Convenient Syntheses of Carboxylic Acid Functionalized Fluoropolymer Surfaces

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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 polychlorotrifluoroethylene (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-butylamine. 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. Since amine-containing polymers (polystyrenes, poly(amine acids), and proteins) are one class of soluble polymers of interest, we have a need for solid polymer substrates containing surface functionality.

We are developing 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. Some of the advantages, in particular the chemical inertness, nonswellability, and spectroscopic uniqueness (particularly high binding energy C₁₆ 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-dimethylloxazoline and subsequent hydrolysis; the hydrolysis is complicated and does not always proceed to completion; thus, the surface contains oxazole as well as carboxylic acid functionality. Carboxylic acid groups are introduced to PTFE by reaction with dipotassium benzoin dianion, thus, the surface contains oxazoline as well as carboxylic acid functionality. 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.

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 sparged with nitrogen prior to use. Tetraphenylcolumbium 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-butylamine was purified as described above. Buffered pH solutions were prepared for polyethylene and polypropylene 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.

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 and adjusted to the desired pH by using a Fisher 825MP pH meter.
mined by measuring the tangent of the drop at the intersection of the air-drop-surface while adding (advancing contact angle, \( \theta_a \)) and withdrawing (receding contact angle, \( \theta_R \)) 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 K\( \alpha \) 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 recorded with a Perkin-Elmer Lambda 3B spectrophotometer with a virgin CO\(_2\)/PCTFE-CO\(_2\) source. Scanning electron micrographs were recorded on a JEOL SEM at magnifications of 2000X and 100 000X.

**Dehydrofluorination of PVF\(_2\) (PVF\(_2\)-CH-CF\(_2\)-)**. 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 (0.05 M) was added via cannula. After 3 min, the solution was removed and the film sample was rinsed with methanol (5 x 20 mL), and then dichloromethane (3 x 20 mL) and dried (48 h, 50 °C, 0.05 mm).

**Reduction of FEP (FEP-OH)**. 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 was rinsed with THF (5 x 20 mL), water (5 x 20 mL), and then THF (2 x 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 sample was rinsed with methanol (-78 °C, 20 mL), methanol (room temperature, 4 x 20 mL), water (5 x 20 mL), and then dichloromethane (5 x 20 mL) and dried (24 h, 50 °C, 0.05 mm).

**Oxidation of Modified Film Samples (PVF\(_2\)-CO\(_2\)H, FEP-CO\(_2\)H, PCTFE-CO\(_2\)H)**. A solution of borane in THF (20 mL, 1.0 M) was added via cannula to a Schlenk tube containing an oxidized film sample. After 1 h at room temperature, the solution was removed and the film sample was rinsed with THF (5 x 20 mL), water (5 x 20 mL), and then methanol (5 x 20 mL) and dried (24 h, 50 °C, 0.05 mm).

**Reaction of Surface Carboxylic Acids with Thallium (PVF\(_2\)-CO\(_2\)TI, FEP-CO\(_2\)TI, PCTFE-CO\(_2\)TI)**. A solution of thallium acetate in THF (20 mL, 1.0 M) was added via cannula to a Schlenk tube containing a carboxylic acid film sample. After 1 h at room temperature, the solution was removed and the film sample was rinsed with THF (5 x 20 mL), water (5 x 20 mL), and then methanol (5 x 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\(_2\)-, FEP, and PCTFE 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 ~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 exists between the polymer and the solution (there is no "wetting"), and hydroxide (in the absence of tetrabutylammonium) in solution cannot access the surface. Tetra- butylammonium 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 autoinhibitory reaction occurs to a depth of ~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 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 agents4,16 we have studied sodium naphthalide and dipotassium benzoin dianion. The product (indicated by C* in eq 3) is an 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 conducting17,18 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-
of the PCTFE-PCTFE-R interface are dependent on the surface each for PVF₂, FEP, and PCTFE.

Yielding a fluoroolefin containing the alkyl group (eq 4).

Of PVF₂ with aqueous sodium hydroxide and tetrabutyrammonium bromide at 40 °C. The thin modified layer 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 PVF₂, FEP, and PCTFE.

PVF₂-CH=CF- was prepared by dehydrofluorination of PVF₂ with aqueous sodium hydride and tetrabutylammonium bromide at 40 °C. The thin modified layer was removed oxidatively with potassium chlorate/sulfuric acid to yield PVF₂-CO₂H. Gravimetric analysis (the mass difference between PVF₂ and PVF₂-CO₂H) indicated that the thickness of the modified layer was ~50 Å. Figure 1 shows the C₁s regions of XPS spectra and the UV-vis spectra for PVF₂, PVF₂-CH=CF-, and PVF₂-CO₂H. The broad absorbance centered at 440 nm that is due to the conjugated CH=CF- double bonds in the modified layer of PVF₂-CH=CF- is completely removed upon oxidation. The high binding energy peaks in the XPS spectrum are due to CF₂ and CO₂H; the low binding energy peaks are from CH₂ and CH=CF carbons present in PVF₂-CH=CF-.

The thickness of the modified layer 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. Alkylithium reacts by metal-halogen exchange, which, in turn, eliminates lithium fluoride to form a difluoroolefin. A second equivalent of alkylithium 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 of the PCTFE-PCTFE-R interface are dependent on the reaction temperature, reaction time, and solvent and very dependent on the structure of the alkylithium. 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 PVF₂, FEP, and PCTFE.

PVF₂-CH=CF- was prepared by dehydrofluorination of PVF₂ with aqueous sodium hydride and tetrabutylammonium bromide at 40 °C. The thin modified layer was removed oxidatively with potassium chlorate/sulfuric acid to yield PVF₂-CO₂H. Gravimetric analysis (the mass difference between PVF₂ and PVF₂-CO₂H) indicated that the thickness of the modified layer was ~50 Å. Figure 1 shows the C₁s regions of XPS spectra and the UV-vis spectra for PVF₂, PVF₂-CH=CF-, and PVF₂-CO₂H. The broad absorbance centered at 440 nm that is due to the conjugated CH=CF- double bonds in the modified layer of PVF₂-CH=CF- is completely removed upon oxidation. The high binding energy peaks in the XPS spectrum are due to CF₂ and CO₂H; the low binding energy peaks are from CH₂ and CH=CF carbons present in PVF₂-CH=CF-

The intensity of the CF₂ photoelectron line decreases upon dehydrofluorination because an overlayer of modified polymer is present and increases upon oxidative removal. The C₁s spectra of PVF₂ and PVF₂-CO₂H are indistinguishable. The only difference in the XPS spectra of PVF₂ and PVF₂-CO₂H is the presence of an O₁s line at 536 eV. Quantitative XPS of the outer 10 Å (15° takeoff angle, measured from the plane of the film) gives an atomic composition of C₁₄F₁₃O (XPS does not detect hydrogen). Assuming that all oxygen is present as carboxylic acids, an approximate structure for the outer 10 Å is (CH₂CF₂)₁₃CO₂H, or one carboxylic acid per 13 repeat units of PVF₂. Three factors make surface density calculations (number of CO₂H 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 PVF₂-CO₂H-solvent interface); (2) the XPS sensitivity decreases exponentially with depth, 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, PVF₂ repeat unit(s), and these may either screen carboxylic acids from photoelectron detection (if CO₂H groups are in pits) or enhance detection (if CO₂H 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 PVF₂-CO₂H (Table I) show it to be more hydrophilic than PVF₂. ATR IR and SEM of film samples showed no changes upon dehydrofluorination or oxidation. PVF₂ 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. The modified layer was removed by oxidation with potassium chlorate/sulfuric acid to form FEP-CO₂H. Figure 2 shows XPS and UV-vis spectra for FEP, FEP-C, and FEP-CO₂H. 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-CO₂H displays an O₁s peak at 533 eV and gives a stoichiometry of C₁₄F₁₃O (15° takeoff angle), indicating an approximate composition of one carboxylic acid group per 16 repeat units (CF₂-CF₂)₁₆CO₂H. Contact angles of FEP-CO₂H 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-CO₂H. Gravimetric...
binding energy (eV)

Figure 2. XPS (C1 region, 15° takeoff angle) and UV—vis spectra of (a) FEP, (b) FEP-C, and (c) FEP-CO2H.

binding energy (eV)

Figure 3. XPS (C1 region, 15° takeoff angle) and UV—vis spectra of (a) PCTFE, (b) PCTFE-Bu, and (c) PCTFE-CO2H.

Figure 4. ATR IR spectra of (a) PCTFE, (b) PCTFE-Bu, and (c) PCTFE-CO2H.

Figure 5. XPS (survey, 15° takeoff angle) spectra of (a) PVF2-CO2Tl, (b) FEP-CO2Tl, and (c) PCTFE-CO2Tl.
have studied pyridine-catalyzed esterifications of surface hydroxyl groups on other hydroxylated FEP surfaces, and poor yields were observed; good yields were observed for esterification reactions of PCTFE-CH2CH2CH2O.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 PVF2, PVF2-CO2H, and PVF2-CH2OH are displayed in Figure 6. Neither PVF2 nor PVF2-CO2H exhibits pH-dependent contact angles; PVF2-CO2H shows pronounced pH-dependent advancing and receding contact angles with \( \theta_A/\theta_R = 77°/39° \) at low pH and \( \theta_A/\theta_R = 68°/25° \) at high pH. This indicates that the surface becomes more hydrophilic when PVF2-CO2H is converted to PVF2-CO2- and that the surface carboxylic acids have pH-dependent contact angles; PVF2-CO2H shows similar behavior to PVF2-CO2- and that the surface carboxylic acids have pronounced pH-dependent advancing and receding contact angles with \( \theta_A/\theta_R = 77°/39° \) at low pH and \( \theta_A/\theta_R = 68°/25° \) at high pH. This indicates that the surface becomes more hydrophilic when PVF2-CO2H is converted to PVF2-CO2- and that the surface carboxylic acids have pH-dependent contact angles ranging from \( \sim 5 \) to \( \sim 10 \). Similar behavior is observed for oxidized polyethylene (PE-CO2H). Scattered in the advancing contact angle data for FEP-CO2H and PCTFE-CO2H is greater than the \( \theta_A \) change over the pH range. The receding contact angles show pH dependences similar to PVF2-CO2H (\( \theta_A \) is \( \sim 15° \) lower at high pH than it is at low pH). Contact angles for FEP, FEP-CH2OH, PCTFE, and PCTFE-CH2OH showed no pH dependences.

Conclusions

Appropriately modified fluoropolymers (PVF2, 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 CO2H 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 \( \theta_A/\theta_R = 71°/9° \) PE-CO2H (which contains 1 CO2H/4 repeat units) exhibits (water) \( \theta_A = 55° \). 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.

Acknowledgment. We are grateful to the National Science Foundation (Grant DMR-8718420) and the Office of Naval Research for financial support.

References and Notes


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


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


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 C1 photoelectron mean free path, which was measured in poly(p-xylene).24


25. We do not indicate in this structure the presence of 8%-CF(CF3)- CF(CF3)= 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.


27. We are less certain of this estimate than we are of those for PVF2 and FEP because the latter measurements were made many more times.12

28. This value was estimated from the reported XPS data.26

Registry No. PVF2, 24937-79-2; FEP, 25067-11-2; PCTFE, 9002-83-9; NaOH, 1310-75-2; n-Buti, 109-72-8; KClO4, 3811-04-9; H2SO4, 7664-93-9; sodium naphthalide, 3481-12-7.