Macromolecules 1987, *20*, 2068-2076

Introduction of Carboxylic Acid, Aldehyde, and Alcohol Functional Groups onto the Surface of Poly(chlorotrifluoroethylene)

Anthony J. Dias[1] and Thomas J. McCarthy*

Polymer Science and Engineering Department, University of Massachusetts, Amherst, Massachusetts 01003. *Received February 17, 1987*

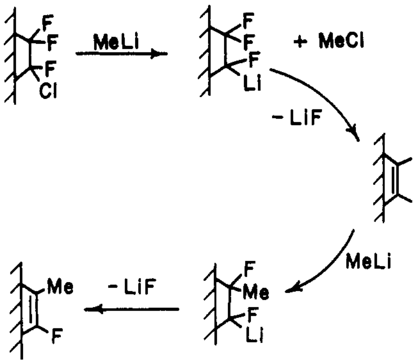
ABSTRACT: Carboxylic acid, aldehyde, and alcohol functionalities have been independently introduced to the surface of poly(chlorotrifluoroethylene) by using two step modification sequences: Lithium reagents containing protected functional groups react with polymer film surfaces via a surface-selective reduction–addition–elimination sequence which incorporates the protected functional group on the surface of the polymer. Deprotection renders polymer film samples containing surface-confined functional groups. Carboxylic acids were introduced using 2-(lithiomethyl)-4,4-dimethyloxazoline, aldehydes were introduced using 2-lithio-1,3-dithiane, and alcohols were introduced using acetaldehyde 3-lithiopropyl ethyl acetal. The depths of the modification reactions were sensitive to solvent and temperature and could be controlled. The depth of reaction was also dependent on the lithium reagent and varied according to acetaldehyde 3-lithiopropyl ethyl acetal $\gg$ 2-lithio-1,3-dithiane > 2-(lithiomethyl)-4,4-dimethyloxazoline; the carboxylic acid functionalization reaction is the most surface selective. The carboxylic acid site density was determined using ^{14}C-labeled (2-position) 2-(lithiomethyl)-4,4-dimethyloxazoline.

Introduction

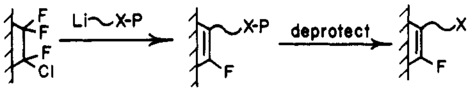
We are interested in studying the role that organic chemistry plays in determining the surface and interface properties of organic solids and are studying organic polymer surfaces in this regard.[2-4] In particular, we'd like to answer the following questions: Can surface properties be controlled by performing standard organic functional group transformations on the outer few angstroms of a polymeric object? Do surface functional groups in contact with reagents in solution react in the same manner as functional groups in solution, or do interfacial conditions (surface energy, solvation, wetting, swelling) and geometric constraints alter their reactivity? What are the thermal and solvent-contact stabilities of functionalized surfaces? Under what conditions and by what mechanisms do functionalized polymer surfaces reorganize? What is the effect of the location (distance from the surface) of functional groups on reactivity and properties? We have chosen to study chemically resistant polymer surfaces containing versatile organic functional groups at their surfaces (Figure 1) and have developed surface modification techniques for poly(vinylidene fluoride),[2] poly(tetrafluoroethylene),[3,4] and poly(chlorotrifluoroethylene).[5]

These materials offer several advantages as substrates for the study of surface chemistry. One, the surfaces are clean under normal laboratory conditions; they do not spontaneously oxidize or hydrate as do metal and inorganic surfaces. Two, they (or low molecular weight analogues) are soluble, and homogeneous solution reactions can be run as controls for surface reactions. Three, many interface environments (between solid polymer and reactive solution) can be designed by choices of solvent and temperature: the degree to which a solvent wets or swells the polymer and the mobility of polymer chains can be controlled. Four, the bulk of the polymers is resistant to chemical attack, so even brutal conditions can be applied to the surface functionality without affecting the bulk. Five, organic chemistry is a highly developed science and wide ranges of functional group transformations can be conceived. Six, the bulk of these materials is UV–vis transparent; thus, surface functionality can be observed by standard transmission spectroscopy. Seven, the carbon is region of the X-ray photoelectron spectra (XPS) is lucid with regard to changes because fluorinated carbon has an especially high binding energy. Eight, film samples of these materials have the integrity necessary to perform gravimetric analysis.

Scheme I
Series of Reactions by Which Methyllithium Reacts with Poly(chlorotrifluoroethylene)



We have reported the surface modification of poly(chlorotrifluoroethylene) (PCTFE) with methyllithium and phenyllithium and the mechanism for this transformation.[5] Scheme I is a depiction of this reaction using methyllithium as an example. Two equivalents of methyllithium react to form an unsaturated surface containing methyl groups. In this paper, we report the extension of this modification technique to introduce carboxylic acids, aldehydes, and alcohols to the PCTFE surface. The strategy involves the use of protected functional groups containing lithium reagents and is described generically as eq 1.



(1)

Experimental Section

Materials. PCTFE film was obtained from two sources: Allied provided 5- and 1-mil samples of Aclar 33A and Aclar 33C; 3M provided 5-mil samples of Kel-F 81. The film samples were extracted with refluxing dichloromethane and dried (0.05 mm, 90 °C) until constant mass (±1 μg) was achieved. This procedure gives films that are consistently free of any detectable contaminants. Film samples were stored in Schlenk tubes under vacuum or nitrogen. PCTFE oil was obtained from Polysciences and purified by fractional vacuum distillation. A fraction (bp 60–80 °C, 0.05 mm) was collected and stored under nitrogen. Tetrahydrofuran and heptane were distilled from sodium benzophenone dianion and stored under nitrogen. Dichloromethane was stirred

0024-9297/87/2220-2068$01.50/0

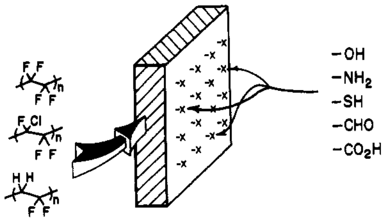


Figure 1. Target substrates for the study of polymer surface organic chemistry.

over sulfuric acid, washed with water, dried with magnesium sulfate, filtered, distilled from phosphorous pentoxide, and stored under nitrogen. Methanol was refluxed over magnesium turnings for 24 h, distilled, and stored under nitrogen. Water was doubly distilled (Gilmont Still), degassed by purging with nitrogen or vacuum distillation, and stored under nitrogen. Dihydropyran, dodecane, 2-amino-2-methyl-1-propanol, 2,4,4-trimethyloxazoline (160 mm), and 2-(2-bromoethyl)-1,3-dioxolane (0.05 mm) were obtained from Aldrich, distilled from calcium hydride, and stored under nitrogen. 3-Bromo-1-propanol (Aldrich) was dissolved in an equal volume of dichloromethane, washed with water, saturated sodium bicarbonate (twice), and saturated sodium chloride, dried with magnesium sulfate, filtered, concentrated by rotary evaporation, vacuum distilled from potassium carbonate (bp 60–64 °C, 5 mm), and stored under nitrogen over potassium carbonate in a freezer. Ethyl vinyl ether (Aldrich) was distilled under nitrogen immediately before use. Acetic acid (Aldrich) was distilled from phosphorous pentoxide and stored under nitrogen. 1,3-Dithiane (Aldrich) was purified by sublimation (0.05 mm, 20 °C). Diphenylacetic acid (Aldrich) was purified by sublimation (0.05 mm, 100 °C). Dichloroacetic acid (Aldrich), trifluoroacetic acid (Aldrich), 1-[^{14}C]acetic acid (Pathfinder Laboratories), mercuric trifluoroacetate (Aldrich), trifluoroacetic acid (Aldrich), heptafluorobutyryl chloride (Aldrich), and OSC scintillation fluid (Amersham) were used as obtained. *n*-Butyllithium, *sec*-butyllithium, and *tert*-butyllithium were obtained from Aldrich and standardized using diphenylacetic acid.

Methods. Contact angles were measured with a Rame-Hart telescopic goniometer. Dynamic angles were obtained using water as the probe fluid. Advancing contact angles (θ_{ADV}) were determined by measuring the tangent normal to the drop at the drop–surface intersection as water was added to the drop (by using a Gilmont syringe), and the drop advanced. Receding contact angles (θ_{REC}) were measured while water was removed from the drop, and the drop receded. The data reported are averages of at least six measurements made on different positions of the film samples and standard deviation of the measured values. Attenuated total reflection infrared (ATR IR) spectra were obtained by using an IBM 38 FTIR at 4-cm^{-1} resolution and a germanium 45° internal reflection element. The spectra were ratioed against a spectrum of the internal reflection element. X-ray photoelectron spectra (XPS) were obtained by using a Perkin-Elmer Physical Electronics 5100 with Mg Kα excitation. Film samples were mounted in a Vacuum Atmospheres glovebox and transferred to the spectrometer antechamber under nitrogen. The base pressure of the vacuum chamber containing the film sample was less than 5×10^{-9} mm. Spectra were recorded at two angles: the film surface 15° and 75° from the analyzer. UV-vis spectra were recorded by using a Perkin-Elmer Lambda 3A spectrophotometer. Transmission spectra were obtained by using a film-holding attachment. Scanning electron micrographs (secondary electron images) (SEM) were obtained with a JEOL 100 STEM. Liquid scintillation counting (LSC) was performed with a Beckman LS3801 instrument. PCTFE films (1 mil) were submersed in the scintillation fluid. Infrared spectra of oils were obtained with a Perkin-Elmer 283 spectrophotometer on thin films cast on NaCl plates. ^{1}H NMR spectra of oils were obtained by using a Varian XL300. Gravimetric analysis was performed by using a Cahn 29 electrobalance containing a polonium source. Samples were maintained under nitrogen or vacuum until just prior to weighing and were weighed in air. The films were charge neutralized by using a Zerostat (Aldrich) just prior to weighing.

Synthesis of Acetaldehyde 3-Lithiopropyl Ethyl Acetal (LiPEAA). 3-Bromo-1-propanol (26 g, 0.187 mol) was introduced to a flask which was equipped with a magnetic stirring bar and septum-stoppered reflux condenser. The system was purged with nitrogen for 15 min, and then ethyl vinyl ether (22.6 g, 0.314 mol) was added via cannula over 30 min. Dichloroacetic acid (0.3 mL) was added via syringe. The temperature rose, and reflux began. After 1 h, 0.1 mL of dichloroacetic acid was added. After 4 more hours, an additional 0.1 mL of dichloroacetic acid was added. The mixture was stirred overnight. The mixture was neutralized by stirring over potassium carbonate for 2 h and filtered, and the excess ethyl vinyl ether was removed at reduced pressure. The remaining liquid, acetaldehyde 3-bromopropyl ethyl acetal (BrPEAA), was dried with magnesium sulfate and distilled (bp 49–51 °C, 1 mm) from potassium carbonate. The distillate (31.6 g, 80% yield) was stored over potassium carbonate. BrPEAA (0.64 g, 3 mmol) was introduced to a nitrogen-purged Schlenk tube containing a magnetic stirring bar which was equilibrated at −78 °C. A solution (which had been equilibrated at −78 °C) of *tert*-butyllithium (1.7 mL, 1.7 M, 2.9 mmol) in heptane (15 mL) was added. The suspension was stirred for 15 min at −78 °C and allowed to warm to −20 °C, at which temperature it was maintained for 15 min and then diluted with 15 mL of THF. The solution was stirred at −20 °C for at least 30 min before it was used for further reaction.

Reaction of PCTFE with LiPEAA (PCTFE–PEAA). A PCTFE film sample was placed, along with a magnetic stirring bar, in a Schlenk tube which was then purged with nitrogen for 15 min. The tube was equilibrated to the desired reaction temperature, and 20 mL of LiPEAA solution (prepared as described above), also at the same temperature, was added via cannula. Reactions were carried out at −78, −20, and 0 °C for 5, 30, and 60 min. After the reaction, the LiPEAA solution was removed via cannula. The reaction tube was not removed from the temperature bath until after the first methanol wash. The methanol used for the first wash was equilibrated to the reaction temperature. The film sample was washed under nitrogen with methanol (5 × 30 mL), water (5 × 30 mL), methanol (1 × 30 mL), and dichloromethane (5 × 30 mL) and dried (24 h, 0.05 mm) before XPS, UV-vis, ATR IR, and contact angle data were obtained. The film sample was further dried (0.05 mm, 90 °C) to constant mass for gravimetric analysis.

Hydrolysis of PCTFE–PEAA (PCTFE-OH). The PCTFE–PEAA film sample was placed in a solution of trifluoroacetic acid (5 mL), water (50 mL), and acetone (50 mL) which was refluxed for 24 h. The film sample was removed, washed under nitrogen with methanol (5 × 30 mL) and dichloromethane (5 × 30 mL), and dried (0.05 mm, 24 h) before XPS, ATR IR, SEM, and contact angle data were obtained. The film sample was further dried (0.05 mm, 90 °C) to constant mass for gravimetric analysis.

Reaction of PCTFE-OH with Heptafluorobutyryl Chloride. One film sample each of PCTFE-OH and PCTFE (control) was placed in a Schlenk tube which was then purged with nitrogen before a solution of heptafluorobutyryl chloride (0.5 g) in THF (10 mL) was added via cannula. The film samples were allowed to react at room temperature for 3 h, the solution was removed via cannula, and the film samples were washed under nitrogen with THF (3 × 30 mL), methanol (3 × 30 mL), and dichloromethane (5 × 30 mL). The film samples were dried (24 h, 0.05 mm) before XPS, ATR IR, and contact angle data were obtained.

Preparation of the Grignard Reagent from 3-Bromopropyl Tetrahydropyranyl Ether (BrMgPTHP). 3-Bromo-1-propanol (24.9 g, 0.179 mol) was added via cannula to a nitrogen-purged, tared, and septum-stoppered flask which contained a magnetic stirring bar. The contents of the flask were stirred while dihydropyran (15.2 g, 0.181 mol) containing dichloroacetic acid (1 g) was added via cannula. After the addition, the mixture was stirred for 3 h and then neutralized with potassium carbonate. The solution was diluted with dichloromethane (100 mL), dried with magnesium sulfate, filtered, and concentrated by rotary evaporation. The concentrate (BrPTHP) was fractionally distilled (bp 105 °C, 15 mm) and stored over potassium carbonate under nitrogen in a freezer. Magnesium turnings (0.2 g, 8.2 mmol) were weighed into a 100-mL flask which was equipped with a magnetic stirring bar and a reflux condenser. The condenser was septum-stoppered, and the system was heated with a heat gun and purged with nitrogen for 15 min and then allowed to cool to room temperature. THF (10 mL) and then 2.0 g (9.0 mmol) of BrPTHP in 10 mL of THF were added via cannula. This mixture was stirred for 2 h under nitrogen, after which time most of the magnesium had reacted.

Reaction of PCTFE with BrMgPTHP and Subsequent Hydrolysis. A PCTFE film sample was placed in a Schlenk tube, the tube was purged with nitrogen for 15 min, and 10 mL of BrMgPTHP solution (prepared as described above) was added via cannula. After 30 min, 5 mL of methanol was added via syringe. The film was removed and washed with 2 N HCl (2 × 30 mL), saturated ammonium chloride (1 × 30 mL), water (3 × 100 mL), and methanol (3 × 100 mL). The film was dried (24 h, 0.05 mm) before XPS and contact angle data were obtained. This film sample was placed in a 100-mL flask which was equipped with a reflux condenser and boiling stone. HCl (2 N, 50 mL) was added and the flask was heated to reflux. After 60 min, the film sample was removed, washed with water (3 × 100 mL) and methanol (3 × 100 mL), and dried (24 h, 0.05 mm) before XPS and contact angle data were obtained.

Preparation of 2-Lithio-1,3-dithiane (LiDT). 1,3-Dithiane (1 g, 8.3 mmol) was placed in a Schlenk tube with a magnetic stirring bar, and the tube was flushed with nitrogen for 15 min. Heptane (10 mL) was added via cannula, and the mixture was stirred until the 1,3-dithiane dissolved. A solution containing *tert*-butyllithium (1.7 M, 4.5 mL, 7.7 mmol) or *n*-butyllithium (1.5 M, 5.0 mL, 7.5 mmol) diluted to 10 mL with heptane was prepared and added to the stirred solution. The suspension was placed in a bath at −20 °C and stirred for 30 min before THF (20 mL) was added via cannula. The colorless solution was stirred for 30 min at −20 °C before it was used in further reactions. The resulting solution was 0.15 M in lithium reagent, and it was possible to store it in a dessicator in the freezer for at least a week without observing a decrease in lithium reagent concentration. LiDT was also prepared in THF with *n*-butyllithium by using a similar procedure.

Reaction of PCTFE with LiDT (PCTFE–DT). A PCTFE film sample was placed in a Schlenk tube which was then purged with nitrogen for 15 min. THF and/or heptane (40 mL) was added (depending on the desired solvent composition—10%–90% THF was studied), and the Schlenk tube was equilibrated to the desired reaction temperature (−78, −20, or 0 °C). LiDT solution (20 mL—making the concentration in the reaction flask 0.05 M) was equilibrated to the reaction temperature and added via cannula. The film sample was allowed to react for the desired time (5, 30, or 60 min), and the solution was removed and replaced with 30 mL of methanol that had been equilibrated to the reaction temperature. The methanol was removed, and the film sample was washed with 0.1 N HCl (30 mL), water (3 × 30 mL), methanol (3 × 30 mL), and dichloromethane (5 × 30 mL), dried (0.05 mm, 24 h) before XPS, UV–vis, ATR IR, and contact angle data were obtained, and further dried (0.05 mm, 90 °C) for gravimetric analysis.

Hydrolysis of PCTFE–DT (PCTFE-CHO). A PCTFE–DT film sample which had only been dried at room temperature was placed, along with a glass boiling chip, in a 100-mL flask, and a solution of mercuric trifluoroacetate (0.5 g), trifluoroacetic acid (1 mL), acetone (10 mL), and water (40 mL) was added. A condenser was attached to the flask, and the mixture was heated to reflux. After 48 h, the film sample was removed, washed with methanol (3 × 30 mL) and dichloromethane (3 × 30 mL), and extracted with dichloromethane for 24 h in a Soxhlet extraction apparatus. The film was dried (24 h, 0.05 mm) before XPS, UV–vis, ATR IR, SEM, and contact angle analyses and further dried (90 °C, 0.05 mm) to constant mass for gravimetric analysis.

Reaction of PCTFE Oil with LiDT and Subsequent Hydrolysis. PCTFE oil (1 g) and a magnetic stirring bar were placed in a Schlenk tube which was then flushed with nitrogen for 15 min. THF (10 mL) was added and the mixture was stirred to dissolve the polymer and then equilibrated to −78 °C. LiDT solution (80 mL, 0.15 M in THF) was cooled to −78 °C and added dropwise over 30 min to the stirred PCTFE solution. After the addition, the reaction was maintained at −78 °C for 60 min and then allowed to warm to room temperature, where it was maintained for 15 min before 5 mL of methanol was added. The solvent was removed at reduced pressure, 100 mL of water was added to the remaining solid, and 1 N HCl was added to neutralize the solution. The solution was extracted with dichloromethane (3 × 50 mL) which was dried with magnesium sulfate, filtered, concentrated by rotary evaporation, and dried (0.05 mm, 50 °C, 72 h) before NMR and IR spectra were obtained. The resulting PCTFE–DT oil was placed, along with a magnetic stirring bar, in a 100-mL flask, 20 mL of acetone was added, and the mixture was stirred to dissolve the polymer. A solution of mercuric trifluoroacetate (5 g), trifluoroacetic acid (1 g), acetone (30 mL), and water (50 mL) was added. A condenser was attached to the flask, and the mixture was refluxed for 48 h, filtered, and extracted with dichloromethane (3 × 50 mL). The combined dichloromethane extracts were dried with magnesium sulfate, filtered, and concentrated by rotary evaporation. The resulting oil was dried (24 h, 0.05 mm) before NMR and IR spectra were obtained.

Reaction of PCTFE with the Grignard Reagent Prepared from 2-(2-Bromoethyl)-1,3-dioxolane and Subsequent Hydrolysis. Magnesium turnings (0.21 g, 8.6 mmol) and a magnetic stirring bar were placed in a 100-mL flask which was equipped with a septum-stoppered condenser. The apparatus was purged with nitrogen, heated with a heat gun for 15 min, and then cooled under a stream of nitrogen. THF (50 mL) was added via cannula, and then a solution of 2-(2-bromoethyl)-1,3-dioxolane (1.2 g, 6.6 mmol) in 5 mL of THF was added dropwise. The solution was maintained at 25 °C, and after 1 h, most of the magnesium had reacted. A 10-mL portion of this solution was added to a Schlenk tube containing a PCTFE film sample and 10 mL of THF. The reaction was allowed to proceed for 60 min before the solution was removed via cannula. The film sample was washed with methanol (30 mL), saturated ammonium chloride (2 × 30 mL), water (2 × 30 mL), methanol (3 × 30 mL), and dichloromethane (3 × 30 mL). The film was dried (24 h, 0.05 mm) before XPS and contact angle data were obtained. An identical film sample was prepared and placed in a 100-mL flask containing a boiling stone. Ethanol (25 mL) and 12 N HCl (25 mL) were added, and the mixture was refluxed for 2 h. The film sample was removed and washed with water (3 × 30 mL), methanol (3 × 30 mL), and dichloromethane (5 × 30 mL). The film was dried (24 h, 0.05 mm) before contact angle data were obtained.

Preparation of 2-(Lithiomethyl)-4,4-dimethyloxazoline (LiTMO). A magnetic stirring bar was placed in a Schlenk tube which was then purged with nitrogen for 15 min. 2,4,4-Trimethyloxazoline (TMO) (1 g, 8.8 mmol) and 10 mL of THF were added, and the tube was agitated to dissolve the TMO and equilibrated to −78 °C. *n*-Butyllithium (1.6 M, 5.2 mL, 8.3 mmol) was added via cannula, and the colorless solution was stirred at −78 °C for 15 min. The reaction was allowed to warm to −20 °C at which temperature it was stirred for 30 min. The yellow solution was diluted with heptane and/or THF (to the desired solvent composition) to 0.05 M before it was used in further reactions. This reagent could also be prepared in THF using *sec*-butyllithium and in heptane using *n*-butyllithium or *tert*-butyllithium.

Reaction of PCTFE with LiTMO (PCTFE–TMO). A PCTFE film sample was placed in a Schlenk tube which was then purged with nitrogen for 15 min. The reaction tube was equilibrated to the desired temperature (−78, −20, or 0 °C), and LiTMO solution (0.05 M, 20 mL) which was equilibrated to the reaction temperature was added. The film sample was allowed to react for the desired time (5, 30, or 60 min), and the solution was removed and replaced with 30 mL of methanol which had been equilibrated to the reaction temperature. The methanol was removed, and the film sample was washed with 0.1 N HCl (30 mL), water (3 × 30 mL), methanol (3 × 30 mL), and dichloromethane (5 × 30 mL). The film sample was dried (0.05 mm, 24 h) before XPS, UV–vis, ATR IR, and contact angle data were obtained and further dried (0.05 mm, 90 °C) for gravimetric analysis.

Hydrolysis of PCTFE–TMO (PCTFE-COOH). A PCTFE–TMO film sample which had been dried only at room temperature was placed along with a glass boiling chip in a Schlenk tube (which had been modified with a water jacket so that refluxing could be carried out in it) which was then purged with nitrogen for 15 min. A solution of trifluoroacetic acid (1 mL), water (20 mL), and acetone (5 mL) was added, and the tube was heated to reflux for 48 h. After this time, the film sample was removed and washed with methanol (3 × 30 mL), water (3 × 30 mL), methanol (30 mL), and dichloromethane (5 × 30 mL). The film sample was dried (24 h, 0.05 mm) before XPS, UV–vis, ATR IR, SEM, and contact angle measurements were obtained. The film was further dried (90 °C, 0.05 mm) to constant mass for gravimetric analysis.

Reaction of PCTFE Oil with LiTMO and Subsequent Hydrolysis. A Schlenk tube containing a magnetic stirring bar was purged with nitrogen for 15 min and PCTFE oil (1 g) and THF (10 mL) were added via cannula. The mixture was agitated to dissolve the polymer and equilibrated at −78 °C before LiTMO solution (50 mL 0.2 M in THF) was added dropwise. The mixture was stirred at −78 °C for 1 h and then allowed to warm to room temperature, where it was maintained for 15 min before 5 mL of methanol was added by syringe. The mixture was centrifuged to remove the precipitated salts, and the supernatant was added to 100 mL of water. The mixture was acidified with 1 N HCl and extracted with dichloromethane (3 × 50 mL). The combined extracts were dried with magnesium sulfate, filtered, and concentrated by rotary evaporation. The oil was dried (0.05 mm, 50 °C, 24 h) before NMR and IR spectra were obtained. PCTFE–TMO oil (1 g) was dissolved in 5 mL of THF in a 100-mL flask containing a magnetic stirring bar. HCl (5 N, 50 mL) was added, a condenser was attached, and the solution was heated to reflux for 3 h. After reflux, the solution was poured into 50 mL of cold water, and the mixture was extracted with dichloromethane (3 × 50 mL). The combined extracts were dried with magnesium sulfate, filtered, and concentrated to an oil by rotary evaporation. The oil was dried (24 h, 50 °C, 0.05 mm) before NMR and IR data were obtained.

Preparation of 2-[^{14}C]-2,4,4-Trimethyloxazoline. 2-Amino-2-methyl-1-propanol (0.525 g, 5.9 mmol) was weighed into a 35-mL flask containing a magnetic stirring bar. Acetic acid (0.347 g, 5.8 mmol) was weighed into a 5-mL V-bottomed flask. The vial containing 1-[^{14}C]acetic acid (1 mCi, 4.5 μL) was cooled to 0 °C and opened, and the unlabeled acetic acid was added. The resulting solution was transferred to the flask containing 2-amino-2-methyl-1-propanol. The flask and vial that contained acetic acid were washed with 20 mL of dodecane which was then added to the reaction flask. The flask was fitted with a 10-cm Vigreux column, a short path distillation head, and receiver that contained 10 mL of dodecane. The mixture was distilled until the temperature at the head of the column reached 140 °C. The contents of the receiver were dried with magnesium sulfate and then calcium hydride and redistilled under nitrogen to yield 0.45 g (68% yield) of [^{14}C]TMO.

Results and Discussion

Most of the results that follow were obtained using three different commercial PCTFE film samples: Kel-F 81 (3M), Aclar 33A (Allied), and Aclar 33C (Allied). Although the films varied in crystallinity (and perhaps other ways unknown to us), no differences in reactivity were observed in our experiments. Film was the chosen substrate form because it is most amenable to surface analytical techniques (contact angle, XPS, SEM, ATR IR, UV–vis, and gravimetric analyses). All of these techniques were used to study each of the functionalized surfaces prepared (PCTFE-OH, PCTFE-CHO, and PCTFE-COOH). Different techniques gave lucid information for different surfaces. UV–vis and XPS data were combined to estimate reaction depths. ATR IR and gravimetric analyses displayed no differences (from PCTFE) for two of the modified surfaces and indicated only that the modification depths were shallow. Contact angle measurements indicated qualitatively that polar functional groups were present on the surfaces and also gave information consistent with reaction kinetics which were determined by UV–vis. Scanning electron micrographs exhibited no changes in surface topography at a resolution of 100 Å and indicated that gross physical changes were not occurring upon modification. XPS spectra were recorded at two takeoff angles, 15° and 75° from the film surface and analyzed the outer 10 and 40 Å of the film samples.[6] The binding energies reported are approximate and not corrected, as the samples charged variably and were not charge-neutralized. In several cases, we used low molecular weight PCTFE oil to model the surface reactions when we could not directly observe functional groups by surface analytical techniques.

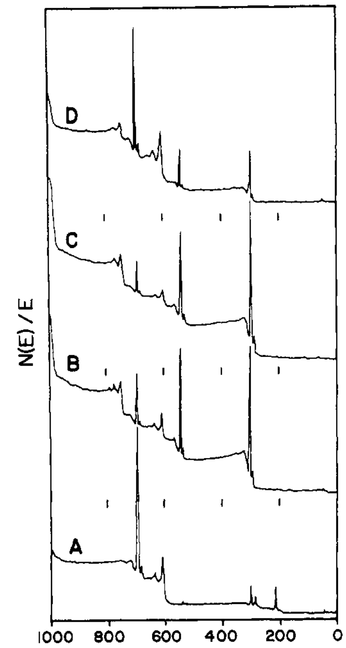
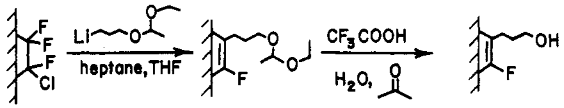


Figure 2. XPS survey spectra for the synthesis and labeling of PCTFE-OH. The reaction with LiPEAA was carried out in 50:50 heptane/THF at −20 °C for 60 min. The takeoff angle was 75° from the film surface. A, PCTFE; B, PCTFE–PEAA; C, PCTFE-OH; D, PCTFE-OCOC$_3$F$_7$.

Introduction of Surface Alcohol Functionality (PCTFE-OH). Equation 2 describes the reactions used to introduce hydroxyl groups onto the surface of PCTFE.



(2)

(PCTFE-OH)

Acetaldehyde 3-lithiopropyl ethyl acetal (LiPEAA) was prepared by using Eatons' procedure[7] as well as by lithium–bromine exchange in heptane at −78 °C. The latter method is faster, more convenient and with this method LiPEAA solutions can be prepared with a range of heptane:THF compositions. Treatment of PCTFE film samples with excess LiPEAA in heptane/THF (50:50) produces changes in the film surface consistent with the chemistry in eq 2 which can be observed by using a range of techniques. XPS indicates that the entire XPS sampling depth at a takeoff angle of 75° (40 Å) has reacted after 60 min at 0 or −20 °C and that most of the outer 40 Å has reacted after 60 min at −78 °C. Figure 2 depicts survey spectra for the reaction sequence in eq 2 as well as a spectrum of the product of the reaction of PCTFE-OH with heptafluorobutyryl chloride. Upon reaction of PCTFE with LiPEAA, there is a large decrease in the relative amount of fluorine present (685 eV), the complete removal of chlorine (208 and 278 eV), and the introduction of a significant amount of oxygen (532 eV). Deprotection of the alcohol increases the relative (to oxygen) amount of carbon (288 eV) present. The esterification of PCTFE-OH with heptafluorobutyryl chloride is indicated by the large increase in fluorine relative to oxygen and carbon. Some of these changes are more easily observed by examining

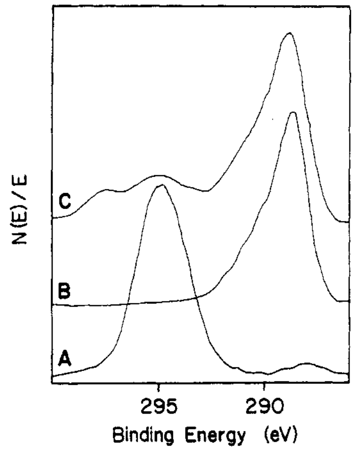


Figure 3. XPS spectra (expanded C_{1s} region) for the PCTFE-OH labeling experiment. Spectra are of the same samples in Figure 2. The takeoff angle was 75° from the film surface. A, PCTFE; B, PCTFE-OH; C, PTCFE-$OCOC_3F_7$.

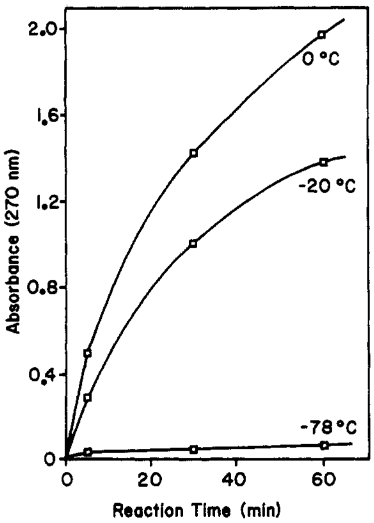


Figure 4. Plots of absorbance (270 nm) vs. reaction time for the reaction of PCTFE with LiPEAA in 50:50 THF/heptane at -78, -20, and 0 °C.

the expanded C_{1s} region (Figure 3): The peak corresponding to the electron-deficient carbon (CF_2 and $CFCl$ at 295 eV) is completely removed upon reaction with LiPEAA, and a complex peak at lower binding energy is observed. After reaction with heptafluorobutyryl chloride, higher binding energy peaks due to CF_3, CF_2, and $C{=}O$ are observed.

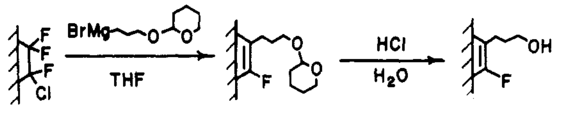
It was possible to estimate the depths of reaction by combining data from UV-vis spectroscopy with the XPS results. The relative amounts of PCTFE reacted during the modification were determined by comparing the absorbance at 270 nm (due to unsaturation) of samples reacted at -78, -20, and 0 °C. Figure 4 shows plots of absorbance vs. reaction time for these temperatures. After 60 min, the reaction at -20 °C has proceeded 23 times as far and the reaction at 0 °C has proceeded 32 times as far as the reaction at -78 °C. We estimate that the reaction at -78 °C has proceeded 50 Å into the film because the expanded C_{1s} region of the XPS (which assays the outer 40 Å) exhibits a small amount of high binding energy carbon due to starting material. The UV-vis relative absorbances thus place depth estimates at 1150 and 1600 Å for the reactions at -20 and 0 °C, respectively. These results indicate that this is not a very surface-selective reaction and that reaction depths can be controlled by temperature and time of reaction. The estimated values of reaction depth should be taken as crude estimates and rely completely on the value of 50 Å estimated from the XPS spectrum of the PCTFE film sample reacted at -78 °C. This may be a poor estimate; the reaction is somewhat corrosive in nature and how much modified PCTFE is present below the XPS sampling region is difficult to assess. We bother to make these estimates only for comparison with other, less deeply modified film samples discussed below. Another problem with these estimates is suggested by gravimetric analysis of the reactions: The films lose mass upon reaction and the stoichiometry in eq 2 predicts a mass gain (before deprotection). Film samples with surface areas of 6 cm² lost 5 ± 5 μg upon reaction at -78 °C for 60 min; higher temperatures rendered irreproducible and greater mass losses. These results suggest that the modified film is soluble in the reaction medium or that a degradative side reaction resulting in mass loss is competing. We prefer the former suggestion: we have observed no chain cleaving reaction with any lithium reagent, and we have completely solubilized PCTFE film samples in THF by grafting polystyrene onto it using polystyryllithium.[8] Contact angle data indicate the introduction of polar functionality and that the sampling depth of this technique is rapidly modified and changes little after its initial modification. The data are summarized in Table I.

Table I
Contact Angle Data (Water) for the Reaction of PCTFE with LiPEAA and Subsequent Deprotection

	-78 °C reaction		0 °C reaction	
surface	θ_{ADV}, deg	θ_{REC}, deg	θ_{ADV}, deg	θ_{REC}, deg
PCTFE	104 ± 1	80 ± 1	104 ± 1	80 ± 1
+ LiPEAA (5 min)	78 ± 2	49 ± 2	95 ± 3	0
(after hydrolysis)	71 ± 2	20 ± 2	64 ± 2	19 ± 2
+ LiPEAA (30 min)	77 ± 2	46 ± 2	98 ± 2	0
(after hydrolysis)	71 ± 2	20 ± 2	73 ± 1	22 ± 1
+ LiPEAA (60 min)	73 ± 1	42 ± 1	98 ± 3	0
(after hydrolysis)	69 ± 1	19 ± 1	66 ± 3	20 ± 3

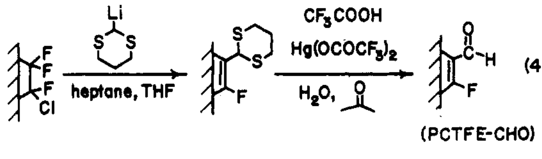
It was possible to obtain ATR IR spectra of the modified PCTFE samples which were lucid and consistent with the chemistry in eq 2. The spectra in Figure 5 indicate that a large quantity of the protected functionality is present when the reaction is carried out at -20 °C and a small amount is incorporated at -78 °C.

It was also possible to introduce hydroxyl groups onto the surface of PCTFE using the protected Grignard reagent and the reaction sequence summarized in eq 3. The resulting surface was not analyzed in detail.



(3)

Introduction of Surface Aldehyde Functionality (PCTFE-CHO). Formyl groups were introduced to the PCTFE surface by using the chemistry described in eq 4.



(4)

2-Lithio-1,3-dithiane (LiDT)[9] was prepared by reacting 1,3-dithiane with either *tert*-butyllithium or *n*-butyllithium in heptane at -20 °C, and the resulting solution was diluted with THF and/or heptane to the desired concentration and solvent ratio. PCTFE film samples were exposed to

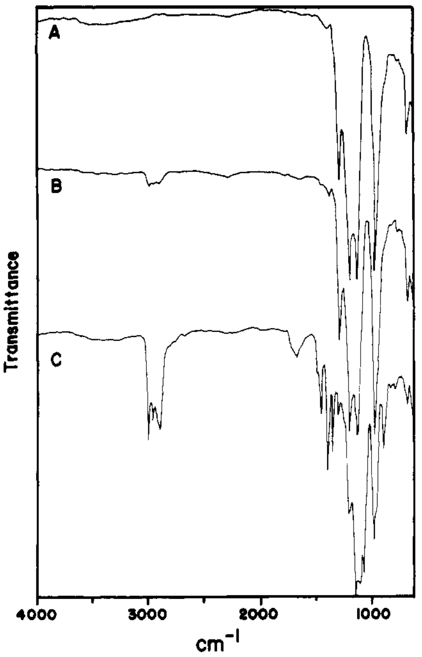


Figure 5. ATR IR spectra (Ge, 45°) for (A) PCTFE, (B) PCTFE reacted with LiPEAA at -78 °C in 50:50 heptane/THF for 60 min, and (C) PCTFE reacted with LiPEAA at -20 °C in 50:50 heptane/THF for 60 min.

LiDT solution at the desired temperatures for the desired lengths of time and were worked up and deprotected. The sulfur in PCTFE–DT served as a convenient XPS label and allowed the monitoring and the optimization of the reactions. Mercuric trifluoroacetate/trifluoroacetic acid induced much more complete deprotection than mercuric chloride, cupric chloride/cupric oxide, or methyl iodide. A probable reason for the success of this method is the solubility of the reagents in the film surface. XPS (as well as other analyses discussed below) indicates that a surface-selective reaction has taken place. The reaction proceeds to a much lower depth than the one used to incorporate alcohol functionality. Figure 6 shows XPS survey spectra for the reactions summarized in eq 4. Reaction with 3-lithio-1,3-dithiane causes decreases in fluorine (685 eV) and chlorine (208 and 278 eV) intensity and the introduction of oxygen (532 eV) from adventitious sources and sulfur (236 and 172 eV). Deprotection of the aldehyde to give PCTFE-CHO causes increases in fluorine (685 eV) and chlorine (208 and 278 eV) intensity (removal of the three methylenes and two sulfur atoms exposes more of the unreacted bulk to the sampling region), an increase in oxygen (532 eV) intensity, and almost complete removal of sulfur (236 and 172 eV). The photoelectron lines at 108, 111, 370, and 390 eV are due to mercury that could not be extracted from the film sample; this residual mercury comprises less than 0.5% of the atomic composition of the XPS sampling region. The presence of chlorine in the outer 40 Å indicates that unreacted PCTFE is present in this region. Figure 7 shows the expanded C_{1s} regions of PCTFE–DT spectra recorded at two different takeoff angles. The upper spectrum (15° takeoff) indicates that the outer 10 Å contains almost no unreacted PCTFE; the lower spectrum (75° takeoff) indicates that a significant amount of unreacted PCTFE is present from 10 to 40 Å from the surface. When the reaction of PCTFE with LiDT is carried out at 0 °C, the outer 40 Å contains no unreacted PCTFE.

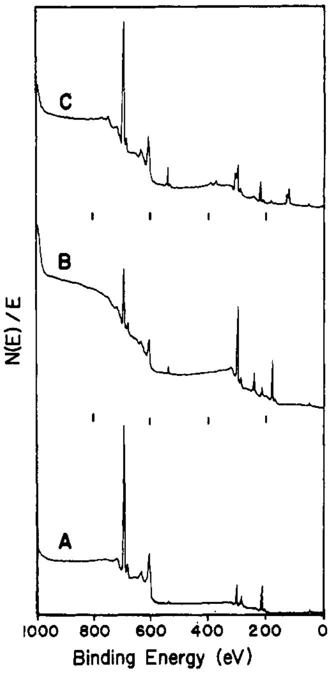


Figure 6. XPS survey spectra for the synthesis of PCTFE-CHO. The reaction of PCTFE with 2-lithio-1,3-dithiane was carried out in 50:50 heptane/THF at -78 °C for 60 min. The takeoff angle was 75° from the film surface. A. PCTFE; B, PCTFE-DT; C, PCTFE-CHO.

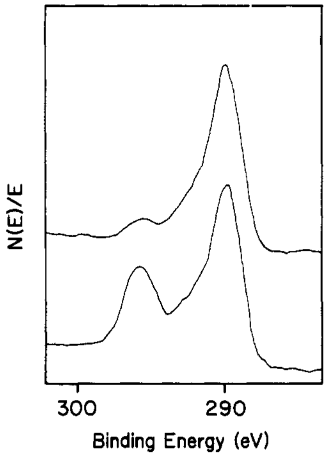


Figure 7. XPS spectra (expanded C_{1s} region) for PCTFE–DT. Spectra are of the same sample in Figure 6. The upper spectrum was recorded at a takeoff angle of 15° from the film surface; the lower spectrum was recorded at a takeoff angle of 75° from the film surface.

The kinetics of the reactions at -78 and 0 °C were obtained by using UV–vis spectroscopy; the data are shown in Figure 8. The plots describe autoinhibiting reactions in which the surface reacts completely in less than 5 min with little further reaction occurring subsequently. We view both of these reactions as surface-selective and emphasize that the thickness of the surface region is a function of temperature: The PCTFE film sample–solution interface is thicker (more diffuse) at 0 °C than it is at -78 °C; more of the PCTFE is exposed to lithium reagent in solution at 0 °C than at -78 °C.

We estimate, using the data in Figure 7, that the thickness of the modified layer in PCTFE-CHO prepared at -78 °C is about 25 Å; using the data in Figure 8, we then can calculate that the modified layer prepared at 0 °C is about 60 Å. ATR IR spectra of the PCTFE–DT and PCTFE-CHO film samples are identical with those of unmodified PCTFE, confirming that a very thin surface layer is modified. Gravimetric analyses are also consistent: no measurable changes in mass (the detection limits are ±1 μg) are observed in samples with 6-cm^2 surface area

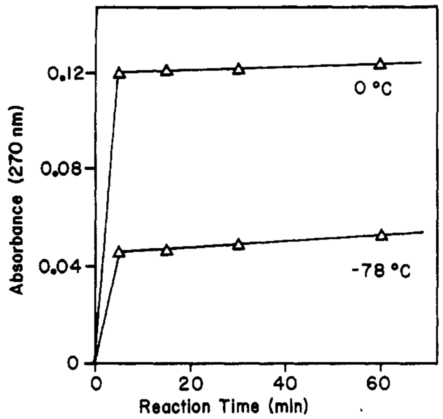


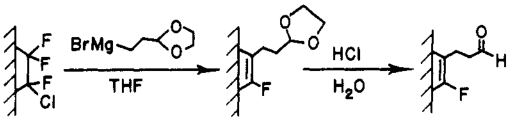
Figure 8. Plots of absorbance (270 nm) vs. reaction time for the reactions of PCTFE film with LiDT in 50:50 heptane/THF at 0 and -78 °C.

Table II
Contact Angle Data (Water) for the Reaction of PCTFE with LiDT and Subsequent Deprotection

	-78 °C reaction		0 °C reaction	
surface	θ_{ADV}, deg	θ_{REC}, deg	θ_{ADV}, deg	θ_{REC}, deg
PCTFE	104 ± 1	80 ± 1	104 ± 1	80 ± 1
+ LiDT (5 min)	90 ± 2	63 ± 2	82 ± 1	45 ± 2
(after hydrolysis)	80 ± 2	36 ± 1	79 ± 1	22 ± 1
+ LiDT (30 min)	89 ± 1	64 ± 2	82 ± 1	44 ± 1
(after hydrolysis)	75 ± 2	20 ± 1	71 ± 1	19 ± 2
+ LiDT (60 min)	88 ± 1	61 ± 1	82 ± 1	41 ± 1
(after hydrolysis)	75 ± 1	25 ± 1	71 ± 1	19 ± 1

upon reaction with LiDT or upon deprotection. Contact angle data are consistent with the introduction of polar functionality (Table II). These data also indicate that the significant changes in the region assayed by this technique occur in the initial stages of of reaction and that little occurs subsequently. That the chemistry described in eq 4 occurs was confirmed by carrying out these reactions on low molecular weight PCTFE oil in solution. The infrared spectrum of PCTFE-DT oil exhibits absorbances consistent with methylene groups (2930, 2878, and 1450 cm^{-1}) and unsaturation (broad absorbances 1600–1700 cm^{-1}). Upon deprotection, an intense carbonyl absorbance appears at 1730 cm^{-1} due to PCTFE-CHO. The ^{1}H NMR spectrum of PCTFE–DT oil exhibits a broad resonance from δ 1 to 2 due to the methylenes in the protecting group; PCTFE-CHO oil exhibits a resonance at δ 9.1 due to the aldehydic proton.

Aldehyde functionality could also be introduced using the protected Grignard reagent and the reaction sequence summarized in eq 5. The resulting surface was not analyzed in detail. An advantage of LiDT that this reagent does not have is a "built in" XPS label (sulfur).



(5)

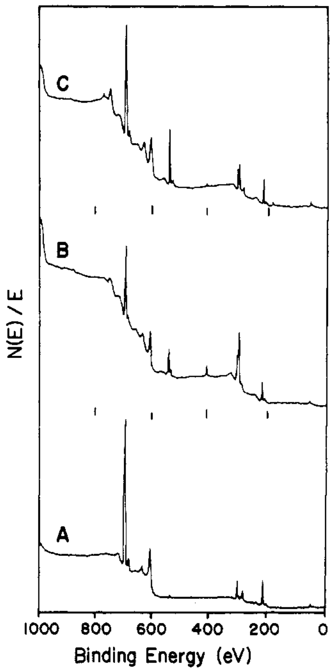
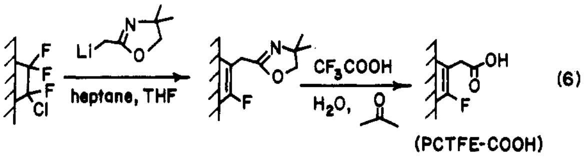


Figure 9. XPS survey spectra for the synthesis of PCTFE-COOH. The reaction of PCTFE with LiTMO was carried out in 50:50 heptane/THF at -78 °C for 60 min. The takeoff angle was 75° from the film surface. A, PCTFE; B, PCTFE–TMO; C, PCTFE-COOH.

Introduction of Surface Carboxylic Acid Functionality (PCTFE-COOH). The strategy of using a protected functional group containing lithium reagent was again employed to introduce carboxylic acid functionality to the surface of PCTFE. 2-(Lithiomethyl)-4,4-dimethyloxazoline (LiTMO)[10] was prepared by reacting 2,4,4-trimethyloxazoline with either *tert*-butyllithium or *n*-butyllithium in heptane or *n*-butyllithium or *sec*-butyllithium in THF at -78 °C followed by dilution with heptane and/or THF to the desired concentration and solvent ratio. The reaction with PCTFE to prepare PCTFE–TMO and subsequent deprotection to prepare PCTFE-COOH are summarized in eq 6. The nitrogen in the TMO serves as a built-in XPS label and allowed the optimization of the deprotection step by monitoring nitrogen and oxygen by XPS. Refluxing trifluoroacetic acid/water/acetone proved to be superior to aqueous HCl, aqueous/ethanolic HCl, *p*-toluenesulfonic acid/water/THF, *p*-toluenesulfonic acid/water/diglyme, and trifluoroacetic acid/water/THF. The ratio of water to acetone was important (probably because of both the liquid surface tension and the reflux temperature) and was optimized at 4:1 water:acetone. The same battery of analytical techniques described above was used to characterize these surfaces. XPS survey spectra for the reactions described in eq 6 are shown in Figure 9. The spectrum of PCTFE–TMO exhibits the expected nitrogen (402 eV) and oxygen (532 eV) photoelectron lines and decreased chlorine (208 and 278 eV) and fluorine (685 eV) intensities. Deprotection of the carboxylic acid group to give PCTFE-COOH causes the removal of most of the nitrogen and an increase in oxygen content. The fluorine and chlorine intensities also increase as the removal of the 4-carbon protecting group exposes more of the unreacted bulk to the sampling region. The expanded C_{1s} regions of PCTFE–TMO are shown in Figure 10. The upper spectrum was obtained at a 15° (from the surface) takeoff angle, the lower spectrum at a 75° takeoff angle. These spectra indicate a very surface-selective reaction and indicate that most of the PCTFE–TMO is contained in the outer 10–20 Å. When the reaction of PCTFE with LiTMO is carried out at -20 °C for 60 min, the outer 10 Å contains no unreacted PCTFE, but a small amount remains in the



(6)

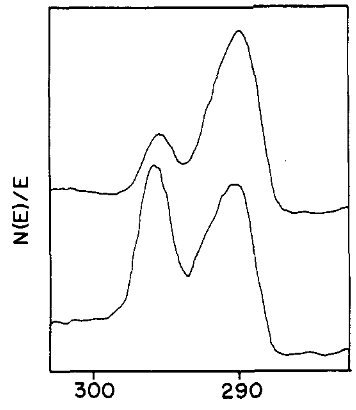


Figure 10. XPS spectra (expanded C_{1s} region) for PCTFE–TMO prepared at −78 °C in 50:50 heptane/THF (reaction time, 60 min). The takeoff angles used to obtain the spectra were 15° for the upper spectrum and 75° for the lower spectrum.

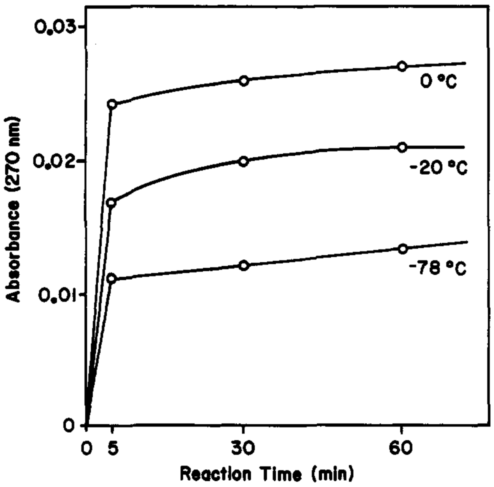


Figure 11. Plots of absorbance (270 mm) vs. reaction time for the reactions of PCTFE film with LiTMO in 50:50 heptane/THF at 0, −20, and −78 °C.

Table III
Contact Angle Data (Water) for the Reaction of PCTFE with LiTMO and Subsequent Deprotection

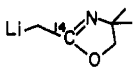
	−78 °C reaction		0 °C reaction	
surface	θ_{ADV}, deg	θ_{REC}, deg	θ_{ADV}, deg	θ_{REC}, deg
PCTFE	104 ± 1	80 ± 1	104 ± 1	80 ± 1
+ LiTMO (5 min)	89 ± 2	45 ± 2	75 ± 1	37 ± 2
(after hydrolysis)	75 ± 3	10 ± 2	70 ± 2	10 ± 1
+ LiTMO (30 min)	87 ± 2	42 ± 2	74 ± 1	34 ± 2
(after hydrolysis)	74 ± 2	10 ± 2	74 ± 1	0
+ LiTMO (60 min)	88 ± 2	43 ± 2	74 ± 1	34 ± 1
(after hydrolysis)	71 ± 1	0	72 ± 1	0

outer 40 Å. At 0 °C, the outer 40 Å is completely reacted after 60 min.

The kinetics of the reaction which were obtained by using UV–vis spectroscopy are consistent with surface selectivity. The data for reactions at −78, −20, and 0 °C are shown in Figure 11; the reactions are autoinhibiting, as is the case for PCTFE–DT, and essentially complete after 5 min. From the data in Figures 10 and 11, we estimate that the thicknesses of the modified layers in PCTFE–TMO and PCTFE-COOH are 20 Å when reacted at −78 °C, 35 Å when reacted at −20 °C, and 50 Å when reacted at 0 °C. ATR IR spectra and gravimetric analyses are consistent with this extent of reaction: PCTFE–TMO and PCTFE-COOH film samples exhibit no spectral or mass (for 6-cm^2 surface area) differences from unreacted PCTFE. Contact angle data are consistent with the introduction of polar functionality. The data are summarized in Table III and indicate that changes in the contact angle sampling region occur primarily in the initial stages of the reaction.

The chemistry to prepare PCTFE–TMO and PCTFE-COOH is also demonstrated by model solution reactions on low molecular weight PCTFE oil. The IR spectrum of PCTFE–TMO oil exhibits absorbances due to methyl (2960 and 2870 cm^{-1}), methylene (2920 and 2850 cm^{-1}), unsaturation (broad absorbance, 1500–1600 cm^{-1}), and C=N (1630 cm^{-1}). Upon deprotection, an intense carbonyl absorbance appears at 1760 cm^{-1} which shifts to 1600 cm^{-1} when triethylamine is added to the oil (forming the triethylammonium carboxylate salt). The ^{1}H NMR spectrum of PCTFE–TMO oil exhibits resonances at δ 1.10 (s), 1.65 (s), and 3.57 (s), corresponding to the methyl and methylene protons; PCTFE-COOH oil exhibits a resonance at δ 10–11, corresponding to the carboxylic acid proton.

Determination of Carboxylic Acid Site Density by Radioisotopic Labeling. It was possible to precisely determine the functional group density (number of carboxylic acids/cm^2 in PCTFE-COOH) by employing ^{14}C-labeled LiTMO (Li[^{14}C]TMO) in the synthesis. The synthesis of [^{14}C]TMO from 1-[^{14}C]acetic acid was essentially that of Meyers,[10] modified for the necessarily small scale (5–6 mmol). The PCTFE film used for these experiments was 25 μm thick. The energy of the β particles emitted from decaying ^{14}C is sufficient for them to pass through the film, so liquid scintillation counting (LSC) could be performed directly on films submersed in liquid scintillation fluid. That fluorescence quenching by the film is not significant was ascertained by LSC of a known amount of [^{14}C]TMO both in the presence and absence of a film sample: the presence of the film reduced the number of counts by 0.5%. The efficiency of the radioassay was established as 87% by comparing the measured counts per minute of a known quantity of [^{14}C]TMO with the predicted decays per minute (dpm) of the true activity. The dpm values were calculated from the efficiency, and a correction was made for the background. The calculated dpm values were divided by the surface area and converted, using the specific activity of the [^{14}C]TMO, into mol/cm^2. The mean value obtained at −20 °C for 60-min reaction is (9.7 ± 0.6) × 10^{-10} mol/cm^2 (95% confidence based on eight measurements, 5.8 × 10^{14} COOH/cm^2). The mean value obtained at −78 °C for 60-min reaction is (4.3 ± 1.0) × 10^{-10} mol/cm^2 (2.6 × 10^{14} COOH/cm^2). Two sources of error may bias these calculations high: (1) The deprotection step may not occur with quantitative yield (there is always residual nitrogen in the XPS spectra), and PCTFE-COOH may contain PCTFE–TMO. (2) Control reactions which consisted of treating PCTFE with [^{14}C]-TMO and exposing these film samples to the identical workup and deprotection conditions used to prepare PCTFE-[^{14}C]COOH gave film samples with significant radioactivity: 23% of the value obtained for PCTFE-[^{14}C]COOH (−20 °C), 25% of the value obtained for PCTFE-[^{14}C]COOH (−78 °C). It is not known whether or not these are appropriate controls; the same physisorption may or may not occur in the reactions of PCTFE with Li[^{14}C]TMO. It is also not known what form the ^{14}C has adsorbed as. Identical controls with cold TMO show no



Li[^{14}C]TMO

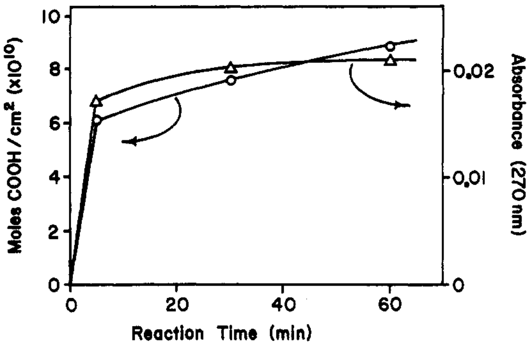


Figure 12. Plots of COOH site density determined by LSC and absorbance (270 nm) vs. reaction time for the reactions of Li-[^{14}C]TMO and LiTMO with PCTFE film at -20 °C in 50:50 heptane/THF. LSC data were obtained on PCTFE-[^{14}C]COOH; UV-vis data were obtained on PCTFE-TMO.

adsorption by any technique we have used.

The kinetics of the reaction at -20 °C were also obtained using LSC (Figure 12). As was indicated by monitoring the reaction by UV-vis, most of the reaction occurs in the first 5 min. The rate of the reaction after the initial 5 min appears to be greater when monitored by LSC than when monitored by UV-vis. This may indicate that the first steps of the reaction which generate the difluoroolefin intermediate (see Scheme I) occur slightly faster than the addition of the lithium reagent to the difluoroolefin. The differences in the kinetics, however, do not indicate substantial rate differences.

Solvent Dependence of Reaction Depth. Each of the reactions described above can be controlled using temperature to affect the depth of modification. This temperature dependence is likely due to differences in mobility of surface chains (both modified and unmodified) at different temperatures. Higher temperatures favor surface mobility, more potential reaction sites are exposed to reagents in solution, and thicker modified layers result. This mobility should also depend on the solvent in contact with the polymer; solvents which wet and/or swell the polymer to greater extents should favor mobility and render thicker modified layers. This effect was examined for the reactions of LiDT and LiTMO with PCTFE at -20 °C using different composition heptane/THF solutions as solvent, and the depths of reaction were compared (relatively) by using UV-vis spectroscopy. The results are summarized in Figure 13. Higher concentrations of THF promote thicker modified layers. We have observed that THF swells PCTFE and that heptane does not by gravimetric analysis of film samples extracted with those solvents. The effect of solvent composition on reaction depth is much more pronounced in the case of PCTFE-DT than in the case of PCTFE-TMO. PCTFE-PEAA synthesis is an extreme example of solvent-product interaction: the reaction is not surface-selective, and the product dissolves in the reaction solvent.

Summary and Conclusions

Alcohol functionality can be introduced to the surface of PCTFE by reaction with LiPEAA and subsequent hydrolysis. The reaction is not very surface-selective and proceeds to depths greater than 1000 Å after 60 min of reaction at temperatures of -20 and 0 °C. A more surface-selective reaction occurs at -78 °C, giving a modified layer with a thickness estimated as 50 Å. Aldehyde functionality can be incorporated in the PCTFE surface

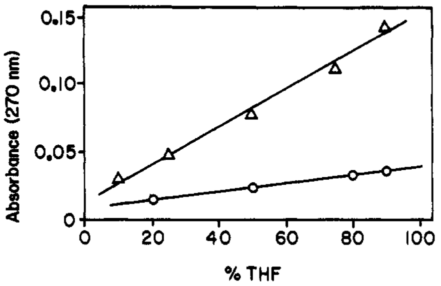


Figure 13. Plots of absorbance (270 nm) vs. composition for the reactions of LiDT and LiTMO with PCTFE film at -20 °C for 60 min.

by reaction with LiDT followed by deprotection. The conversion of the 1,3-dithiane moiety to an aldehyde was not straightforward and illustrates that reactions at condensed phase interfaces may have requirements different than the same reactions in solution. The reactions which form PCTFE-DT are autoinhibiting and surface-selective. The thicknesses of the modified layers in PCTFE-CHO are estimated to be 25 and 60 Å for reactions carried out for 60 min at -78 and 0 °C, respectively. Carboxylic acid functional groups are incorporated in the PCTFE surface upon reaction with LiTMO and subsequent hydrolysis. The reactions which form PCTFE-TMO are autoinhibiting and surface-selective and give modified layers with thicknesses of 20, 35, and 50 Å for reactions carried out for 60 min at -78, -20, and 0 °C, respectively. The site density of carboxylic acids contained on the PCTFE surface was determined to be $(4.3 \pm 1.0) \times 10^{-10}$ mol/cm^2 for samples prepared at -78 °C and (9.7 ± 0.6) mol/cm^2 for samples prepared at -20 °C.

The depth of reaction of PCTFE with lithium reagents is dependent on the temperature of the reaction, the solvent used, and the structure of the lithium reagent. Low temperatures favor shallow reaction depths. The extent to which the solvent interacts (wets, swells, dissolves) with the product is a major contributor to reaction depth. The experiments reported herein point out that the structure and reactivity of a polymer surface are strongly affected by the environment and are (and can be) controlled by temperature and the solvent in contact.

Acknowledgment. We are indebted to the National Science Foundation Materials Research Laboratory at the University of Massachusetts and the Office of Naval Research for financial support. T.J.M. acknowledges the support of the National Science Foundation in the form of a Presidential Young Investigator Award.

References and Notes

(1) Current address: Exxon Chemical Company, Linden, NJ 07036.
(2) Dias, A. J.; McCarthy, T. J. *Macromolecules* **1984**, *17*, 2529.
(3) Costello, C. A.; McCarthy, T. J. *Macromolecules* **1984**, *17*, 2940.
(4) Costello, C. A.; McCarthy, T. J. *Macromolecules* **1985**, *18*, 2087.
(5) Dias, A. J.; McCarthy, T. J. *Macromolecules* **1985**, *18*, 1826.
(6) Clark, D. T.; Thomas, H. R. *J. Polym. Sci., Polym. Chem. Ed.* **1977**, *15*, 2843.
(7) Eaton, P. E.; Cooper, G. F.; Johnson, R. C.; Mueller, R. H. *J. Org. Chem.* **1972**, *37*, 1947.
(8) Patton, P. A.; McCarthy, T. J., unpublished results, 1987.
(9) Corey, E. J.; Seebach, D. *Angew. Chem., Int. Ed. Engl.* **1965**, *4*, 1075.
(10) Meyer, A. I.; Temple, D. L.; Nolen, R. L.; Mihelich, E. D. *J. Org. Chem.* **1974**, *39*, 2778.