Acknowledgment. Financial support of the Deutsche Forschungsgemeinschaft, Bonn-Bad Godesberg (projects Schu 416/3 and Schu 416/12-1), is gratefully acknowledged. We thank Dr. C. Puglisi and Professor G. Montaudo, University of Catania, for providing the butandiol diacetate model compound and helpful comments.

References and Notes

(1) Grassie, N.; Murray, E. J.; Holmes, P. A. *Polym. Degr. Stab.* **1984,** *6,* 47.
(2) Lüderwald, I. In *Developments in Polymer Degradation, Volume 2;* Grassie, N., Ed.; 1979; pp 77-98.
(3) Garozzo, D.; Giuffrida, M.; Montaudo, G. *Macromolecules* **1986,** *19,* 1643.
(4) Maravigna, P.; Montaudo, G. Formation of cyclic oligomers. In Comprehensive Polymer Science; Eastmond, G. C., Ledwith, A., Russo, S., Sigwalt, P., Eds.; Pergamon Press: Oxford, 1989.
(5) Giuffrida, M.; Maravigna, P.; Montaudo, G.; Chiellini, E. *J. Polym. Sci.; Polym. Chem. Ed.* **1986,** *24,* 1643.
(6) Plage, B.; Schulten, H.-R. *J. Anal. Appl. Pyrolysis* **1989,** *15,* 197.
(7) Schulten, H.-R.; Lattimer, R. P. *Mass Spectrom. Rev.* **1984,** *3,* 231.
(8) Schulten, H.-R. *J. Anal. Appl. Pyrolysis* **1987,** *12,* 149.
(9) Simmleit, N.; Schulten, H.-R. *Chemosphere* **1989,** *18,* 1855.
(10) Hempfling, R.; Zech, W.; Schulten, H.-R. *Soil Sci.* **1988,** *146,* 262.
(11) Beckey, H. D. Field Ionization Mass Spectrometry. In *International Series of Monographs in Analytical Chemistry, Volume 42;* Belcher, R., Freiser, H., Eds.; Pergamon Press: Oxford, 1971.
(12) Schulten, H.-R.; Simmleit, N.; Müller, R. *Anal. Chem.* **1987,** *59,* 2903.
(13) Schulten, H.-R.; Simmleit, N.; Müller, R. *Anal. Chem.* **1989,** *61,* 221.
(14) Lüderwald, I.; Urrutia, H. *Makromol. Chem.* **1976,** *177,* 2093.
(15) Lüderwald, I.; Urrutia, H.; Herlinger, H.; Hirt, P. *Angew. Makromol. Chem.* **1976,** *50,* 163.
(16) Adams, R. E. *J. Polym. Sci.; Polym. Chem. Ed.* **1982,** *20,* 119.
(17) Doerr, M.; Lüderwald, I.; Schulten, H.-R. *Fresenius Z. Anal. Chem.* **1984,** *318,* 339.
(18) Ballistreri, A.; Garozzo, D.; Giuffrida, M.; Montaudo, G. *Anal. Chem.* **1987,** *59,* 2024.
(19) Schulten, H.-R.; Plage, B. *J. Polym. Sci.; Polym. Chem. Ed.* **1988,** *26,* 2381.
(20) Plage, B.; Schulten, H.-R. *J. Appl. Polym. Sci.* **1989,** *38,* 123.
(21) Ohtani, H.; Nagaya, T. Sugimara, Y.; Tsuge, S. *J. Anal. Appl. Pyrolysis* **1982,** *4,* 117.
(22) Schulten, H.-R.; Murray, K. E.; Simmleit, N. *Z. Naturforsch.* **1987,** *42c,* 178.
(23) Jacobi, E.; Lüderwald, I.; Schulz, R. C. *Makromol. Chem.* **1978,** *179,* 429.
(24) Garozzo, D.; Giuffrida, M.; Montaudo, G. *Polymer Bull.* **1986,** *15,* 353.
(25) Garozzo, D.; Montaudo, G.; Giuffrida, M. *Polym. Deg. Stab.* **1986,** *15,* 143.
(26) Iwabuchi, S.; Jaacks, V.; Kern, W. *Makromol. Chem.* **1976,** *177,* 2675.
(27) Lüderwald, I. *Makromol. Chem.* **1977,** *178,* 2603.
(28) Foti, S.; Giuffrida, M.; Maravigna, P.; Montaudo, G. *J. Polym. Sci.; Polym. Chem. Ed.* **1984,** *22,* 1201.

Registry No. I (copolymer), 28158-21-6; I (SRU), 28725-67-9; II (copolymer), 24938-37-2; II (SRU), 24937-05-1; III (copolymer), 36568-42-0; III (SRU), 36221-42-8; IV (copolymer), 26745-88-0; IV (SRU), 26762-10-7; V (SRU), 25038-59-9; VI (copolymer), 26062-94-2; VI (SRU), 24968-12-5; VII (copolymer), 28158-15-8; VII (SRU), 28759-54-8; VIII (homopolymer), 26100-51-6; VIII (SRU), 26023-30-3; IX (homopolymer), 26063-00-3; IX (SRU), 126296-86-4; X (homopolymer), 24980-41-4; X (SRU), 25248-42-4; XI (homopolymer), 30729-36-3; XI (SRU), 26099-71-8.

Surface Modification of Poly(tetrafluoroethylene-*co*-hexafluoropropylene). Introduction of Alcohol Functionality[1]

Robert C. Bening and Thomas J. McCarthy*

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

Received October 6, 1989; Revised Manuscript Received November 21, 1989

ABSTRACT: The reduction of poly(tetrafluoroethylene-*co*-hexafluoropropylene) (FEP) was studied with regard to the kinetics of reaction and the product structure. The thickness of the resulting modified surface layer (depth of reaction) can be controlled by using reaction time and temperature. At -78 °C the thickness can be controlled in the range of 45-90 Å using reaction time; at 0 °C the thickness can be controlled in the range of 250-800 Å. The air-sensitive reduction product contains carbon-carbon double and triple bonds, aliphatic C-H bonds, alcohols, carbonyls, and very little fluorine. The sources of the oxygen and C-H functionality were studied. Hydroboration followed by oxidation introduces alcohol functionality to the surfaces. The alcohols exhibit low reactivity in esterification reactions, but yields can be improved by using acylation catalysts; their reactivity is analogous to hindered alcohols in solution. Base-catalyzed addition of ethylene oxide renders surface-bound primary alcohols, increasing the reactivity of the surface toward esterification. Lower yields of primary alcohols can be directly introduced to the surface by reaction of the reduced layer with 9-BBN, followed by carbonylation and reduction.

Introduction

Our study of the surface chemistry of fluorinated polymers[2-6] has been with the objective of preparing model substrates from which surface structure-property and structure-reactivity correlations can be drawn. Chemically resistant polymer film samples were chosen[7] to prepare substrates with reactive surfaces and inert interiors so that

0024-9297/90/2223-2648$02.50/0

subsequent chemical modification would occur exclusively at the surface, allowing property differences to be correlated with surface-chemical differences.

We have developed surface-selective modification reactions for poly(chlorotrifluoroethylene)[4,6] (PCTFE) and poly(vinylidene fluoride)[3,8] (PVF_2). The strategy for achieving surface selectivity in both cases involved carrying out reactions at sharp (not diffuse) interfaces between polymer film samples and reactive solutions; autoinhibiting kinetics were observed, indicating that reaction is limited to that part of the film sample that is accessible to reagents in solution. The depth of modification reactions (the thickness of the modified layer) could be controlled by adjusting the diffuseness of the interface using temperature (for PCTFE and PVF_2) and solvent composition (for PCTFE).

The surface chemistry that we developed for poly(tetrafluoroethylene)[5] (PTFE), however, is not surface-selective. Reaction of PTFE with benzoin dianion produces an unsaturated surface that serves as a reactive handle upon which further modification chemistry can be effected; however, the reaction proceeds corrosively. Unreacted PTFE is present in the outer 40 Å of samples with modified layers of less than 500-Å (average) thickness; thus homogeneous (within the XPS sampling region) surfaces could be prepared only by deeply modifying film samples. Average reaction depth (modified layer thickness) could only be crudely controlled by varying reaction time. Attempts to extend the range of modification depths by varying reaction temperature failed. A consistent explanation for the corrosive nature of this modification reaction is that the product exhibits electronic conductivity[9] which facilitates reaction by conducting electrons from solution to virgin PTFE.

The work reported in this paper concerns the surface modification of poly(tetrafluoroethylene-*co*-hexafluoropropylene) (FEP). We chose to study this chemically resistant material specifically because it contains trifluoromethyl groups, which should introduce defects in the reduction product that are not present in reduced PTFE, lowering the conductivity, thus increasing the surface selectivity of the reaction. It has been reported[10] that the electronic conductivity of reduced FEP is lower than that of reduced PTFE.

Experimental Section

Materials. FEP film samples (Du Pont 5-mil) were extracted with THF (Soxhlet extractor) for 24 h and dried (0.02 mm, 25 °C) overnight. This procedure gives film samples that are consistently free of any detectable contaminants. Samples used for gravimetric analysis (1.5 × 1.5 cm) were dried (0.02 mm, 75 °C) until constant mass (±1 μg) was achieved. THF was distilled from sodium benzophenone dianion; methanol and ethanol were refluxed over and distilled from magnesium turnings. House distilled water was redistilled with a Gilmont still and deoxygenated by sparging with nitrogen. 2,4-Dinitrophenylhydrazine (Aldrich) was recrystallized from petroleum ether. Heptafluorobutyryl chloride (Aldrich) was distilled at reduced pressure trap-to-trap and stored under nitrogen. Pyridine (Fisher, 100 mm) and ethylene oxide (Eastman, trap-to-trap) were distilled from calcium hydride. Sodium (Aldrich) was washed with two portions of hexane and cut under nitrogen. Borane–tetrahydrofuran ($BH_3 \cdot THF$) complex (1.0 M in THF, Aldrich), potassium chlorate (Alfa), hydrogen peroxide (30%, VWR), D_2O (Aldrich), THF-d_8 (Aldrich), lithium diisopropylamide (LDA, Aldrich), 4-(dimethylamino)pyridine (DMAP, Aldrich), 9-BBN (0.5 M in THF, Aldrich), $LiAlH_4$ (Aldrich), benzoyl peroxide (Aldrich), dichloromethane (Fisher), and carbon monoxide (Linde) were used as received. All reactions and manipulations involving air-sensitive materials (including reduced polymers) were performed under an atmosphere of prepurified nitrogen (Linde) that was further purified by passing through columns of BASF-BTS catalyst and P_2O_5.

Methods. Gravimetric analysis was performed with a Cahn 29 electrobalance equipped with a polonium source. Samples were stored under nitrogen or vacuum and charge neutralized with a Zerostat (Aldrich) just prior to weighing and then weighed in air. Samples were dried under vacuum (0.02 mm) at 75 °C and weighed at 24-h intervals until constant mass was observed. We estimate that our results are accurate to ±1 μg. X-ray photoelectron spectroscopy (XPS) was performed with a Perkin-Elmer-Physical Electronics 5100 spectrometer (Mg Kα excitation, 300 W) using a pass energy of 71.5 eV. Charge neutralization was not employed so that, unless otherwise specified, spectra are not corrected for charging. Samples were mounted in a nitrogen atmosphere drybox (Vacuum Atmospheres) and transferred to the nitrogen-purged antechamber by using Schlenk techniques. Atomic sensitivity factors used to calculate atomic composition data were as follows: F_{1s}, 1.00; O_{1s}, 0.66; N_{1s}, 0.42; C_{1s}, 0.25; Cl_{2p}, 0.53. Attenuated total reflectance infrared (ATR IR) spectra were recorded under nitrogen by using an IBM 38 FTIR and a 45° germanium internal reflection element. UV–vis spectra were recorded in air by using a Perkin-Elmer Lambda 3A spectrophotometer. Quantitative absorbance data were read off the digital meter at the desired wavelength. The absorbance differences between virgin and reacted film samples were obtained by subtracting the average value for virgin FEP (determined from four film samples) at that wavelength. The accuracy of the absorbance difference is estimated to be ±0.004 au. Dynamic advancing and receding contact angles were measured with a Ramé-Hart telescopic goniometer while adding and removing water (purified as described above—pH 5–7) using a Gilmont syringe.

Reaction of FEP with Sodium Naphthalide (FEP-C). Sodium naphthalide was prepared by adding 5 g (40 mmol) of naphthalene to 250 mL of THF and cutting ~1.7 g (74 mmol) of sodium (very small pieces) into the solution under nitrogen. After being stirred for ~3 h, the dark green solution was transferred via cannula to a nitrogen-purged storage flask. FEP samples (1.5 × 4 cm) were placed in a Schlenk tube that was subsequently purged with nitrogen; THF (5 mL) was added, and the flask was allowed to equilibrate to the reaction temperature (0 or −78 °C). The sodium naphthalide reagent (which was equilibrated to −78 °C for the low temperature reaction) was added to the reaction tube. After the desired time, the reaction solution was removed and the film was rinsed by one of the following procedures: A, water (5 × 20 mL) and then THF (5 × 20 mL); B, THF (3 × 20 mL), water (5 × 20 mL), and then THF (5 × 20 mL); C, methanol (5 × 20 mL) and then THF (5 × 20 mL); D, D_2O (2 × 5 mL) and then THF (5 × 20 mL). Film samples were then dried at reduced pressure. We note that the sodium naphthalide reagent exhibited a reversible color change and slow precipitation at −78 °C, indicative of reduced solubility at that temperature. Product film samples were dull black colored until rinsing with water, after which they appeared brown.

Oxidation of FEP-C with $KClO_3/H_2SO_4$. The reduced surface layer was removed from FEP-C samples by oxidation with a sulfuric acid solution of potassium chlorate (1 g in 50 mL) at room temperature in an open beaker; film samples were then washed with water (5 × 20 mL) followed by THF (5 × 20 mL) and dried (0.02 mm, 75 °C) for gravimetric analysis.

Reaction of FEP-C with Oxygen and Air. FEP-C samples were prepared by using rinsing procedure C and exposed either to dry oxygen (Linde, <3 ppm H_2O) for 96 h or to laboratory atmosphere for 7 days.

Hydroboration and Subsequent Oxidation of FEP-C (FEP-OH). Borane in THF (10 mL, 0.5 M) was introduced to a Schlenk tube containing a FEP-C film sample at room temperature. After ~18 h the solution was removed and the film sample was washed with THF (3 × 20 mL). A solution of basic aqueous peroxide (1.2 g NaOH, 20 mL of H_2O, 10 mL of 30% H_2O_2) was prepared at 0 °C and introduced to the reaction flask. After 3 h at 0 °C the solution was removed and the film sample was washed with dilute aqueous NaOH (5 × 20 mL), dilute aqueous HCl (5 × 20 mL), water (5 × 20 mL), and then THF (5 × 20 mL) and dried at reduced pressure.

Reaction of FEP-OH with Ethylene Oxide and LDA. LDA (0.25 g) was dissolved (a small amount remained suspended) in 25 mL of THF, and the solution was equilibrated at 0 °C. Ethylene oxide (5 mL) was added, and the solution was transferred via cannula to a nitrogen-purged Schlenk tube containing a FEP-OH film sample. The reaction was allowed to proceed at 5 °C. After the desired time, the reagent was removed and the film sample was washed with THF (2 × 20 mL), extracted with methanol (Soxhlet, overnight), and dried (0.02 mm, 45 °C).

Reaction of FEP-C with Methanol and Benzoyl Peroxide. A solution of 0.5 g of benzoyl peroxide in 25 mL of methanol was introduced to a Schlenk tube containing a FEP-C film sample. The tube was heated at 50 °C for 24 h; the solution was removed, and the film sample was washed with methanol (5 × 20 mL), extracted (Soxhlet) with dichloromethane, and dried (0.02 mm, 45 °C).

Reaction of FEP-C with 9-BBN (FEP-9-BBN). A 0.5 M solution of 9-borobicyclo[3.3.1]nonane (9-BBN) (20 mL) was introduced to a nitrogen-purged Schlenk tube containing a FEP-C film sample. Reaction was allowed to proceed overnight at either room temperature or reflux temperature (a condenser was attached). The reagent was removed, and the film sample was washed with THF (3 × 20 mL) and dried (25 °C, 0.02 mm).

Carbonylation and Subsequent Basic Workup of FEP-9-BBN. A solution of $LiAlH(OCH_3)_3$ in THF (0.47 M) was prepared by slowly adding, under nitrogen, 1.7 g of methanol (0.043 mol) in 16 mL of THF to 14 mL of 1.0 M $LiAlH_4$ (0.014 mol) in THF. Heat evolved and a milky white suspension was produced. After the solution cooled to room temperature, it was transferred to a nitrogen-purged Schlenk tube containing a FEP-9-BBN film sample. Carbon monoxide was bubbled through the solution for 5 min, and the tube was sealed under a positive pressure of CO. After 4 h the tube was repressurized with CO, and, after an additional 22 h, the reagent was removed and the film sample washed with THF (2 × 20 mL). A solution of 2.1 g of KOH in 30 mL of ethanol was added, and the flask was heated at 60 °C for 45 min. The solution was removed, and the film sample was washed with slightly acidic (HCl) methanol (5 × 20 mL), methanol (5 × 20 mL), and then dichloromethane (5 × 20 mL) and dried (0.02 mm, 45 °C).

Reaction of Hydroxylated Surfaces with Heptafluorobutyryl Chloride (HFBC). Surface hydroxyl groups were acylated with HFBC by using the following conditions: A: A solution of 0.5 mL of HFBC in 20 mL of THF was added to a nitrogen-purged Schlenk tube containing a film sample; 100 μL of pyridine was then added. B: Pyridine (15 mL) was added to a Schlenk tube containing a film sample, and then 0.5 mL of HFBC was introduced. Gas evolved and a pale yellow precipitate formed; after ~2 h the precipitate dissolved, resulting in a bright yellow solution. C: A solution of 0.082 g of DMAP in 20 mL of pyridine was introduced to the reaction tube (containing a film sample) and then 0.5 mL of HFBC was added. Gas evolved, a white precipitate formed, and the solution became yellow-orange colored. D: A THF solution (20 mL) of 0.082 g of DMAP and 1.3 mL of pyridine was added to a Schlenk tube containing a film sample, and then 0.5 mL of HFBC was introduced. A pale yellow solution and a white precipitate formed. After the desired reaction time, the solution (and precipitate if present) was removed via cannula and the film sample was washed with THF (2 × 20 mL), methanol (5 × 20 mL), and then THF (3 × 20 mL) and dried (0.02 mm).

Reaction of FEP-C and FEP-OH with 2,4-Dinitrophenylhydrazine. A solution of 0.2 g of 2,4-dinitrophenylhydrazine (DNPH), 8 drops of concentrated HCl, 1 mL of water, and 20 mL of THF was transferred via cannula to a Schlenk flask containing a film sample (FEP-C or FEP-OH). Reaction was allowed to proceed at room temperature for 48 h. The solution was removed and the film sample washed with THF (5 × 20 mL), ethanol (5 × 20 mL), and then heptane (5 × 20 mL) and dried (0.02 mm).

Results and Discussion

Perfluorinated polymers are the least generally reactive polymeric materials; however, they react faciley with single electron reducing agents.[5,10–21] We have studied[5] the reduction of PTFE with dipotassium benzoin dianion in Me_2SO and proposed a reduction mechanism that proceeds by a series of electron transfers and fluoride eliminations (and other competing reactions) to render a cross-linked carbonaceous material. The skeleton of this mechanism (eq 1) can be applied to any of the reported

$$CF_2 + 4\,e^- \longrightarrow \underbrace{4\,F^- + C}_{\text{crosslinks, condensed aromatics, free spins, C=C,C≡C}} \qquad (1)$$

perfluorinated polymer reductions. We have needs for surface-functionalized chemically resistant polymers and report here results of our studies on the reduction of FEP with sodium naphthalide and the further modification of the reaction product. The reaction of FEP with sodium naphthalide has been studied previously, and it is reported that the product contains unsaturation[17] and oxygen-containing functional groups.[21] Only this minimal structural characterization and no attempts to study or control reduction kinetics have been reported. Additionally, it is not apparent from previous reports what attempts were made to exclude air and water during reaction, workup, and subsequent analysis.

Reduction Kinetics. FEP film reacts rapidly with THF solutions of sodium naphthalide at room temperature as evidenced by an instantaneous blackening of the initially clear/white film. We determined kinetics (depth of reaction versus time) for reaction of FEP film with 0.2 M sodium naphthalide at 0 °C and −78 °C using a combination of gravimetric analysis and UV–vis spectroscopy. Accurate measurements of reaction depth could be made without stoichiometric assumptions for samples reacted at 0 °C using gravimetric analysis. Film samples (5-mil, 1.5 × 1.5 cm²) were weighed, reacted for various times, isolated by using rinsing procedure A (we abbreviate these reduced samples FEP-C^a with the superscript indicating the rinsing procedure used), oxidized with $KClO_3/H_2SO_4$ and reweighed. Figure 1 shows XPS spectra of FEP, FEP-C^a (0 °C, 4 h), and a sample of FEP-C^a that had been oxidized with $KClO_3/H_2SO_4$. It is apparent from these spectra that the reduced layer in FEP-C^a is essentially completely removed by the oxidation; thus the mass loss upon reduction and oxidation is equivalent to the mass of FEP that is reduced. The depth of reaction (thickness of the carbonaceous layer in FEP-C^a) can be directly determined by using eq 2, where M_v is

$$\text{depth of reaction} = \frac{M_V - M_O}{(2.15)\cdot A} \qquad (2)$$

the mass of the virgin film sample, M_o is the mass of the reduced-then-oxidized film sample, and A is the surface area (neglecting the edges) of the sample; 2.15 is the density of FEP. UV–vis spectra of FEP-C samples exhibit a broad absorbance tailing out to 700 nm with a distinct peak centered at 266 nm; comparison of spectra with gravimetric data indicate the absorbance at 250 nm is proportional to the depth of reaction with a proportionality constant of 0.08 ± 0.005 μm/au. The depth of reaction for samples reduced at −78 °C could not be determined by gravimetric analysis (mass losses were too small) but could be determined from the UV–vis data by using the proportionality constant determined from the 0 °C data. The accuracy of these data depends on the similarity of product structures prepared at 0 and −78 °C; the similarities of XPS, ATR IR, and UV–vis spectra of samples prepared at these temperatures and the similarity between

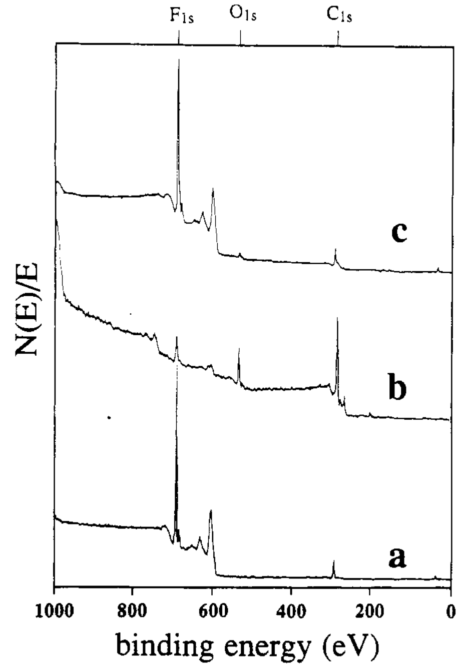


Figure 1. XPS spectra (75° takeoff angle) of FEP (a), FEP-C^a (b), and FEP-C^a after oxidative removal of the modified layer (c).

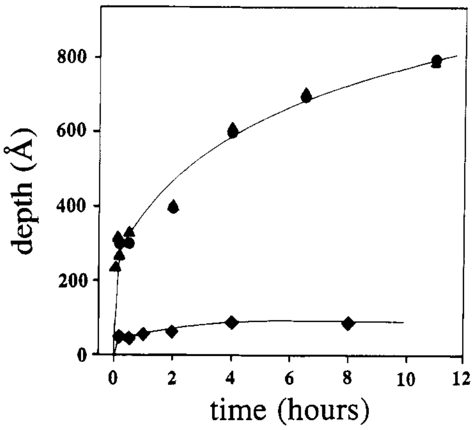


Figure 2. Reaction depth (thickness of modified layer) versus reaction time for FEP reacted at 0 °C (●, ▲) and -78 °C (♦): (●), determined from gravimetric data; (▲), determined from absorbance at 250 nm.

reaction depths obtained from gravimetric and UV-vis kinetics of the 0 °C reduction support the use of this proportionality.

Figure 2 summarizes the kinetics data for FEP reductions at 0 and -78 °C. At 0 °C, the reaction proceeds rapidly to a depth of ~250 Å and then slows. At -78 °C, the initial burst renders a more shallow modification (~45 Å) and is followed by a very slow reaction. We emphasize that these experiments do not comprise a careful kinetics analysis and that we did not investigate the reason(s) for the observed differences in rate with temperature. We note that the sodium naphthalide reagent exhibits a reversible color change and slow precipitation at -78 °C indicating reduced solubility. Reducing agent concentration, thermal activation of the reduction, polymer chain mobility differences, mass transport differences, or temperature-dependent interfacial properties may have an impact on the temperature dependence of this reaction. The data in Figure 2 are, however, reproducible, and these conditions allow practical control of reaction depths in the ranges of 45-90 and 250-800 Å.

FEP-C Structure. The principal objective of the work reported here was to prepare reactive FEP surfaces of controlled thickness. It was not to determine the structure of FEP-C but rather to prepare FEP-C for use as a reactive intermediate which was expected to be similar in structure and reactivity to PTFE-C.[5] The previous section demonstrates that the objective of controlling modified layer thickness has been met, and in this sense, FEP-C offers advantages over PTFE-C. It was clear, however, from our initial characterization of FEP-C, that the assumption of structural similarity with PTFE-C was incorrect and that further characterization of FEP-C was warranted.

PTFE-C, prepared by reaction of PTFE with dipotassium benzophenone dianion in Me_2SO, is metallic gold-colored and contains carbon-carbon double and triple bonds, fluorine and hydrogen bound to sp^2 and sp^3 carbons, and a small amount of oxygen. The corrosive reaction produces a gradient structure of highly reduced carbonaceous material close to the surface, less reduced material (containing more fluorine) at greater depths, and unreacted PTFE extending into the reacted region from the bulk. FEP-C is brown and not metallic in appearance, suggesting shorter conjugation of unsaturation than is present in PTFE-C; this is also indicated by the lower wavelength absorbance in the UV-vis spectrum (PTFE-C exhibits a broad absorbance centered at ~580 nm). That this difference is due to the copolymer composition (the presence of $-CF_3$ groups) and not the reducing agent is indicated by the fact that FEP reduced with dipotassium benzoin dianion in Me_2SO is brown colored and shows UV-vis and ATR IR spectra similar to FEP-C. Other differences are described in the following paragraphs.

Variable angle XPS yields information concerning the atomic composition and the chemical homogeneity (as a function of depth) of the outer ~40 Å of film samples. Spectra were recorded at two takeoff angles: 15° and 75°—measured from the film surface. The spectrum recorded at a 15° takeoff angle is representative of the outer ~10 Å of the film sample (94% of the photoelectrons measured are ejected from this region[22]). The 75° takeoff angle spectrum represents the composition of the outer ~40 Å of the sample (95% of the photoelectrons measured are ejected from this region). Figure 3 displays the C_{1s} regions of XPS spectra (corrected for differential charging) for FEP and FEP-C^a prepared at 0 (4 h) and -78 °C (4 h). The reaction at 0 °C rapidly removes fluorine from the outer 40 Å; the high binding energy peak, which is due to CF_2 and CF_3 in the FEP spectrum, is replaced after 2 min of reaction by a peak at lower binding energy due to more highly reduced carbon species. The survey spectra indicate that a significant amount of oxygen is incorporated, and empirical formulas of $C_{100}F_{4\pm3}O_{17\pm3}$ (15° takeoff angle) and $C_{100}F_{5\pm3}O_{16\pm3}$ (75° takeoff angle) are obtained from atomic composition data (XPS does not detect hydrogen). The similarity of the data obtained at the different takeoff angles indicates that the composition is similar throughout the outer 40 Å of the film sample. The XPS data for samples prepared at -78 °C indicate that the composition of the outer 10 Å is similar to that obtained at 0 °C and that more fluorine is present in deeper regions. The data give empirical formulas of $C_{100}F_{3.5\pm2}O_{20\pm5}$ (15° takeoff angle) and $C_{100}F_{10\pm4}O_{17\pm4}$ (75° takeoff angle). The presence of a small peak due to CF_2/CF_3 in the 75° takeoff angle spectrum, and its absence from the 15° spectrum suggest that the *minimum*-modified layer thickness is ~40

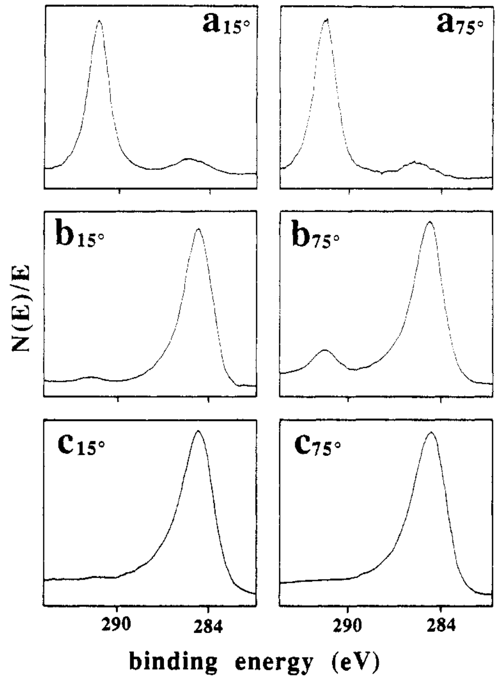


Figure 3. XPS spectra (C$_{1s}$ region) of FEP (a), FEP-C^a (−78 °C, 4 h) (b), and FEP-C^a (0 °C, 4 h) (c), recorded at 15° and 75° takeoff angles.

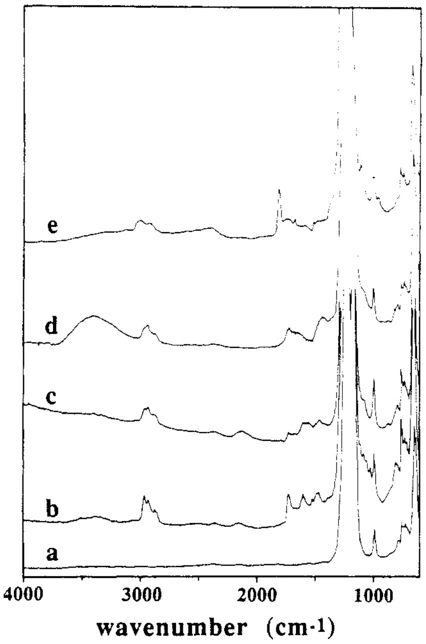


Figure 4. ATR IR spectra of (a) FEP, (b) FEP-C^a, (c) FEP-C^b, (d) FEP-OH, and (e) FEP-OC(O)C$_3$F$_7$.

Å. These data alone give only a *minimum thickness* as the FEP–FEP-C interface may be diffuse, with reduced material extending deeper than 40 Å. Coupled with the UV-vis data, which indicates a thickness of 45 Å, the data suggest a reasonably sharp FEP–FEP-C interface.

Additional information concerning the structure of FEP-C was obtained from ATR IR spectra; the extensively reduced samples showed more lucid product features. Figure 4 shows ATR IR spectra of FEP and FEP-C^a (0 °C, 4 h). The only feature present in the FEP spectrum above 1210 cm^{-1} is a weak overtone at 2360 cm^{-1}. The spectrum of FEP-C^a shows O—H stretching (3400 cm^{-1}), three aliphatic C—H$_x$ stretching bands (2960, 2930, 2870 cm^{-1}), C=O stretching (1720 cm^{-1}), and conjugated and/or condensed aromatic C=C stretching (1597, 1462 cm^{-1}—the 1462 cm^{-1} band is also consistent with aliphatic C—H$_x$ bending). Unlike PTFE-C^5, no sp^2 C–H stretching (>3000 cm^{-1}) is observed.

IR and XPS analyses indicate that FEP-C worked up by using rinsing procedure A contains the expected unsaturation (C=C and C≡C), very little fluorine, significant amounts of oxygen present as alcohols and carbonyls, and aliphatic C—H bonds. The C—H stretching region suggests that both CH$_3$-groups (2960 cm^{-1}—ν_{as}) and -CH$_2$- groups (2930 cm^{-1}—ν_{as}) are present. Further evidence for the presence of hydroxyl and carbonyl groups was provided by labeling for XPS analysis with heptafluorobutyryl chloride (HFBC) and 2,4-dinitrophenylhydrazine (DNPH), respectively. Treatment with HFBC in THF containing a small amount of pyridine resulted in an increase in fluorine content and features in the C$_{1s}$ region characteristic of the heptafluorobutyrate^5 as well as the expected carbonyl band (1780 cm^{-1}) in the ATR IR spectrum. Quantitative analysis of the XPS data indicates that ~15% of the oxygen present reacts to form the ester. Labeling with DNPH results in the introduction of two nitrogen photoelectron lines (hydrazone, nitro) and quantitation indicates that ~8% of the oxygen reacts to form hydrazone. These labeling reactions account for less than 25% of the oxygen present. ATR IR spectra of labeled (HFBC, DNPH) FEP-C^a show no significant decrease in O—H or C=O features.

These analyses of FEP-C^a reveal that several features unexpected from the idealized reduction (eq 1), in particular carbon–oxygen and carbon–hydrogen species, are present in sigificant concentration. These side products compromise the utility of FEP-C as a substrate for functionalization. The sources of these side products were considered (THF, naphthalene, and adventitious impurities in the reduction, water and THF in the rinsing, and air in the drying and transferring), and a series of experiments was performed to determine the source(s) and to thus prepare a cleaner substrate, more suitable for functionalization.

Four different rinsing procedures were studied: D$_2$O was substituted for water, and the resulting ATR IR spectrum shows an O–D band at 2580 cm^{-1} as well as an O–H stretching band. The C—H and C=O regions are unchanged, and no C—D stretching absorbances are observed; however, small C—D features may be obscured by the C≡C band that appears in the same region. When THF alone or methanol (followed by THF) was used for rinsing, the O—H and C=O bands in the infrared are significantly decreased in intensity, but the C—H region is unchanged. The oxygen concentration determined by XPS is increased substantially, and both samples contain Na$^+$ and F$^-$, suggesting that some hydroxide or methoxide may be present. When the reduced sample was rinsed with THF, then water, and then THF, the O—H and C=O absorbances in the infrared are descreased, but the C—H region is unchanged. XPS indicates that slightly less oxygen is present relative to film samples rinsed first with water and then THF. We interpret these data as follows: the majority of the C–H bonds are not formed in the rinsing step and thus must form during the reduction. A significant amount of hydroxyl and carbonyl groups are formed in the rinsing step by reaction of water in the presence of sodium naphthalide with the reduced surface. A likely mechanism involves the addition of hydroxide to conjugated olefins and alkynes. Removing unreacted sodium naphthalide by rinsing with THF prior to exposure to water limits this reaction. The fact that oxygen functionality can be limited in the ATR IR sampling region (which includes the entire modified layer) with more success than in the outer 40 Å (XPS sampling region) suggests that FEP-C is air-sensitive and that a portion of the oxygen functionality is introduced during drying and transferring. Deliberate exposure of FEP-C to air resulted in large increases in intensity of both O—H and C=O infrared bands, and exposure to dry oxygen resulted in a large increase in C=O intensity with little change in the O—H absorbance. These results suggest that atmospheric moisture reacts with FEP-C to yield hydroxyl groups (and likely also carbonyls), perhaps by addition of H_2O or ^-OH to electrophilic olefins, while reaction with O_2 results primarily in carbonyls.

To determine the source(s) that contribute to the formation of C-H bonds during reduction, a series of reactions was performed in which one of the following changes were made in the reaction conditions: THF was "spiked" with D_2O prior to distillation, THF-d_8 was substituted for THF, naphthalene-d_8 was substituted for naphthalene, the reaction flask was treated with D_2O/–OD prior to drying, and the reduction was carried out in a PTFE vessel. In each case, the intensity of the C–H stretching bands, relative to the C–F bands, remained essentially unchanged, and no C–D features were observed. The changes were not significantly large in any experiment to identify one reaction component as the major source of hydrogen, and no potential source was eliminated. It was concluded that there is no unique hydrogen source and that adventitious moisture and reactive C–H bonds in any reagent can contribute. The purity of the sodium was not assessed. A reaction was run with all deuterated reagents and solvents in a PTFE vessel in a drybox. Only very weak C-H bands and no O—H or C=O bands were exhibited in the product's spectrum. An O–D vibration (2592 cm^{-1}) and an unusually intense C≡C band were observed. No C-D bonds were evident; however, their presence may be obscured by the C≡C band. XPS indicates that less oxygen was present ($C_{100}F_3O_9$). A reduction was also run by using sodium naphthalide reagent that was spiked with 1,4-dihydronaphthalene (the Birch reduction product of naphthalene[23]) to determine whether this serves as a general hydrogen transfer agent between ultimate sources and product. It does not: no infrared changes were observed.

As a substrate for further modification, FEP-C is not ideal. Although the thickness of the modified layer can be controlled with precision, we have not been completely successful at controlling (or understanding) its chemical composition. It is very air-sensitive, and the presence of oxygen in the XPS sampling depth cannot be practically avoided. The presence of hydroxyl groups and carbonyl groups in the ATR IR sampling depth can be limited by appropriate rinsing but not completely avoided. The presence of aliphatic C–H bonds cannot be practically avoided, and the chemistry of their formation is not clear. It is also unclear why they appear, as indicated by the infrared spectra, to be present principally as methyl and methylene groups and not sp^2 C–H bonds.

A practical decision was made, at this point in the research, to carry out further modification reactions to incorporate hydroxyl groups using FEP-C prepared at 0 °C (~4-h reaction time) using rinsing procedure B (THF, followed by water and then THF); FEP-C produced in this fashion is hereafter abbreviated FEP-C^b). This procedure reproducibly yields a ~600-Å thick modified surface. ATR IR and XPS spectra of FEP-C^b are shown in Figures 4 and 5, respectively. Atomic composition data yield empirical formulas of $C_{100}F_{4\pm2}O_{13\pm3}$ for 15° takeoff angle and $C_{10}F_{4\pm2}O_{11\pm3}$ for 75° takeoff angle. Alcohol functionality was chosen because (1) hydroxyl groups are already present in FEP-C^b, (2) carbonyls that are present in FEP-C^b can, in principal, be reduced to alcohols, and (3) we have found[6] that surface-confined hydroxyl groups are quite versatile.

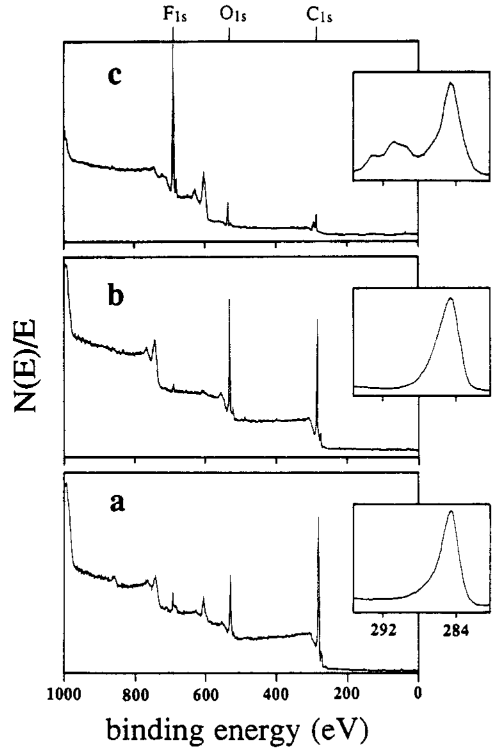
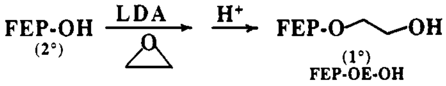


Figure 5. XPS spectra of (a) FEP-C^b, (b) FEP-OH, and (c) FEP-$OC(O)C_3F_7$ (each spectrum was recorded by using a 15° takeoff angle).



(3)

Synthesis and Reactivity of FEP-OH. Treatment of FEP-C^b with BH_3·THF complex followed by oxidation with basic hydrogen peroxide produces film samples (FEP-OH) exhibiting very little of the color present in FEP-C^b and properties and spectra consistent with the presence of hydroxyl groups. Contact angles of water on FEP-OH are consistent with the presence of polar functionality; θ_a/θ_r values of FEP-OH are 59° ± 2°/30° ± 3° (FEP exhibits values of 108° ± 1°/100 ± 1°). Figure 5b shows XPS spectra of FEP-OH; oxygen concentration increases upon hydroboration/oxidation (compare with Figure 5a), and the XPS empirical formula (15° takeoff angle) is $C_{100}F_{1.5\pm0.5}O_{27\pm3}$. Changes in the ATR IR spectrum (Figure 4d—compare with 4c) are also consistent with alcohol introduction: the intensity of the O—H absorbance (~3300 cm^{-1}) increases, the C≡C absorbance (~2120 cm^{-1}) disappears, the C=C band at 1597 cm^{-1} decreases in intensity, and the C=O stretching vibration shifts from 1720 to 1710 cm^{-1}. The shift in the carbonyl absorbance can be explained by reduction of carbonyls to alcohols and hydroboration/oxidation of alkynes to (different) ketones.

Esterification of FEP-OH with HFBC in THF containing pyridine (acylation procedure A in the Experimental Section) rendered a rather poor yield of heptafluorobutyrate. XPS atomic composition data for this product are given in Table I (entry 2). These data (75° takeoff

Table I
XPS Relative Atomic Composition Data for Surfaces Reacted with Heptafluorobutyryl Chloride

entry	sample	procedure	takeoff angle, deg	C	F	O	% esterificatn[a]
1	FEP[b]-C	A, 72 h	15	100	17	12	19
			75	100	15	12	17
2a	FEP-OH	A, 24 h	15	100	42	29	46
			75	100	27	22	30
2b	FEP-OH	A, 72 h	15	100	39	29	43
			75	100	25	27	27
3	FEP-OH	B, 48 h	15	100	36	16	40
			75	100	31	15	35
4	FEP-OH	C, 48 h	15	100	82	23	91
			75	100	53	20	58
5	FEP-OH	D, 48 h	15	100	42	26	46
			75	100	37	21	41
6	FEP-OE-OH	A, 24 h	15	100	66	26	92
			75	100	62	28	86
7	FEP-C (BPO/MeOH)	A, 24 h	15	100	13	26	15
			75	100	10	22	11
8	FEP-CH_2OH	A, 24 h	15	100	33	15	55
			75	100	29	14	48

[a] Calculated from C:F ratio—see text.

angle) indicate that only ~30% of the oxygen in FEP-OH reacts to form ester. This suggests that the majority of hydroxyl groups present are unreactive. Under less severe conditions (HFBC in THF, no pyridine, room temperature, 3 h) surface hydroxyl groups on PCTFE-OH[4] react quantitatively with HFBC. The low reactivity of FEP-OH is also apparent by ATR IR analysis: a new absorbance characteristic of the heptafluorobutyrate carbonyl (1780 cm^{-1}) is observed, but the intensity of the O–H stretching vibration decreases only slightly. The hydroxyl groups in PCTFE-OH are primary and are separated from the polymer chain by three methylene units. The majority of the alcohols in FEP-OH are secondary and are attached directly to polymer chain which is cross-linked (to an unknown extent). These structural differences, as well as the differences between the FEP-OH–THF and PCTFE-OH–THF interfaces, are likely reasons for the difference in reactivity and the low reactivity of FEP-OH.

Several different acylation conditions were tried to increase the esterification yield, and these are summarized in Table I and the Experimental Section. Using pyridine as the solvent and DMAP catalysis (Experimental Section, procedure C) gave the best yield (Table I, entry 4). The ATR IR spectrum (Figure 5e) shows an intense heptafluorobutyrate carbonyl absorbance at 1778 cm^{-1} and the near complete disappearance of the O–H stretching band. The absorbances at 3070, 1688, and 1645 cm^{-1} indicate the presence of (dimethylamino)pyridinium hexafluorobutyrate (which shows bands (KBr) pellet) at 3070, 1685, and 1649 cm^{-1}). No nitrogen was observed by XPS indicating that this salt was removed from the outer 40 Å during rinsing. The XPS spectrum shows an intense F_{1s} photoelectron line (Figure 5c) and the C_{1s} region indicates the presence of the CF_3, CF_2, and C=O moieties present in FEP-OC(O)C_3F_7. Analysis of the 15° takeoff angle atomic composition data (Table I, entry 4) indicates a 91% yield of heptafluorobutyrate in the outer 10 Å based on the FEP-OH atomic composition (1 hydroxyl per 3.7 surface carbons). The predicted stoichiometry is $C_{3.7}O_1$-C(O)C_3F_7 ($C_{100}F_{91}O_{26}$). The product empirical formula is $C_{100}F_{82}O_{23}$. This experiment indicates that most of the oxygen in FEP-OH is present as alcohol functionality.

Other Approaches to Hydroxylated FEP. Three other strategies were studied to prepare more reactive (primary) alcohol-containing FEP surfaces. One involved the conversion of secondary alcohols in FEP-OH to primary alcohols; the others were direct reactions of FEP-C[b] aimed at introducing primary alcohols.

FEP-OH was treated with LDA and ethylene oxide in an attempt to prepare the hydroxyethyl ether surface (eq 3). There are several potential difficulties with this reaction: (1) Although LDA is basic enough to quantitatively deprotonate FEP-OH (in principle, based on solution pK_a values), this may not occur. (2) The resulting lithium surface alkoxides may not react well with ethylene oxide due to surface steric effects and the covalent nature of the O–Li bond. (3) The product (FEP-OE-OLi) may react with ethylene oxide to form oligomeric species. (4) The yield of primary alcohols (or the extent of deprotonation, addition, and oligomerization) cannot be unambiguously determined by XPS because primary alcohols, secondary alcohols, and ethers cannot be distinguished and XPS is relatively insensitive to the addition of ethylene oxide (two carbons and one oxygen) to FEP-OH (C:O ratio = 3.7:1). XPS and ATR IR spectra indicate that ethylene oxide addition occurs: upon reaction, the C:O ratio changes from 3.7:1 to 2.9:1 and the intensity of the methylene stretching band increases. The reactivity of FEP-EO-OH with HFBC is increased (entry 6, Table I—compare with entry 2) over FEP-OH, indicating that this strategy was successful. Using mild esterification conditions (procedure A), the yield is increased over FEP-OH, particularly at greater depths. The predicted stoichiometry of the product of addition of one ethylene oxide molecule to each oxygen in FEP-OH is $C_{3.7}O_1$-CH_2CH_2OH ($C_{100}O_{35}$) which agrees well with the stoichiometry of the product ($C_{100}F_2O_{35}$). Addition of HFBC to this structure predicts the following stoichiometry: $C_{3.7}O_1$-CH_2CH_2O-C(O)C_3F_7 ($C_{100}F_{72}O_{30}$). Comparison with the stoichiometry of the HFBC-labeled product ($C_{100}F_{66}O_{26}$) suggests that ~90% of the surface hydroxyl groups have reacted. Analysis of this esterified product by ATR IR indicates that a significant amount of hydroxyl groups are unreacted; thus the XPS results are not representative of deeper regions. These results indicate that oligomerization is not extensive.

FEP-C[b] was treated with benzoyl peroxide in methanol in an attempt to add $^{\bullet}CH_2OH$ radicals to the unsaturated surface.[23] ATR IR, XPS, and reaction with HFBC indicate that few primary alcohols are introduced by this procedure. The ATR IR spectrum showed only a weak O–H band and a relatively intense carbonyl band at 1730 cm^{-1}. XPS indicates an increase in oxygen concentration (15°, $C_{100}F_3O_{27}$; 75°, $C_{100}F_3O_{24}$), but reaction with HFBC (Table I, entry 7) indicates that little of this oxygen is present as reactive hydroxyl groups.

Reaction of FEP-C^b with 9-BBN, carbonylation, and reduction[24] to prepare FEP-CH_2OH introduced fewer, but more reactive hydroxyl groups than are in FEP-OH. The hydroboration with 9-BBN was less efficient than with BH_3·THF as evidenced by XPS ($C_{surface}$:B = 17:1 (9-BBN) versus 10:1 (BH_3·THF)) and ATR IR (less decrease in intensity of unsaturated regions), and this, coupled with the fact that only one hydroxyl group can be introduced per B with 9-BBN versus as many as three with BH_3·THF, accounts for the lower yield of alcohols. That these alcohols are more reactive than those in FEP-OH is indicated by their reactivity with HFBC (Table I, entry 8—compare with entry 2).

Conclusion

The reduction of FEP with sodium naphthalide in THF results in an unsaturated modified surface layer, the thickness of which can be controlled with reaction time and temperature. The air-sensitive surface layer contains alcohols, carbonyls (likely ketones), and aliphatic C—H bonds in addition to C=C and C≡C. This surface layer can be further modified by hydroboration and subsequent oxidation to prepare a surface containing predominantly hydroxyl groups. Esterification reactions of these alcohols are slow and proceed to low yield, unless strong acylating catalysts are used. Their reactivity is similar to the reactivity of hindered alcohols in solution. The reactivity of the surface can be enhanced by "chain extension" of secondary surface alcohols with ethylene oxide to form a surface containing primary hydroxyl groups separated from the polymer backbone by a two-carbon spacer. Primary alcohols can be directly introduced to the surface in lower yield by reaction of the reduced layer with 9-BBN, carbonylation, and reduction.

Acknowledgment. We thank the Office of Naval Research and the University of Massachusetts Materials Research Laboratory for financial support.

References and Notes

(1) A preliminary account of a portion of this work has been presented: Bening, R. C.; McCarthy, T. J. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1988**, *29* (2), 336.
(2) Dias, A. J.; McCarthy, T. J. *Macromolecules* **1984**, *17*, 2529.
(3) Dias, A. J.; McCarthy, T. J. *Macromolecules* **1985**, *18*, 1826.
(4) Dias, A. J.; McCarthy, T. J. *Macromolecules* **1987**, *20*, 2068.
(5) Costello, C. A.; McCarthy, T. J. *Macromolecules* **1987**, *20*, 2819.
(6) Lee, K.-W.; McCarthy, T. J. *Macromolecules* **1988**, *21*, 2318.
(7) Reference 4 summarizes the advantages of these materials as substrates for surface chemical studies.
(8) Brennan, J. V.; McCarthy, T. J. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1988**, *29* (2), 338.
(9) Costello, C. A.; McCarthy, T. J. *Macromolecules* **1985**, *18*, 1087.
(10) Varma, A. J.; Jog, J. P.; Nadkarni, V. M. *Makromol. Chem., Rapid Commun.* **1983**, *4*, 715.
(11) Jansta, J.; Dousek, F. P. *Electrochim. Acta* **1973**, *18*, 673.
(12) Jansta, J.; Dousek, F. P. *Electrochim. Acta* **1981**, *26*, 233.
(13) Jansta, J.; Dousek, F. P.; Patzelova, V. *Carbon* **1975**, *13*, 377.
(14) Yoshino, K.; Yanagida, S.; Sakai, T.; Azuma, T.; Inuishi, Y.; Sakurai, H. *Jpn. J. Appl. Phys.* **1982**, *21*, L301.
(15) Nelson, E. R.; Kilduff, T. J.; Benderly, A. A. *Ind. Eng. Chem.* **1985**, *50*, 329.
(16) Barker, D. J.; Brewis, D. M.; Dahm, R. H. *J. Mater. Sci.* **1979**, *14*, 749.
(17) Dwight, D. W.; Riggs, W. J. *J. Colloid Interface Sci.* **1974**, *47*, 650.
(18) Brecht, H.; Mayer, F.; Binder, H. *Angew. Makromol. Chem.* **1973**, *33*, 89.
(19) Barker, D. J.; Brewis, D. M.; Dahm, R. H.; Hoy, L. R. *Polymer* **1978**, *19*, 865.
(20) Chakrabarti, N.; Jacobus, J. *Macromolecules* **1988**, *21*, 3011.
(21) Borosova, F. K.; Galkin, G. A.; Kiselev, A. V.; Korolev, A.; Lygin, V. I. *Colloid J. USSR (Engl. Transl.)* **1965**, *27*, 265.
(22) These calculations use the value of 14 Å for the mean free path of C_{1s} electrons excited with Mg Kα irradiation. This value was measured in poly(*p*-xylylene): Clark, D. T.; Thomas, H. R. *J. Polym. Sci., Polym. Chem. Ed.* **1977**, *15*, 2843.
(23) Tsubokawa, N.; Fujiki, K.; Sone, Y. *J. Polym. Sci., Polym. Chem. Ed.* **1986**, *24*, 191.
(24) Brown, H. C.; Knights, E. F.; Coleman, R. A. *J. Am. Chem. Soc.* **1969**, *91* (8), 2144.