Thermal Reconstruction of Surface-Functionalized Poly(chlorotrifluoroethylene)[1]

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ABSTRACT: The heterogeneous reaction of poly(chlorotrifluoroethylene) (PCTFE) film with lithium reagents in THF or heptane/THF solution results in a modification that introduces the alkyl group of the lithium reagent into the surface region of PCTFE. 2-(Lithiomethyl)-4,4-dimethyloxazoline reacts to incorporate the trimethyloxazoline functionality in the outer 10–20 Å of the PCTFE film (PCTFE-TMO). Hydrolysis of PCTFE-TMO renders surface carboxylic acid groups (PCTFE-COOH). Hydroxyl groups are incorporated by reaction of PCTFE with 3-lithiopropyl ethyl acetal and subsequent hydrolysis (PCTFE-OH). The thickness of the modified layer in PCTFE-OH depends on the conditions of reaction; we have studied film samples with modified layers of ~30- and ~1150-Å thickness. PCTFE-OH (30 Å) was further modified to yield PCTFE-OC(O)-CH_3, PCTFE-OC(O)CF_3, and PCTFE-OSiMe_3. All of the surfaces are stable (give reproducible surface analytical data) indefinitely at room temperature. On heating for days at 80–110 °C the surface regions of PCTFE-TMO, PCTFE-OH(30 Å), PCTFE-OH(1150 Å), PCTFE-COOH, and PCTFE-OC(O)CH_3 reconstruct as evidenced by contact angle analysis. X-ray photoelectron spectroscopy (XPS) indicates the reconstruction of PCTFE-TMO and PCTFE-OH(30 Å), but little or no changes in XPS spectra occur on heating PCTFE-OH(1150 Å), PCTFE-COOH, and PCTFE-OC(O)CH_3. PCTFE-OC(O)CF_3 and PCTFE-OSiMe_3 show no tendency to reconstruct. A reconstruction process that involves the concomitant migration of modified repeat units from the outer 10 Å of the film sample to a deeper region and migration of unmodified PCTFE repeat units from a deeper region into the outermost 10 Å is evident in PCTFE-TMO and PCTFE-OH(30 Å). The distance scale of these motions is small; the majority of the modified repeat units remains in the outer 10 Å. Another reorganization process is evident from contact angle measurements of PCTFE-OC(O)CH_3 and PCTFE-OH(1150 Å) and it involves motions of even smaller distance; repeat units do not measurably migrate (the composition of the outermost 10 Å remains constant) and we propose that they rotate.

Introduction

Interfacial properties, e.g., adhesion and wettability, of solid materials depend upon, among other parameters, the chemical composition of the outer few angstroms at the physical boundaries (surfaces) of the solid object. Organic polymer surfaces are uniquely complex, in a number of regards, among materials surfaces: Most polymers under many conditions exhibit dynamic surfaces with chains rotating and reptating on time scales and dimension scales that depend on the polymer structure and the environment. Surface chain mobility varies greatly from polymer to polymer; surface regions can have different degrees of crystallinity, and common polymers exhibit glass transition temperatures (T_g) over a temperature range greater than 400 °C. Polymers are used in a wide variety of environments, and the structure of the polymer surface component of the polymer–environment interface is environment dependent. Polymers are used in contact with vacuum, noninteracting gases, gases that adsorb to the polymer surface, gases that penetrate the polymer to varying extents, liquids that do not wet the surface, liquids that wet the surface to varying extents, liquids that swell the polymer to varying extents and depths, solids (amorphous, crystalline, and semicrystalline) that the polymer does not interact with, and solids that the polymer adheres to varying extents. Each of these interactions can take place at various temperatures (in particular, temperatures relative to the polymer's T_g). There is thus no generic description of a polymer surface or interface.

The mobility of polymer surfaces in materials that can display different surface structures is of practical importance as desired surface properties can be the result of one particular surface orientation. A rather extensive literature has grown in the past 20 years[2] that describes surface reconstruction in a variety of polymer materials of this type. A portion of this literature has been reviewed.[3] Homopolymer surfaces can display different properties by selective orientation of surface functionality which can vary depending on the processing conditions and/or the environment.[4-16] Random, graft, and block copolymers as well as polymer blends can concentrate one (or another) component at the surface in response to processing or the environment.[17-35] Surface-modified polymers can also display different surface structure and properties.[19,36-45] These materials can be regarded as a blend of unmodified polymer and modified polymer in which the modified chains are concentrated (initially after the modification reaction, at least) at the surface. The heterogeneous reaction conditions of surface modifications suggest that modified polymer chains are blocky copolymers of virgin and reacted repeat units but also that structure should vary greatly system to system depending on polymer structure (crystallinity, chain orientation), modification chemistry (chain cleavage or no chain cleavage), and surface selectivity (how deeply and uniformly the modification proceeds).

Solid organic polymer objects, because of the high molecular weight of their molecules are inherently nonequilibrium structures[46] and because of relaxation and transition phenomena, their structures and properties are time and temperature dependent. Polymer surface modifications are often carried out with the objective of increasing the surface free energy of the material to permit or enhance adhesion. Normally polar functional groups are introduced by chemical reaction. These modified structures are inherently unstable with respect to other structures that display lower surface free energies that the material can assume (relax to) given sufficient chain mobility. The spontaneous "migration" of polar functional groups from the surface toward the bulk has been described

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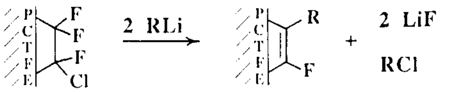
for many surface-functionalized polymers.[19,36–42,45]

We are developing the surface chemistry of poly(chlorotrifluoroethylene) (PCTFE) with the overall objective of controlling surface properties (wettability, adhesive behavior, adsorptive behavior, coefficient of friction) by manipulating the structure of the surface (functionality, orientation, cross-link density, depth of modified layer). PCTFE film reacts with lithium reagents to incorporate their alkyl groups as summarized in eq 1.[47,48]



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We have introduced carboxylic acid, aldehyde, and alcohol functionalities by using lithium reagents containing protected functional groups and have shown that the depth of reaction (thickness of the modified layer) can be controlled by varying reaction temperature and solvent composition.[48] We have reported a range of further reactions of the hydroxylated surface (PCTFE-OH)[49,50] and that adhesive properties can be controlled by surface chemistry.[51]

Throughout the course of this work we have ignored polymer surface mobility and have assumed that surface structures remain stable with respect to reorganization over the time periods and under the conditions that we handle the samples.[52] Analyses by the techniques that we employ (contact angle, X-ray photoelectron spectroscopy (XPS), and attenuated total reflectance infrared spectroscopy (ATR IR)) suggest that this assumption is, for the most part,[52] analytically valid. The motivation behind the study reported in this paper was practical: we need to know under what conditions and for what time periods our surface-modified PCTFE samples are stable. We have also studied, and comment herein on, the length (depth) scale of surface reorganization and the sensitivities of contact angle and XPS to this process.

Experimental Section

Materials. PCTFE was obtained from Allied as 1- and 5-mil film (Aclar 33C), extracted with refluxing dichloromethane for 30 min, and dried (<0.05 mm, 110 °C) for at least 24 h. Tetrahydrofuran and heptane were distilled from sodium benzophenone dianion. Methanol was distilled from magnesium. Dichloromethane was distilled from calcium hydride. All solvents were used immediately or stored for short periods under nitrogen in Teflon stopcock sealed storage flasks. 3-Bromo-1-propanol (Aldrich) was distilled under nitrogen 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. 2,4,4-Trimethyloxazoline (TMO) (Aldrich) was distilled from calcium hydride (70 °C, 160 mm) and stored under nitrogen. Heptafluorobutyryl chloride (Aldrich) was purified by freeze–pump–thaw cycles and trap-to-trap distillation. Trifluoroacetic acid, trifluoroacetic anhydride, acetic acid, acetone, *n*-butyllithium, *tert*-butyllithium, acetyl chloride, and dichloroacetic acid were obtained from Aldrich and used as received. Concentrated hydrochloric acid (Fisher) was used as received. House distilled water was redistilled with a Gilmont still and redistilled again under nitrogen.

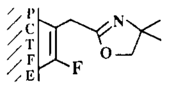
Methods. All reactions on polymer film surfaces were carried out under nitrogen; reactions were not stirred. Product film samples were stored under nitrogen or vacuum prior to analysis. Contact angle measurements were obtained with a Ramé-Hart telescopic goniometer and a Gilmont syringe with a 24-gauge flat-tipped needle. Water was used as the probe fluid to measure advancing and receding (dynamic) contact angles. The values reported are averages of at least five measurements made on different areas of the film surface. X-ray photoelectron spectra (XPS) were recorded with a Perkin-Elmer Physical Electronics 5100 spectrometer with Mg Kα excitation (300 W). Spectra were recorded at two angles, 15° and 75° from the film surface, and the reported binding energies are not corrected for charging. Atomic composition data and peak area calculations were determined by using the instrument's supplied software and programmed sensitivity factors: F_{1s}, 1.00; O_{1s}, 0.66; N_{1s}, 0.42; C_{1s}, 0.25; Cl_{2p}, 0.53. Attenuated total reflectance infrared (ATR IR) spectra were obtained under nitrogen using an IBM 38 FT IR and a germanium internal reflection element. UV–vis spectra were recorded on a Perkin-Elmer Lamda 3A spectrophotometer.

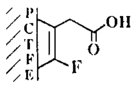
Modified-Surface Syntheses. The syntheses of modified PCTFE film samples used in this work have been reported for PCTFE-TMO,[48] PCTFE-COOH,[48] PCTFE-OH,[48,50] PCTFE-OC(O)CH_3,[50] PCTFE-OSiMe$_3$,[50] and PCTFE-OC(O)C_3F_7.[48] PCTFE-OC(O)CF_3 and PCTFE-OC(O)C_3H_7 were prepared from PCTFE-OH and trifluoroacetic anhydride or *n*-butyryl chloride, respectively, using conditions analogous to those used for PCTFE-OC(O)CH_3 and PCTFE-OC(O)C_3F_7.

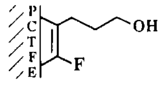
Annealing of Film Samples. Film samples were heated under vacuum (<0.05 mm) either with an Abderhalden drying pistol at 100° (refluxing water) or 110 °C (refluxing toluene) or in a vacuum oven equilibrated at 80, 90, or 100 °C. Data obtained at 100 °C with both the drying pistol and the vacuum oven established that equivalent thermal environments were produced by both methods. Annealing of film samples in refluxing water was carried out in a condenser-jacketed Schlenk tube. Film samples that were annealed in water were rinsed with methanol (2 × 20 mL) and then dichloromethane (2 × 20 mL) and dried (room temperature, 0.05 mm) for 24 h prior to analysis.

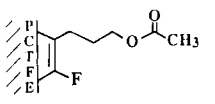
Results and Discussion

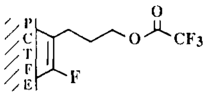
All of the experiments reported in this paper were carried out with commercial PCTFE film samples that were extracted with dichloromethane and dried/annealed at reduced pressure at 110 °C for at least 24 h and then cut to 1 × 2 cm (a convenient size for our analyses). Five-mil-thick films were used, except for UV experiments for which 1-mil films were used. This procedure consistently yields film samples that are free from contaminants detectable by any technique that we used and also may serve to relax certain types of residual strain incorporated during processing.[53] Film samples were modified by using reported[48,50] procedures to prepare surfaces with structures indicated below:

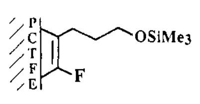












PCTFE-TMO,PCTFE-COOH, and PCTFE-OH were screened in preliminary annealing experiments and it was found that PCTFE-TMO was the most appropriate substrate for our analytical techniques; thus the majority of the studies were carried out with PCTFE-TMO.

PCTFE-TMO Structure. PCTFE-TMO film samples that were used in this work were prepared by allowing PCTFE film to react with 0.15 M 2-(lithiomethyl)-4,4-dimethyloxazoline (LiTMO) in THF at 0 °C for 60 min. We have discussed[48] the surface-selective and autoinhibitive nature of these reactions. Figure 1 shows XPS survey spectra for PCTFE and PCTFE-TMO recorded at a 75° takeoff angle (measured from the plane of the film sample). The survey spectra indicate the replacement of PCTFE repeat units (CF_2CFCl) with PCTFE-TMO units upon reaction by the decrease in intensity of the F_{1s}, Cl_{2s}, and

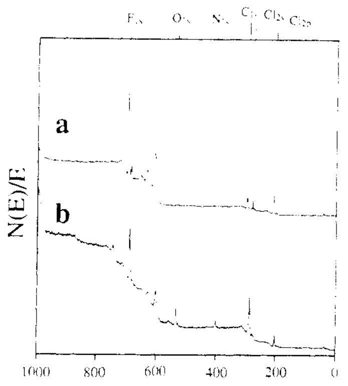


Figure 1. XPS survey spectra of PCTFE (a) and PCTFE-TMO (b).

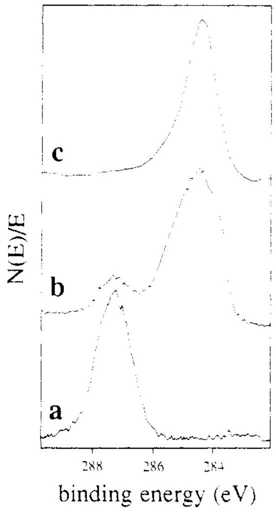


Figure 2. C_{1s} regions of XPS spectra of PCTFE (a) and PCTFE-TMO recorded at takeoff angles of 75° (b) and 15° (c).

Cl_{2p} photoelectron lines and introduction of N_{1s} and O_{1s} signals. Figure 2 shows C_{1s} region spectra for PCTFE and PCTFE-TMO. The high binding energy peak due to CF_2 and CFCl decreases in intensity upon reaction, and a low binding energy peak due to all of the carbons in the PCTFE-TMO repeat unit appears. The PCTFE-TMO spectrum shows takeoff angle dependent intensities. The spectrum recorded at a 15° takeoff angle (c) is representative of the outer 10 Å of the film sample (94% of the photoelectrons measured are ejected from this region[54]) and indicates that this region is comprised of almost entirely PCTFE-TMO repeat units. The 75° takeoff angle spectrum (b) represents the composition of the outer 40 Å of the film sample (95% of the photoelectrons measured originate within this region[54]) and indicates that an appreciable amount of virgin PCTFE repeat units are present in the outer 40 Å. The relative area of these two peaks is indicative of the ratio of PCTFE:PCTFE-TMO repeat units in this region but is biased by two factors that overestimate the amount of PCTFE-TMO present: One, the sensitivity of XPS decreases exponentially with depth, and 52%[54] of the 75° takeoff angle spectrum is due to photoelectrons originating in the outer 10 Å. The 15° takeoff angle spectrum shows that this region is essentially only PCTFE-TMO; thus the region between the depths of 10 and 40 Å is richer in PCTFE than the 75° takeoff angle spectrum in Figure 2 indicates. Two, the PCTFE-TMO repeat unit contains eight carbons that contribute to the spectrum and the PCTFE repeat unit contains only two, so the analysis is more sensitive to PCTFE-TMO repeat units by a factor of 4.

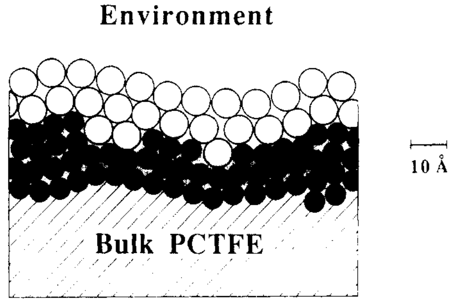


Figure 3. 2-D cross sectional model of the surface region of PCTFE-TMO: (○) PCTFE-TMO repeat unit; (●) PCTFE repeat unit.

On the basis of these takeoff angle dependent XPS spectra viewed with regard to the factors discussed above, the inherent surface selectivity of this type of reaction,[48] and other analytical data (ATR IR and gravimetric analyses show no indication of reaction for PCTFE → PCTFE-TMO),[48] we have developed the model for the surface region of PCTFE-TMO described in Figure 3. The figure depicts a cross section of the surface region with small shaded circles representing PCTFE repeat units and large open circles representing PCTFE-TMO repeat units. The sizes of the circles are drawn to approximate the relative size of the repeat units.[55] The figure is not meant to convey topographical information. The outer 10 Å is very PCTFE-TMO-rich, and all PCTFE-TMO is confined to the outer ~20 Å. The samples contain ~2 "molecular layers" of PCTFE-TMO.

Contact angle analysis (using water as the probe liquid) indicates substantial changes in wettability upon conversion of PCTFE to PCTFE-TMO: θ_A/θ_R (advancing contact angle/receding contact angle) for PCTFE = 104°/80°; θ_A/θ_R for PCTFE-TMO = 72°/25°. PCTFE and all of its surface-modified derivatives[48,50] show pronounced contact angle hysteresis. The origin of this hysteresis is likely a combination of surface roughness, surface chemical heterogeneity, and the reorganization of surface functionality during analysis. We do not know the relative importance of these factors.

Thermal Annealing of PCTFE-TMO. The surface of PCTFE-TMO is stable (shows reproducible contact angle and XPS data) for weeks at room temperature when stored under nitrogen or reduced pressure. When PCTFE-TMO film samples are heated at 80–110 °C, changes occur in surface structure which are observed by contact angle and XPS. Figure 4 shows advancing contact angle (θ_A) data as a function of time of heating at the various temperatures studied.[56] PCTFE-TMO before heating exhibits θ_A = 72°; virgin PCTFE has θ_A = 104°. Upon heating, θ_A increases, indicating that reconstruction occurs which lowers the surface energy and increases the hydrophobicity of the PCTFE-TMO. The scatter in the data is not due to the precision of the measurement or to the reproducibility of heating conditions, but most likely to the reproducibility of the PCTFE-TMO synthesis (see below). The thermal reorganizations are very slow at these temperatures, occurring over days. Film samples heated at 110 °C showed slight discoloration and an increase in absorbance from 190 to 600 nm, so higher temperatures were not studied. The 100 °C data points are darkened for emphasis because we compare these data with XPS results below. Note that at 100 °C, a "rapid" increase in contact angle occurs over the first ~30 h of heating (θ_A changes from 72° to ~90°) and little further increase occurs after an additional ~200 h of heating. We do not know if wettability will decrease further upon more weeks of heating or if a final-state structure has been reached.

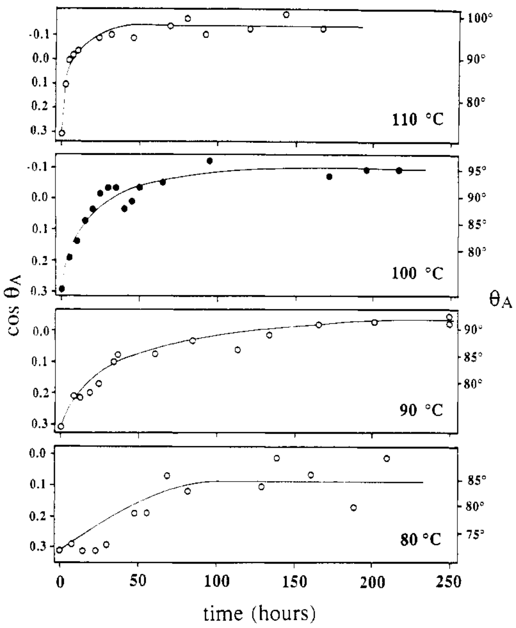


Figure 4. Dependence of θ_A (water) of PCTFE-TMO on time of heating at various temperatures.

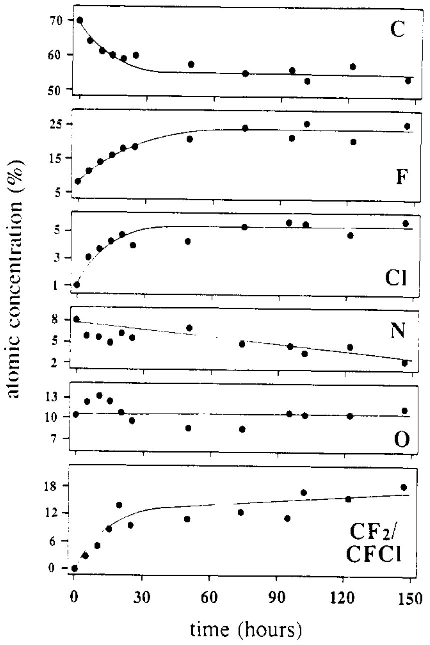


Figure 5. Atomic concentration and % CF_2/CFCl changes for PCTFE-TMO on annealing at 100 °C. The data are representative of the outer 10 Å of film samples.

The contact angle changes upon heating PCTFE-TMO are reflected by XPS spectra of heated samples. Figure 5 shows atomic concentrations determined by XPS for each of the elements as a function of time upon annealing at 100 °C. The spectra used to calculate these data were recorded at a takeoff angle of 15° and represent the atomic concentration of the outer 10 Å of the film sample. The obvious changes are as follows: fluorine and chlorine increase in concentration relatively rapidly over the first ~30 h and then level; carbon decreases in concentration relatively rapidly over the first ~30 h and then levels. The nitrogen concentration decreases slightly and the oxygen concentration remains the same within experimental error. There is one major source of error in these measurements (and likewise all measurements reported in this paper): each data point in Figure 5 was obtained with a different film sample of PCTFE-TMO. The reproducibility of the PCTFE-TMO synthesis is such that seven samples gave nitrogen analyses of 4.97, 5.93, 9.68, 4.37, 6.17, 6.08, and 7.93% (mean = 6.45%). The scatter in the data reflects this level of synthetic reproducibility. Another problem is that PCTFE-TMO is air sensitive (samples for XPS analysis are mounted in air); thus oxygen analyses are suspect. Also shown in Figure 5 is a plot of % CF_2/CFCl vs time of heating. Upon heating, the high binding energy C_{1s} photoelectron line due to CF_2 and CFCl in virgin PCTFE appears in the 15° takeoff angle spectrum and increases in intensity with time of heating. The data plotted are the percentages of the total carbon that is present as CF_2 or CFCl. These data indicate that upon heating PCTFE-TMO at 100 °C for >50 h, ~45% of the repeat units present in the outer 10 Å are virgin PCTFE repeat units. Analogous data for samples heated at 80, 90, and 110 °C are 17, 33, and 77%, respectively. Figure 6 shows a representation, in the format of Figure 3, of the structure of PCTFE-TMO heated at 100 °C for >50 h, based on the %CF_2/CFCl data.

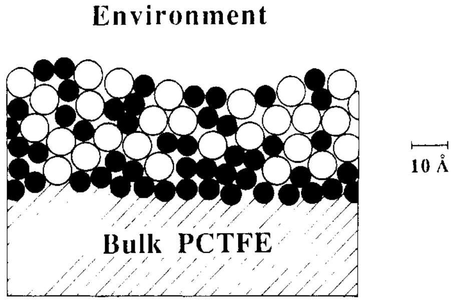


Figure 6. Pictorial representation of the surface region of PCTFE-TMO after heating at 100 °C for 150 h: (○) PCTFE-TMO repeat unit; (●) PCTFE repeat unit.

The similarity in rates of change in contact angle and composition of the outer 10 Å as assessed by XPS suggests that the same molecular level processes are responsible for changes observed by both techniques. The comparative sensitivity of XPS and contact angle analyses toward surface reconstruction for this system is very different from what was observed for oxidized polyethylene (PE-COOH).[36] PE-COOH reconstructs in the same temperature regime as does PCTFE-TMO, but the carboxylic acid groups diffuse rapidly (in minutes) from the region assessed by contact angle and more slowly (over several hours) from the region assessed by XPS. This marked contrast emphasizes the point made in the Introduction that polymer surfaces should not be generalized. A major difference between the polyethylene and PCTFE reconstructions is the relative differences in reconstruction temperature and glass transition temperature. The T_g of polyethylene is ~-125 °C; for PCTFE T_g = ~84 °C. We suspect that the type of reconstruction observed for PCTFE-TMO is occurring rapidly and reversibly in PE-COOH at room temperature.

Our view of the molecular-level processes responsible for the surface reconstruction of PCTFE-TMO is vague despite the XPS and contact angle data described above. It is clear that PCTFE-TMO repeat units are replaced by PCTFE repeat units at the surface by some process and that a decrease in surface energy drives this process. That surface energy is the driving force is supported by the fact that PCTFE-TMO does not reconstruct when heated in refluxing water (100 °C)[57] and experiments described below. The reconstruction appears to be irreversible as evidenced by the fact that annealed (100 °C, 100 h) PCTFE-TMO surfaces are unchanged by heating in contact with water at 100 °C for 100 h. XPS indicates that the thermal reorganization involves very short range events.

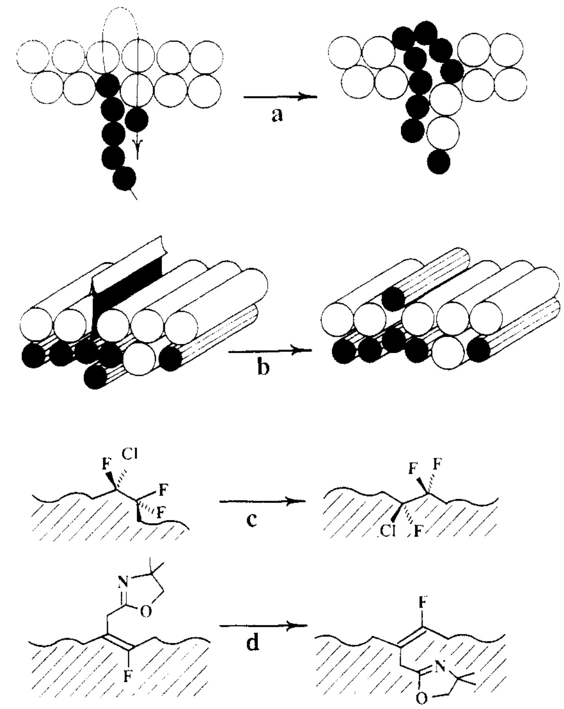


Figure 7. Plausible processes for reconstruction. Shaded figures represent PCTFE units or chain segments; unshaded figures represent PCTFE-TMO.

Virgin PCTFE repeat units migrate from sub-10-Å locations into the outer 10 Å, whereas PCTFE-TMO repeat units migrate very little and a significant portion of them remain in the outer 10 Å. Comparisons of 15° and 75° takeoff angle spectra indicate that the outer 10 Å is more PCTFE-TMO rich than the 10–40-Å-deep region in all except for the most extensively (110 °C) annealed samples. The PCTFE-TMO repeat units do not migrate far on the time scale of our experiments: they appear to stop. We suggest that they stop for two reasons: (1) migrating further does not lower surface energy; (2) the modified polymer is not compatible with virgin polymer.

Figure 7 describes plausible molecular-level processes for the observed PCTFE-TMO reconstruction. The migration of repeat units can be explained by reptation-like motions that bury PCTFE-TMO units and expose PCTFE units (a) or chain segments slipping by one another to expose PCTFE and bury PCTFE-TMO (b). Rotations of PCTFE (c) and PCTFE-TMO (d) units are shorter range motions that do not measurably alter the XPS composition but do affect contact angle. These are observed for PCTFE-OH (below) and likely occur in PCTFE-TMO as well.

Annealing of PCTFE-OH. The reaction used to prepare PCTFE-OH is not nearly as surface selective as the one used to prepare PCTFE-TMO. The reasons for this have been discussed.[48] Two PCTFE-OH surfaces were used in this work. One was prepared at -78 °C using a 5-min reaction time; these conditions yield an *average* reaction depth determined by UV–vis absorbance[48] of ~30 Å. This surface-modified material differs from PCTFE-TMO in that the interface between modified and unmodified regions is not sharp (there are modified repeat units deeper than 30 Å and unreacted repeat units throughout the outer 30 Å). The 15° takeoff angle XPS spectrum (C_{1s} region) reveals that 14% of the carbon in the outer 10 Å is present as PCTFE repeat units (29% of the repeat units are CF_2CFCl). The other PCTFE-OH surface studied was prepared at -20 °C using a 30-min reaction time to yield a surface-modified film sample with an average reaction depth of ~1150 Å. This sample contains no PCTFE repeat units in the outer 40 Å.

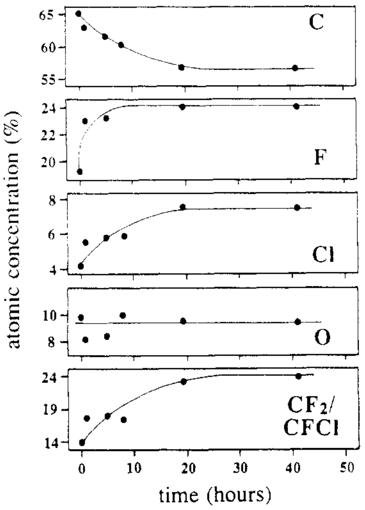


Figure 8. Atomic concentration and % $CF_2/CFCl$ changes for PCTFE-OH(30 Å) on annealing at 110 °C. The data are representative of the outer 10 Å of film samples.

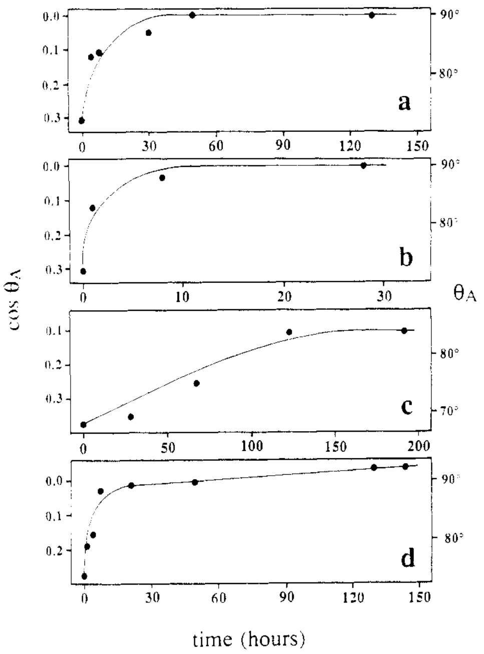


Figure 9. Contact angle data as a function of time of heating for (a) PCTFE-OH(30 Å), 110 °C; (b) PCTFE-OH(30 Å), 100 °C; (c) PCTFE-OH(1150 Å), 100 °C; and (d) PCTFE-COOH, 100 °C. Note that abscissas are not uniform.

Annealing studies of the 30-Å-modified PCTFE-OH were carried out at 100 and 110 °C. XPS and contact angle data from these experiments are shown in Figures 8 and 9a,b. The plots are similar to those for PCTFE-TMO shown in Figures 4 and 5 and we interpret the data similarly. PCTFE repeat units migrate into the outer 10 Å, and PCTFE-OH repeat units migrate from the outer 10 Å. After ~20 h of heating at 110 °C the reorganization is complete (or continues very slowly), and the outer 10 Å is composed of 43% PCTFE repeat units and 57% PCTFE-OH repeat units. The majority of the PCTFE-OH units in this region remain there.

The 1150-Å-modified PCTFE-OH was annealed at 100 °C; no changes were observed by XPS or ATR IR (this is the only surface discussed in this paper that shows infrared features due to modified polymer) after 288 h of heating. No PCTFE repeat units migrate into the outer

40 Å. The contact angle does change (Figure 9c), revealing that reconstruction occurs. Rotation of PCTFE-OH repeat units, as described in Figure 7d for PCTFE-TMO, to bury the polar hydroxyl groups is a plausible process for this reconstruction. This result indicates that contact angle is more sensitive than XPS to very short range reorganizations and suggests that similar events likely occur on heating PCTFE-OH(30 Å) and PCTFE-TMO as well. The process(es) that account for functional group migration in PCTFE-TMO and PCTFE-OH(30 Å) are likely at play in PCTFE-OH(1150 Å); however, PCTFE-OH repeat units are replaced by identical groups.

Annealing of PCTFE-COOH. PCTFE-COOH was prepared by hydrolysis of PCTFE-TMO.[48] Film samples were heated at 100 °C and assayed by XPS and contact angle. XPS gave little useful information and was compromised by the facts that the hydrolysis reaction does not proceed to completion[48] (PCTFE-TMO repeat units are observed) and that the COOH carbon peak is not resolved from the CF_2/CFCl carbon in the C_{1s} spectrum. The atomic concentrations of C, F, Cl, O, and N did not change within experimental error (at either 15° or 75° takeoff angles) after heating at 100 °C for 150 h. The high binding energy photoelectron line in the C_{1s} spectrum at 15° takeoff angle decreased in intensity slightly, indicating that PCTFE-COOH repeat units are likely migrating from the outer 10 Å. This change in the spectrum was likely attenuated by the migration of CF_2CFCl units into the outer 10 Å. The contact angle changed appreciably (increased) with heating (Figure 9d) and at a greater rate than the θ_A changes for PCTFE-TMO or PCTFE-OH. We offer no explanation for these rate differences as different surfaces are reconstructed to still different surfaces and direct comparisons are not appropriate.

Annealing of PCTFE-OC(O)R and PCTFE-OSiMe$_3$ Surfaces. PCTFE-OH(30 Å) was further modified to yield PCTFE-OC(O)CH_3 (θ_A/θ_R = 79°/47°), PCTFE-OC(O)CF_3 (θ_A/θ_R = 100°/65°), and PCTFE-OSiMe$_3$ (θ_A/θ_R = 90°/58°). Annealing experiments were carried out in an attempt to gain insight into structure–mobility relationships. These film samples were heated at 100 °C for ~100 h and no changes in XPS occurred in any of them. The contact angles were likewise unchanged for PCTFE-OC(O)CF_3 and PCTFE-OSiMe$_3$ but increased for PCTFE-OC(O)CH_3. This material was studied further, and the contact angles (θ_A/θ_R) were found to change from 79°/47° to 90°/56° upon heating at 110 °C for 98 h. The XPS spectra showed no changes after this treatment. This line of study was abandoned; it suggests that a sufficiently high surface energy is necessary for surfaces to reconstruct.

Summary and Conclusions

Poly(chlorotrifluoroethylene) film samples containing sufficiently polar functional groups in the outer 10–30 Å reconstruct when heated to ~100 °C (T_g = 84 °C) to yield lower energy surfaces. At least two processes are responsible for this reconstruction. One involves the migration of virgin PCTFE (CF_2CFCl) repeat units from a region below 10 Å deep into the outer 10 Å and concomitant migration of the polar modified repeat unit from the outer 10 Å into a slightly deeper region. This process is observed for PCTFE-TMO and PCTFE-OH(30 Å) by contact angle and grazing (15° takeoff) angle XPS analyses. The distance scale of this process is small: the majority of the modified repeat units initially present in the outer 10 Å remains there; the average distance the modified repeat units migrate increases with temperature. A shorter distance scale process that is likely rotation of repeat units was observed when PCTFE-OH(1150 Å) and PCTFE-OC(O)CH_3 were heated; it is likely also operative in PCTFE-OH and PCTFE-TMO. This process is observable by contact angle, but not XPS.

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(53) Any residual strain in PCTFE film is likely unimportant with regard to the experiments reported here. The fact that certain samples are stable with respect to thermal treatment indicates that residual strain is not responsible for surface reconstruction. The modification reactions and particularly the swelling of the modified surfaces by the reaction solutions significantly restructure the surface so that any residual strain incorporated in the surface region during processing is removed.

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(56) Receding contact angle (θ_R) changes parallel the θ_A changes; θ_R data were generally more scattered than those for θ_A.

(57) This experiment is also evidence that PCTFE-TMO groups remain attached during annealing. The XPS results and UV-vis spectroscopy also support this.

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Kinetics of the Gas-Phase Halogenation of a Polyethylene Surface As Studied with X-ray Photoelectron Spectroscopy

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ABSTRACT: X-ray photoelectron spectroscopy (XPS) has been used to determine the kinetics of gas-phase halogenation of a polyethylene surface. XPS allows the determination of the concentration of each carbon species present based upon chemical bonding. With this information detailed information about the kinetics has been obtained. The gas-phase chlorination of polyethylene was shown to follow predictable kinetics based on the XPS results. A time distribution of the monochlorinated and dichlorinated species was found, with the monochlorinated species more predominant. Chlorination kinetics are shown to predictably proceed for up to 600-s exposure to chlorine gas. At this exposure a $CH_2/CHCl/CCl_2$ ratio of 1/1/0.5 was found. For exposures >600 s, chlorination slows drastically. It is postulated that this latter effect is due to steric effects. Angular-dependent XPS data have shown that chlorination of polyethylene is uniform throughout the sampling depth (~10–70 Å). The XPS results suggest the bromination kinetics are also first order but $\sim 10^5$ slower than that of chlorination. The rate of iodination was found to be orders of magnitude slower than that of bromination.

Introduction

Polymer surface properties control wettability,[1] adhesion,[1] and in some cases electronic properties.[2] These properties are many times altered via chemical modification of the surface. This modification can be made via chemical reaction with a contacting solution,[3,4] corona discharge treatment (CDT),[5,6] plasma or glow discharge treatment,[7,8] gas-phase reactions,[5,6] and combinations of the aforementioned treatments.[9] We have investigated the effects of CDT on polymer surfaces and the physisorption of surfactant molecules on the treated surfaces.[10,11] The chemistry involved in CDT treatment is complicated, with a series of hydrophilic chemical moieties created. These structures are dependent upon treatment power and treatment atmosphere and have been analyzed by gas-phase derivatization followed by XPS. In order to understand more completely the effect of gas-phase reactions on polymer surfaces, the gas-phase halogenation of polyethylene has been studied. XPS can be used to identify the various chemical species formed in the surface region (~10–70 Å) and can differentiate a chemical gradient within this region. It is the purpose of this study to (1) ascertain if the kinetics of formation of the various chemical species can be modeled and (2) determine whether this study can verify the selective chlorination kinetics observed by others.[12–14] These latter studies indicate that a halogenated carbon atom greatly affects the halogenation of an adjacent atom.

Experimental Section

The XPS spectra were obtained on either a Hewlett-Packard 5950A or a Surface Science Laboratories SSX-100 photoelectron spectrometer, both of which have monochromatic Al $K\alpha$ X-ray sources (1486.6 eV). The use of a monochromatic source minimizes sample radiation damage, which is especially important

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