid and corrosive, yielding a very diffuse (rough) FEP–FEP-C interface. We have reported a scanning electron micrograph of poly(tetrafluoroethylene) film that had been reduced and had its reduced layer removed by oxidation;[19] the surface is very rough. At lower temperatures the reduction of FEP film with sodium naph-
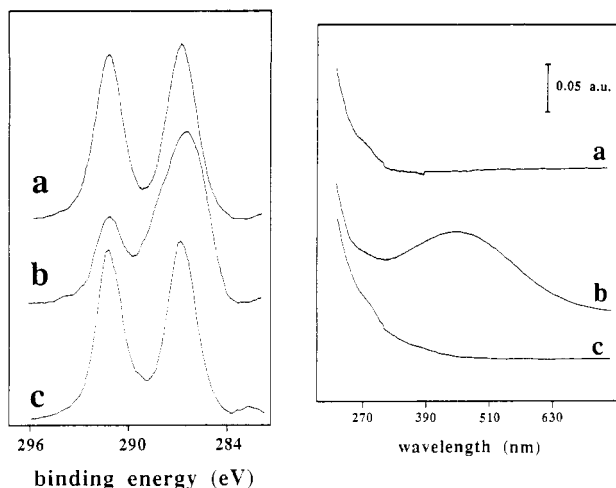
Figure 1. XPS (C_{1s} region, 15° takeoff angle) and UV-vis spectra of (a) PVF_2, (b) PVF_2-CH=CF-, and (c) PVF_2-CO_2H.

Table I
Advancing (θ_A) and Receding (θ_R) Contact Angle Data (Water)

sample	θ_A	θ_R
PVF_2	86	65
PVF_2-CO_2H	75	29
FEP	115	100
FEP-CO_2H	99	47
PCTFE	104	76
PCTFE-CO_2H	96	50

thalide can be controlled. At -78 °C the modified layer thickness can be controlled quite accurately with reaction time in the range of 45-90 Å; the FEP-FEP-C interface is sharp as evidenced by a combination of XPS, UV-vis, and gravimetric analyses. At 0 °C the thickness can be controlled in the range of 250-800 Å with reaction time.

PCTFE is modified by reaction with lithium reagents.[2,3,20,21] Alkyllithium reacts by metal-halogen exchange to yield alkyl chloride and lithiated polymer, which, in turn, eliminates lithium fluoride to form a difluoroolefin. A second equivalent of alkyllithium adds to the difluoroolefin, and lithium fluoride is eliminated, yielding a fluoroolefin containing the alkyl group (eq 4). Both the depth of reaction into PCTFE and the diffuseness

$$
\begin{array}{c}
\text{P}\\\text{C}\\\text{T}\\\text{F}\\\text{E}
\end{array}
\left\langle
\begin{array}{c}
\text{F}\\\text{F}\\\text{F}\\\text{Cl}
\end{array}
\right.
\xrightarrow{\text{2 RLi}}
\begin{array}{c}
\text{P}\\\text{C}\\\text{T}\\\text{F}\\\text{E}
\end{array}
\left\langle
\begin{array}{c}
\text{R}\\\\\text{F}
\end{array}
\right.
\qquad (4)
$$

of the PCTFE-PCTFE-R interface are dependent on the reaction temperature, reaction time, and solvent and very dependent on the structure of the alkyllithium. The degree to which the reaction solvent interacts with the modified product is the major controlling factor. We have prepared modified layers ranging in thickness from ~10 Å (certain conditions show autoinhibition) to thousands of angstroms.

We have not undertaken a study with the objective of preparing modified films with variable modified layer-virgin polymer interface topographies but are convinced that a wide latitude of topographies are accessible for each of these fluoropolymers through manipulation of the appropriate variables. All of the modified structures described are susceptible to oxidation; thus, carboxylic acid surfaces of controlled roughness could be prepared. In the work described here we have chosen one modified surface each for PVF_2, FEP, and PCTFE.

PVF_2-CH=CF- was prepared by dehydrofluorination of PVF_2 with aqueous sodium hydroxide and tetrabutylammonium bromide at 40 °C. The thin modified layer was removed oxidatively with potassium chlorate/sulfuric acid to yield PVF_2-CO_2H. Gravimetric analysis[22] (the mass difference between PVF_2 and PVF_2-CO_2H) indicated that the thickness of the modified layer was ~50 Å. Figure 1 shows the C_{1s} regions of XPS spectra and the UV-vis spectra for PVF_2, PVF_2-CH=CF-, and PVF_2-CO_2H. The broad absorbance centered at 440 nm that is due to the conjugated -CH=CF- double bonds in the modified layer of PVF_2-CH=CF- is completely removed upon oxidation. The high binding energy peaks in the XPS spectrum are

due to CF_2 and CO_2H; the low binding energy peaks are from CH_2 and CH=CF carbons present in PVF_2-CH=CF-. The intensity of the CF_2 photoelectron line decreases upon dehydrofluorination because an overlayer of modified polymer is present and increases upon oxidative removal. The C_{1s} spectra of PVF_2 and PVF_2-CO_2H are indistinguishable. The only difference in the XPS spectra of PVF_2 and PVF_2-CO_2H is the presence of an O_{1s} line at 536 eV. Quantitative XPS of the outer 10 Å[23] (15° takeoff angle, measured from the plane of the film) gives an atomic composition of $C_{14}F_{13}O$ (XPS does not detect hydrogen). Assuming that all oxygen is present as carboxylic acids, an approximate structure for the outer 10 Å is $(CH_2CF_2)_{13}CO_2H$, or one carboxylic acid per 13 repeat units of PVF_2. Three factors make surface density calculations (number of CO_2H groups per centimeter squared) suspect from these data: (1) the XPS technique assesses the composition of a finite thickness (~10 Å in this case) so the carboxylic acid density may be greater in a thinner region (closer to solvent in a PVF_2-CO_2H-solvent interface); (2) the XPS sensitivity decreases exponentially with depth,[24] and this factor would bias the density high if carboxylic acids were concentrated near the surface (meaning line of site of the XPS detector optics) of the outer 10 Å; (3) the dehydrofluorination and oxidation reaction may form "pits" of the size of a, or several, PVF_2 repeat unit(s), and these may either screen carboxylic acids from photoelectron detection (if CO_2H groups are in pits) or enhance detection (if CO_2H groups are projecting from pit edges). The extent to which these factors contribute to the data is unknown, and we choose not to make density calculations but to report "raw" XPS stoichiometries. The water contact angle data of PVF_2-CO_2H (Table I) show it to be more hydrophilic than PVF_2. ATR IR and SEM of film samples showed no changes upon dehydrofluorination or oxidation. PVF_2 film showed no changes upon identical oxidation treatment.

FEP-C was prepared by reduction with sodium naphthalide in THF at -78 °C for 1 h. The depth of the modified layer was calculated from a combination of UV-vis and gravimetric analysis to be 55 Å.[6] The modified layer was removed by oxidation with potassium chlorate/sulfuric acid to form FEP-CO_2H. Figure 2 shows XPS and UV-vis spectra for FEP, FEP-C, and FEP-CO_2H. The low binding energy photoelectron line and the broad absorbance in the UV-vis are due to the modified layer and are removed upon oxidation. XPS of FEP-CO_2H displays an O_{1s} peak at 533 eV and gives a stoichiometry of $C_{16}F_{32}O$ (15° takeoff angle), indicating an approximate composition of one carboxylic acid group per 16 repeat units (CF_2-CF_2)$_{16}CO_2H$.[25] Contact angles of FEP-CO_2H show it to be more hydrophilic than FEP (Table I). ATR IR and SEM of FEP samples showed no evidence of reaction. An FEP control showed no changes under the oxidation conditions.

PCTFE film was reduced/alkylated with n-butyllithium in THF-heptane at -78 °C for 1 h to prepare PCTFE-Bu. The modified layer was removed with potassium chlorate/sulfuric acid to yield PCTFE-CO_2H. Gravimet-
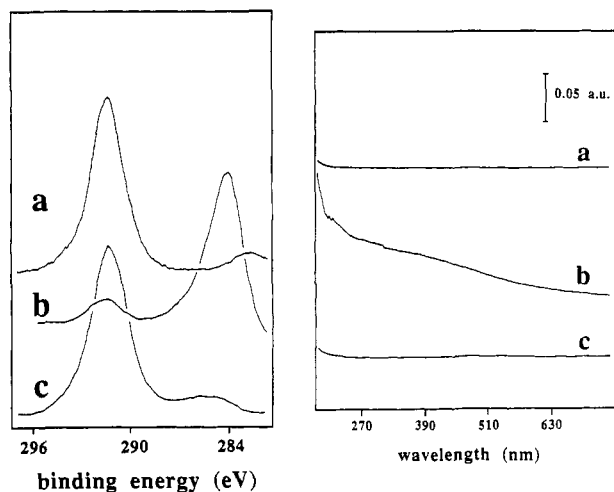
Figure 2. XPS (C_{1s} region, 15° takeoff angle) and UV–vis spectra of (a) FEP, (b) FEP-C, and (c) FEP-CO_2H.
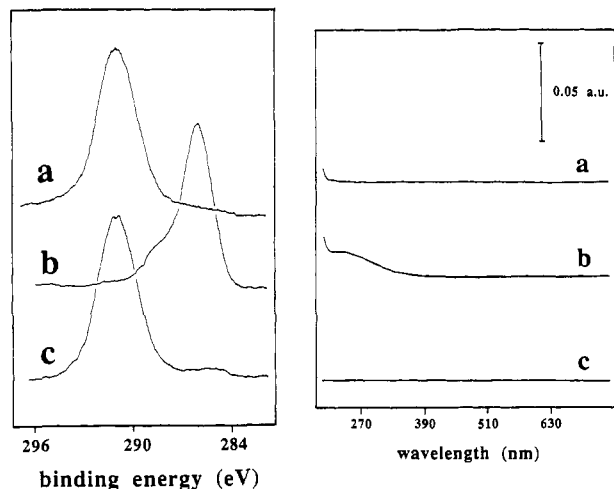

Figure 3. XPS (C_{1s} region, 15° takeoff angle) and UV–vis spectra of (a) PCTFE, (b) PCTFE-Bu, and (c) PCTFE-CO_2H.

ric analysis indicated that the thickness of the modified layer in PCTFE-Bu was ~35 Å.[27] Figure 3 shows XPS and UV–vis spectra in the style of Figures 1 and 2. We interpret the data similarly. XPS shows an O_{1s} peak at 534 eV for PCTFE-CO_2H and the stoichiometry to be $C_{13}F_{18}Cl_6O$, which corresponds to 1 carboxylic acid/12 repeat units, $(CF_2CFCl)_{12}CO_2H$. Because of the introduction of n-butyl groups, ATR IR changes were observed in PCTFE upon reaction with n-butyllithium and upon oxidation. Figure 4 shows spectra for PCTFE, PCTFE-Bu, and PCTFE-CO_2H. The PCTFE-Bu spectrum shows methyl and methylene stretching (2961, 2936, and 2876 cm^{-1}) and bending (1462, 1428, and 1383 cm^{-1}) bands (the peak at ~2200 cm^{-1} is an overtone). These are removed upon oxidation. The contact angle data indicated PCTFE-CO_2H to be more hydrophilic than PCTFE (Table I). SEM showed no changes upon oxidation. A PCTFE control sample was unaffected by the oxidation conditions.

The carboxylic acid functionalized surfaces were labeled for XPS analysis by reaction with thallous ethoxide.[14] This reagent selectively labels carboxylic acids in the presence of alcohols, ketones, and aldehydes. Figure 5 shows survey XPS spectra for PVF$_2$-CO_2Tl, FEP-CO_2Tl, and PCTFE-CO_2Tl. The oxygen–thallium ratio should be 2:1 if all of the oxygen present is carboxylic acids and reacts to form the salt. The O to Tl ratios for labeled surfaces are as follows: PVF$_2$-CO_2Tl, 2.0:1; FEP-CO_2Tl, 2.7:1; PCTFE-CO_2Tl, 3.0:1. In FEP-CO_2H and PCTFE-CO_2H, 24% and 33%, respectively, of the oxygen does not react with thal-
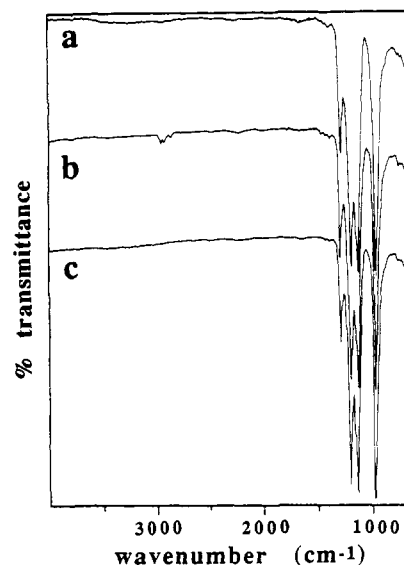

Figure 4. ATR IR spectra of (a) PCTFE, (b) PCTFE-Bu, and (c) PCTFE-CO_2H.
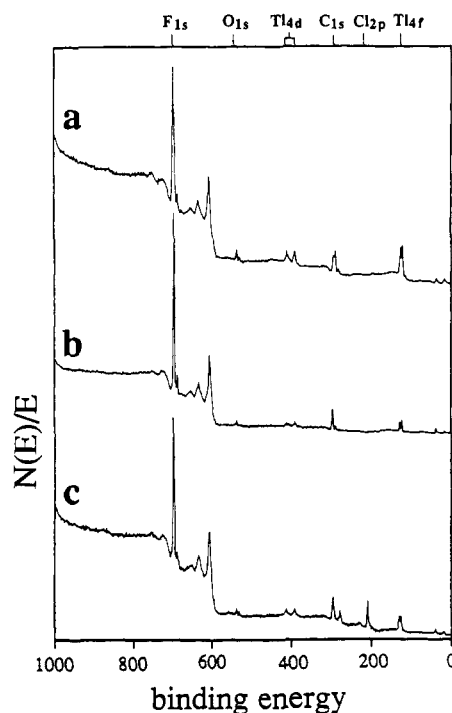
Figure 5. XPS (survey, 15° takeoff angle) spectra of (a) PVF$_2$-CO_2Tl, (b) FEP-CO_2Tl, and (c) PCTFE-CO_2Tl.[*]

lous ethoxide. We do not know whether oxygen is present as another functional group (mechanistically unlikely) or the labeling reaction did not proceed quantitatively. The factors described above that make quantitative carboxylic acid density calculations suspect also compromise estimates of reaction yields. Fluoropolymer control films showed no reaction with thallous ethoxide.

The carboxylic acid surfaces were also reduced to alcohols with borane in THF, and the alcohols were labeled for XPS analysis with trichloroacetyl chloride. Upon quantitative reduction (polymer–CO_2H → polymer–CH_2-OH), the carbon to oxygen ratio should double. Yields of reductions were calculated from C to O ratios to be 60%, 120%, and 50%, respectively, for PVF$_2$-CH_2OH, FEP-CH_2-OH, and PCTFE-CH_2OH. The yields of esterification with trichloroacetyl chloride (based on Cl to O ratios, assuming that all oxygen present was in the form of alcohols) were somewhat poor (33%, 42%, and 70% for PVF$_2$-CH_2OH, FEP-CH_2OH, and PCTFE-CH_2OH, respectively). We
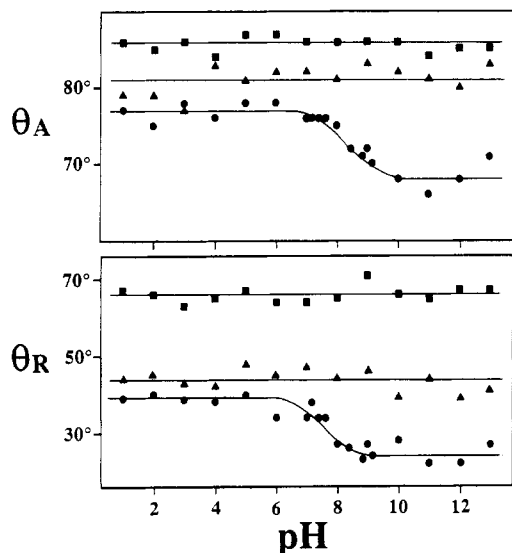
Figure 6. Dependence of θ_A and θ_R on pH (buffered aqueous solutions): (■) PVF$_2$, (▲) PVF$_2$-CH$_2$OH, (●) PVF$_2$-CO$_2$H.

have studied pyridine-catalyzed esterifications of surface hydroxyl groups on other hydroxylated FEP surfaces, and poor yields were observed;[6] good yields were observed for esterification reactions of PCTFE-CH$_2$CH$_2$CH$_2$OH.[4]

We have measured the pH dependence of the advancing and receding contact angles for each of the carboxylic acid surfaces as well as the alcohol surfaces (from borane reduction) and virgin fluoropolymer surfaces using buffered pH solutions ranging between pH 1 and 13. The data for PVF$_2$, PVF$_2$-CO$_2$H, and PVF$_2$-CH$_2$OH are displayed in Figure 6. Neither PVF$_2$ nor PVF$_2$-CH$_2$OH exhibits pH-dependent contact angles; PVF$_2$-CO$_2$H shows pronounced pH-dependent advancing and receding contact angles with θ_A/θ_R = 77°/39° at low pH and θ_A/θ_R = 68°/25° at high pH. This indicates that the surface becomes more hydrophilic when PVF$_2$-CO$_2$H is converted to PVF$_2$-CO$_2^-$ and that the surface carboxylic acids have pK_a values ranging from ~5 to ~10. Similar behavior is observed for oxidized polyethylene (PE-CO$_2$H).[26] Scatter in the advancing contact angle data for FEP-CO$_2$H and PCTFE-CO$_2$H is greater than the θ_A change over the pH range. The receding contact angles show pH dependences similar to PVF$_2$-CO$_2$H (θ_R is ~15° lower at high pH than it is at low pH). Contact angles for FEP, FEP-CH$_2$OH, PCTFE, and PCTFE-CH$_2$OH showed no pH dependences.

Conclusions

Appropriately modified fluoropolymers (PVF$_2$, FEP, and PCTFE) can be converted to carboxylic acid containing surfaces by removal of their modified surface layer with strong oxidation. The density of acid functionality is small (1 CO$_2$H group/12–16 repeat units) and is controlled by the number of covalent bonds between virgin fluoropolymer and the modified surface layer (partially modified chains). We have no control over this density, which depends on surface region morphology, but likely can control the number of acids per square centimeter of film surface by adjusting the virgin polymer–modified polymer interface topography as described above. The contact angles are higher (Table I) than other reported carboxylic acid surfaces, likely because of this low density. A different carboxylic acid functionalized PCTFE surface (which contains a carboxylic acid on each repeat unit) exhibits water contact angles of θ_A/θ_R = 71°/0°.[3] PE-CO$_2$H (which contains 1 CO$_2$H/~4 repeat units[28]) exhibits (water) θ_A = 55°.[26] Further chemical modification (we have shown thallation and reduction) can be effected on

the majority of surface carboxylic acids. We are presently studying adsorptions to these surfaces.

References and Notes

(1) A preliminary account of some of the research reported here has been presented: Shoichet, M. S.; McCarthy, T. J. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1990**, *31* (1), 418.

(2) Some of our objectives have been detailed in: Kolb, B. V.; Patton, P. A.; McCarthy, T. J. *Macromolecules* **1990**, *23*, 336.

(3) Dias, A. J.; McCarthy, T. J. *Macromolecules* **1987**, *20*, 2068.

(4) Lee, K.-W.; McCarthy, T. J. *Macromolecules* **1988**, *21*, 2318.

(5) Costello, C. A.; McCarthy, T. J. *Macromolecules* **1987**, *20*, 2819.

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

(7) Brennan, J. V.; McCarthy, T. J. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1989**, *30*(2), 152.

(8) For examples see: Holmes-Farley, S. R.; Reamey, R. H.; Nuzzo, R. G.; McCarthy, T. J.; Whitesides, G. M. *Langmuir* **1987**, *3*, 799 and references sited therein.

(9) For example see: Briggs, D.; Brewis, D. M.; Konieczo, M. B. *J. Mater. Sci.* **1976**, *11*, 1270.

(10) Lipton, M. F.; Sorensen, C. M.; Sadler, A. C.; Shapiro, R. H. *J. Organomet. Chem.* **1980**, *186*, 155.

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

(12) Dias, A. J.; McCarthy, T. J. *Macromolecules* **1984**, *17*, 2529.

(13) Brennan, J. V.; McCarthy, T. J. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1987**, *29*(2), 338.

(14) Reilley, C. N.; Everhart, D. S.; Ho, F. F. L. In *Applied Electron Spectroscopy for Chemical Analysis*; Windawi, H., Ho, F. F. L., Eds.; John Wiley and Sons: New York, 1982; Chapter 6.

(15) Reference 2 contains a discussion of the factors that control thickness and diffuseness in solid polymer–solution interface reactions.

(16) Dwight, D. W.; Riggs, W. J. *J. Colloid Interface Sci.* **1974**, *47*, 650.

(17) Varma, A. J.; Jog, J. P.; Nadkarni, V. M. *Makromol. Chem., Rapid Commun.* **1983**, *4*, 715.

(18) Costello, C. A.; McCarthy, T. J. *Macromolecules* **1985**, *18*, 1087.

(19) Costello, C. A.; McCarthy, T. J. *Macromolecules* **1984**, *17*, 2592.

(20) Dias, A. J.; McCarthy, T. J. *Macromolecules* **1985**, *18*, 1826.

(21) Danielson, N. D.; Taylor, R. T.; Huth, J. A.; Siergiej, R. W.; Galloway, J. G.; Paperman, J. B. *Ind. Eng. Chem. Prod. Res. Dev.* **1983**, *22*, 303.

(22) Bonafini, J. A.; Dias, A. J.; Guzdar, Z. A.; McCarthy, T. J. *J. Polym. Sci., Polym. Lett. Ed.* **1985**, *23*, 33.

(23) The 15° takeoff angle spectrum is representative of the outer 10 Å of the film sample to the extent that 94% of the photoelectrons measured are ejected from this region; this calculation uses a value of 14 Å for the C$_{1s}$ photoelectron mean free path, which was measured in poly(p-xylylene).[24]

(24) Clark, D. T.; Thomas, H. R. *J. Polym. Sci., Polym. Chem. Ed.* **1977**, *15*, 2843.

(25) We do not indicate in this structure the presence of 8% -CF$_2$-CF(CF$_3$)- repeat units. This does not affect the C to F to O ratio; if it were included, the calculated number of carboxylic acids per repeat unit would be slightly higher.

(26) Holmes-Farley, S. R.; Reamey, R. H.; McCarthy, T. J.; Deutch, J.; Whitesides, G. M. *Langmuir* **1985**, *1*, 725.

(27) We are less certain of this estimate than we are of those for PVF$_2$ and FEP because the latter measurements were made many more times.[6,12]

(28) This value was estimated from the reported XPS data.[26]

Registry No. PVF$_2$, 24937-79-9; FEP, 25067-11-2; PCTFE, 9002-83-9; NaOH, 1310-73-2; n-BuLi, 109-72-8; KClO$_4$, 3811-04-9; H$_2$SO$_4$, 7664-93-9; sodium naphthalide, 3481-12-7.