2318 *Macromolecules* **1988**, *21*, 2318–2330

Chem. Ed. **1976**, *14*, 1735. (d) Endo, T.; Katsuki, H.; Bailey, W. J. *Makromol. Chem.* **1976**, *177*, 3231. (e) Bailey, W. J.; Endo, T. *J. Polym. Sci., Polym. Symp.* **1978**, *64*, 17.
(3) (a) Endo, T.; Arita, H. *Makromol. Chem., Rapid Commun.* **1985**, *6*, 137. (b) Endo, T.; Sato, H.; Takata, T. *Macromolecules* **1987**, *20*, 1416. (c) Endo, T.; Maruoka, S.; Yokozawa, T. *J. Polym. Sci., Polym. Chem. Ed.* **1988**, *25*, 2925; (d) *Macromolecules* **1987**, *20*, 2690.
(4) (a) Pigott, M. R.; Lam, W. K.; Lim, J. T.; Woo, M. S. *Comp. Sci. Technol.* **1985**, *23*, 247. (b) Bailey, W. J.; Amone, M. J.; Issari, B.; Lin, Y.-N.; No, K.; Pan, C.-Y.; Saigo, K.; Stansbury, J.; Tan, S.-R.; Wu, C.; Yamazaki, N.; Zhou, *Prepr. Am. Chem. Soc., Div. Polym. Mater.* **1986**, *54*, 23. (c) Ogasawara, T.; Mizutani, K.; Kato, H.; Endo, T. *Polym. Prepr. Jpn.* **1982**, *31*, 11.
(5) (a) Sigwalt, P.; Spassky, N. In *Ring-Opening Polymerization*; Ivin, K. J., Saegusa, T., Eds.; Elsevier Applied Science: New York, 1984; Chapter 9. (b) Goethals, E. *J. Macromol. Sci.—Rev. Macromol. Chem.* 1968, *C2* (1), 73. (c) Sigwalt, P. In *Ring Opening Polymerization*; Frisch, K. C., Reegen, S. L., Eds.; Marcel Dekker: New York, 1969; Chapter 4.
(6) Goethals, E. J.; DuPrez, E. *J. Polym. Sci. Part A* **1966**, *14*, 2893.
(7) Endo, T.; Uno, H. *J. Polym. Sci., Polym. Lett. Ed.* **1985**, *23*, 359.
(8) Coffen, D. L. *J. Heterocycl. Chem.* **1970**, *7*, 201.
(9) Backer, H. J.; Stedhouder, P. L. *Recl. Trav. Chim. Pays-Bas* **1933**, *52*, 923.
(10) Cooper, W. *Br. Polym. J.* **1971**, *3*, 28.
(11) (a) Padias, A. B.; Hall, Jr., H. K. *Macromolecules* **1982**, *15*, 2. (b) Yokoyama, Y.; Padias, A. B.; Bratoeff, E. A.; Hall, H. K., Jr. *Macromolecules* **1982**, *15*, 11.
(12) (a) Endo, T.; Saigo, K.; Bailey, W. J. *J. Polym. Sci., Polym. Lett. Ed.* **1980**, *18*, 457. (b) Saigo, K.; Bailey, W. J.; Endo, T. *J. Polym. Sci., Polym. Chem. Ed.* **1983**, *21*, 1435.
(13) Takata, T.; Endo, T. *Macromolecules* **1988**, *21*, 900.

Chemistry of Surface-Hydroxylated Poly(chlorotrifluoroethylene)[1]

Kang-Wook Lee and Thomas J. McCarthy*

Polymer Science and Engineering Department, University of Massachusetts, Amherst, Massachusetts 01003. *Received November 16, 1987*

ABSTRACT: Hydroxyl groups have been introduced to the surface of poly(chlorotrifluoroethylene) (PCTFE) by reaction of PCTFE film samples with the protected alcohol-containing lithium reagent, acetaldehyde lithiopropyl ethyl acetal (LiPrO*P*), and subsequent deprotection. The density of hydroxyl groups (the depth of the modification reaction) in the modified film surface (PCTFE-OH) can be controlled with reaction temperature. The concentration of hydroxyl groups has been determined to be four OH groups per five PCTFE repeat units. PCTFE-OH has been converted to a range of modified surfaces using standard hydroxyl group transformations: Reaction with *p*-toluenesulfonyl chloride yields the *p*-toluenesulfonate (PCTFE-OTs). PCTFE-OTs reacts with chloride, bromide, and cyanide to yield PCTFE-Cl, PCTFE-Br, and PCTFE-CN, respectively. PCTFE-OH reacts with acetyl chloride, trichloroacetyl chloride, pentafluorobenzoyl chloride, and adipoyl chloride to give the corresponding surface-confined esters. Adipoyl chloride reacts to give primarily the diester. Trichloroacetyl isocyanate, α,α,α-trifluoro-*p*-tolyl isocyanate, and hexamethylene diisocyanate react with PCTFE-OH to yield the urethanes and diurethane. Trimethylchlorosilane reacts with PCTFE-OH to yield the trimethyl(surface alkoxy)silane; dimethyldichlorosilane yields the dimethyl(surface dialkoxy)silane. PCTFE-OH reacts with methyltrichlorosilane to yield what analyzes to be methylchloro(surface dialkoxy)silane and with tetrachlorosilane to yield what analyzes to be chloro(surface trialkoxy)silane. Reactions of PCTFE-OH with (2-cyanoethyl)trichlorosilane, (3-cyanopropyl)dimethylchlorosilane, and (3-(methacryloxy)propyl)dimethylchlorosilane yield (2-cyanoethyl)(surface trialkoxy)silane, (3-cyanopropyl)dimethyl(surface alkoxy)silane, and (3-(methylacryloxy)propyl)dimethyl(surface alkoxy)silane, respectively. Thionyl chloride reacts with PCTFE-OH to give the sulfite. Reaction of PCTFE-OH with phosphorous tribromide does not yield a single functional group containing product: It yields surface-confined phosphite, surface phosphinous acid, and PCTFE-Br. Oxidation of PCTFE-OH with dicyclohexyl carbodiimide, Me_2SO, and anhydrous phosphoric acid yields the aldehyde (PCTFE-CHO) and with pyridinium dichromate in DMF yields the carboxylic acid (PCTFE-COOH). The modified surfaces were characterized by X-ray photoelectron spectroscopy (XPS), attenuated total reflectance infrared spectroscopy (ATR IR), and contact angle analysis. Monitoring the reaction of PCTFE-OH with pentafluorobenzoyl chloride by each of these techniques suggests that the reactions proceed at a uniform rate throughout the hydroxylated layer. The reactions were carried out on PCTFE-OH samples that contained ~1500 Å thick modified surfaces to facilitate ATR IR analysis. That the same chemistry is feasible by using PCTFE-OH containing ~50 Å thick modified surfaces was demonstrated by carrying out three reactions on this substrate: the preparation of the ester using trichloroacetyl chloride, the preparation of PCTFE-OTs, and the displacement of the tosylate with bromide.

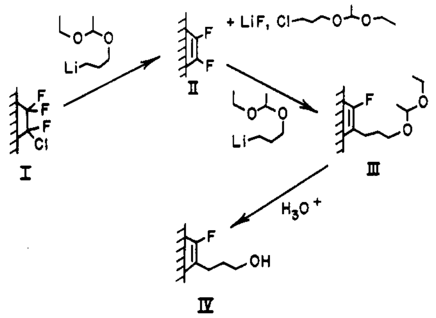
Introduction

Chemistry at polymer surfaces and interfaces is central to many polymer materials applications.[2,3] We have begun a research program directed at preparing specific polymer surfaces and interfaces with well-defined chemical compositions. With these model substrates we hope to be able to draw surface structure-property and structure-reactivity relations and learn how to predict particular properties with knowledge of the chemical structure as well as impart desired properties by introducing specific functional groups in specific locations, densities, and patterns. We have chosen to study chemically resistant (unreactive) polymers containing versatile organic functional groups at their surfaces to meet the above objectives. The advantages of these materials as substrates have been discussed in detail.[4] Briefly, polymer film samples with inert bulk and reactive surfaces can be modified by using a range of conditions which limit changes to surface chemical ones and do not alter the structure or properties of the bulk. The first phase of this research has involved developing surface-selective modification reactions for poly(chlorotrifluoroethylene) (PCTFE),[4] poly(tetrafluoroethylene) (PTFE),[5] poly(vinylidene fluoride) (PVF_2),[6] and polypropylene (PP).[7,8] The second phase involves incorporation of specific versatile functional groups, either in the modification reactions or by further reactions of modified surfaces. We have reported the introduction of carboxylic acid, aldehyde, and alcohol functional groups onto the surface of

0024-9297/88/2221-2318$01.50/0

PCTFE,[9] the introduction of alcohol, amine, and carboxylic acid functional groups onto the surface of PTFE,[10] and the introduction of alcohol functionality onto the surface of PP.[7,8]

In this paper we report chemical transformations of one functionalized surface: PCTFE containing alcohol functionality, abbreviated PCTFE-OH. This was chosen for three reasons: First, hydroxylated surfaces are routinely exploited by using coupling agents to prepare composite materials,[11,12] modified electrodes,[13] and chromatography supports;[14] thus PCTFE-OH chemistry[15] may impact on a range of adhesion technologies. Second, the depth of the hydroxylated surface in PCTFE-OH can be conveniently controlled so that infrared spectroscopy, which is essential in analyzing organic functionality, can be employed. Third, PCTFE-OH is expected to be relatively reactive as the alcohol is primary and is attached to the polymer chain by a three-carbon spacer. Equation 1 summarizes the synthesis of PCTFE-OH; the depth of the reaction with acetaldehyde lithiopropyl ethyl acetal (LiPrO*P*) (which controls the density of hydroxyl groups in PCTFE-OH) is extremely temperature-sensitive, and we have estimated[9] that reactions for 60 min at −78, −20, and 0 °C yield modified layers of ~50-, ~1150-, and ~1600-Å thickness, respectively.



(1)

Experimental Section

Materials. PCTFE was obtained from Allied as 1- and 5-mil film (Aclar 33C) and extracted with refluxing dichloromethane for 15 min and dried (0.02 mm, 70 °C) for at least 24 h. This procedure gives film samples that are consistently free of detectable contaminants. Tetrahydrofuran was distilled from sodium benzophenone dianion; methanol was distilled from magnesium/magnesium methoxide; heptane, hexane, dimethyl sulfoxide, and pyridine were distilled from calcium hydride; dichloromethane and dimethylformamide were distilled from phosphorous pentoxide. House distilled water was redistilled by using a Gilmont still. All solvents were stored under nitrogen. 3-Bromo-1-propanol (Aldrich) was distilled from potassium carbonate (60–64 °C, 5 mm) and stored under nitrogen over potassium carbonate. Ethyl vinyl ether (Aldrich) was distilled under nitrogen immediately prior to use. *tert*-Butyllithium (Aldrich) was standardized by using diphenylacetic acid. Acetyl chloride, trichloroacetyl chloride, pentafluorobenzoyl chloride, adipoyl chloride, trichloroacetyl isocyanate, α,α,α-trifluoro-*p*-tolyl isocyanate, hexamethylene diisocyanate, methyltrichlorosilane, dimethyldichlorosilane, trimethylchlorosilane, *p*-toluenesulfonyl chloride, thionyl chloride, phosphorous tribromide, potassium cyanide, 18-crown-6 ether, tetrabutylammonium chloride, tetrabutylammonium bromide, dibutyltin dilaurate, pyridinium dichromate, and dicyclohexyl carbodiimide were purchased from Aldrich and used without further purification. Tetrachlorosilane, (3-cyanopropyl)dimethyldichlorosilane, (3-(methacryloxy)propyl)dimethylchlorosilane, and (2-cyanoethyl)trichlorosilane were purchased from Petrarch and used without further purification. Anhydrous phosphoric acid was purchased from Fluka and used as received.

Methods. Air-sensitive reactions were carried out under dry nitrogen. Reactions with films were not stirred. Contact-angle measurements were obtained with a Ramê-Hart telescopic goniometer and a Gilmont syringe with a 24-gauge flat-tipped needle. Water purified as described above was used as the probe fluid. Dynamic advancing and receding angles were determined by measuring the tangent of the drop at the intersection of the air/drop/surface while adding (advancing) and withdrawing (receding) water to and from the drop. The values reported are averages of five measurements made on different areas of the film sample surface. Attenuated total reflectance infrared (ATR IR) spectra were obtained under nitrogen by using an IBM 38 FTIR spectrometer and either a germanium or a KRS-5 (thallium bromide iodide) (45°) internal reflection element. The absorbances listed in the experimental section do not include (in most cases) bands due to PCTFE and PCTFE-OH and include bands between 4000 and 700 cm^{-1}. Relative intensities for the bands due only to the modified surfaces are described. X-ray photoelectron spectra (XPS) were recorded by using a Perkin Elmer-Physical Electronics 5100 spectrometer with Mg Kα excitation (300 W). The samples charged variably during analysis, and the reported binding energies are not corrected for charging. Spectra were recorded at two angles, 15° and 75°, from the film surface. Atomic composition data were determined by using the instrument's computer and programmed sensitivity factors: F_{1s}, 1.00; O_{1s}, 0.66; N_{1s}, 0.42; C_{1s}, 0.25, Cl_{2p}, 0.73; S_{2p}, 0.54; P_{2p}, 0.39; Si_{2p}, 0.27; Br_{3d}, 0.83. The reported atomic composition data were obtained from spectra recorded with the analyzer 75° from the film surface. UV–vis spectra were recorded by using a Perkin-Elmer Lamda 3A spectrophotometer. Scanning electron microscopy (SEM) (secondary electron images) was performed by using JEOL 60 SEM and JEOL 100 STEM instruments.

Acetaldehyde bromopropyl ethyl acetal (BrPrO*P*) was prepared from 3-bromo-1-propanol and ethyl vinyl ether by using the previously described procedure.[9]

Acetaldehyde lithiopropyl ethyl acetal (LiPrO*P*) was prepared by a modification of the previously described procedure.[9] This method renders a more pure product. A Schlenk flask containing a magnetic stirring bar was dried in an oven (200 °C) and then purged with nitrogen for 20 min. BrPrO*P* (0.99 g, 4.69 mmol) and heptane (15 mL) were added to the Schlenk flask that was then equilibrated to −78 °C. A solution of *tert*-butyllithium (2.7 mL, 1.7 M, 4.59 mmol) in heptane (10 mL) (which had been equilibrated to −78 °C) was added slowly via cannula to the vigorously stirred solution. The resulting white suspension was stirred for 15 min at −78 °C and then allowed to warm to −20 °C at which temperature it was maintained for 15 min. The solution was recooled to −78 °C, and 15 mL of THF was added. The suspension dissolved yielding a clear, colorless solution and an unidentified yellow precipitate. If too little THF is added, the suspension does not dissolve; if too much THF is added, the yellow precipitate dissolves. The solution is separated from the yellow precipitate via cannula at the time of further reaction.

Preparation of PCTFE-O*P* (3) from PCTFE (1) and LiPrO*P*. PCTFE-O*P* film samples were prepared as described previously.[9] Reactions were carried out at −15 or −78 °C for 30 min.

For 1: contact angles θ_A/θ_R = 104°/77°; ATR IR 1287 (m), 1194 (s), 1125 (s), 968 (s) cm^{-1}. XPS Atomic Ratios Calcd for C_2F_3Cl: C, 33; F, 50; Cl, 17. Obsd: C, 34; F, 51; Cl, 15.

For 3: contact angles θ_A/θ_R = 88°/37°; ATR IR 2978 (s), 2936 (s), 2899 (s, sh), 2876 (s), 1680 (w, br), 1480 (w), 1445 (m), 1381 (s), 1341 (s), 1127 (s), 1061 (s, sh), 872 (m) cm^{-1}. XPS Atomic Ratios Obsd: C, 73; F, 12; O, 15.[16]

Hydrolysis of PCTFE-O*P* (PCTFE-OH, 4). PCTFE-O*P* film samples were placed in a solution of concentrated HCl (5 mL), water (30 mL), and methanol (65 mL) which was then refluxed for 3 h. The film samples were removed and washed with water (3 × 30 mL), methanol (3 × 30 mL), and then dichloromethane (3 × 30 mL) and dried (0.02 mm, 24 h). Contact angles: θ_A/θ_R = 67°/17°. ATR IR: 3335 (s, br), 2946 (s), 2878 (m), 1451 (w), 1381 (w), 1063 (m) cm^{-1}. XPS Atomic Ratios Calcd for $C_{22}F_6O_4$: C, 69; F, 19; O, 13. Obsd: C, 69; F, 16; O, 15.

Reactions of PCTFE-OH with Acid Chlorides (Acetyl Chloride, Trichloroacetyl Chloride, Pentafluorobenzoyl Chloride, Adipoyl Chloride). PCTFE-OH film samples were placed in a Schlenk tube which was then purged with nitrogen for 20 min. Solvent (20 mL) was added via cannula, and then the acid chloride (4–7 mmol) was introduced via syringe. Each reaction was carried out at room temperature. The reactions with trichloroacetyl chloride and adipoyl chloride were complete after 40 h in THF to yield PCTFE-OC(O)CH_3 (**5**) and PCTFE-[OC(O)$CH_2CH_2]_2$ (**6**), respectively. The reaction of PCTFE-OH with trichloroacetyl chloride was complete after 12 h in THF to give PCTFE-OC(O)CCl_3 (**7**). The reaction of pentafluorobenzoyl chloride with PCTFE-OH was extremely sluggish in THF; it was complete, however, in 24 h in pyridine as a solvent/catalyst to yield PCTFE-OC(O)C_6F_5 (**8**). In each case the reaction solution was removed via cannula and the film samples were washed under nitrogen with THF (4 × 30 mL) and then dichloromethane (4 × 30 mL) and dried (0.02 mm, 24 h). PCTFE film samples were exposed to identical reaction conditions as controls; no reaction occurred in each case.

For PCTFE-OC(O)CH_3 (**5**): contact angles θ_A/θ_R = 75°/35°; ATR IR 2961 (m), 2905 (w, sh), 2874 (w), 1740 (s), 1451 (m), 1387 (m), 1368 (m), 1238 (s), 1074 (m), 1042 (m) cm^{-1}. XPS Atomic Ratios Calcd for $C_{30}F_6O_8$: C, 68; F, 14; O, 18. Obsd: C, 67; F, 15; O, 18.

For PCTFE-[OC(O)$CH_2CH_2]_2$ (**6**): contact angles θ_A/θ_R = 76°/43°; ATR IR 2959 (m), 2936 (m, sh), 2874 (w), 1734 (s), 1456 (w), 1420 (w), 1389 (w), 1356 (w), 1267 (s), 1078 (m), 1038 (w), 741 (m) cm^{-1}. XPS Atomic Ratios Calcd for $C_{34}F_6O_8$: C, 71; F, 13; O, 17. Obsd: C, 69; F, 13; O, 18; Cl, 0.2.

For PCTFE-OC(O)CCl_3 (**7**): contact angles θ_A/θ_R = 87°/67°; ATR IR 2967 (m), 2936 (w, sh), 2873 (w), 1767 (s), 1235 (s), 828 (s) cm^{-1}. XPS Atomic Ratios Calcd for $C_{30}F_6O_8Cl_{12}$: C, 54; F, 11; O, 14; Cl, 21. Obsd: C, 54; F, 11; O, 15; Cl, 19.

For PCTFE-OC(O)C_6F_5 (**8**): contact angles θ_A/θ_R = 94°/62°; ATR IR 2967 (m), 2903 (w, sh), 1742 (s), 1653 (s), 1526 (s), 1499 (s), 1424 (m), 1385 (m), 1329 (s), 1225 (s), 1001 (s, sh) cm^{-1}. XPS Atomic Ratios Calcd for $C_{50}F_{26}O_8$: C, 60; F, 31; O, 10. Obsd: C, 56; F, 34; O, 11.

Reactions of PCTFE-OH with Isocyanates (α,α,α-Trifluoro-*p*-tolyl Isocyanate, Trichloroacetyl Isocyanate, Hexamethylene Diisocyanate). PCTFE-OH film samples were placed in a Schlenk flask that was then purged with nitrogen for 20 min. THF was added via cannula and then the isocyanate (3–4 mmol) was added via syringe. Each reaction was carried out at room temperature. Control reactions were run by using PCTFE (**1**) and PCTFE-O*P* (**3**); no reactions were observed for any of the controls. The reactions of PCTFE-OH with α,α,α-trifluoro-*p-tolyl* isocyanate and trichloroacetyl isocyanate were complete after 12 h to yield PCTFE-OC(O)NHC_6H_4-*p*-CF_3 (**9**) and PCTFE-OC(O)NHC(O)CCl_3 (**10**), respectively. The reaction of PCTFE-OH with hexamethylene diisocyanate was complete after 24 h when dibutyltin dilaurate (2–3 mol %, based on hexamethylene diisocyanate) was used as a catalyst to yield PCTFE-[OC(O)-NH$CH_2CH_2CH_2]_2$ (**11**). In each case the reaction solution was removed via cannula and the film samples were washed under nitrogen with THF (3 × 20 mL) and then dichloromethane (3 × 20 mL) and dried (0.02 mm, 24 h).

For PCTFE-OC(O)NHC_6H_4-*p*-CF_3 (**9**): contact angles θ_A/θ_R = 83°/50°; ATR IR 3441 (m), 3320 (m, br), 3206 (w), 3137 (w), 3067 (w), 2959 (m), 2884 (w), 1744 (s, sh), 1719 (s), 1618 (s), 1607 (s), 1541 (s), 1514 (w, sh), 1416 (s), 1329 (s), 1073 (s, sh), 1017 (m), 843 (m) cm^{-1}. XPS Atomic Ratios Calcd for $C_{54}F_{18}O_8N_4$: C, 64; F, 21; O, 10; N, 5. Obsd: C, 59; F, 25; O, 11; N, 5.

For PCTFE-OC(O)NHC(O)CCl_3 (**10**): contact angles θ_A/θ_R = 77°/48°; ATR IR 3411 (w), 3289 (m, br), 3227 (w), 2967 (m), 2907 (w), 1806 (s, sh), 1796 (vs), 1746 (s,), 1730 (s, sh), 1495 (vs), 1393 (w), 1246 (m, sh), 1167 (m, sh), 1046 (w), 847 (s), 824 (m), 770 (m) cm^{-1}. XPS Atomic Ratios Calcd for $C_{34}F_6O_{12}N_4Cl_{12}$: C, 50; F, 9; O, 18; N, 6; Cl, 18. Obsd: C, 52; F, 9; O, 19; N, 6; Cl, 15.

For PCTFE-[OC(O)NH$CH_2CH_2CH_2]_2$ (**11**): contact angles θ_A/θ_R = 73°/38°; ATR IR 3455 (w, sh), 3333 (m, br), 2936 (s), 2963 (m), 2272 (w), 1723 (m, sh), 1705 (s), 1530 (s), 1453 (w), 1262 (m, sh), 1235 (m, sh), 777 (w) cm^{-1}. XPS Atomic Ratios Calcd for $C_{38}F_6O_8N_4$: C, 68; F, 11; O, 14; N, 7. Obsd: C, 68; F, 10; O, 15; N, 7.

Reaction of PCTFE-OH with *p*-Toluenesulfonyl Chloride. PCTFE-OH film samples and *p*-toluenesulfonyl chloride (0.77 g, 4.0 mmol) were placed in a Schlenk tube that was then flushed with nitrogen for 20 min. Pyridine (20 mL) was added via cannula, and the tube was stored in a freezer at −20 °C for 40 h. After this period, the solution was removed via cannula and the film samples were washed with benzene (3 × 20 mL), THF (2 × 20 mL), methanol (2 × 20 mL), benzene (2 × 20 mL), and hexane (2 × 20 mL) in this order and dried (0.02 mm, 24 h). Control reactions of PCTFE and PCTFE-OP rendered no changes. For PCTFE-OTs (**12**): contact angles θ_A/θ_R = 80°/50°; ATR IR 3067 (w), 3034 (w), 2961 (m), 2932 (w), 2899 (w), 2876 (w), 1599 (m), 1495 (w), 1451 (w), 1358 (s), 1177 (s), 936 (s,sh), 916 (m), 743 (w) cm^{-1}. XPS Atomic Ratios Calcd for $C_{50}F_6O_{12}S_4$: C, 69; F, 8; O, 17; S, 6. Obsd: C, 67; F, 10; O, 18; S, 5.

Reactions of PCTFE-OTs with Nucleophiles (Chloride, Bromide, Cyanide). PCTFE-OTs film samples and tetrabutylammonium chloride (0.8 g, 2.88 mmol) or tetrabutylammonium bromide (0.67 g, 2.08 mmol) were placed in a 200-mL flask equipped with a reflux condenser. Methanol (50 mL) was added, and the solution was heated and allowed to reflux for 24 h. Film samples were washed with methanol (4 × 20 mL) and dichloromethane (3 × 20 mL) and dried (0.02 mm, 24 h) to give PCTFE-Cl (**13**) and PCTFE-Br (**14**). A control reaction of PCTFE with tetrabutylammonium bromide rendered no changes. PCTFE-OTs film samples were placed in a Schlenk tube that was then purged with nitrogen for 20 min. A solution of KCN (0.125 g, 1.92 mmol) and 18-crown-6 ether (0.35 g, 1.32 mmol) in THF (20 mL) was added via cannula. The film samples were allowed to react at room temperature for 4 h to give PCTFE-CN (**15**). The film samples were washed with water (2 × 20 mL), methanol (2 × 20 mL), THF (3 × 20 mL), and dichloromethane (3 × 20 mL) in this order and dried (0.02 mm, 24 h). A control reaction of PCTFE produced a darkened film sample with a high C:F ratio and no nitrogen.

For PCTFE-Cl (**13**): contact angles θ_A/θ_R = 84°/33°; ATR IR 2959 (m), 2870 (w), 1680 (w, br), 1487 (w), 1447 (w) cm^{-1}. XPS Atomic Ratios Calcd for $C_{22}F_6Cl_4$: C, 69; F, 19; Cl, 12. Obsd: C, 69; F, 18; Cl, 10; O, 3.

For PCTFE-Br (**14**): contact angles θ_A/θ_R = 84°/30°; ATR IR 2961 (m), 2878 (w), 1444 (w), 1407 (m), 754 (w) cm^{-1}. XPS Atomic Ratios Calcd for $C_{22}F_6Br_4$: C, 69; F, 19; Br, 12. Obsd: C, 73; F, 16; Br, 8; O, 4.

For PCTFE-CN (**15**): contact angles θ_A/θ_R = 75°/42°; ATR IR 2959 (m), 2892 (w), 2247 (m, sharp), 1460 (w), 1428 (w), 1354 (m) cm^{-1}. XPS Atomic Ratios Calcd for $C_{26}F_6N_4$: C, 72; F, 17; N, 11. Obsd: C, 72; F, 11; N, 10; O, 5; S, <1.

Reactions of PCTFE-OH with $ClSiMe_3$, Cl_2SiMe_2, Cl_3SiMe, and Cl_4Si. PCTFE-OH film samples were placed in a Schlenk tube that was then purged with nitrogen for 20 min prior to the introduction of reagents and solvents via cannula. $ClSiMe_3$ (0.514 g, 4.73 mmol) in THF (20 mL) was added and allowed to react at 0 °C for 18 h to give PCTFE-$OSiMe_3$ (**16**). Cl_2SiMe_2 (0.63 g, 4.01 mmol) in THF (18 mL) and pyridine (2 mL) was added and allowed to react at room temperature for 48 h to yield PCTFE-$(O)_2SiMe_2$ (**17**). Cl_3SiMe (0.764 g, 5.11 mmol) in THF (20 mL) was added and allowed to react at room temperature for 40 h to yield PCTFE-$(O)_2SiMeCl$ (**18**). Cl_4Si (1.48 g, 8.72 mmol) in THF (20 mL) was added and allowed to react at room temperature for 48 h to give PCTFE-$(O)_3SiCl$ (**19**). After reactions, solutions were removed and film samples were washed with THF (5 × 20 mL) and hexane (3 × 20 mL) and dried (0.02 mm, 24 h).

For PCTFE-$OSiMe_3$ (**16**): contact angles θ_A/θ_R = 90°/58°; ATR IR 2957 (s), 2899 (m), 2867 (m), 1678 (w, br), 1451 (w), 1385 (w), 1252 (s), 868 (m), 841 (s), 748 (w) cm^{-1}. XPS Atomic Ratios Calcd for $C_{34}F_6O_4Si_4$: C, 71; F, 13; O, 8; Si, 8. Obsd: C, 68; F, 13; O, 11; Si, 8.

For PCTFE-$(O)_2SiMe_2$ (**17**): contact angles θ_A/θ_R = 106°/55°; ATR IR 2961 (s), 2974 (m), 1449 (w), 1387 (w), 1262 (s), 901 (m), 868 (m, sh), 802 (s), 743 (m) cm^{-1}. XPS Atomic Ratios Calcd for $C_{26}F_6O_4Si_2$: C, 68; F, 16; O, 11; Si, 5. Obsd: C, 58; F, 15; O, 18; Si, 9; Cl, 1.

For PCTFE-$(O)_2SiClMe$ (**18**): ATR IR 2957 (m), 2882 (m), 1451 (w), 1386 (w), 1269 (s), 864 (w), 795 (w), 745 (m) cm^{-1}. XPS Atomic Ratios Calcd for $C_{24}F_6O_4Si_2Cl_2$: C, 63; F, 16; O, 11; Si, 5; Cl, 5. Obsd: C, 58; F, 13; O, 17; Si, 8; Cl, 5.

For PCTFE-$(O)_3SiCl$ (**19**): ATR IR 2959 (m), 2886 (m), 1451 (w), 1385 (w), 745 (w) cm^{-1}. XPS Atomic Ratios Calcd for $C_{66}F_{18}O_{12}Si_4Cl_4$: C, 63; F, 17; O, 12; Si, 4; Cl, 4. Obsd: C, 54; F, 15; O, 18; Si, 6; Cl, 7.

Reaction of PCTFE-OH with (2-Cyanoethyl)trichlorosilane, (3-Cyanopropyl)dimethylchlorosilane and (3-(Methacryloxy)propyl)dimethylchlorosilane. PCTFE-OH film samples were reacted as described for the other silane reactions with (2-cyanoethyl)trichlorosilane (0.57 g, 3.02 mmol) in THF (20 mL) at room temperature for 40 h to yield PCTFE-$(O)_3SiCH_2CH_2CN$ (**20**), (3-cyanopropyl)dimethylchlorosilane (0.497 g, 3.07 mmol) in THF (20 mL) at room temperature for 48 h to yield PCTFE-$OSi(Me)_2CH_2CH_2CH_2CN$ (**21**) and (3-(methacryloxy)propyl)dimethylchlorosilane (0.60 g, 2.72 mmol) in THF (20 mL) at room temperature for 48 h to yield PCTFE-$OSi(Me)_2CH_2CH_2CH_2OC(O)C_3H_5$ (**22**). Film samples were washed with THF (3 × 20 mL) and then dichloromethane (3 × 20 mL) and dried (0.02 mm, 24 h).

For PCTFE-$(O)_3SiCH_2CH_2CN$ (**20**): ATR IR 2982 (m), 2946 (m), 2880 (m), 2313 (m), 2253 (s), 1428 (w), 1385 (w), 747 (w) cm^{-1}. XPS Atomic Ratios Calcd for $C_{78}F_{18}O_{12}Si_4N_4$: C, 67; F, 16; O, 10; Si, 3; N, 3. Obsd: C, 58; F, 10; O, 18; Si, 7; N, 6; Cl, 1.

For PCTFE-$OSi(Me)_2CH_2CH_2CH_2CN$ (**21**): contact angles $\theta_A/\theta_R = 77°/55°$; ATR IR 3470 (w, br), 2955 (m), 2976 (m), 2247 (w, sharp), 1657 (w, br), 1428 (w), 1383 (m), 1254 (m), 865 (m) cm^{-1}. XPS Atomic Ratios Calcd for $C_{46}F_6N_4O_4Si_4$: C, 72; F, 9; N, 6; O, 6; Si, 6. Obsd: C, 71; F, 13; O, 11; N, 2; Si, 3.

For PCTFE-$OSi(Me)_2CH_2CH_2CH_2OC(O)C_3H_5$ (**22**): contact angles $\theta_A/\theta_R = 88°/60°$; ATR IR 3434 (w, br), 2957 (s), 2874 (m), 1721 (s), 1640 (w), 1453 (w), 1387 (m), 1260 (s), 855 (s), 802 (s) cm^{-1}. XPS Atomic Ratios Calcd for $C_{54}F_6O_{12}Si_4$: C, 73; F, 8; O, 15; Si, 5. Obsd: C, 67; F, 11; O, 16; Si, 5.

Reaction of PCTFE-OH with Thionyl Chloride. PCTFE-OH film samples were reacted under nitrogen with thionyl chloride (0.816 g, 6.86 mmol) in THF (20 mL) at room temperature for 24 h to give PCTFE-$(O)_2SO$ (**23**). The film samples were washed with THF (3 × 20 mL) and then dichloromethane and dried (0.02 mm, 24 h). Contact angles: $\theta_A/\theta_R = 82°/50°$. ATR IR: 2955 (m), 2890 (w), 1593 (w), 1497 (w), 1383 (w), 1194 (s, overlapped with PCTFE band), 907 (m, sh), and 741 (m) cm^{-1}. XPS Atomic Ratios Calcd for $C_{22}F_6O_6S_2$: C, 61; F, 17; O, 17; S, 6. Obsd: C, 59; F, 16; O, 20; S, 5, Cl, <1.

Reaction of PCTFE-OH with Phosphorous Tribromide. PCTFE-OH film samples were reacted under nitrogen with phosphorous tribromide (1.152 g, 4.26 mmol) in THF (20 mL) at room temperature to yield the modified surface PCTFE-OH/PBr_3 (**24**). Film samples were washed with THF (4 × 20 mL) and dichloromethane (4 × 20 mL) and dried (0.03 mm, 24 h). Contact angles: $\theta_A/\theta_R = 74°/20°$. ATR IR: 2961 (m), 2903 (w), 2855 (w), 2427 (w, br), 1680 (w, br), 1449 (m), 1383 (w), 1267 (m), 745 (m) cm^{-1}. XPS Atomic Ratios Obsd: C, 58; F, 16; O, 17; Br, 3, P, 6.

Oxidation of PCTFE-OH to PCTFE-CHO (25). A PCTFE-OH film sample and dicyclohexyl carbodiimide (0.825 g, 4.00 mmol) were placed in a Schlenk tube which was then purged with nitrogen for 15 min; Me_2SO (10 mL) was added. Anhydrous phosphoric acid (0.04 g, 0.41 mmol) was placed in another Schlenk tube that was then purged with nitrogen for 15 min; Me_2SO (10 mL) was added. The phosphoric acid solution was slowly transferred to the tube containing the film sample at room temperature, and the reaction was allowed to proceed for 24 h. The reaction solution was removed, and the film sample was washed with Me_2SO (2 × 20 mL), THF (3 × 20 mL), methanol (3 × 20 mL), and dichloromethane (3 × 20 mL) in this order and dried (0.02 mm, 24 h). Contact angles: $\theta_A/\theta_R = 80°/30°$. ATR IR: 2932 (m), 2861 (w), 2730 (w), 1725 (s), 1665 (m), 1453 (w), 1385 (w) cm^{-1}. XPS Atomic Ratios Calcd for $C_{22}F_6O_4$: C, 69; F, 18; O, 13. Obsd: C, 65; F, 18; O, 17.

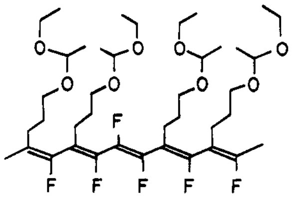
Oxidation of PCTFE-OH to PCTFE-COOH (26). PCTFE-OH film samples were reacted with pyridinium dichromate (0.31 g, 0.32 mmol) in DMF (20 mL) at room temperature for 24 h. The reaction solution was removed, and the film samples were washed with 1 M HCl (2 × 20 mL), water (2 × 20 mL), methanol (4 × 20 mL), and dichloromethane (4 × 20 mL) in this order and dried (0.03 mm, 24 h). Contact angles: $\theta_A/\theta_R = 68°/12°$. ATR IR: 3381 (s, br), 2959 (s), 2928 (s), 2870 (m, sh), 1736 (s), 1649 (s), 1599 (s), 1564 (s), 1449 (m), 1428 (m), 1389 (s), 812 (m) cm^{-1}. XPS Atomic Ratios Calcd for $C_{22}F_6O_8$: C, 61; F, 17; O, 22. Obsd: C, 63; F, 14; O, 24.

Results and Discussion

All of the experiments reported in this paper involve modification reactions of hydroxylated poly(chlorotrifluoroethylene) (4) (IV in eq 1—which we abbreviate PCTFE-OH), the synthesis of which is summarized in eq 1. The PCTFE film used for this synthesis was obtained from Allied (Aclar 33C): 5 mil film was used to prepare samples for analysis by X-ray photoelectron spectroscopy (XPS), attenuated total reflectance infrared spectroscopy (ATR IR), scanning electron microscopy (SEM), and contact angle analysis; 1 mil film was used for UV–vis analysis. PCTFE-OH was prepared under conditions (−15 °C for 30 min) which yield modified layers of ~1500-Å thickness. These relatively thick modified layers were necessary to facilitate analysis by ATR IR which was critical in defining functional group transformations. Several experiments were performed on thinner modified layers (~50 Å) to ascertain that the same chemistry occurs in these samples. Gravimetric analysis that we have adapted to surface characterization[17] was not useful in this work because the modified film samples dissolve to a small (but significant to gravimetric analysis) extent in the reaction solvents. The extent of dissolution likely varies depending on the structure of the modified surface, and we have not studied this process in detail. We estimate[18] that a ~10-Å layer dissolves; this does not compromise any of the analytical techniques employed but precludes gravimetric analysis.

Atomic composition data of each modified surface were obtained from XPS multiplex spectra and are reported in the Experimental Section: this deserves some comment in that these data are seldom reported and compared with the expected values. Indeed, in no other system which we have studied are these data so consistent and reproducible. The degree to which these data agree with the expected chemistry and infrared analyses is self-evident, and, for the chemistry reported here, this technique has proven to be quite quantitative. The reactions evidently proceed in high yield and occur homogeneously throughout the XPS sampling depth. (Angle resolved XPS analysis indicates that the latter suggestion is so.)

Preparation of PCTFE-OH. PCTFE film reacts with LiPrO*P* in THF/heptane via the reduction–addition–elimination sequence described in eq 1 to yield the protected alcohol-containing surface PCTFE-O*P* (**3**).[9] Contact angles exhibit the expected decreased values, $\theta_A/\theta_R = 88°/37°$ (from PCTFE—104°/77°), and the ATR IR spectrum (Figure 1) shows bands due to PCTFE as well as absorbances with the same pattern as the spectrum of acetaldehyde bromopropyl ethyl acetal, indicating that acetaldehyde propyl ethyl acetal group is incorporated into the film. The film is unchanged (from PCTFE) in color and texture to the eye, and SEM exhibits no changes in surface topography at the limits of resolution: both samples appear flat. The XPS spectrum (Figure 2) indicates the incorporation of oxygen, the partial removal of fluorine, and complete removal of chlorine. The high binding energy C_{1s} photoelectron line (301 eV) due to PCTFE is completely removed and replaced by the complex line at lower binding energy (290 eV) due to all of the carbons in **3**. XPS atomic ratios for **3** were consistently and reproducibly determined to be 73:12:15 for C:F:O. The predicted ratios for III (eq 1) are 75:8:17 for C:F:O, thus



3, PCTFE-O*P*

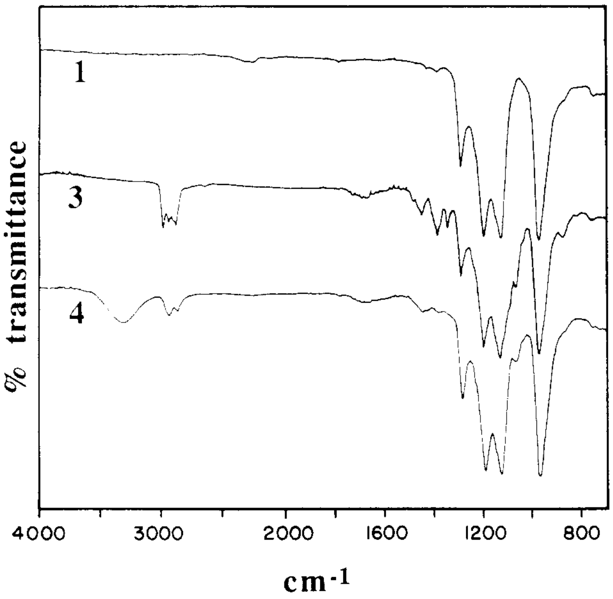


Figure 1. ATR IR spectra of PCTFE (1), PCTFE-O*P* (3), and PCTFE-OH (4).

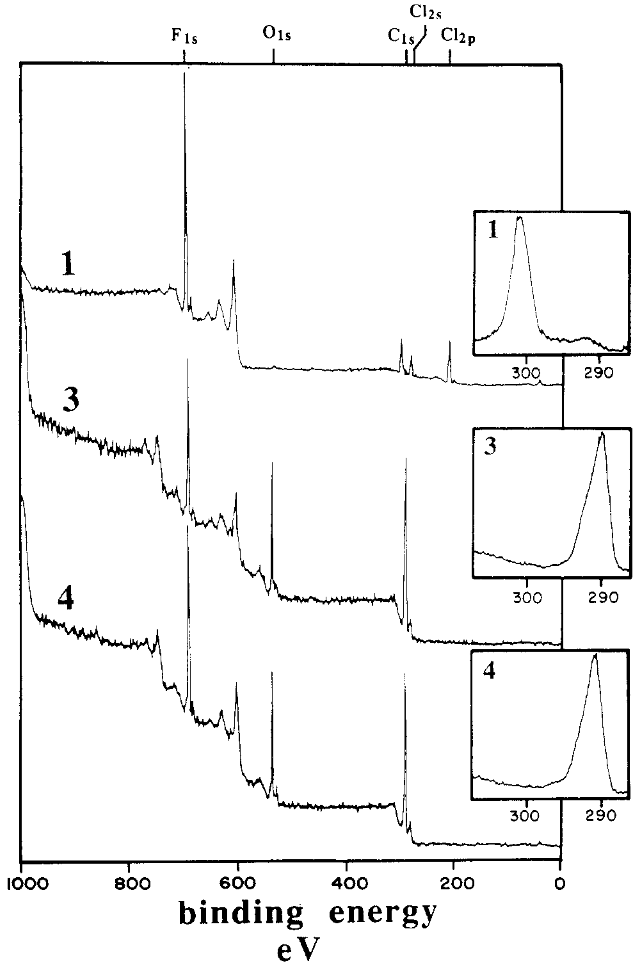
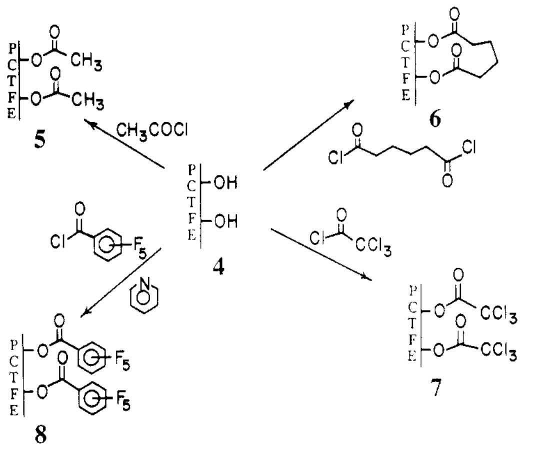


Figure 2. XPS survey and C_{1s} region spectra of PCTFE (1), PCTFE-O*P* (3), and PCTFE-OH (4).

Scheme I



PCTFE-O*P* exhibits lower values than predicted for carbon and oxygen and a higher value than predicted for fluorine based on structure III. In that these differences are counter to what would be expected from sample contamination or oxidation, we propose that 3 consists of 80% III and 20% II. The validity of this proposition is supported by many of the data which follow and is explained by proposing that the first step in eq 1 proceeds quantitatively and the second step proceeds in 80% yield. We have observed this in reactions of other lithium reagents with PCTFE, and steric requirements appear to determine the extent of the second step.[19]

Hydrolysis of **3** using refluxing aqueous/methanolic HCl for 3 h renders colorless PCTFE-OH (**4**). The contact angles for **4** are depressed further (θ_A/θ_R = 67°/17°), indicating the presence of the polar and hydrophilic hydroxyl group. The ATR IR spectrum of PCTFE-OH (Figure 1) displays a broad hydrogen-bonded O–H band (3335 cm^{-1}), a C–O stretching band (1063 cm^{-1}), and methylene C–H stretching bands (2946 and 2878 cm^{-1}). The XPS spectrum (Figure 2) is consistent with deprotection and the atomic ratios match well with those calculated on the basis of four hydroxyl groups per five PCTFE repeat units.

Esterification of PCTFE-OH. Reactions with Acetyl Chloride, Adipoyl Chloride, Trichloroacetyl Chloride, and Pentafluorobenzoyl Chloride. The reactions of **4** with acid chlorides (Scheme I) in THF at room temperature for 12–40 h were complete and rendered PCTFE-OC(O)CH_3 (**5**), PCTFE-[OC(O)CH_2CH_2]$_2$ (**6**), and PCTFE-OC(O)CCl_3 (**7**). The corresponding reaction with pentafluorobenzoyl chloride was sluggish but was complete after 24 h in the presence of pyridine to give PCTFE-OC(O)C_6F_5 (**8**).

ATR IR spectra (Figure 3) of **5**–**8** indicate the complete reaction of the hydroxyl group (disappearance of the O–H band at 3335 cm^{-1}–Figure 1) and the presence of carbonyl bands (1740, 1734, 1767, and 1742 cm^{-1} for **5**, **6**, **7**, and **8**, respectively), and methylene bands due to the product esters. The spectrum of **6** displays an increased intensity of the methylene bending absorbance (741 cm^{-1}); **7** exhibits C–Cl stretching (828 cm^{-1}); **8** exhibits aromatic bands (1526 and 1499 cm^{-1}), and aromatic C–F stretching (1653 cm^{-1}).

XPS analysis was also consistent with high yield esterification reactions. Figure 4 exhibits survey spectra for **5**, **6**, **7**, and **8**: noteworthy are photoelectron lines corresponding to Cl_{2s} (278 eV) and Cl_{2p} (207 eV) for **7** and F_{1s} (693 eV) for **8**. The observed atomic ratios are consistent with those calculated (Experimental Section). The C_{1s} regions of the XPS spectra of **5**, **6**, and **7** could be nicely curve-fitted with three peaks. Figure 5 shows these data along with a two-peak-curve fitted spectrum of **4** for comparison. We assign the higher binding energy peak fitted to the spectrum of **4** to the carbons bonded to fluorine or oxygen (indicated by ■ in the figure) and the lower binding energy peak to the remaining carbons (●). The calculated percentage of the high binding energy carbons (■) is 47% of the total carbon; the observed value is 45%. The data agree well with the proposed structure. The spectra of **5**, **6**, and **7** are fitted with higher binding energy peaks (▲)

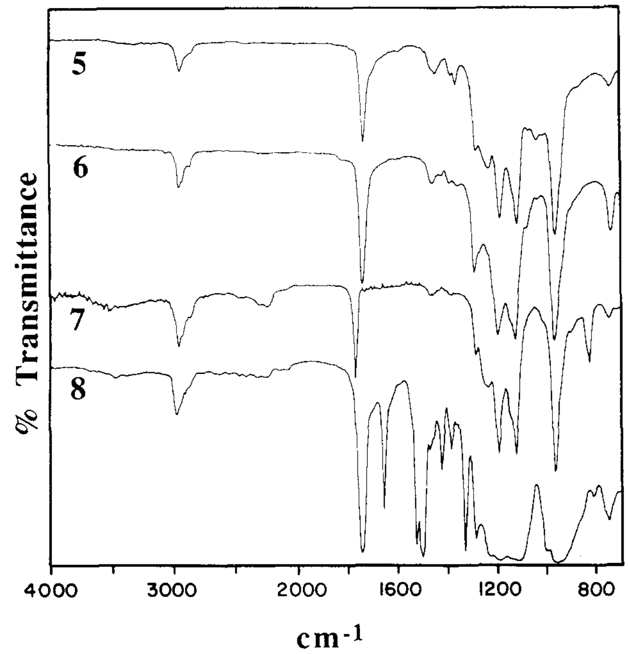


Figure 3. ATR IR spectra of esterified surfaces: PCTFE-OC(O)CH_3 (5), PCTFE-[OC(O)CH_2CH_2]$_2$ (6), PCTFE-OC(O)CCl_3 (7), and PCTFE-OC(O)C_6F_5 (8).

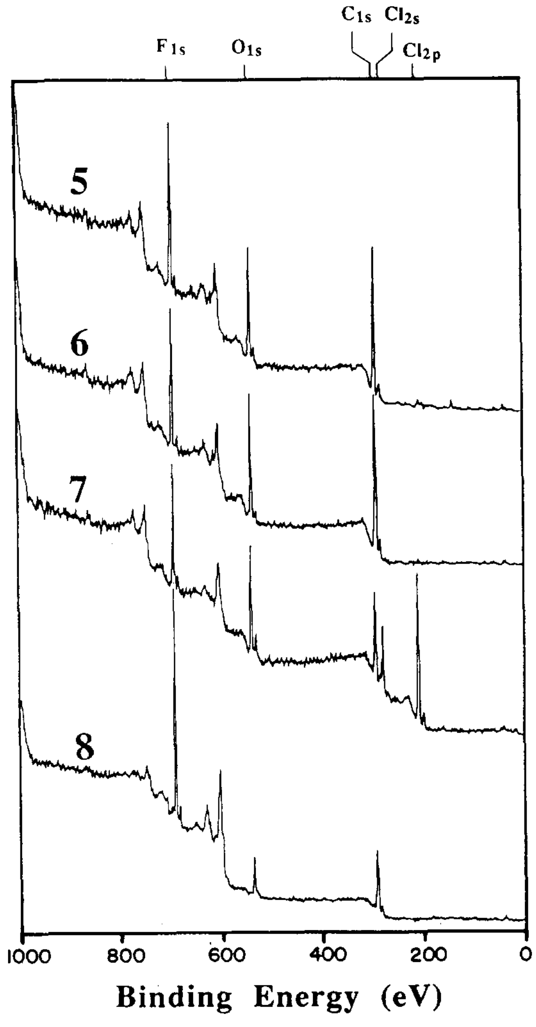


Figure 4. XPS spectra of esterified surfaces: PCTFE-OC(O)CH_3 (5), PCTFE-[OC(O)CH_2CH_2]$_2$ (6), PCTFE-O(O)CCl_3 (7), and PCTFE-OC(O)C_6F_5 (8).

as well as two peaks which we assign as we did for 4. We assign these high binding energy regions to the carbonyl carbons in 5 and 6 and to the carbonyl carbons and trichloromethyl carbons in 7. The observed percentages for the ▲, ■, and ● carbon peaks of 5 are 12, 34, and 54%, respectively; the calculated values are 13, 33, and 54%, respectively. The observed percentages for the ▲, ■, and ● carbon peaks of 6 are 13, 23, and 64%, respectively; the calculated values are 12, 29, and 59%, respectively. The observed percentages for the ▲, ■, and ● carbon peaks of 7 are 29, 37, and 34%, respectively; the calculated values are 27, 33, and 40%, respectively. In each case the observed areas agree well with the values predicted for the proposed structures. The C_{1s} region of 8 was less well resolved and not suited for this treatment.

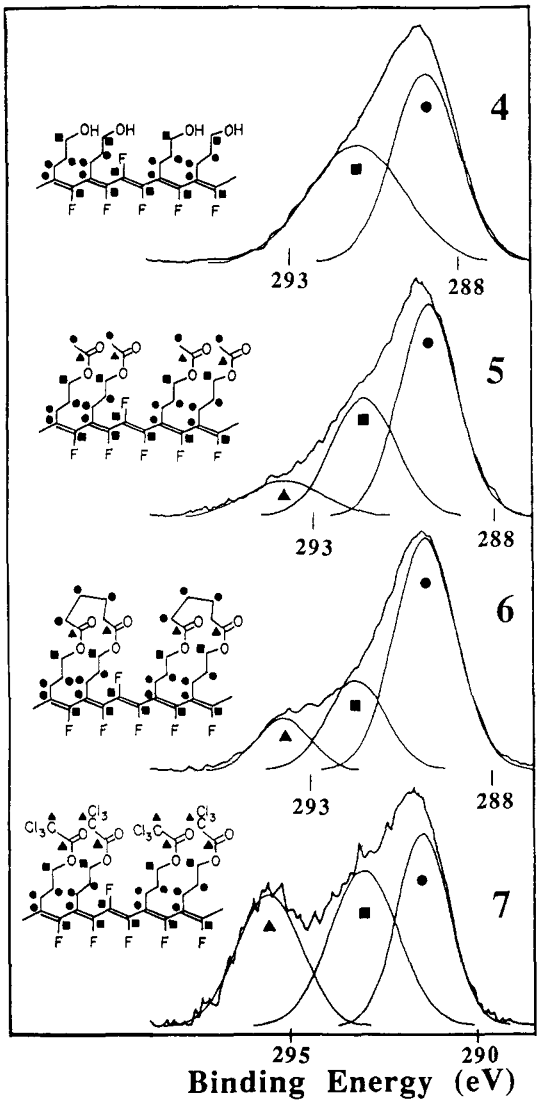
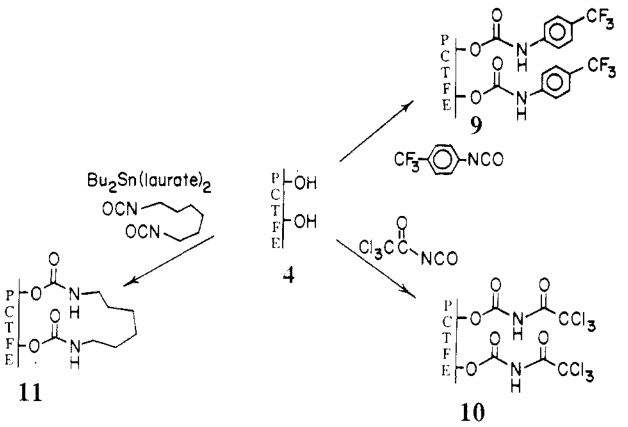


Figure 5. C_{1s} regions of XPS spectra of 4, PCTFE-OH, 5, PCTFE-OC(O)CH_3, 6, PCTFE-[OC(O)CH_2CH_2]$_2$, and 7, PCTFE-OC(O)CCl_3.

Contact angles changed upon esterification from θ_A/θ_R = 67°/17° for PCTFE-OH to 75°/35° for 5, 76°/43° for 6, 87°/67° for 7, and 94°/62° for 8. These increases indicate decreases in hydrophilicity and are consistent with changing a hydroxylated surface to ester-containing surfaces. The hydrophilicity is lowest in the halogenated surfaces (7 and 8).

The formation of the diester 6 from adipoyl chloride is indicated by the single carbonyl band in the infrared and the low amount (less than 1% atomic composition) of chlorine observed by XPS. A small amount of half ester/half acid chloride is formed as evidenced by the fact that treatment of 6 with water removes the small amount

Scheme II



of chlorine present (as observed by XPS) and lowers the contact angles by 4–6°; these changes are consistent with hydrolysis of the acid chloride. That predominantly diester is formed from a many order-of-magnitude excess (over the hydroxyl groups) of adipoyl chloride suggests that the half ester/half acid chloride, which is initially formed and already bound to the polymer chain, reacts with another alcohol faster than adipoyl chloride in solution does. This can be explained by the fact that the hydroxyl group concentration in the modified surface layer is ~8.5 M[20] and the concentration of adipoyl chloride in solution is 0.2 M; thus at the site of reaction, there is a large excess of hydroxyl groups.

Reaction of PCTFE-OH with Isocyanates: α,α,α-**Trifluoro-*p*-tolyl Isocyanate, Trichloroacetyl Isocyanate, and Hexamethylene Diisocyanate.** The reactions of 4 with α,α,α-trifluoro-*p*-tolyl isocyanate and trichloroacetyl isocyanate in THF at room temperature (Scheme II) are complete after 12 h to yield PCTFE-OC(O)NHC$_6$H$_4$-*p*-CF$_3$ (*9*) and PCTFE-OC(O)NHC(O)CCl$_3$ (**10**). The reaction with hexamethylene diisocyanate is considerably slower and takes 24 h in THF in the presence of catalytic amounts of dibutyltin dilaurate to yield PCTFE-[OC(O)NHCH$_2$CH$_2$CH$_2$]$_2$ (**11**). The contact angles of the products are increased from θ_A/θ_R = 67°/17° for 4 to 83°/50° for **9**, 77°/48° for **10**, and 73°/38° for **11**. The hydrophobicity varies in the order: fluorine-containing surface > chlorine-containing surface > nonhalogenated surface.

ATR IR spectra (Figure 6) are consistent with urethane formation. This technique does not ascertain that all of the hydroxyl groups have reacted since the N–H bands appear in the same region as the O–H band; however, doubling the reaction time causes no further changes in XPS and ATR IR spectra, suggesting that the reactions are complete. The spectrum of **9** shows three N–H stretching bands: 3441 (free N–H), 3320 (hydrogen bonded N–H), 3206 cm^{-1}, aromatic and aliphatic C–H stretching (3137, 3067, 2959, 2884 cm^{-1}), two carbonyl bands (1744 free, 1719 cm^{-1} hydrogen bonded), two aromatic C=C stretching bands (1618, 1607 cm^{-1}), a coupled N—H/C—N deformation (1541 cm^{-1}), two C—F stretching bands (1416, 1329 cm^{-1}), and a C—O stretching band (1073 cm^{-1}). The spectrum of **10** exhibits three N–H stretching bands (3411 (free N–H), 3289 (hydrogen-bonded N–H), 3227 cm^{-1}), two methylene bands (2967, 2907 cm^{-1}), two free carbonyl bands (1806, 1746 cm^{-1}), two hydrogen-bonded carbonyl bands (1796, 1730 cm^{-1}), a coupled N-H/C-N deformation (1495 cm^{-1}), and two C-Cl stretching bands (847, 824 cm^{-1}). The spectrum of **11** shows two N–H bands: 3455 (free N–H), 3333 (hydrogen-bonded N–H) cm^{-1}, two methylene bands (2936, 2863 cm^{-1}), a weak N=C=O stretching band (2272 cm^{-1}), two strong carbonyl bands (1723, 1705 cm^{-1}), a coupled N-H/C-N deformation (1530 cm^{-1}), and two C–O–C stretching bands (1262, 1235 cm^{-1}). The very weak intensity of N=C=O band compared to the strong C=O band indicates that the half isocyanate/half urethane is present but it is a small contributor to the structure of **11**.

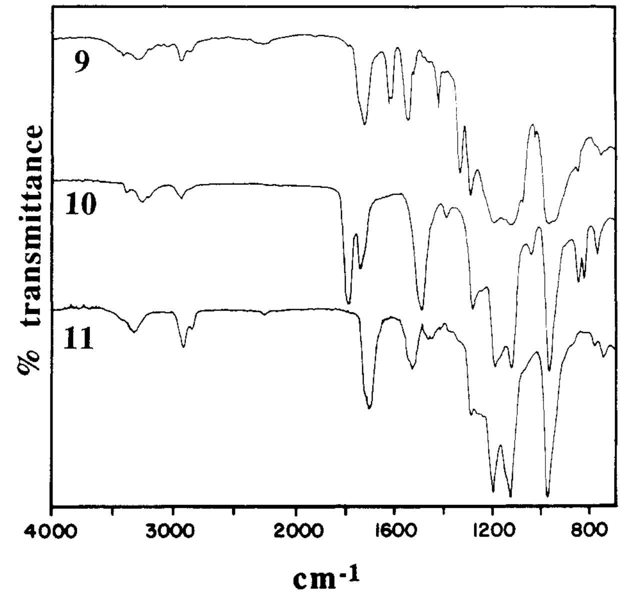


Figure 6. ATR IR spectra of **9**, PCTFE-OC(O)NHC$_6$H$_6$H$_4$-*p*-CF$_3$, **10**, PCTFE-OC(O)NHC(O)CCl$_3$, and **11**, PCTFE-[OC(O)NHCH$_2$CH$_2$CH$_2$]$_2$.

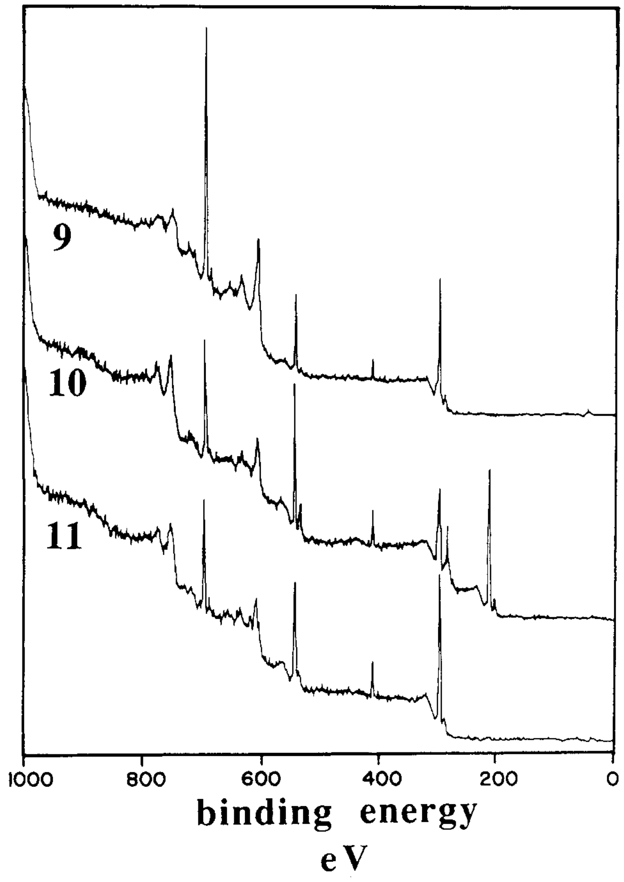


Figure 7. XPS spectra of **9**, PCTFE-OC(O)NHC$_6$H$_4$-*p*-CF$_3$, **10**, PCTFE-OC(O)NHC(O)CCl$_3$, and **11**, PCTFE-[OC(O)NHCH$_2$CH$_2$CH$_2$]$_2$.

The XPS spectra for **9**, **10**, and **11** (Figure 7) are consistent with the chemistry summarized in Scheme II, and the atomic ratios (Experimental Section) match well with

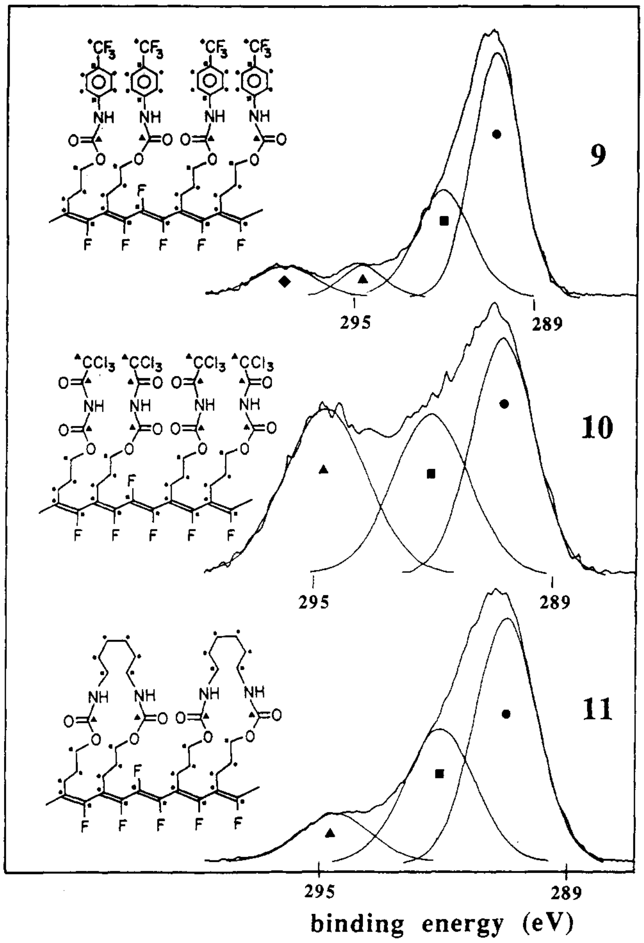
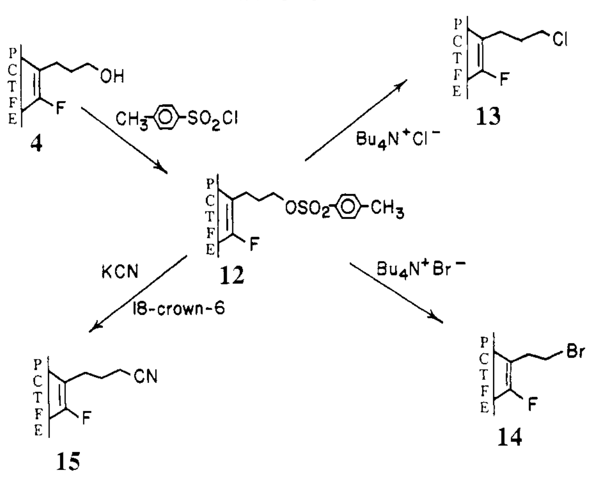


Figure 8. C_{1s} regions of XPS spectra of **9**, PCTFE-OC(O)NHC$_7$H$_4$-*p*-CF$_3$, **10**, PCTFE-OC(O)NHC(O)CCl$_3$, and **11**, PCTFE-[OC(O)NHCH$_2$CH$_2$CH$_2$]$_2$.

the calculated values. Noteworthy are photoelectron lines corresponding to F_{1s} (693 eV) and N_{1s} (406 eV) for **9**, N_{1s} (406 eV), Cl_{2s} (278 eV), and Cl_{2p} (206 eV) for **10**, and N_{1s} (405 eV) for **11**. The C_{1s} regions of these spectra along with fitted curves are shown in Figure 8. The spectrum of **9** is fitted with two high binding energy peaks which we assign to the trifluoromethyl carbons (297.5 eV) and the carbonyl carbons (294.8 eV). We assign the lower binding energy peaks as we did above for **4**. The spectrum of **10** is fitted with a high binding energy peak (294.9 eV) which we assign to the two carbonyl carbons and the trichloromethyl carbons. It is noteworthy that the trichloromethyl carbons of PCTFE-OC(O)CCl$_3$ and PCTFE-OC(O)NHC(O)CCl$_3$ appear at the same binding energy as the carbonyl(s) in each case. We assign the high binding energy peak (294.7 eV) fitted to the spectrum of **11** to the carbonyl carbons. The observed percentages for the ♦, ▲, ■, and ● carbon peaks of **9** are 8, 6, 30, and 56%, respectively; the calculated values are 8, 8, 32, and 52%, respectively. The observed percentages for the ▲, ■, and ● carbon peaks of **10** are 34, 30, and 36%, respectively; the calculated values are 35, 30, and 35%, respectively. The observed percentages for the ▲, ■, and ● carbon peaks of **11** are 12, 34, and 54%, respectively; the calculated values are 11, 36, and 53%, respectively. The data agree well with the proposed structures in each case.

XPS atomic composition data for **11** also support the formation of the diurethane: Nitrogen should be present as 7% of the atomic composition if structure **11** (Scheme II) is correct. If the structure were entirely half isocyanate/half urethane, the nitrogen should be 10% of the atomic composition. The observed value is 7%.

Scheme III



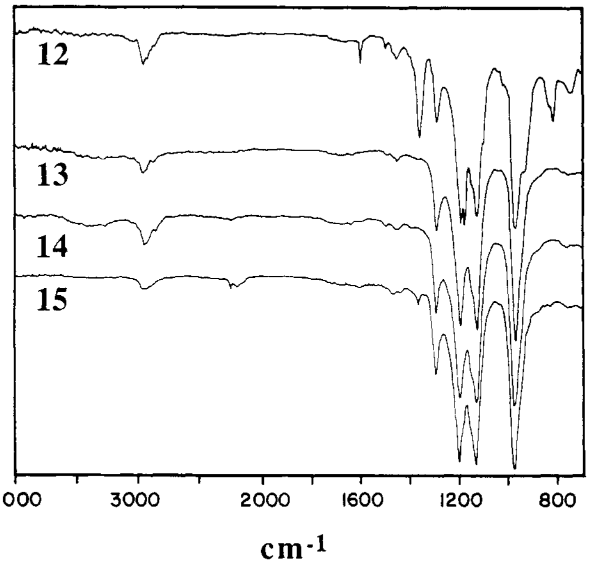


Figure 9. ATR IR spectra of **12**, PCTFE-OTs, **13**, PCTFE-Cl, **14**, PCTFE-Br, and **15**, PCTFE-CN.

Reaction of PCTFE-OH with *p*-Toluenesulfonyl Chloride and Substitution Reactions of PCTFE-OTs with Chloride, Bromide, and Cyanide Ions. The reaction of **4** with *p*-toluenesulfonyl chloride in pyridine at −20 °C for 40 h yields PCTFE-OTs (**12**) (Scheme III). The contact angles increase from θ_A/θ_R = 67°/17° for **4** to 80°/50° for **12**. The ATR IR spectrum of **12** (Figure 9) illustrates that the O–H band has disappeared and that bands due to SO$_2$ stretching (1358, 1177 cm^{-1}), S–O–C stretching (936 cm^{-1}), and aromatics (1599 and 816 cm^{-1}) are present. XPS (Figure 10) displays the expected photoelectron lines, and the observed atomic ratios (experimental section) are consistent with the theoretical values.

Reaction of **12** with tetrabutylammonium chloride or bromide in refluxing methanol for 24 h gives PCTFE-Cl (**13**) or PCTFE-Br (**14**). Reaction of **12** with potassium cyanide and 18-crown-6 ether in THF at room temperature for 3 h yields PCTFE-CN (**15**). The ATR IR spectra for **13**, **14**, and **15**, (Figure 9) show that the *p*-toluenesulfonate has been removed, and the methylene bands are still present. The C≡N stretching band (2247 cm^{-1}) is present in the spectrum of **15**. XPS spectra (Figure 10) illustrate the disappearance of the S_{2s} (237 eV) and S_{2p} (173 eV) bands and appearance of new photoelectron lines corresponding to Cl_{2s} (276 eV) and Cl_{2p} (206 eV) for **13**; Br_{3s} (262 eV), $Br_{3p1/2}$ (194 eV), $Br_{3p3/2}$ (188 eV), and Br_{3d} (75 eV) for **14**; and N_{1s} (403 eV) for **15**. The oxygen (O_{1s}, 537 eV) has

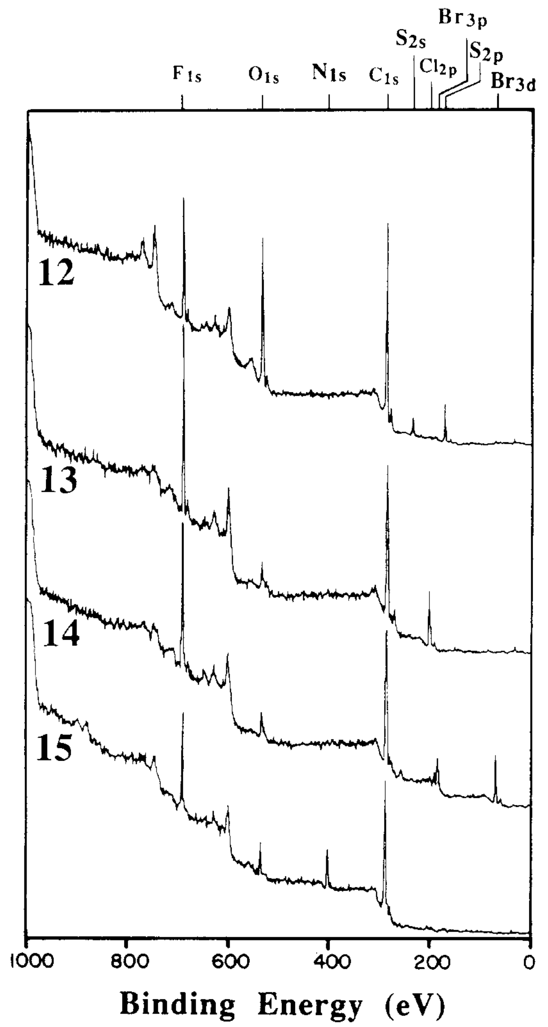


Figure 10. XPS spectra of **12**, PCTFE-OTs, **13**, PCTFE-Cl, **14**, PCTFE-Br,and **15**, PCTFE-CN.

not been completely removed from **13**, **14**, and **15**. This may be due to a side reaction, residual *p*-toluenesulfonate (which was not observable by ATR IR), or adventitious oxidation. The XPS atomic ratios (Experimental Section) support these assignents. The reaction with cyanide ion may be more complex than is indicated: PCTFE reacts with cyanide under the same conditions. A control reaction consisting of treating PCTFE-OTs with refluxing methanol caused a slow elimination that was not observed in substitution reaction.

Reaction of PCTFE-OH with Chlorosilanes ($ClSiMe_3$,Cl_2SiMe_2, Cl_3SiMe, Cl_4Si, $Cl_3SiCH_2CH_2CN$, $Cl(Me)_2SiCH_2CH_2CH_2CN$, $Cl(Me)_2SiCH_2CH_2CH_2OC(O)C_3H_5$). PCTFE-OH film samples react readily with chlorosilanes to give surface-confined silanes (Scheme IV). $ClSiMe_3$ reacts with **4** in THF at 0 °C to yield PCTFE-$OSiMe_3$ (**16**) after 18 h. The contact angles increase from $\theta_A/\theta_R = 67°/17°$ for **4** to 90°/58° for **16**. The ATR IR spectrum of **16** (Figure 11) indicates that the hydroxyl groups have reacted (the O-H (3335 cm^{-1}) and C-O (1063 cm^{-1}) bands have disappeared) to form trimethylsilyl ethers. The spectrum displays the methyl asymmetric stretching band (2957 cm^{-1}) and three other strong bands characteristic of $-OSiMe_3$ (1252, 868, 841 cm^{-1}). The XPS spectrum of **16** (Figure 12) displays the expected silicon photoelectron lines, Si_{2s} (157 eV) and Si_{2p} (106 eV); the observed atomic ratios agree well with the calculated values for **16**. The reaction of Cl_2SiMe_2 with **4** (THF, pyridine, room temperature, 48 h) yields PCTFE-$(O)_2SiMe_2$ (**17**). A large contact angle increase accompanies the reaction, $\theta_A/\theta_R = 106°/55°$ for **17**. The ATR IR spectrum (Figure 11) shows the expected absorbances characteristic of $SiMe_2$ (2961, 1262, 901, 802 cm^{-1}). The XPS spectrum shows the Si_{2s} (158 eV) and Si_{2p} (107 eV) photoelectron lines; atomic ratios are consistent with the proposed structure, chlorine being present as less than 1% of the atomic composition. Cl_3SiMe and Cl_4Si react with **4** in THF at room temper-

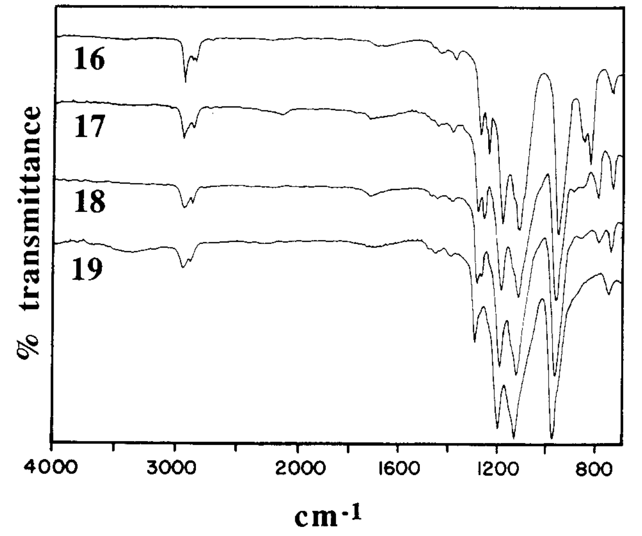


Figure 11. ATR IR spectra of **16**, PCTFE-$OSiMe_3$, **17**, PCTFE-$(O)_2SiMe_2$, **18**, PCTFE-$(O)_2Si(Me)Cl$, and **19**, PCTFE-$(O)_3SiCl$.

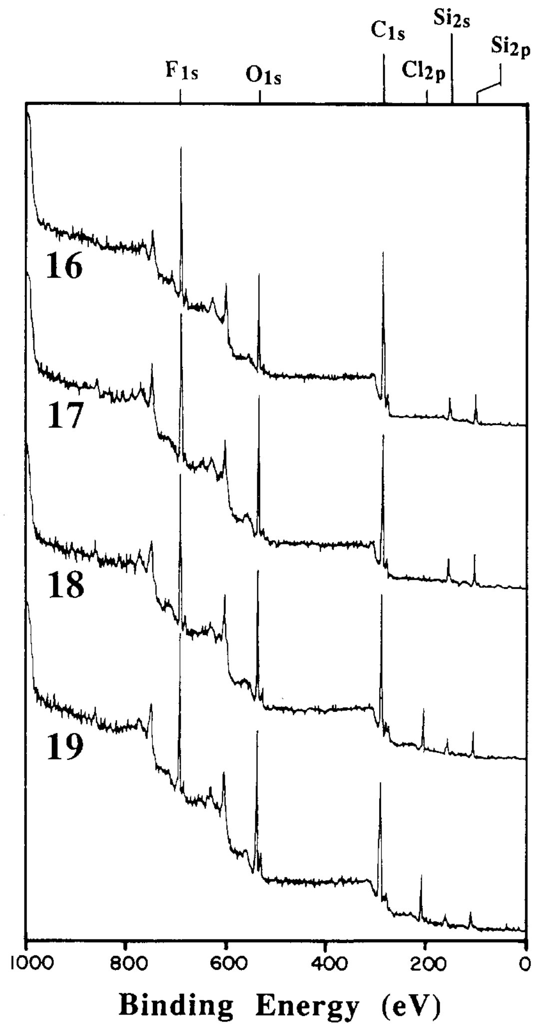
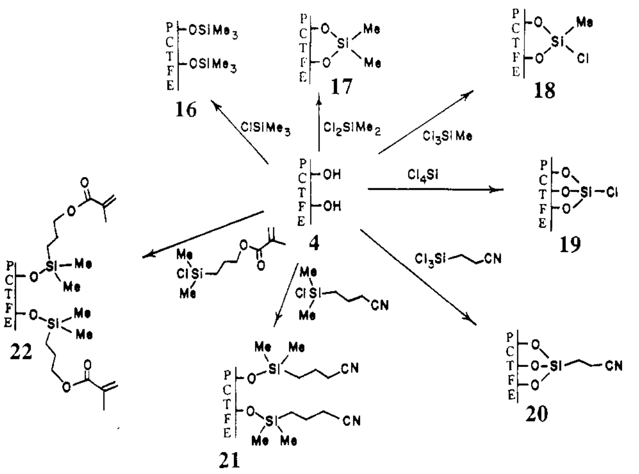


Figure 12. XPS spectra of **16**, PTCFE-$OSiMe_3$, **17**, PCTFE-$(O)_2SiMe_2$, **18**, PCTFE-$(O)_2SiMe(Cl)$, and **19**, PCTFE-$(O)_3SiCl$.

Scheme IV



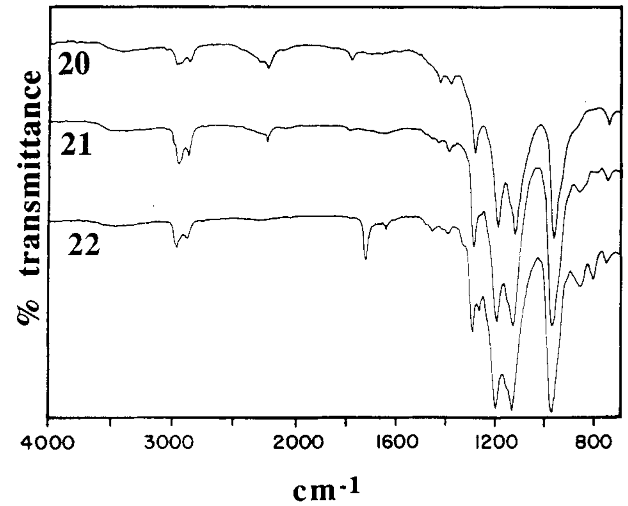


Figure 13. ATR IR spectra of **20**, PCTFE-$(O)_3SiCH_2CH_2CN$, **21**, PCTFE-$OSi(Me)_2CH_2CH_2CH_2CN$, and **22**, PCTFE-$OSi(Me)_2CH_2CH_2CH_2OC(O)C_3H_5$.

ature for 40 and 48 h, respectively, to yield **18** and **19**. These structural assignments were made on the basis of XPS atomic ratios and indicate the average surface composition. The observed Si:O and Si:Cl ratios for **18** are 1:2.1 and 1:0.6, respectively, indicating that some PCTFE-$(O)_3SiMe$ is likely present as well as PCTFE-$(O)_2SiClMe$. The observed Si:O and Si:Cl ratios for **19** are 1:3 and 1:1, respectively, indicating that an average of three Si–Cl bonds reacts to give PCTFE-$(O)_3SiCl$. As is the case for adipoyl chloride, hexamethylene diisocyanate, and Cl_2SiMe_2, these multifunctional reagents react multiply. Surfaces **17**, **18** and **19** exhibit somewhat high silicon and oxygen concentrations. This may be due to siloxane formation due to adventitious water. The ATR IR spectra of **18** and **19** (Figure 11) support the structural assignments: **18** displays four bands characteristic of Si(Me)Cl (2957, 1269, 864, 795 cm^{-1}); **19** shows only methylene bands (2959, 2886 cm^{-1}). **18** and **19** were too hygroscopic to obtain meaningful contact angle data.

Functionalized silanes can also be reacted with **4** to incorporate new functional groups onto the surface. $Cl_3SiCH_2CH_2CN$, $Cl(Me)_2SiCH_2CH_2CH_2CN$, and $Cl(Me)_2SiCH_2CH_2CH_2OC(O)C_3H_5$ react to form **20**, **21**, and **22**. Surface **20** exhibits high silicon and oxygen concentrations which is perhaps due to siloxane formation. XPS indicates that the reaction to form **21** was not brought to completion. ATR IR and XPS data are shown in Figures 13 and 14.

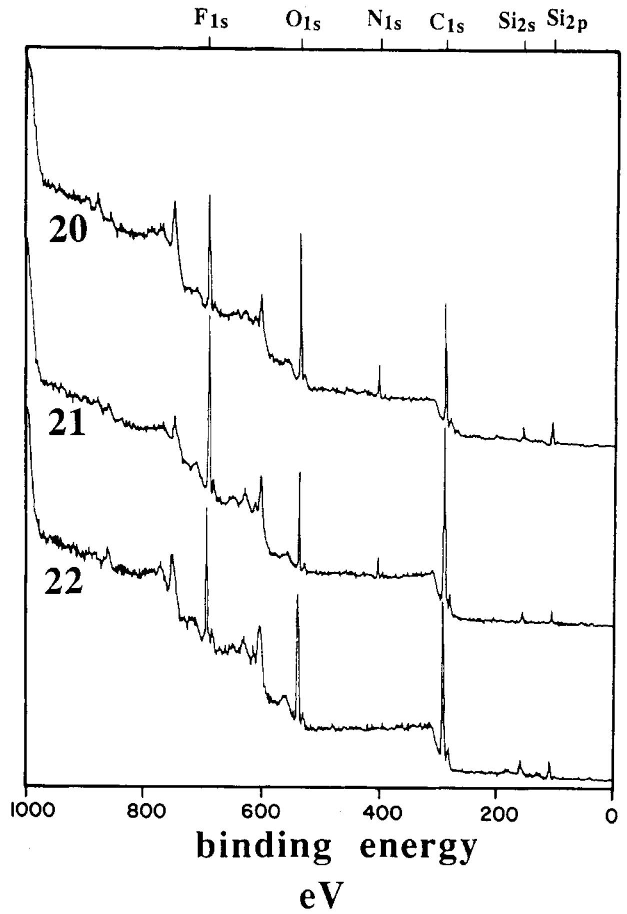
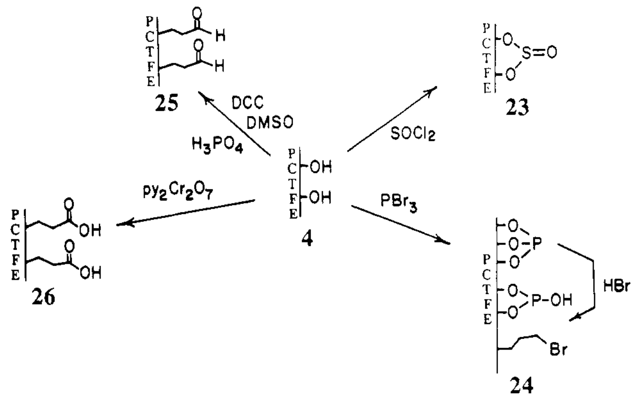


Figure 14. XPS spectra of **20**, PCTFE-$(O)_3SiCH_2CH_2CN$, **21**, PCTFE-$OSi(Me)_2CH_2CH_2CH_2CN$, and **22**, PCTFE-$OSi(Me)_2CH_2CH_2CH_2OC(O)C_3H_5$.

Scheme V



Reaction of PCTFE-OH with Thionyl Chloride and Phosphorous Tribromide. In initial attempts to prepare surfaces PCTFE-Cl (**13**) and PCTFE-Br (**14**), **4** was reacted in THF at room temperature with thionyl chloride (for 24 h) and phosphorous tribromide (for 12 h) (Scheme V). The expected products were not obtained. Reaction with thionyl chloride produced the sulfite PCTFE-$(O)_2SO$ (**23**). Contact angles are $\theta_A/\theta_R = 82°/50°$. The ATR IR spectrum (Figure 15) exhibits the OS(O)O bands (1194, 970 cm^{-1}) and two methylene bands (2955, 2890 cm^{-1}). The XPS spectrum (Figure 16) shows the sulfur photoelectron lines (S_{2s} at 238 eV, S_{2p} at 174 eV). The observed atomic ratios are consistent with the sulfite: less than 1% of the atomic composition is Cl. Treatment of **23** with water removes the chlorine and lowers the receding contact angle by 4–7°, indicating that the chlorine is likely present as the chlorosulfite. Reaction with PBr_3 yields a surface (**24**)

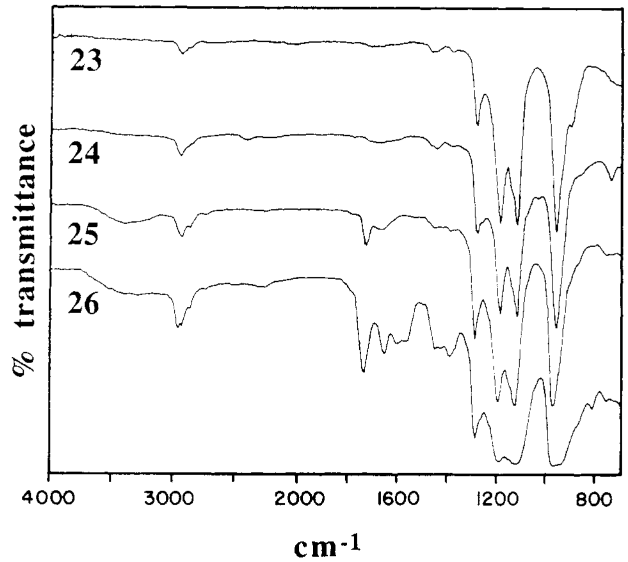


Figure 15. ATR IR spectra of **23**, PCTFE-(O)$_2$SO, **24**, PCTFE-OH/PBr$_3$, **25**, PCTFE-CHO, and **26**, PCTFE-COOH.

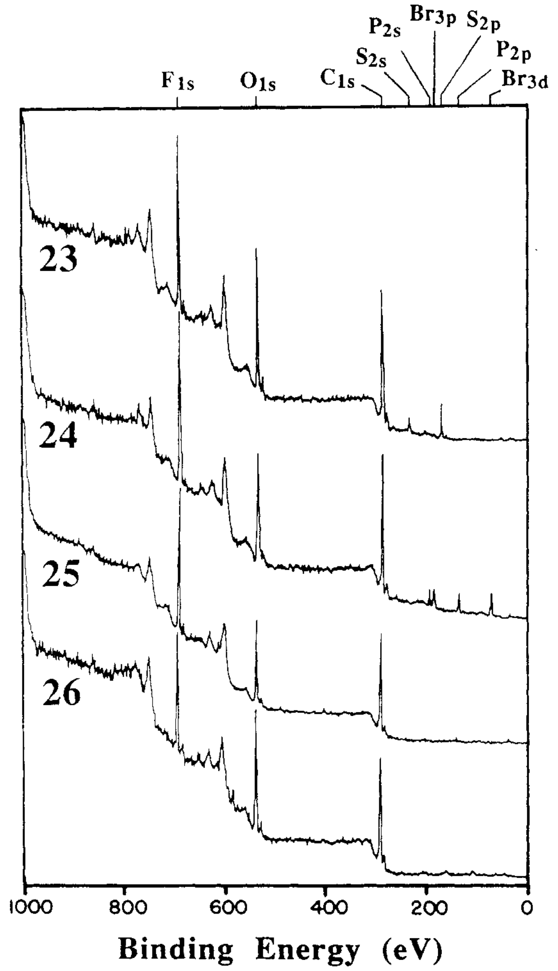


Figure 16. XPS spectra of **23**, PCTFE-(O$_2$)SO, **24**, PCTFE-OH/PBr$_3$, **25**, PCTFE-CHO, and **26**, PCTFE-COOH.

which analyses to be a mixture of products. The ATR IR spectrum (Figure 15) indicates that the O–H bands have reacted, and bands due to P–O–H (2427 cm^{-1}), P–O–C (1267 cm^{-1}), and methylenes (2961, 2903, 2855, 745 cm^{-1}) are present. The XPS spectrum (Figure 16) displays photoelectron lines due to P$_{2s}$ (197 eV), Br$_{3p3/2}$ (189 eV), P$_{2p}$ (140 eV), and Br$_{3d}$ (76 eV). The atomic ratios of Br:P:O are 1:2:6. Treatment of **24** with water does not reduce the bromine concentration, indicating that the bromine is not bonded to phosphorus but to carbon. The structure we proposed for **24** arises from phosphite formation and subsequent partial reaction with the HBr produced.

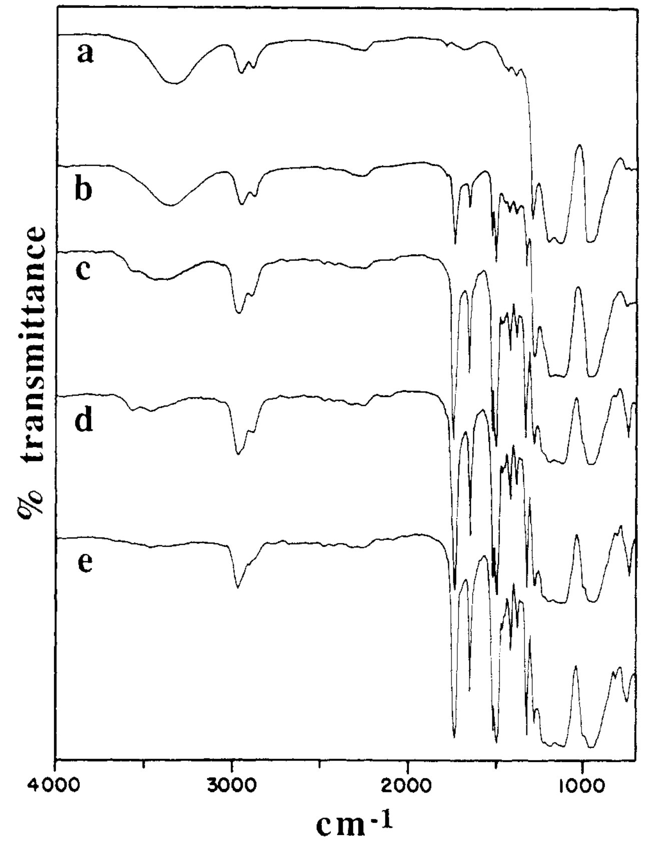


Figure 17. ATR IR spectra for the product film surfaces from the reactions of **4** with ClC(O)C$_6$F$_5$ in THF at room temperature for 0 h (a), 12 h (b), 24 h (c), 48 h (d), and 24 h in the presence of pyridine (e).

Oxidation of PCTFE-OH to PCTFE-CHO and PCTFE-COOH. Oxidation of **4** with Moffatt's reagent[21,22] (dicyclohexyl carbodimide, anhydrous H$_3$PO$_4$, DMSO) at room temperature for 24 h yields the aldehyde PCTFE-CHO (**25**). This reaction was not complete; alcohol functionality is present in **25**. Reaction with pyridinium dichromate in DMF at room temperature for 24 h yields the carboxylic acid (PCTFE-COOH (**26**)). The ATR IR spectrum of **25** shows characteristic aldehyde bands (2730, 1725 cm^{-1}) and of **26** shows a broad O–H band (3381 cm^{-1}) and a carbonyl band (1736 cm^{-1}) indicative of COOH (Figure 15). Contact angles are θ_A/θ_R = 80°/30° for **25** and 68°/12° for **26**. XPS spectra (Figure 16) and atomic ratios are consistent with these transformations.

Kinetics of the Reaction of PCTFE-OH with Pentafluorobenzoyl Chloride Monitored at Different Depths. To gain insight into the surface reactions of PCTFE-OH, the experiments described in this section were designed and carried out. **4** was treated with pentafluorobenzoyl chloride in THF at room temperature, and the reaction progress was monitored by contact angle, XPS, and ATR IR after 12-, 24-, and 48-h reaction. Contact angle assays the outer few angstroms, XPS assays the outer few tens of angstroms, and ATR IR assays the entire modified region. These experiments distinguish between a surface-selective reaction (reaction in the contact angle and XPS sampling regions will be complete before reaction in the ATR IR sampling region) and a homogeneous reaction (reaction will proceed at an equal rate in each sampling region). The results of contact angle and XPS atomic concentration are listed in Table I. The ATR IR spectra are displayed in Figure 17. Both contact angles

Table I
Contact Angle and XPS Atomic Concentration Data for Reactions of 4 with Pentafluorobenzoyl Chloride

reactn conditns	contact angles		atomic concns		
	θ_A	θ_R	C	F	O
0 h	67	17	68.8	16.3	14.9
12 h	83	34	61.1	25.1	13.7
24 h	90	55	56.3	32.2	11.5
48 h	91	57	56.0	33.4	10.7
24 h[a]	94	62	55.6	33.8	10.6

[a] In the presence of pyridine.

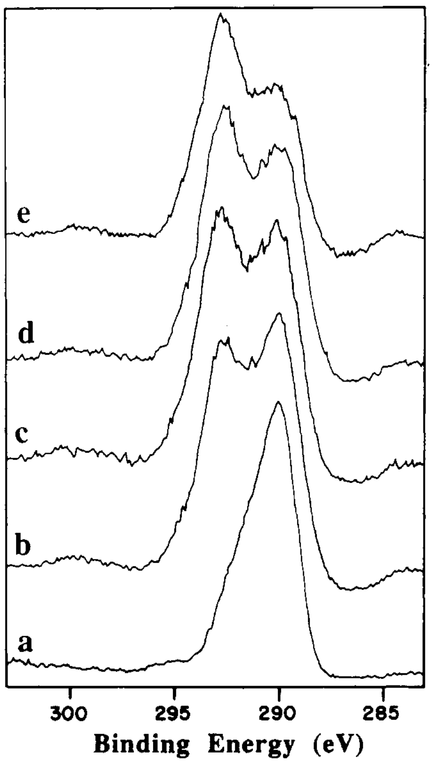


Figure 18. C_{1s} regions of XPS spectra for the product film surfaces from the reactions of 4 with $ClC(O)C_6H_5$ in THF at room temperature for 0 h (a), 12 h (b), 24 h (c), 48 h (d), and 24 h in the presence of pyridine (e).

and XPS atomic concentrations change until the reaction is complete as judged by IR spectra. The ATR IR spectra show that the intensity of the O—H band corresponding to the starting material decreases, and the intensity of the C=O band corresponding to the product increases as the reaction progresses. The C_{1s} regions of XPS spectra (Figure 18) illustrate that the photoelectron line at 293.0 eV which is due to the product increases relative to the 290.5 eV line which is due to both starting material and product throughout the reaction. We have obtained similar but less complete kinetics data for most of the reactions described in this paper as each reaction was monitored to give maximum conversion with the minimum reaction time. These observations clearly indicate that reaction occurs at approximately equal rates in each sampling region, that is reaction is equally probable for any hydroxyl group in 4 irrespective of its distance from the surface. This suggests that diffusion into the modified surface is fast relative to reaction. The ease with which excess reagents can be washed from reacted films also indicates a facile partitioning of reagents between solvent and modified polymer.

Reactions of PCTFE-OH (~50 Å). Each of the reactions discussed thus far was performed on PCTFE-OH containing a modified layer of ~1500-Å thickness to allow ATR IR analysis. Three reactions were carried out on PCTFE-OH which was prepared to have a ~50 Å thick modified surface (−78 °C, 30 min).[9] The trichloroacetyl ester was prepared, and the *p*-toluenesulfonate was prepared and displaced with bromide as described above. XPS and contact angle analyses indicate that the same reactions occur. The only bands observable by ATR IR are very weak absorbances due to the trichloroacetate carbonyl (1769 cm^{-1}) and the SO_2 asymmetric stretching (1360 cm^{-1}). The UV–vis spectrum of PCTFE-OTs (~50 Å) shows intense peaks at 224 and 253 nm, indicating the presence of the *p*-toluenesulfonyl group. These absorbances disappear when the tosylate is displaced with Br^- to give PCTFE-Br.

Summary and Conclusions

The hydroxylated surface of poly(chlorotrifluoroethylene) (PCTFE-OH) is chemically versatile. Reactions in which the nucleophile is attached to the surface and the electrophile is in solution (most of the chemistry described) and in which the electrophile is attached to the surface and the nucleophile is in solution (the displacement reactions of PCTFE-OTs) proceed. Di- and poly-functional reagents tend to react multiply, even though a large excess of reagent is present in solution: at the site of reaction, there is a large excess of hydroxyl groups. Reactions proceed uniformly throughout the modified region of PCTFE-OH.

Acknowledgment. We are grateful to the Office of Naval Research and the University of Massachusetts Institute for Interface Science (supported by IBM) 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) A preliminary account of part of the work reported here has been published: Lee, K.-W.; McCarthy, T. J. *Macromolecules* **1987**, *20*, 1437.
(2) Clark, D. T.; Feast, W. J. *Polymer Surfaces*; Wiley-Interscience: New York, 1978.
(3) Feast, W. J.; Munro, H. S. *Polymer Surfaces and Interfaces*; Wiley: New York, 1987.
(4) Dias, A. J.; McCarthy, T. J. *Macromolecules* **1985**, *18*, 1826.
(5) Costello, C. A.; McCarthy, T. J. *Macromolecules* **1984**, *17*, 1592.
(6) Dias, A. J.; McCarthy, T. J. *Macromolecules* **1984**, *17*, 2529.
(7) Lee, K.-W.; McCarthy, T. J. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1987**, *28*(2), 10.
(8) Lee, K.-W.; McCarthy, T. J. *Macromolecules* **1988**, *21*, 309.
(9) Dias, A. J.; McCarthy, T. J. *Macromolecules* **1987**, *20*, 2068.
(10) Costello, C. A.; McCarthy, T. J. *Macromolecules* **1987**, *20*, 2819.
(11) Plueddemann, E. P. *Silane Coupling Agents*; Plenum: New York, 1982.
(12) Leyden, D. E., Ed. *Silane Surfaces and Interfaces*; Gordon and Breach: New York, 1986; Vol. 1.
(13) Wrighton, M. S. *Science (Washington, D.C.)* **1986**, *231*, 32.
(14) Sander, L. C.; Wise, S. A. *Anal. Chem.* **1984**, *56*, 504.
(15) There is a large body of work on the surface modification of polymers containing hydroxyl groups, e.g. poly(vinyl alcohol), cellulose. For examples, see ref 23–26. These materials are not appropriate for surface studies of the type reported here. They interact extensively with polar solvents (swell, dissolve) are not chemically resistant, and the derivatized materials contain unreacted hydroxyl groups that make analyses difficult. We found[26] that it is difficult to control the extent of these reactions.
(16) Calculated XPS atomic ratios for PCTFE-OH and its derivatives are based on the analysis of PCTFE-O*P* (3). Justification for this is given in the text.
(17) Bonafini, J. A.; Dias, A. J.; Guzdar, Z. A.; McCarthy, T. J. *J. Polym. Sci., Polym. Lett.* Ed. **1985**, *23*, 33.
(18) Small mass losses were observed when modified samples were stored in THF (the principal reaction solvent for this work). PCTFE-$OSO_2C_6H_4$-*p*-CH_3 (~50 Å) was stored in THF at room temperature for 48 h. The absorbance at 224 nm de-

creased by 20%, indicating that ~10 Å of the modified layer dissolved.

(19) Kolb, B. U.; Patton, P. A.; McCarthy, T. J. *Polym. Prepr. (Am. Chem. Soc., Div.* Polym. *Chem.)* 1987, *28*(2), 248. This paper presents an extreme case of steric requirements: polystyryllithium, a secondary benzylic lithium reagent, reduces PCTFE (the first step of eq 1) but does not add to the difluoroolefin.

(20) This is based on estimating that the density of the modified layer of **4** is 1 g/mL.

(21) Pfitzner, K. E.; Moffatt, J. G. *J. Am. Chem. Soc.* **1965**, *87*, 5661.

(22) Fenselan, A. H.; Moffatt, J. G. *J. Am. Chem. Soc.* **1966**, *88*, 1762.

(23) Taniguchi, M.; Samal, R. K.; Suzuk, M.; Iwata, H.; Ikada, Y. *ACS Symp. Ser.* **1982**, No. *187*.

(24) Caro, S. V., Jr.; Sung, C. S. P.; Merrill, E. W. *J. Appl. Polym. Sci.* **1976**, *20*, 3241.

(25) Geblein, C. G.; Burnfield, K. E. *ACS Symp. Ser.* **1980**, *No. 121*, 83.

(26) Bonafini, J. A.; McCarthy, T. J. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1985**, *26*(1), 178.

Stereoselective Hydrolysis of Amino Acid Esters in Branched or Linear Poly(ethylenimine) Derivatives

Mamoru Nango,* Yoshiharu Kimura, Yasuji Ihara,† and Nobuhiko Kuroki

Department of Applied Chemistry, College of Engineering, University of Osaka Prefecture, Sakai, Osaka 591, Japan. *Received August 11, 1987*

ABSTRACT: The viscosity behavior of modified poly(ethylenimine) derivatives and fluorescence behavior of sulfonated fluorophore and binding behavior of sulfonated dye in branched or linear poly(ethylenimine) derivatives showed characteristics of the structural nature of the polymers. Stereoselective hydrolysis of chiral substrates was examined in branched or linear poly(ethylenimine) derivatives with covalently linked dipeptide-containing histidine. A high stereoselective effect, $k_L/k_D = 3.6$, is observed. Added copper ions influenced both the rate and stereoselective ratio as catalyzed by the polymers with covalently linked active groups, depending on the nature of the polymers. A large rate enhancement and a stereoselective preference also are exhibited in the hydrolysis as catalyzed by *N*-decanoyl-L-histidine (I) or a dipeptide containing an L-histidyl residue (II) in the environment of branched or linear poly(ethylenimine) domain. The dipeptide catalyst revealed the highest stereoselectivity, $k_L/k_D = 8.6$, in a linear poly(ethylenimine) derivative. The effect of the substrate structure influenced both the rate constant and stereoselective ratio in the hydrolyses by the modified poly(ethylenimine) derivatives.

Introduction

Developments in the area of synthetic macromolecular catalysts with enzymelike behavior are impressive.[1-4] However, there has been little study of stereochemical effect with synthetic macromolecular catalysts although the stereoselective preference is one of the most important properties in many enzymatic actions.[5-13] Our laboratory has been involved in the stereochemical effect on the catalysis in macromolecular systems as models for enzymatic reactions.[14]

In the previous article,[14a] we first observed stereoselective preference of amino acid *p*-nitrophenyl esters hydrolysis by branched poly(ethylenimine)s with optically active histidine moieties. Similar results have been reported by others with imidazole-containing polymers.[6,7] Following in this direction, this paper describes a high stereoselective effect in the hydrolysis of chiral esters by modified poly(ethylenimine) derivatives with a covalently linked dipeptide substituent containing a histidyl residue.[15] Furthermore, this paper describes the results of the catalytic activities of chiral ester hydrolysis in linear or branched poly(ethylenimine) domains.[16] The results of quarternization of branched poly(ethylenimine) and of the addition of surfactants on the kinetics of optically active ester hydrolysis in the branched poly(ethylenimine)s were reported previously,[14b] indicating that the rate and stereoselectivity are remarkably enhanced in the presence of quaternized branched poly(ethylenimine) derivatives. However, the branched poly(ethylenimine) has several kinds of amino groups which occasionally made the behavior of catalysis puzzling. In contrast, linear poly(ethylenimine) has only secondary amino groups on the polymer chain and this provides a simpler local macromolecular environment in aqueous solution than does the branched polymer.

A comparison of rate constants and stereoselectivity of the catalyst in the linear or branched polymer domains provides some insight into the influence of local macromolecular environment on the behavior of the imidazole nucleophile.

Experimental Section

A Jasco ORD/UV-5 spectropolarimeter was used to measure specific rotation, $[\alpha]_D$, at room temperature.

Branched poly(ethylenimine) (PEI) and linear poly(ethylenimine) ($\overline{\mathrm{PEI}}$) with an average molecular weight of about 50 000 were gifts from Professor I. M. Klotz (obtained from Dow Chemical Co.). These materials were purified by ultrafiltration in an Amicon ultrafiltration apparatus, using a Toyo Roshi UK-50 ultrafilter. *N*-Decanoyl-L-histidine (I) was prepared and purified by standard methods. CBZ-L-Leu-L-His (II) was prepared by the reaction of the *N*-hydroxysucciniimide ester of *N*-[(benzoyloxy)carbonyl]-L-leusine with L-histidine (Anal. Found: C, 59,30; H, 6.60; N, 13.20. Calcd: C, 59.68; H, 6.52; N, 13.92; mp 121–122 °C; $[\alpha]_D = +7.3°$; 80% EtOH–H_2O).[17] Lauryl iodide was distilled before use [bp 117 °C (1.1 mmHg)]. 1,8-Bis(dimethylamino)naphthalene, or "proton sponge" (from Aldrich Co.), was recrystallized from ethanol–water. 1-Ethyl-3-(3-(dimethylamino)propyl)carbodiimide (Sigma Chemical Co.), L-histidine methyl ester, $CuCl_2$ (Nakarai Chemical Co.), lauryl bromide, and *N*-(2-bromoethyl)phthalimide (Tokyo Kasei Co.) were used without further purification. The substrate *p*-nitrophenyl esters of L-*N*-carbobenzoxyalanine (CBZ-Ala) and L-*N*-CBZ-phenylalanine (CBZ-Phe) (from Sigma Chemical Co.) were used without further purification. The preparation of D-CBZ-Ala nitrophenyl ester has been described previously.[14b] The other substrates, D- and L-*N*-(methoxycarbonyl) (MOC)-Phe and D-CBZ-Phe were

---

* To whom all correspondence should be addressed.

† Present address: Yamaguchi Women's University, Sakurabatake, Yamaguchi 753, Japan.

0024-9297/88/2221-2330$01.50/0