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Surface-Selective Introduction of Specific Functionalities onto Poly(tetrafluoroethylene)[1]

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ABSTRACT: Exposure of poly(tetrafluoroethylene) film samples to Me$_2$SO solutions of the potassium salt of benzoin dianion renders metallic gold-colored, air-sensitive film samples. The color and property changes of the film are due to a carbonaceous reduction product, the thickness of which can be controlled by the duration of the exposure to benzoin dianion. Reduced layers of ca. 150–20 000 Å have been prepared. The chemical structure of the carbonaceous product is complex: it is a cross-linked polymeric carbon containing carbon–carbon single, double, and triple bonds, fluorine and hydrogen bound to sp^2 and perhaps sp^3 carbon, and a small amount of oxygen. Reduced film samples react with a range of reagents which are reactive toward unsaturation. Strong oxidants completely remove the reduced layer. Chlorine and bromine react readily, turning gold-colored films white and pale yellow, respectively. The reduced layer can be used as a reactive "handle" to incorporate hydroxyl, amino, and carboxylic acid functionalities on the surface of poly(tetrafluoroethylene): Hydroboration followed by oxidation introduces hydroxyl groups. Maleic anhydride adds radically and can be hydrolyzed to carboxylic acids. Substitution reactions of brominated films introduce amino groups.

Introduction

Modification of the chemical composition of polymer surfaces is important to a range of materials applications.[3] We are concerned with modified polymer surfaces at the functional group level and wish to answer the questions: how does the location of polymer surface functional groups at the polymer–reactive environment interface affect functional group reactivity? Can interface conditions (solvent in contact, temperature) be manipulated to control functional group chemistry? Can we use standard functional group manipulations to regulate surface properties of the polymer, in particular adsorption (of other polymers from solution), wetting, and adhesion (to metals or standard adhesives)? To address these questions we have been developing methods for introducing polar organic functionalities onto the surfaces of chemically resistant polymers.[4,5] Because these polymers are resistant to most reagents, a range of reactions can be directed at the surface functionality, not further modifying the bulk of the polymer. This paper reports two-step and multistep reactions for modifying the surface of poly(tetrafluoroethylene) (PTFE). The first step in each modification is the benzoin dianion reduction/cross-linking[1] of the PTFE surface. Throughout this manuscript this material is abbreviated PTFE-C. Subsequent reactions of this intermediate are devised to render cross-linked PTFE surfaces containing covalently attached chlorine, bromine, hydroxyl, amino, and carboxylic acid functionalities.

The work reported in this manuscript had four objectives: (1) to study the reaction of benzoin dianion with PTFE, particularly with regard to controlling the depth of reaction; (2) to characterize the chemical composition of the reduced layer (PTFE-C) to govern choices of subsequent reactions; (3) to introduce functionalities by using

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reagents expected to react with the reduced layer; (4) to characterize these modified PTFE surfaces.

The modified PTFE surfaces described here do not approach "two-dimensional arrays" of functional groups on polymer surfaces (the modified layers are thicker) as closely as do the modifications[6] of poly(vinylidene fluoride)[5] and poly(chlorotrifluoroethylene).[4] The thickness can, however, be controlled to as low as ca. 150 Å and the ultimate chemical resistance of PTFE makes these modified polymers attractive substrates for the study of problems in organic surface and interface science. The modification procedures reported here are significantly different than other reported reactions of PTFE. PTFE can be surface modified by flame[7] or plasma[8] treatments, which are corrosive and nonspecific in the functional groups introduced. PTFE can be reduced electrochemically or with strong reducing agents, particularly alkali metals, and there is considerable disagreement concerning the structure of the products: the black materials have been described as carbonaceous,[9,10] containing carbon and oxygen in the ratio of 1:0.3,[11,12] containing carbon radicals and carbon–carbon double bonds,[11] amorphous carbon interspersed with alkali-metal fluoride,[13] intercalated carbon,[14] polymeric carbon and alkali fluoride,[15] polymeric anion radicals,[16] and alkali fluoride doped poly(fluoroacetylene).[17]

Experimental Section

General. Virgin PTFE film (Commercial Plastics/Du Pont Teflon) and PTFE powder (Polysciences no. 1344, 500-μm chromatographic) were extracted (Soxhlet extractor) with THF for 24 h and dried under vacuum at 60 °C to constant weight (overnight). Benzoin (Aldrich) was recrystallized twice (constant melting point) from 95% ethanol and stored in a desiccator. Potassium *tert*-butoxide (Aldrich) was sublimed (at temperatures less than 165 °C to avoid degradation) and stored under nitrogen. Doubly distilled water (Gilmont still) was deoxygenated by purging with nitrogen; tetrahydrofuran (THF) (Fisher) was distilled from sodium benzophenone dianion; dimethyl sulfoxide (Me_2SO) (Aldrich) was distilled from P_2O_5; heptane (Fisher) was distilled from sodium benzophenone dianion (a small amount of diglyme was added to solubilize the dianion); pyridine was distilled from calcium hydride; dichloromethane (Fisher) was deoxygenated by purging with nitrogen; ethanol and methanol were refluxed over magnesium for 6 h and distilled under nitrogen. Maleic anhydride (Aldrich) was recrystallized twice from chloroform. Trifluoroacetic anhydride (Alfa) and pentafluorobenzaldehyde (Aldrich) were degassed by using three successive freeze–pump–thaw cycles and stored under nitrogen. Heptafluorobutyryl chloride (Alfa) was distilled at reduced pressure, trap to trap, and stored under nitrogen. AIBN (Aldrich) was recrystallized twice from methanol. Chlorine (Linde) was passed through a fine glass-fritted filter packed with glass wool; a 0.2 M Br_2 solution in CCl_4 was degassed by using three successive freeze–pump–thaw cycles and stored under nitrogen in the dark at 4 °C. Borane–tetrahydrofuran complex (1.0 M, Aldrich), potassium chlorate (Alfa), tetrabutylammonium bromide (Aldrich), hydrogen peroxide (30%, VWR), and carbonyldiimidazole (Sigma) were used without further purification. All reactions and manipulations of the extracted polymers (with the exceptions of the oxidation reactions) were performed under an atmosphere of prepurified nitrogen (Linde) which was further purified by passage through columns of BASF BTS catalyst and phosphorous pentoxide.

Gravimetric analyses were performed with a Cahn 29 electrobalance stabilized with a polonium source. PTFE samples of 1 cm × 1 cm were used. Film samples were stored in a Schlenk tube under vacuum until just prior to weighing. They were removed and held by one corner with tweezers and cleaned of dust by blowing freon over them and charge neutralized with a Zerostat antistatic instrument (Aldrich). The balance is accurate to ±0.2 μg; we estimate that our results are accurate to ±1 μg.

Elongation and Scanning Electron Microscopy. Tensile specimens were cut from "dogbone" patterns and reduced as described below for 12 h. Control samples and PTFE-C were elongated with an Instron TT-BM tensile tester to 300% elongation. Samples were gold sputter coated and secondary electron images were obtained by using an ETEC autoscan.

Solid-State CPMAS NMR. A 10 cm × 2 cm PTFE film sample was reduced as described below for 6 days, rolled up, and inserted into the spinner under nitrogen. The spectrum was recorded by using an IBM/Bruker 200-AF with solids accessory operating cross-polarized with matching Hartmann/Hann conditioning at 50 MHz. The cross polarization (contact time) was 2 ms. The protons were irradiated with a 90° pulse for 5 μs.

Contact angle measurements were obtained with a Rame-Hart telescopic goniometer and a Gilmont syringe. Water purified as described above was used; the pH varied from 5 to 7.[18] 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.

X-ray Photoelectron Spectroscopy (XPS). Spectra were obtained on a Perkin-Elmer–Physical Electronics 5100 spectrometer (Mg Kα source, 300 W). The pressure in the analysis chamber was 10^{-8} to 10^{-9} Torr during data acquisition. The chemical shifts reported are approximate as the samples charged differentially and were not charge neutralized. Survey spectra were recorded with a pass energy of 89.95 eV; high-resolution spectra were recorded with a pass energy of 7.44 eV. Samples were analyzed at two angles, 15° and 75° from the surface. The samples were mounted on the holder in a glovebox and transferred to the nitrogen-purged antechamber by using Schlenk techniques. Atomic composition data were determined by using the instrument's computer and programmed sensitivity values.

Attenuated Total Reflectance IR Spectroscopy (ATR IR). Spectra were obtained under nitrogen by using either a Perkin-Elmer 283 or an IBM 38 spectrometer and a 45° KRS-5 (thallium bromide iodide) crystal. Samples were reduced for 3 days in order to achieve a measurable thickness of PTFE-C.

Raman spectra were recorded on a Jobin-Yvon Ramanor H6 25 laser Raman spectrometer with a helium (6328 Å) laser. Samples were reduced for 2 days and transferred under nitrogen to glass tubes which were sealed under vacuum.

UV–vis spectra were recorded by using a Perkin-Elmer Lamda 3A spectrophotometer. Two PTFE film samples were selected that exhibited a flat base line when one was placed in the sample beam and one in the reference beam. One of the film samples was reduced for 8 h as described below and a spectrum was recorded in air with it in the sample beam and the unreacted one in the reference beam.

EPR spectra were obtained with a Varian E109 Spectrometer with a TE-102 cavity. Powder samples (100 mg) were reduced as outlined below for 24 h. The powder was packed under nitrogen in quartz EPR tubes which were sealed under vacuum.

Reaction of PTFE with Benzoin Dianion (PTFE-C). Benzoin (0.27 g, 1.3 mmol) in 5 mL of Me_2SO was added to a solution of 1.0 g (8.9 mmol) of potassium *tert*-butoxide in 30 mL of Me_2SO. The dark purple solution was transferred by cannula to a Schlenk tube containing 1 cm × 1 cm PTFE film samples which had been equilibrated to 50 °C. The reaction was allowed to proceed for the desired length of time. The solution was removed via cannula from the tube and the film was washed successively with 10 25-mL portions of water and then five 25-mL portions of THF. The samples were dried under vacuum to constant weight.

Oxidation of PTFE-C with $KClO_3/H_2SO_4$. Film samples of PTFE-C were oxidized with a sulfuric acid solution of potassium chlorate (1 g of $KClO_3$ in 50 mL of H_2SO_4) at room temperature in an open flask for gravimetric analysis and XPS. Oxidized film samples were washed with copious amounts of water and then THF and dried under vacuum at 60 °C to constant weight.

Air Oxidation of PTFE-C (PTFE-O). PTFE-C samples (24-h reduction) were exposed to ambient laboratory atmosphere for 2 weeks, turning from gold to brown to pale yellow. Before obtaining XPS spectra, films were washed with THF and then heptane and dried under vacuum overnight.

Chlorination of PTFE-C (PTFE-Cl). A PTFE-C film sample was equilibrated at 0 °C for 30 min under nitrogen in a Schlenk tube. The tube was flushed with chlorine for several minutes and then closed with a slight positive chlorine pressure and kept in the dark at 0 °C for 2 h. The film color turned from gold to white. The tube was flushed with nitrogen, washed with two portions of dichloromethane and then two portions of THF, and dried under vacuum overnight.

Bromination of PTFE-C (PTFE-Br). Fifteen milliliters of 0.2 M Br_2 in CCl_4 was introduced to a Schlenk tube containing a film sample of PTFE-C at 0 °C in the dark. After 11 h, the bromine solution was removed and the pale yellow film sample was rinsed with copious amounts of CCl_4, dichloromethane, and THF in that order and dried under vacuum overnight.

Hydroboration and Subsequent Oxidation of PTFE-C (PTFE-OH). Ten milliliters of 1.0 M borane in THF was introduced to a Schlenk tube containing a PTFE-C film sample at room temperature. After 12 h (the gold color of the film was discharged), the borane solution was removed and 10 mL of water was added. Ten milliliters of 3 M NaOH was introduced followed by the slow addition of 10 mL of 30% hydrogen peroxide. The tube was immersed in an ice bath for 3 h. The solution was then removed and the film washed with dilute NaOH, water, dilute HCl, water, THF, and heptane in that order and dried under vacuum overnight.

Reaction of PTFE-OH with Trifluoroacetic Anhydride (PTFE-$OCOCF_3$). A film sample of PTFE-OH was treated with 1 mL of trifluoroacetic anhydride in 9 mL of THF at room temperature overnight. The solution was removed and the film was rinsed with THF and then heptane and dried under vacuum overnight.

Reaction of PTFE-OH with Heptafluorobutyryl Chloride (PTFE-$OCOC_3F_7$). A film sample of PTFE-OH was treated with 1 mL of heptafluorobutyryl chloride and 1 drop of pyridine in 9 mL of THF at room temperature for 24 h. The solution was removed and the film sample was rinsed with methanol, THF, and then heptane and dried under vacuum overnight.

Reaction of PTFE-C with Maleic Anhydride and Subsequent Hydrolysis (PTFE-COOH). A film sample of PTFE-C was placed in a water-jacketed Schlenk tube with 0.50 g (5.1 mmol) of maleic anhydride, 0.15 g (0.9 mmol) of AIBN, and 5 mL of THF under nitrogen. The reaction mixture was photolyzed (254 nm) under nitrogen for 2 h at 12 °C in a Rayonet Photochemical Reactor. The solution was removed and the film sample was washed with five portions of THF and transferred to a Schlenk tube modified with a water jacket for reflux. Trifluoroacetic acid (0.5 mL) and 9.5 mL of water were added and the solution was heated to reflux for 24 h. The solution was removed and the film sample was washed with water, THF, and then heptane and dried under vacuum overnight.

Reaction of PTFE-COOH with Carbonyldiimidazole (PTFE-$COC_3H_3N_2$). A PTFE-COOH film sample was treated with a solution of 0.2 g (1.23 mmol) of carbonyldiimidazole in 10 mL of THF at room temperature overnight. The solution was removed and the film sample was washed with copious amounts of THF and then heptane and dried under vacuum overnight.

Preparation of PTFE-NH_2. Approximately 0.5 mL of ammonia was condensed at −78 °C onto sodium and then trap-to-trap distilled into a tube containing a PTFE-Br film sample at −196 °C. The tube was sealed under vacuum and allowed to warm to room temperature. Upon warming, the pale yellow film sample became purple/brown. The tube was maintained at room temperature for 7 h, after which time it was opened under nitrogen and the film sample was transferred to a Schlenk tube and washed with ethanol, THF, and then heptane and dried under vacuum overnight.

Reaction of PTFE-NH_2 with Pentafluorobenzaldehyde (PTFE-$N{=}CC_6F_5$). Pentafluorobenzaldehyde (0.5 mL) was diluted to 10-mL total volume with THF and transferred to a Schlenk tube containing a PTFE-NH_2 film sample. The reaction was allowed to proceed for 24 h, after which time the solution was removed and the film sample was washed with copious amounts of THF and then two portions of heptane and dried under vacuum overnight.

Preparation and Purification of Deuteriated Reagents. Benzoin-d_{12} was prepared from benzaldehyde-d_6 (ICN Biomedicals) via benzoin condensation in CH_3CH_2OD (ICN Biomedicals) according to a literature procedure.[19] Benzaldehyde-d_6 was extracted 3 times with saturated Na_2CO_3 in D_2O (Aldrich), dried over $MgSO_4$, and distilled at 10 mm. The fraction distilling at 66 °C was collected and stored under nitrogen. Me_2SO-d_6 (Aldrich) was distilled from calcium hydride at reduced pressure.

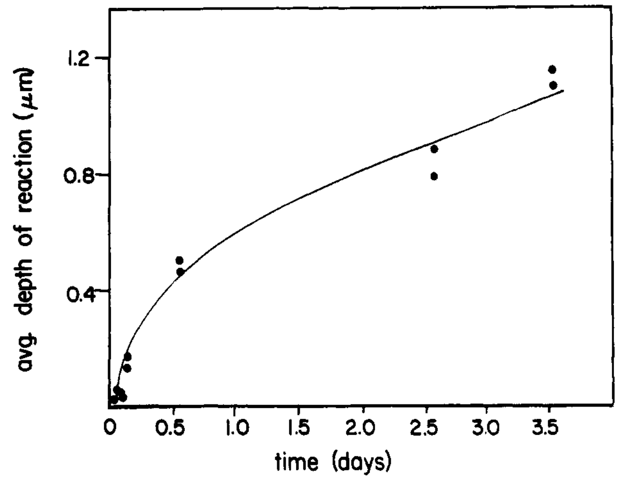


Figure 1. Gravimetric analysis. The data are average depths computed by using eq 1 from the masses of the virgin PTFE sample (M_V) and the reduced then oxidized film sample (M_O).

Results and Discussion

Reaction of PTFE with Benzoin Dianion in Me_2SO. When solid PTFE is exposed to Me_2SO solutions of the potassium salt of benzoin dianion (prepared from benzoin and potassium *tert*-butoxide) at 50 °C, a reaction takes place at and near the surface of the PTFE object. Control experiments with Me_2SO solutions of benzoin or potassium *tert*-butoxide alone under identical conditions render no reaction. The principal reaction which takes place involves electron transfer from benzoin dianion to PTFE and loss of fluoride from PTFE. This reaction is discussed in detail below. The use of benzoin dianion as a reducing agent has been reported.[20] The reduced product is called, throughout this paper, PTFE-C. PTFE film, powder, stirring bars, and Goretex all react with this reagent; most of the results reported here were obtained by using film samples, which are most suited for the analytical techniques. Short reaction times (less than 15 min) produce purple film samples; metallic gold-colored film samples are produced with longer reaction times. The gold color is due to absorbance/reflectance and not interference as evidenced by the morphology[1] and the fact that the color is independent of thickness (beyond a certain minimum) and sample roughness. The gold-colored surface is air sensitive; samples exposed to air (PTFE-O) show increased levels of oxygen by XPS and the presence of carbonyls and C–O bonds by ATR IR spectroscopy. When a PTFE film sample is weighed before and after reaction, a measurable amount of mass is lost, due to the loss of fluorine (see below). The reacted layer on the PTFE film can be completely removed oxidatively by using strong oxidants such as $KClO_3$ in H_2SO_4. This allows measurements of the mass of PTFE reacted and the thickness of the reacted layer. Figure 1 summarizes the effect of reaction time on the extent of reaction: the thickness of the PTFE-C layer can be conveniently controlled. PTFE-C samples with reduced layer thicknesses of 150 Å to 20 000 Å (2 μm) have been prepared. The depths of reaction reported in Figure 1 are *average* depths of reaction. The minimum and maximum are significantly different as the PTFE–PTFE-C interface is quite rough.[1] Equation 1 was used to calculate these

$$\text{depth} = \frac{M_V - M_O}{2(2.13)LW} \tag{1}$$

data; 2.13 is the density of PTFE; the factor 2 appears in

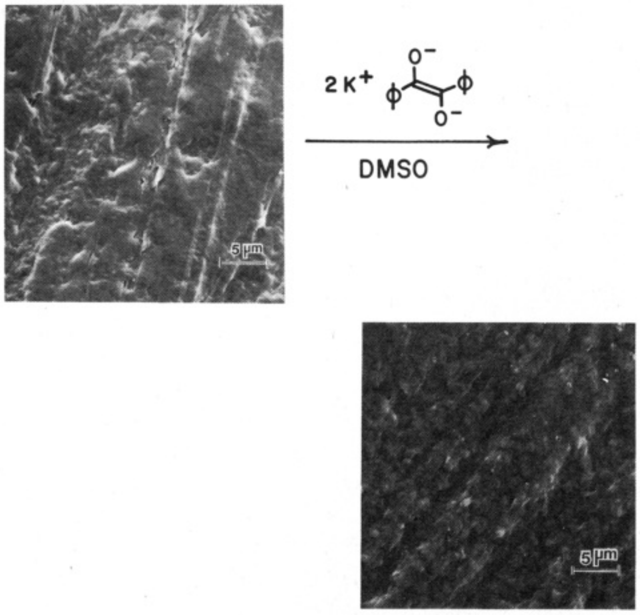
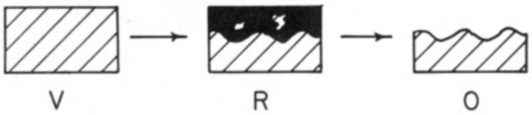


Figure 2. Scanning electron micrographs of PTFE and PTFE-C film samples indicating increased rugosity at the submicron level upon reaction.

the denominator because both sides of the film sample are reacted. M_V is the mass of the virgin film, M_O is the mass of the reduced-then-oxidized film sample, L is the sample length, and W is the sample width. Equation 2 is a graphic



(2)

representation of the reduction and oxidation reactions. V, R, and O indicate virgin, reduced, and reduced-then-oxidized samples, respectively. In that the reaction involves an electron transfer (which requires close contact between donor and acceptor[21]) from benzoin dianion solution to virgin PTFE, initially it was surprising that reaction occurs at distances greater than 10 000 Å from the solution–PTFE interface. This result is rationalized when the electronic conductivity of the product is considered.[22] The product conducts electrons from the solution down to the virgin PTFE. An alternative explanation is that PTFE-C is permeated by reactive solution. Both processes may be at play. It is difficult to draw conclusions from the slope changes of the plot in Figure 1: autocatalysis (due to increased interface area) and electron transport rates may cancel one another to an unpredictable extent.

The surface rugosity changes dramatically at the submicron level upon reduction: Figure 2 displays scanning electron micrographs of virgin and reduced (8 h, ca. 300 Å) PTFE. This change is likely due to contraction (and cross-linking—see below) as the surface layer loses a large percentage of its mass. Attempts at obtaining water contact angle data on PTFE-C also indicate increased roughness. Samples reacted for times greater than 30 min display very high (>150°) and unstable (the drop skips across the surface) advancing contact angles and 0° receding contact angles. These values are not indicative of the surface chemistry; reasonable contact angle data can be obtained from samples prepared with shorter reaction times.

It was possible to visualize the PTFE-C layer on the PTFE film sample because of their different tensile properties. Elongation (300%) of a sample reduced for 8 h produced a fractured "island-like" PTFE-C structure. PTFE film samples treated identically exhibited no changes of this sort. Figure 3 depicts the experiment and exhibits a scanning electron micrograph of the elongated region. This experiment suggests that PTFE-C is cross-linked and has tensile properties considerably different than PTFE.

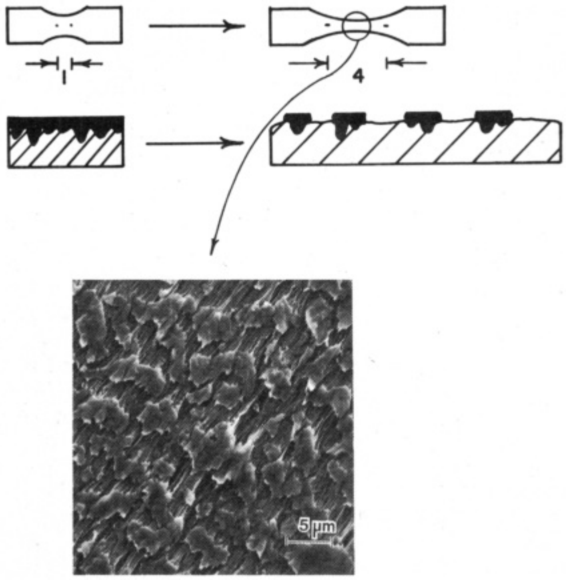


Figure 3. Graphic description of the tensile elongation (300%) of PTFE-C and scanning electron micrograph of the elongated sample.

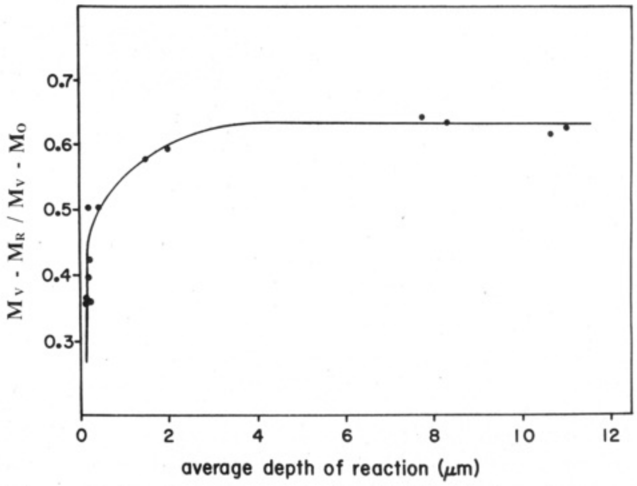


Figure 4. Fraction of mass lost by PTFE (that reacts) upon conversion to PTFE-C.

Chemical Analyses of PTFE-C. Quantitative information concerning the stoichiometry of the benzoin dianion reduction can be obtained from gravimetric analysis of the reactions depicted in eq 2 and used to help predict the structure of PTFE-C. The ratio of $M_V - M_R$ to $M_V - M_O$ is the fraction of mass lost by the PTFE that reacts to form PTFE-C. Figure 4 depicts these data for different reaction depths. After the stoichiometry levels off, PTFE loses over 60% of its mass on conversion to PTFE-C. If we assume that the only source of mass loss is loss of fluoride, three out of four fluorines are lost ($C_2F_4 \rightarrow C_2F$). Several points warrant mention: the unreacted "islands" depicted in Equation 2 bias the fluorine loss low, thus the structure of PTFE-C has a higher C/F ratio. These islands are expected by the nature of the reaction and we have observed small white particles in oxidation solutions which may be they. Incomplete reduction ($CF_2 \rightarrow CF$) does occur and is discussed below. PTFE-C contains both hydrogen

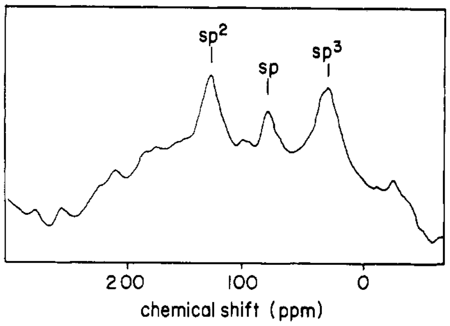


Figure 5. ^{13}C CPMAS NMR spectrum of PTFE-C sample reduced for 6 days.

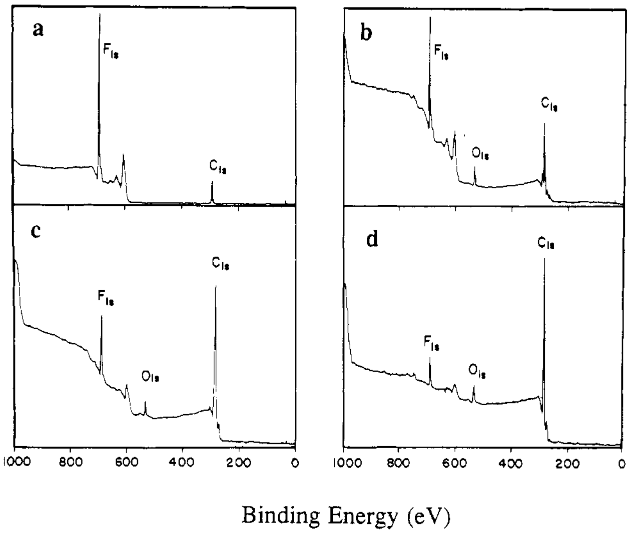


Figure 6. XPS survey spectra of PTFE reduction to various extents: (a) unreacted PTFE; (b) PTFE-C reduced 10 min (150 Å); (c) PTFE-C reduced 25 min (450 Å); (d) PTFE-C reduced 24 h (6000 Å).

and oxygen (discussed below), which also bias the fluorine loss low. Taken by itself, this "quantitative" information from gravimetric analysis is rather qualitative but is useful when combined with the other analyses, particularly for measuring reaction depths.

Several lucid pieces of information were obtained by ^{13}C CPMAS NMR spectroscopy of a PTFE-C sample reduced for 6 days. That a spectrum was obtained at all indicates that hydrogen is present in the sample. The spectrum (Figure 5) exhibits broad and poorly resolved signals due to sp^3 (δ 29.87), sp^2 (δ 130.36), and sp (δ 80.70) carbons. The broadness of these peaks can be attributed to the presence of paramagnetic species (observed by EPR) and dipolar interactions between ^{13}C and ^{19}F nuclei. Broad peaks of this sort have been observed in ^{13}C CPMAS of various coals.[23] The presence of tetrahedral carbon and double and triple bonds is indicated; the poor signal/noise precludes quantitation; however, each is an important feature.

EPR spectroscopy at −196 °C of a powder sample of PTFE-C reduced for 24 h indicates the presence of free mobile spins (singlet, $\Delta H = 9$ G, $g = 2.0030$). Signals of this type are observed for highly conjugated polymers such as polyacetylene[24] and poly(*p*-phenylenevinylene).[25]

XPS gives information on the outer ca. 40 Å of film samples. Although this is a small percentage of the PTFE-C thickness, it is the region of interest for surface chemistry and the technique gives useful information that could not have been obtained by another method. Figure 6 shows XPS survey spectra of PTFE (a), PTFE-C (10 min, b), PTFE-C (25 min, c), and PTFE-C (24 h, d). The spectra indicate the gradual loss of fluorine (F$_{1s}$, 696 eV) in the outer 40 Å which occurs while the reaction proceeds thousands of angstroms deep. The presence of oxygen is indicated and varies somewhat from sample to sample. This may be due to exposure during sample preparation and analysis, reaction with water in the workup, and/or reaction with *tert*-butoxide during the reaction (see below). Further information concerning the nature of the fluorine is obtained from high-resolution C$_{1s}$ spectra of the same samples. Figure 7 shows these spectra. The higher binding energy CF$_2$ signal (293 eV) is replaced by a lower binding energy signal (286 eV) due to the much less oxidized carbon in PTFE-C. Noteworthy is the fact that at longer reaction times the signal due to CF$_2$ completely disappears even though fluorine is still present (survey spectrum, Figure 7d). It must be present as CF, bound to sp^2 and/or sp^3 carbon. Indicated also, from comparison of Figures 6 and 7 is a stepwise reduction CF$_2$ → CF → C, the second step of which is slower than the first. The signals for CF$_2$ (293 eV) in Figure 7b,c are due to islands (or "peninsulas" extending from the virgin PTFE) in the outer 40 Å of PTFE-C which is 150 Å (Figure 7b) and 450 Å (Figure 7c) thick. The atomic composition of PTFE-C (reduced for 24 h) calculated from Figure 6d is CF$_{0.07}$O$_{0.07}$ (in addition hydrogen is present). Samples reduced for times greater than 24 h show increased amounts of oxygen present.

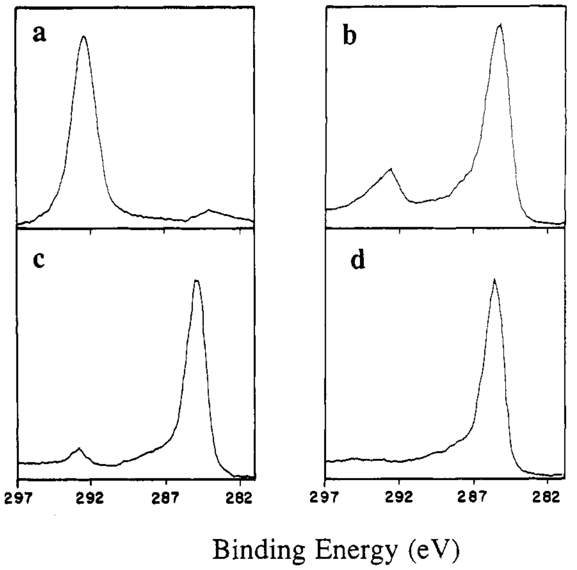


Figure 7. High-resolution C$_{1s}$ XPS spectra of PTFE reduction to various extents. See Figure 6 caption for details.

The combination of isotopic labeling and vibrational spectroscopy yielded further information concerning the structure of PTFE-C and determined the sources of the hydrogen present. Figure 8 shows FT ATR IR spectra of (a) PTFE, (b) PTFE-C prepared by using all hydrogen-containing reagents and solvents, (c) PTFE-C prepared as for (a) except that Me$_2$SO-d_6 was used as the reaction solvent, and (d) PTFE-C prepared as for (b) except that D$_2$O was used in the workup. The absorbances from 2960 to 2860 cm^{-1} which are present in each spectrum are due to aliphatic C–H stretching, principally due to *tert*-butoxy groups incorporated by reaction of *tert*-butoxide with reduced PTFE (Scheme I, below). The lower relative intensity of these absorbances in (c) (prepared by using Me$_2$SO-d_6) suggests that the solvent is also a source of this hydrogen. The absorbance at 3012 cm^{-1} is present in (b) and (d) but absent in (c); this is due to sp^2-C–H stretch and Me$_2$SO is the source of this hydrogen. This absorbance is shifted to 2220 cm^{-1} ($\nu_{\text{C–D}}$) in (c). The absorbances at 1008 cm^{-1} in (b) and (d) and 740 cm^{-1} in (c) are due to sp^2-C–H and sp^2-C–D out-of-plane bending. The absor-

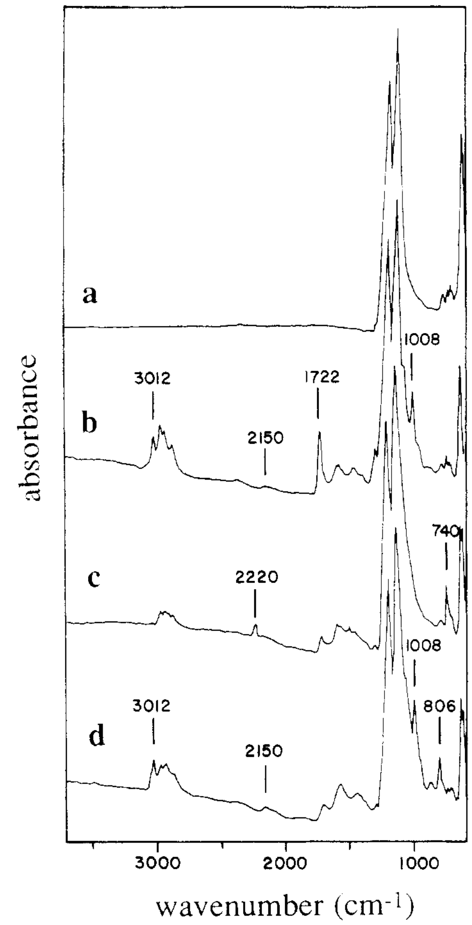


Figure 8. FT ATR IR spectra (KRS-5, 45°) of PTFE (a), PTFE-C (b), PTFE-C (Me_2SO-d_6) (c), and PTFE-C (Me_2SO-h_6, D_2O) (d). Film samples were reduced for 3 days.

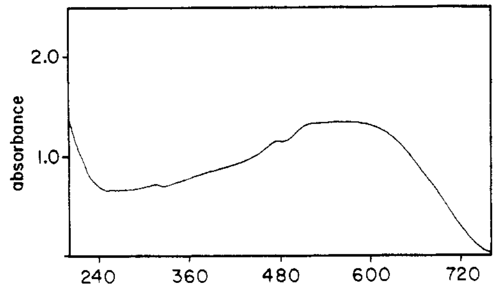


Figure 9. UV–vis spectrum of PTFE-C. A PTFE sample matched to give a flat base line with the PTFE sample used to prepare PTFE-C was placed in the reference beam.

bance at 806 cm^{-1} in (d) may be due to C–D bending (D_2O being the source of D) but this assignment is suspect as no absorbance due to C–D stretching is observed. The absorbance at 2150 cm^{-1} is due to C≡C; the absorbances from 1600 to 1400 cm^{-1} indicate skeletal vibrations of condensed aromatic-like carbon. We tentatively assign the absorbances at 1722 cm^{-1} to monofluorinated olefin C=C stretch.[26] The XPS data suggest that one should exist, but we cannot explain the relative intensities of this absorbance in (b)–(d). There was no indication of deuterium incorporation when benzoin-d_{12} was used.

Raman spectra were recorded by using red (6328 Å) excitation. The UV–vis spectrum exhibits a broad absorbance consistent with an extended conjugated π-system (Figure 9) and we emphasize that the Raman spectrum obtained with red excitation exhibits structural information concerning only a small percentage (the most highly conjugated) of PTFE-C.[26] The Raman spectra of PTFE-C and PTFE-C (Me_2SO-d_6) are exhibited in Figure 10. Spectrum a is that of PTFE-C; we make the following assignments: 1003 (δ_{C-H}), 1100 (ν_{C-C}), 1476 ($\nu_{C=C}$), 2176 ($\nu_{C\equiv C}$ + overtone δ_{C-C}), 2554 (combination $\nu_{C-C} + \nu_{C=C}$), 2942 cm^{-1} (overtone $\nu_{C=C}$). Spectrum b is that of PTFE-C (Me_2SO-d_6); we assign the following: 740 (δ_{C-D}), 857 (ν_{C-C}), 1197 (δ_{C-C-D}), 1382 ($\nu_{C=C}$), 1715 (overtone ν_{C-C}), 2058 (combination $\nu_{C-C} + \delta_{C-C-D}$), 2239 ($\nu_{C\equiv C}$ + combination $\nu_{C-C} + \nu_{C=C}$), 2580 combination ($\nu_{C=C} + \delta_{C-C-D}$), 2755 cm^{-1} (overtone $\nu_{C=C}$). The lines at 1100 and 1476 cm^{-1} in PTFE-C and 1382, 1197, and 857 cm^{-1} in PTFE-C (Me_2SO-d_6) are intense due to resonance enhancement similar to that seen in polyacetylene,[27-29] polydiacetylene,[30] and other highly conjugated materials. The frequency shifts on deuteriation indicate that hydrogen (deuterium) is bonded to these extended conjugated segments. No quantitative information can be interpreted from these Raman data in light of the resonance enhancement, the excitation (discussed above), and the inherent nature of the Raman process; nonetheless the features observed are present to some extent. There was no indication of deuterium incorporation when benzoin-d_{12} was used.

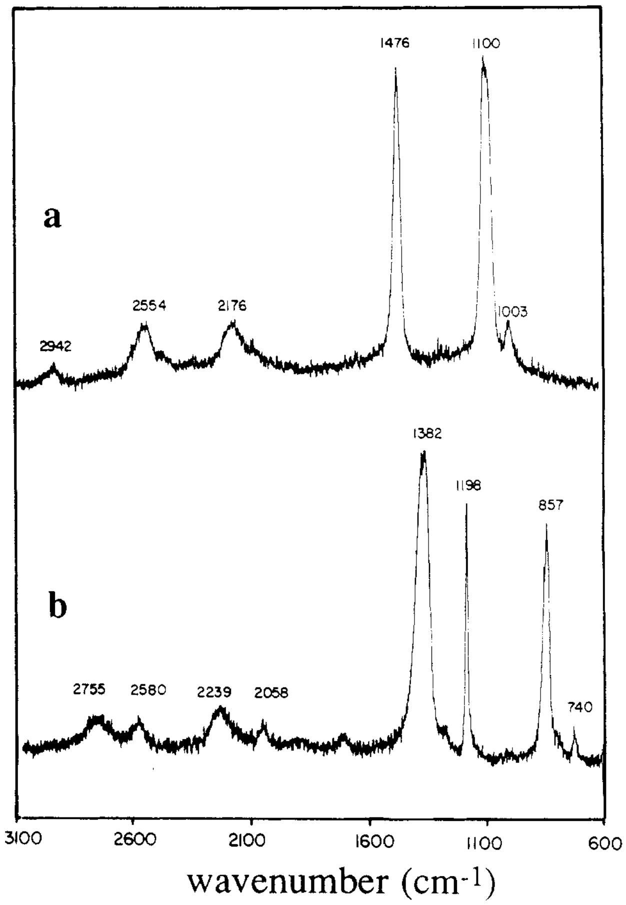
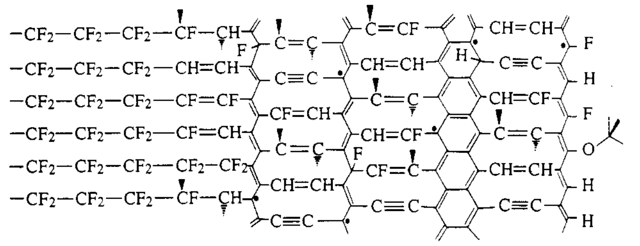


Figure 10. Raman spectra obtained with red (6328 Å) excitation of (a) PTFE-C and (b) PTFE-C (Me_2SO-d_6). Samples were reduced for 2 days.

The analyses, when scrutinized together, present a composite picture of PTFE-C. The major features of the structure include single, double, and triple bonds, extended conjugation, condensed aromatic-like cross-links, fluorine bound to sp^2 carbon, hydrogen bound to a polyacetylene-like structure, oxygen (from adventitious sources and as *tert*-butyl ethers), and free mobile spins. The importance of the reaction which incorporates *tert*-butoxy groups is difficult to assess. The samples prepared for IR

Chart I
Two-Dimensional Pictorial Representation Exhibiting Structural Features Present in PTFE-C



spectroscopy were reacted for 3 days which was necessary to observe non-PTFE absorbances. XPS data (small amounts of oxygen) suggest that this reaction is not as important for shorter reaction times. The XPS data (at different reduction times) suggest a gradient structure of highly reduced carbonaceous material at the surface, less reduced (containing more fluorine) at greater depths and virgin (unreacted) PTFE in the bulk. These observations are depicted in Chart I. This two-dimensional pictorial representation is meant to convey only a qualitative image and expresses nothing concerning homogeneity (the material may be homogeneous or quite mosaic), relative amounts of specific features, or expanse of the reduced layer. A plausible reaction scheme describing the transformation of PTFE to PTFE-C is exhibited in Scheme I. These analyses and their interpretation should not be construed as a detailed structure analysis. Further studies such as radioisotope labeling (to quantitate hydrogen incorporation and identify oxygen sources), scattering experiments (to determine crystalline order, if any), and Rutherford backscattering spectroscopy (to quantitate and confirm the gradient concept) would give useful structural information but would not have advanced us toward our objective of surface functionalization. From the standpoint of being interested in reactivity, we were content to have double and triple bonds as reactive intermediates and are satisfied in describing PTFE-C as carbonaceous.

Halogenation of PTFE-C (PTFE-Cl, PTFE-Br). Treatment of PTFE-C film samples (that had been reduced for 10 min) with chlorine vapor or bromine/CCl_4 produces changes consistent with formation of C–halogen bonds. PTFE-Cl is white; PTFE-Br is pale yellow. Film samples gain weight on halogenation and it is possible to calculate the C/halogen ratios in PTFE-Cl and PTFE-Br, assuming the weight lost on reduction is due only to loss of fluorine (qualifications of this assumption are discussed above) and weight gained on halogenation is due only to gain of halogen: PTFE-Cl has a C/Cl ratio of 1:1 (net reaction $CF_2 \rightarrow CFCl$). PTFE-Br has a C:Br ratio of 1.6:1 (net reaction of $CF_2 \rightarrow CBr_{0.63}$). High-resolution C_{1s} XPS spectra nicely reflect changes due to halogenation. Figure 11 exhibits spectra which show that bromination causes a shift of a component of the carbon peak to higher binding energy (more highly oxidized carbon) and chlorination renders a distinct shoulder on the high binding energy side (Cl being more electronegative than Br).

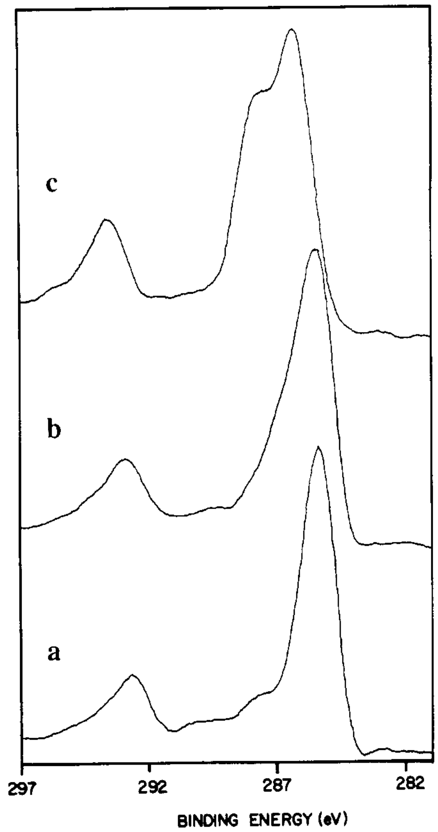


Figure 11. High-resolution C_{1s} XPS spectra for halogenation reactions of PTFE-C (reduced for 10 min): (a) PTFE-C; (b) PTFE-Br; (c) PTFE-Cl.

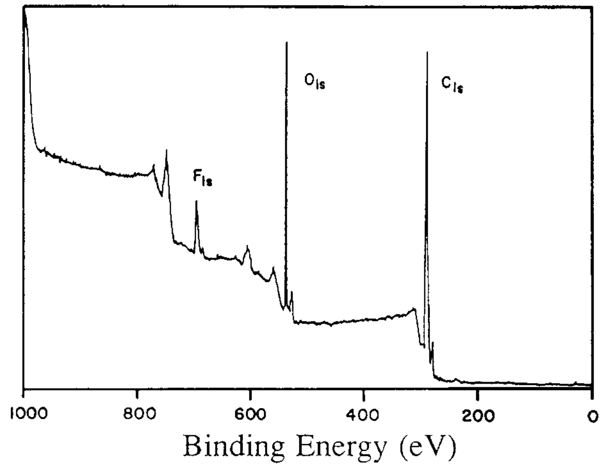


Figure 12. XPS survey spectrum of PTFE-OH prepared from PTFE-C (24-h reduction).

Table I
Contact Angle (Water) Data for PTFE-OH Synthesis

sample	θ_a	θ_r
PTFE	120°	89°
PTFE-C	114°	68°
PTFE-OH	62°	0°

Hydroboration and Subsequent Oxidation of PTFE-C (PTFE-OH). The reactivity of the unsaturation in PTFE-C was further exploited to introduce hydroxyl groups onto the PTFE surface. Treatment of PTFE-C film samples with borane–THF complex followed by oxidation with basic peroxide produces film samples (PTFE-OH) exhibiting spectra and properties consistent with the presence of hydroxyl groups. Contact angles of water on PTFE-OH are consistent with the presence of a polar functionality; Table I summarizes these data. The PTFE-C samples used for these analyses were prepared by reduction for 10 min. Samples reduced for longer times are too rough (discussed above) to obtain this type of data. The values reported in Table I are averages of at least six measurements taken at different locations on the sample and are estimated to be accurate to ±5°. The XPS survey spectrum (Figure 12) of PTFE-OH prepared from a PTFE-C sample reduced for 24 h shows an increased level of oxygen (compare with Figure 6) and gives a calculated atomic composition ratio for C/O of 3.4:1. ATR IR

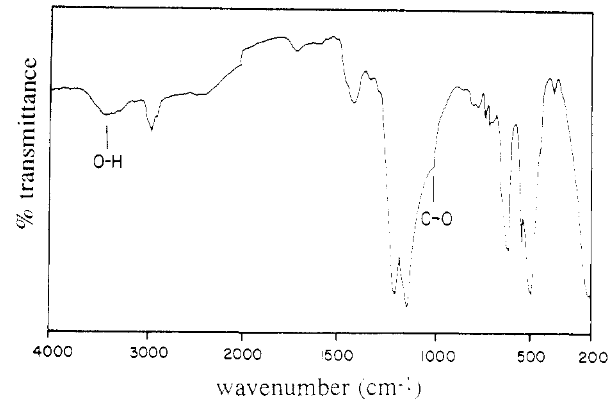


Figure 13. ATR IR spectrum (KRS-5, 45°) of PTFE-OH prepared from PTFE-C (reduced for 24 h).

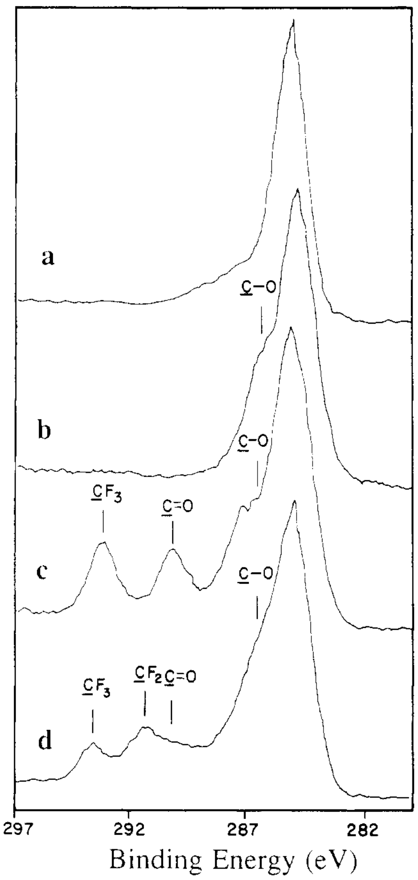


Figure 14. High-resolution C_{1s} XPS spectra of PTFE-OH synthesis and labeling experiments: (a) PTFE-C (reduced for 24 h); (b) PTFE-OH; (c) PTFE-OCOCF$_3$; (d) PTFE-OCOC$_3$F$_7$.

(KRS-5, 45°) also supports hydroxyl group introduction. The spectrum of a PTFE-OH film sample prepared from PTFE-C (24-h reduction) appears in Figure 13. Absorbances at 3500 and 1020 cm^{-1} are due to $\nu_{\text{O-H}}$ and $\nu_{\text{C-O}}$. The intensity of these signals indicates that reaction has taken place throughout most of the PTFE-C layer (6000 Å). The hydroxyl groups in PTFE-OH can be labeled for analysis by XPS by using trifluoroacetic anhydride and heptafluorobutyryl chloride. The high-resolution C_{1s} XPS spectra (Figure 14) definitively prove the presence of hydroxyl groups. The fluorinated ester-labeled PTFE-OH samples show well-resolved spectra; the PTFE-C was reduced for 24 h to eliminate the CF$_2$ signal.

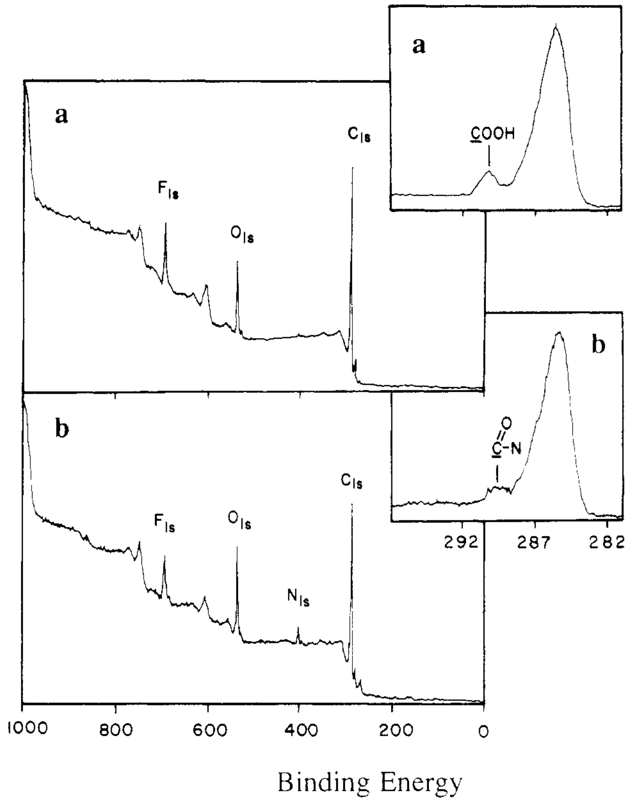


Figure 15. XPS spectra of (a) PTFE-COOH and (b) PTFE-COC$_3$H$_3$N$_2$; the PTFE-C sample had been reduced for 24 h.

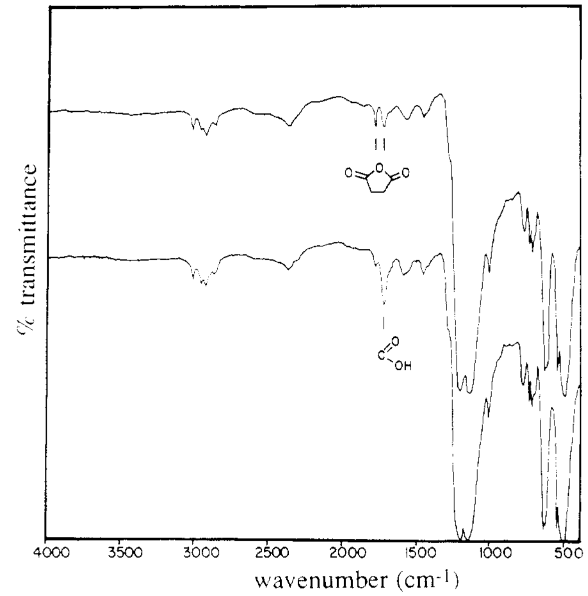
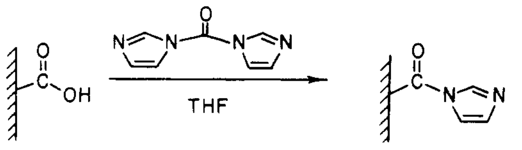


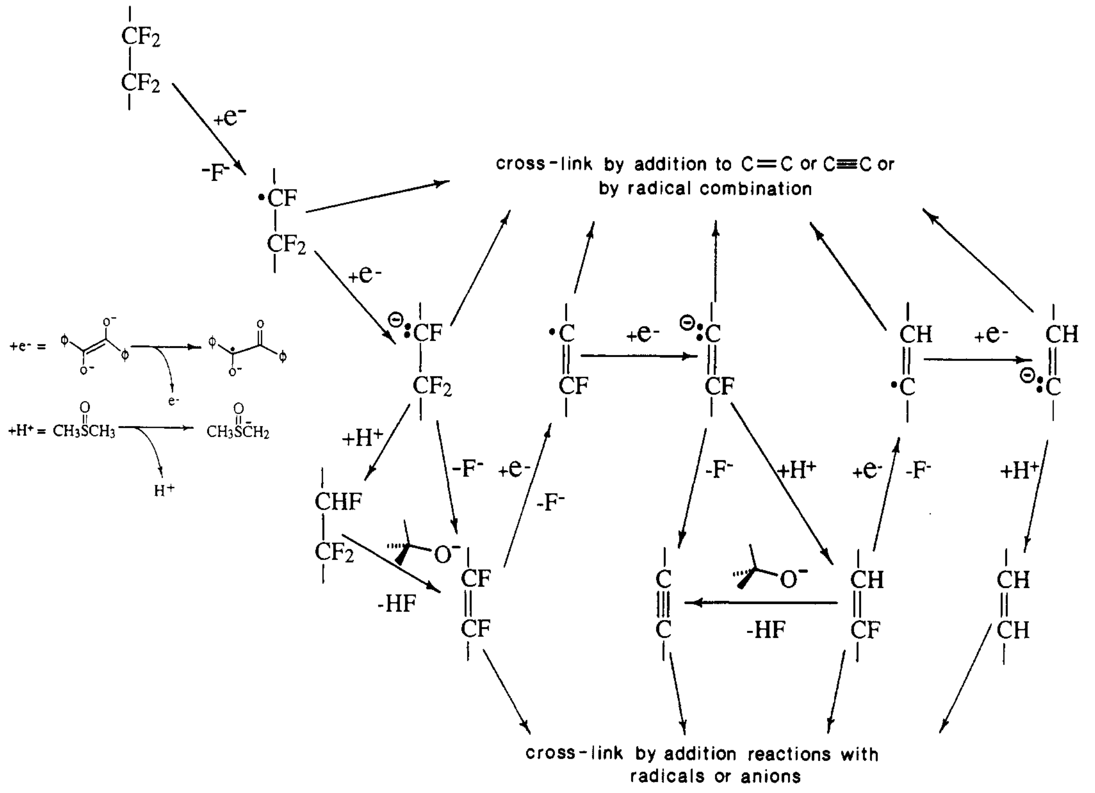
Figure 16. ATR IR spectra for the synthesis of PTFE-COOH.

Synthesis of PTFE-COOH. Irradiation of a solution of maleic anhydride and AIBN in contact with a film sample of PTFE-C produces changes in the film surface consistent with incorporation of an anhydride functionality. Trifluoroacetic acid catalyzed hydrolysis converts this surface to PTFE-COOH. Figures 15 and 16 exhibit the lucid XPS and ATR IR spectra for these transformations. The XPS spectra of PTFE-COOH indicate the presence of oxygen (the C/O ratio is 6.6:1) and a highly oxidized carbon component at 290 eV. The presence of a carboxylic acid functionality is confirmed by the labeling reaction with carbonyldiimidazole (eq 3). The ATR IR spectra show the presence of the anhydride (symmetric and



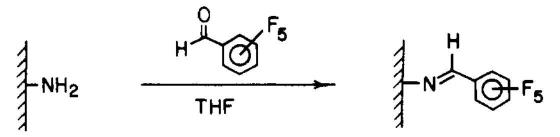
(3)

Scheme I
Plausible Reaction Sequences for Conversion of PTFE to PTFE-C



asymmetric C═O stretching at 1722 and 1784 cm^{-1}) which can be almost entirely hydrolyzed to the carboxylic acid (1723 cm^{-1}). The mechanism of the maleic anhydride incorporation was not examined: surface-confined radicals may add to maleic anhydride and/or AIBN-initiated maleic anhydride radicals may add to PTFE-C unsaturation. A small amount of nitrogen was present in the XPS and its intensity varied from sample to sample. It is not known whether one maleic anhydride molecule reacts with one PTFE-C radical or the maleic anhydride is graft polymerized or oligomerized. Maleic anhydride polymerizes under certain conditions.[31-33] It is clear from the XPS spectra that there is a not a poly(maleic anhydride) coating of any appreciable thickness on the surface: the fluorine in PTFE-C remains in the XPS sampling depth. The advancing and receding water contact angles of PTFE-COOH are 69° and 0°, respectively.

Synthesis of PTFE-NH$_2$. PTFE-Br was treated with liquid ammonia to prepare a surface containing amino groups. Figure 17 shows XPS spectra for this conversion: the bromine photoelectron lines at 256, 189, 182, and 69 eV are replaced by the nitrogen photoelectron line at 402 eV. That a significant portion of the nitrogen is present as amino groups is evidenced by the labeling reaction with pentafluorobenzaldehyde, a reagent specific for primary amines (eq 4).[34] The high-resolution F$_{1s}$ XPS spectrum



(4)

of PTFE-NH═CC$_6$F$_5$ shows two fluorine signals: one from the fluorine from PTFE-C and one from the label. The advancing and receding water contact angles for PTFE-NH$_2$ are 79° and 24°, respectively.

Summary

Reaction of PTFE with Me$_2$SO solutions of the potassium salt of benzoin dianion creates a modified layer at the PTFE surface, the thickness of which can be controlled with reaction time. This carbonaceous product is complex

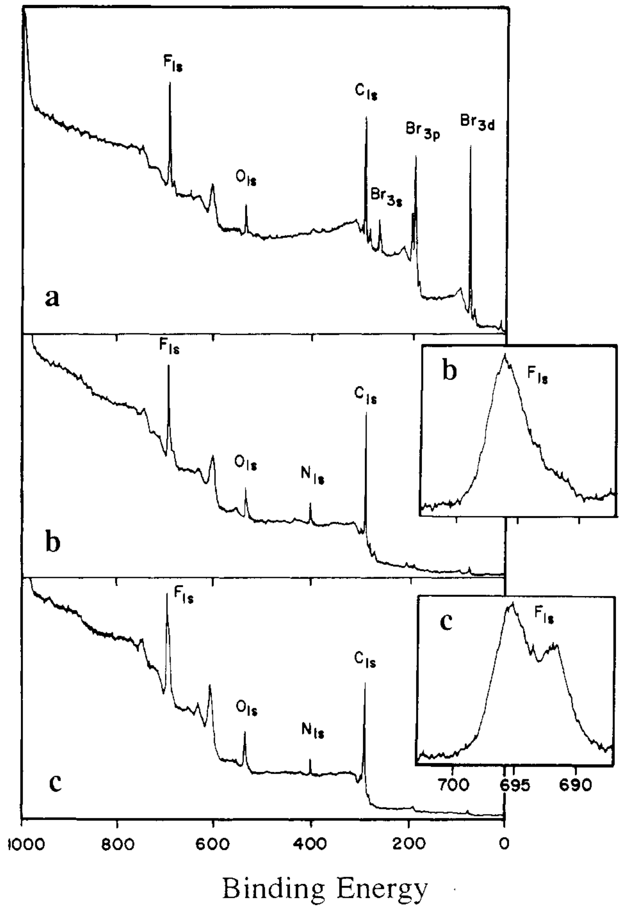


Figure 17. XPS spectra for the synthesis and labeling of (a) PTFE-Br, (b) PTFE-NH$_2$, and (c) PTFE-NCC$_6$F$_5$.

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but contains carbon–carbon double and triple bonds which are capable of further reaction to yield PTFE, surface derivatized with halogen, hydroxyl, amino, or carboxylic acid functionalities.

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Registry No. $KClO_3$, 3811-04-9; BH_3, 13283-31-3; $F_3CCO_2COCF_3$, 407-25-0; $ClCOC_3F_7$, 375-16-6; HO_2CCO_2H, 108-31-6; C_6F_5CHO, 653-37-2; $N_2H_3C_3COC_3H_3N_2$, 530-62-1.

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Miscibility of Blends of Tetramethylbisphenol A Polycarbonate and Styrene/Methyl Methacrylate Copolymers

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ABSTRACT: The phase behavior of blends of tetramethylbisphenol A polycarbonate, MPC, with styrene/methyl methacrylate copolymers, SMMAs, was examined by differential scanning calorimetry and for lower critical solution temperature behavior. MPC was found to be completely miscible with SMMAs having MMA contents less than 35%. Small amounts of MMA in the copolymer greatly increase the temperature at which phase separation occurs on heating relative to that observed for polystyrene blends with MPC. The phase behavior of MPC with SMMA copolymers appears to be strongly affected by intramolecular repulsion between the styrene and MMA units in addition to the intermolecular interactions of these units with MPC.

Introduction

The miscibility behavior of polymer blends has been an active area of investigation for more than a decade.[1–3] For high molecular weight components, the free-energy conditions for miscibility are primarily dominated by energetic considerations. The needed exothermic heat of mixing can arise from intermolecular specific interactions or from intrachain repulsion effects as recognized recently for systems based on copolymers.[4–6] These "pull" and "push"

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