in these solvents. OH moieties did not affect the molecular weight decrease and cross-linking during photolysis.

Registry No. Ph-p, 111351-17-8; Ph-p (homopolymer), 111351-25-8; Ph-p (SRU), 111351-32-7; Me-p-1, 111495-40-0; Me-p-1 (homopolymer), 111351-33-8; Me-p-1 (SRU), 111351-26-9; Ph-m, 111351-18-9; Ph-m (homopolymer), 111351-34-9; Ph-m (SRU), 111351-27-0; Me-m-1, 111351-19-0; Me-m-1 (homopolymer), 111556-64-0; Me-m-1 (SRU), 111524-60-8; Me-p-2, 111351-20-3; Me-p-2 (homopolymer), 111351-35-0; Me-p-2 (SRU), 111351-28-1; Ph-p-2, 111351-21-4; Ph-p-3, 111351-22-5; Me-m-2, 111351-23-6; Me-m-2 (homopolymer), 111351-36-1; Me-m-2 (SRU), 111351-29-2; Ps-2, 111351-24-7; Ps-2 (homopolymer), 111351-39-4; Ps-2 (SRU), 111351-30-5; Ps-3 (homopolymer), 111351-40-7; Ps-3 (SRU), 111351-31-6; (Ph-p)(Me_2SiCl_2) (copolymer), 111351-41-8; (Ph-m)(Me_2SiCl_2) (copolymer), 111351-42-9; (Ph-p-2)(Me_2SiCl_2) (copolymer), 111378-53-1; (Ph-p-3)(Me_2SiCl_2) (copolymer), 111351-43-0; $PhSiHCl_2$, 1631-84-1; 3-$Me_3SiOC_6H_4CH{=}CHMe$, 111351-14-5; $MeSHCl_2$, 75-54-7; 4-$Me_3SiOC_6H_4CH{=}CHMe$, 25195-80-6; $PhCH{=}CH_2$, 100-42-5; 4-$MeOC_6H_4CH{=}CHCH_3$, 104-46-1; ($MeSiCl_2CH(Ph)CH_2CH_3$)($MeSiCl_2CH_2CH(Ph)Me$) (copolymer), 111351-38-3; 1-[4-[(trimethylsilyl)oxy]-3-methoxyphenyl]-1-propene, 6689-41-4; eugenol trimethylsilyl ether, 4515-52-0; isosafrole trimethylsilyl ether, 111351-15-6; isosafroeugenol trimethylsilyl ether, 111351-16-7.

References and Notes

(1) Trujillo, R. E. *J. Organomet. Chem.* **1980**, *198*, C27.

(2) West, R.; David, L. D.; Djurovitch, P. I.; Stearley, K. L.; Srinivasan, K. S. V.; Yu, H. J. *J. Am. Chem. Soc.* **1981**, *103*, 1352.

(3) Trefonas, P.; Djurovich, P. I.; Zhang, X.-H.; West, R.; Miller, R. D.; Hofer, D. *J. Polym. Sci., Polym. Lett. Ed.* **1983**, *21*, 819.

(4) West, R.; David, L. D.; Djurovich, P. I.; Yu, H.; Sinclair, R. *Ceram. Bull.* **1983**, *62* (8), 899.

(5) Zhang, X.-H.; West, R. *J. Polym. Sci., Polym. Chem. Ed.* **1984**, *22*, 159.

(6) Zhang, X.-H.; West, R. *J. Polym. Sci., Polym. Chem. Ed.* **1984**, *22*, 225.

(7) Stuger, H.; West, R. *Macromolecules* **1985**, *18*, 2349.

(8) Wesson, J. P.; Williams, T. C. *J. Polym. Sci., Polym. Chem. Ed.* **1980**, *15*, 720.

(9) Wesson, J. P.; Williams, T. C. *J. Polym. Sci., Polym. Chem. Ed.* **1981**, *19*, 65.

(10) Uhsirogauchi, T.; Tada, T.; Watanabe, H. *Proceedings of Conference on Radiation Curing Ashia*, 1986; p 101.

(11) Zeigler, J. M.; Harrah, L. A.; Johnson, A. W. *Proc. SPIE-Int. Soc. Opt. Eng.* **1985**, *539*, 166.

(12) Wolff, A. R.; West, R.; Peterson, D. C. paper presented at the 18th Organosilicon Symposium, Schenectady, NY, April 4, 1984.

(13) Mazdyshi, K. S.; West, R.; David, L. D. *J. Am. Ceram. Soc.* **1978**, *61*, 504.

(14) Yajima, S.; Hasegawa, Y.; Hayashi, J.; Iimura, M. *J. Mater. Sci.* **1980**, *15*, 720.

(15) Hayase, S.; Onishi, Y.; Suzuki, S.; Wada, M. *Macromolecules* **1985**, *18*, 1799.

(16) Ishikawa, M.; Hongzhi, N.; Matsusaki, K. *J. Polym. Sci., Polym. Lett. Ed.* **1984**, *22*, 669.

(17) Trefonas, P., III; Damewood, J. R., Jr.; West, R. *Organometallics* **1985**, *4*, 1318.

(18) Trefonas, P., III; West, R.; Miller, R. D. *J. Am. Chem. Soc.* **1985**, *107*, 2739.

(19) Gu, T. Y. Y.; Weber, W. P. *J. Organomet. Chem.* **1980**, *184*, 7.

(20) Steele, K. P.; Tzeng, D.; Weber, W. P. *J. Organomet. Chem.* **1982**, *231*, 291.

(21) Kilb, R. W. *J. Phys. Chem.* **1959**, *63*, 1838.

(22) Schnabel, W.; Kuvi, J. In *Aspects of Degradation and Stabilization of Polymers*; Jellinek, H. H. G., Ed.; Elsevier: New York, 1978.

(23) West, R.; Miller, R. D.; Hofer, D. *J. Polym. Sci., Polym. Lett. Ed.* **1983**, *21*, 823.

Surface-Selective Hydroxylation of Polypropylene

Kang-Wook Lee and Thomas J. McCarthy*

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

Received June 18, 1987

ABSTRACT: Room-temperature oxidation of polypropylene film with chromium(VI) oxide in acetic acid/acetic anhydride introduces hydroxyl groups, olefins, ketones, and esters to a thin layer at the surface of the film. Analysis using a combination of analytical techniques (UV–vis, XPS, ATR IR, contact angle, and gravimetric analysis) indicates that the density of functionality increases over the first 4 h of reaction and remains essentially constant thereafter. Gravimetric analysis reveals an initial mass gain (over the first 4 h) and subsequent mass loss, indicating the gradual dissolution of modified polymer and the maintenance of a modified layer on the order of 100 Å thick. SEM reveals no changes in surface topography at the limits of resolution: all film surfaces appear flat. Treatment of the oxidized polypropylene with borane reduces the ketones, the esters, and more slowly, the olefins and increases the density of hydroxyl groups. Hydroxyl groups on oxidized and oxidized/reduced polypropylene were labeled (for XPS and ATR IR identification) by reaction with heptafluorobutyryl chloride.

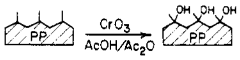
Introduction

Isotactic polypropylene (PP) film is widely used, often in laminates, as a barrier polymer due to its moisture-resistant properties.[1] Its relatively low surface energy and relatively high chemical resistance impede its materials applications, particularly those which require an adhesive bond between PP and another condensed phase (ink, metal, another polymer, inorganic filler). This problem has led to copious research associated with PP surface chemistry and an extensive literature of PP surface modification techniques. Gas discharge treatments[2,3] in air and other atmospheres introduce a range of functionality. Sulfuric acid[4] and chromic–sulfuric acid[4–6] introduce sulfonic acid, carboxylic acid, and likely other less oxidized functional groups. Photohalogenation[7–9] produces printable surfaces. Hydroperoxide-catalyzed oxidation[10] introduces hydroperoxide groups. Ozone treatment[11,12] renders wettable surfaces. Graft polymerizations from free radical sites generated on the surface give access to a range of surface functionality.[12–15] A thin layer of vapor-deposited copper catalyzes surface autoxidation.[16] Radical addition reactions with maleic anhydride produce maleated polypropylene.[17]

We are interested in developing an understanding of the molecular basis (at the functional group level) for macroscopic polymer surface properties. For this study, we need unreactive polymers containing surface-confined versatile organic functional groups. Ideally, the substrates should contain an array of a single functional group covalently attached and located in a position (the surface) where each

0024-9297/88/2221-0309$01.50/0

can react with reagents in solution. The bulk polymer should be inert to the reaction conditions, and the modification reactions (both to introduce the initial functionality and to carry out subsequent transformations) should induce no topographical changes in the polymer surface. These restrictions would limit changes in the polymer surface to chemical ones and allow direct functional group–property correlations. Our work, thus far, has focused on fluorinated polymers as substrates because of their ultimate chemical resistivity.[18-21] We report here the surface selective hydroxylation of PP. Our approach involved the selective oxidation of the tertiary carbon to a tertiary alcohol (eq 1), a reaction with precedence in solution chemistry.[22-24]



(1)

Experimental Section

Materials. Isotactic polypropylene (PP) film samples (1 and 24 mil) were obtained from Hercules and extracted with refluxing dichloromethane for 15 min and dried (0.02 mm, 70 °C) until constant mass (±1 μg) was achieved. Tetrahydrofuran was distilled from sodium benzophenone dianion and stored under nitrogen. Dichloromethane was distilled from phosphorous pentoxide and stored under nitrogen. Chromium(VI) oxide, acetic anhydride, acetic acid, methanol (each obtained from Fisher), borane/THF, heptafluorobutyryl chloride, and trichloroacetyl isocyanate (each obtained from Aldrich) were used without further purification.

Methods. Air-sensitive reactions were carried out under dry nitrogen. Dynamic contact angles were measured by using a Ramê-Hart telescopic goniometer and water as the probe fluid. Advancing (θ_A) and receding (θ_R) angles were measured as water was added and removed, respectively, by using a Gilmont syringe. The values reported are averages of five measurements made on different positions of the film samples. Attenuated total reflectance infrared (ATR IR) spectra were obtained by using an IBM 38 FTIR with 4 cm^{-1} resolution, triangular apodization, a deuteriated triglycine sulfate detector, and a germanium (45°) internal reflection element. X-ray photoelectron spectra (XPS) were obtained by using a Perkin-Elmer Physical Electronics 5100 with Mg Kα excitation (300 W, 15 KeV). Spectra were recorded at two angles: 15° and 75° from the film surface. UV–vis spectra were recorded by using a Perkin-Elmer Lambda 3A spectrophotometer. Scanning electron micrographs (SEM) were obtained with a JEOL 100 STEM. Gravimetric analysis was performed by using a Cahn 29 electrobalance containing a polonium source. The film samples were charge-neutralized by using a Zerostat (Aldrich) immediately prior to weighing.

Oxidation of PP Film. Three 24 mil and three 1 mil film samples were placed in a Schlenk tube which was subsequently purged with nitrogen for 15 min. A solution of chromium(VI) oxide (1.0 g, 10 mmol), acetic acid (10 mL), and acetic anhydride (10 mL) was added via cannula, the film samples were allowed to react at room temperature for 0.5–16 h, and the oxidation solution was removed. The film samples were washed with 1 M NaOH (2 × 20 mL), 1 M HCl (2 × 20 mL), water (2 × 20 mL), methanol (3 × 20 mL), and dichloromethane (3 × 20 mL) in this order and then dried at reduced pressure (0.02 mm) for at least 24 h prior to XPS, ATR IR, UV–vis, SEM, and contact angle analyses. Two tared (prior to oxidation) film samples were further dried (0.02 mm, 70 °C) to constant mass (24 h) for gravimetric analysis. In a control experiment, the oxidized film was stored in acetic acid/acetic anhydride (10 mL each) at room temperature for 16 h and washed and dried as described above. XPS and gravimetric analyses were performed.

Reduction of Oxidized PP Film with Borane. Oxidized PP film samples were placed in a Schlenk tube which was then flushed with nitrogen for 15 min. Borane (2.0 mL, 1.0 M in THF) and THF (15 mL) were added via cannula. The film samples were allowed to react at room temperature for 6 h. The solution was removed via cannula, and the film samples were washed with THF (1 × 20 mL), 1 M aqueous acetic acid (3 × 20 mL), methanol (3 × 20 mL), and dichloromethane (3 × 20 mL) in this order. Alternatively, after removal of the borane solution, the film samples were washed with THF (4 × 20 mL) and treated with a mixture of hydrogen peroxide (30% aqueous, 10 mL) and sodium hydroxide (3 M, 10 mL) for 3 h. The basic peroxide solution was removed, and the films were washed with water (2 × 20 mL), 1 M HCl (3 × 20 mL), water (3 × 20 mL), methanol (3 × 20 mL), and dichloromethane (3 × 20 mL) in this order. The samples were dried (room temperature, 0.02 mm, 24 h) before XPS, ATR IR, UV–vis, SEM, and contact angle analyses.

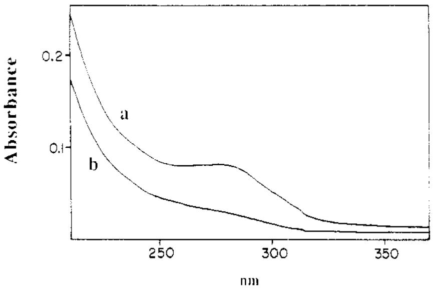


Figure 1. UV–vis spectra of (a) PP-[O], oxidized for 4 h, and (b) PP-OH, oxidized for 4 h, borane reduction worked up with acetic acid. An unreacted PP film was placed in the reference beam.

Reaction of PP-[O] with Aqueous NaOH. PP-[O] film samples were placed in a Schlenk tube, and a solution of aqueous sodium hydroxide (2 M, 20 mL) was added. The film samples were allowed to react at room temperature for 24 h. The solution was removed and the film samples were washed with methanol (3 × 20 mL) and dichloromethane (3 × 20 mL). The samples were dried (room temperature, 0.02 mm, 24 h) before ATR IR spectra were recorded. Protonation consisted of storing the base-treated films in 1 M aqueous HCl for 2 h. The film samples were washed with water (3 × 20 mL), methanol (3 × 20 mL), and dichloromethane (3 × 20 mL). The samples were dried at reduced pressure before ATR IR spectra were recorded.

XPS/ATR IR Labeling Reaction with Heptafluorobutyryl Chloride. An oxidized film sample, an oxidized, then reduced film sample, and a PP film sample (control) were placed in a Schlenk tube which was then purged with nitrogen for 15 min. THF (20 mL) was added via cannula followed by addition of heptafluorobutyryl chloride (0.856 g, 3.68 mmol) via syringe. Pyridine (2 mL) was added, and the films were allowed to react at room temperature for 48 h. The solution was removed, and the film samples were washed with THF (3 × 20) mL) and dichloromethane (3 × 20 mL) prior to XPS, ATR IR, and contact angle analyses.

Results

Two types of isotactic PP film (provided by Hercules) were used for this work: 24 mil film containing no additives and 1 mil film containing antioxidants. Both were extracted with refluxing dichloromethane and dried to constant mass prior to use. The 24 mil film was used for X-ray photoelectron spectroscopy (XPS), attenuated total reflectance infrared spectroscopy (ATR IR), scanning electron microscopy (SEM), and contact angle analysis. The 1 mil film was used for UV–vis spectroscopy and gravimetric analysis.

Oxidation of PP Film (PP-[O]). Hydroxylation of PP film was attempted, as depicted in eq 1, by treating the film with chromium(VI) oxide in acetic acid/acetic anhydride at room temperature for 0.5–16 h; we abbreviate these products: PP-[O]. Upon oxidation, the film samples take on a slight yellow tint, which is indicated in the UV–vis spectrum (Figure 1a). The spectrum exhibits a broad absorbance from low wavelength tailing out to 330 nm. The intensity of this absorbance increases rapidly over the first 4 h of reaction and levels off thereafter; this autoinhibiting behavior is observed in Figure 2, a plot of the absorbance at 260 nm[25] versus reaction time. The XPS spectrum indicates the incorporation of oxygen upon re-

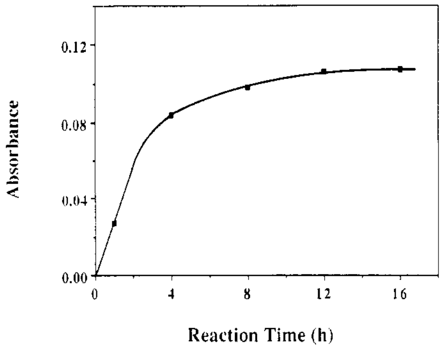


Figure 2. Absorbance (260 nm) of PP-[O] samples versus reaction time.

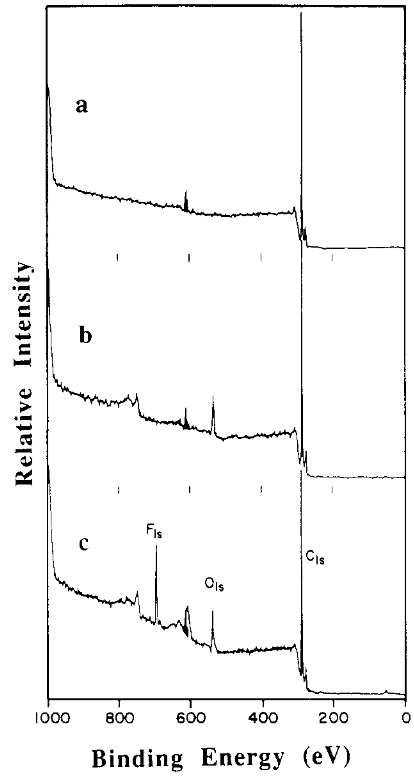


Figure 3. XPS survey spectra of (a) PP, (b) PP-[O] (4 h), and (c) PP-[O]-COC_3F_7. Data were recorded with an angle of 15° between the film surface and the analyzer. The shaded peaks at 611–613 eV are C_{1s} ghosts due to a copper impurity on the anode.

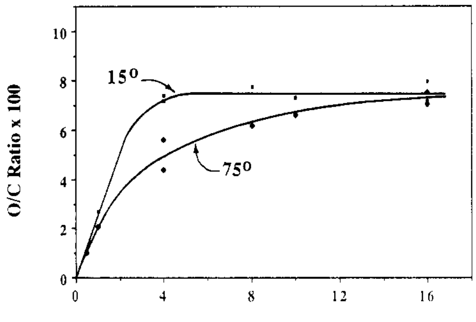


Figure 4. Oxygen:carbon ratio in the XPS sampling depth versus reaction time (75° and 15° indicate the angle between the film surface and the analyzer).

action. Survey spectra of PP and PP-[O] (4 h) are shown in Figure 3, parts a and b. The reactions that incorporate oxygen exhibit kinetics similar to those observed by UV–vis. Figure 4 shows plots of the oxygen:carbon ratio versus reaction time. Two curves are shown: The one labeled 75° was drawn from data obtained with an angle of 75° between the film surface and the analyzer; these data indicate the composition of the outer ca. 40 Å of the sample. The one labeled 15° likewise indicates the geometry of the analysis and is indicative of the outer 10 Å of the sample. The ATR IR spectrum of PP-[O] (8 h) (Figure 5b) exhibits, in addition to strong PP bands, weak absorbances at 1742, 1711, 1620, and 1551 cm^{-1} which we assign to ester carbonyl, ketone, trisubstituted olefin, and disubstituted olefin, respectively. There is no indication of hydroxyl absorbances,[26] but other analyses indicate that they are present (below). The advancing and particularly the receding contact angles (water) decrease upon oxidation, indicating the incorporation of polar functionality on the surface. Table I summarizes these data. Gravimetric analysis (Figure 6) shows that an increase in mass occurs over the first four hours of reaction, followed by a decrease

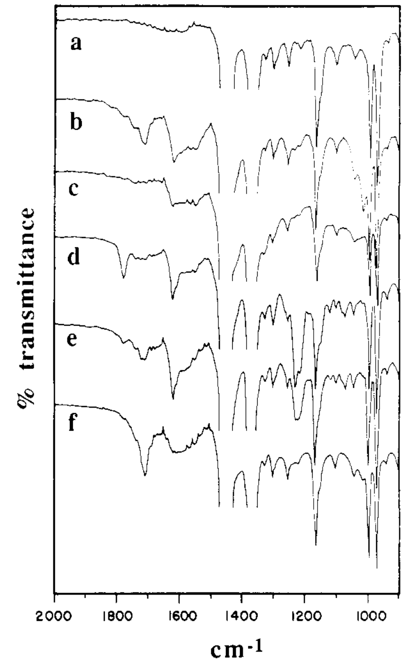


Figure 5. ATR IR spectra: a, PP; b, PP-[O] (8 h); c, PP-OH; d, PP-$OCOC_3F_7$; e, PP-[O]-COC_3F_7; f, PP-[O] after treatment with 2 M NaOH for 24 h.

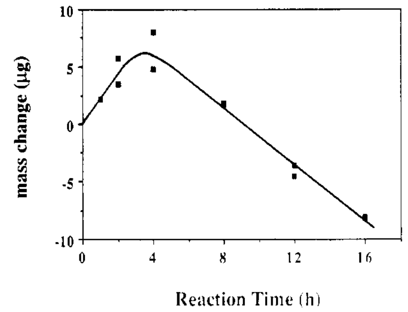


Figure 6. Mass change versus reaction time for PP → PP-[O]. Film samples had 6 cm^2 surface area.

Table I
Contact Angle Data (Water) for PP Oxidation

reactn time, h	θ_A, deg	θ_R, deg
0	111 ± 3	88 ± 3
0.5	111	70
1	107	62
4	104	55
8	102	49
10	101	49
16	104	46

Table II
XPS Atomic Ratios

	C		O		F	
	75°	15°	75°	15°	75°	15°
PP	100	100	0	0	0	0
PP-[O] (4 h)	96	93	4	7	0	0
PP-OH (4 h)	96	93	4	7	0	0
PP-[O]-COC_3F_7	94	93	4	4	2	3
PP-O-COC_3F_7	91	86	5	8	4	6

in mass thereafter. These data should be regarded as rather qualitative because of the different hydrophilicities of the film samples (we weigh them in air), but we emphasize that this information could not have been obtained by another surface analytical technique and was not at all apparent from the other analyses. SEM analysis of PP, PP-[O] (4 h), and PP-[O] (16 h) indicates that no discernible changes in surface topography at the limits of SEM resolution occur upon reaction: all surfaces appear flat.

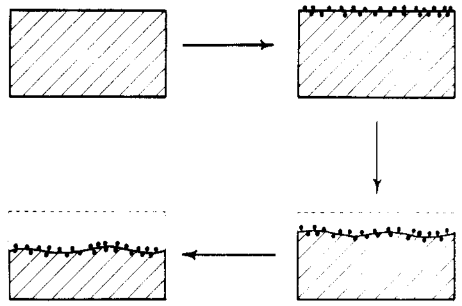
Reduction of PP-[O] with Borane (PP-OH).[27] To reduce esters, ketones and olefins in PP-[O], film samples were treated with BH_3 in THF for 6 h at room temperature and worked up with either aqueous acetic acid or basic peroxide.[28] The yellow tint of the film disappears immediately upon contact with the borane solution. UV–vis absorbance decreases (Figure 1b) and infrared absorbances at 1742 and 1711 cm^{-1} and a portion of the absorbance at 1551 cm^{-1} disappear (Figure 5c).[29] XPS, SEM, contact angle, and gravimetric analyses exhibited no significant changes upon reduction.

Reaction of PP-[O] with Aqueous NaOH. To interpret the infrared spectrum of PP-[O] and to gain insight into the mechanism of mass loss, a film sample was treated with 2 M sodium hydroxide for 24 h.[30] The ATR IR spectrum of the product (Figure 5f) reveals that the absorbance at 1742 cm^{-1} has disappeared, the band at 1711 cm^{-1} is unchanged, and the region in the mid-1500 cm^{-1} has flattened slightly, perhaps due to a new absorbance. Similar treatments with less concentrated base and shorter reaction time rendered less change. Protonation of the base-treated PP-[O] with aqueous HCl induces no changes in the infrared spectrum.

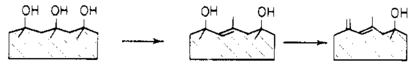
Reaction of PP-[O] and PP-OH with Heptafluorobutyryl Chloride (PP-[O]-COC_3F_7, PP-O-COC_3F_7). To label hydroxyl groups (for XPS and ATR IR analysis) in PP-OH and PP-[O] (to prove their existence and determine their relative concentration), film samples were treated with heptafluorobutyryl chloride and pyridine (catalyst) in THF and analyzed by XPS, ATR IR, and contact angle.[31] Figure 3c shows the XPS survey spectrum for PP-[O]-COC_3F_7. The photoelectron line at 693 eV corresponds to F_{1s}. ATR IR spectra (Figure 5, parts d and e) indicate an ester carbonyl band[32] at 1779 cm^{-1} and C–F stretching modes at 1233 and 1219 cm^{-1}. Contact angles (θ_A/θ_R) of PP-$OCOC_3F_7$ are = 115°/61°. Table II gives atomic ratios as determined by XPS for these transformations.

Discussion

Scheme I



Oxidation of hydrocarbons with CrO_3 in acetic acid/acetic anhydride is reported to give hydroxylated hydrocarbons.[22–24] Retention of configuration is observed, and the relative rates of oxidation at primary, secondary, and tertiary carbons is 1:65:3500.[23] Reaction of PP film surfaces with $CrO_3/AcOH/Ac_2O$ does not, however, accomplish the simple and selective hydroxylation as depicted in eq 1. UV–vis and ATR IR spectra (Figures 1a and 5b) indicate the presence of carbonyls and olefins, conjugated to varying extents. Olefins and carbonyl-containing compounds are observed in prolonged oxidations of hydrocarbons.[23] Acid-catalyzed dehydration of initially tertiary and subsequently tertiary allylic alcohols (eq 2) is the likely



(2)

source of olefins. Carbonyls likely arise from oxidation of this unsaturation and esterification of the hydroxyl groups. We assign the carbonyl bands to a mixture of ketones and esters (predominantly ketones) and specifically not carboxylic acids. If carboxylic acids were present to a significant extent, brief treatment with aqueous base would shift a portion of the peak at 1711 cm^{-1} to lower frequency.[30] Long exposure removes the 1742 cm^{-1} (Figure 5f), and we interpret this change as due to ester hydrolysis. PP-$OCOCH_3$ can be formed from the reaction of PP-OH with acetic anhydride. If the ester functionality were present as PP-$OCOCH_3$, hydrolysis by aqueous NaOH would yield PP-O^-. If, however, the esters were PP-CO_2CH_3, hydrolysis would yield PP-COO^- and protonation should give a more intense carbonyl peak at 1711 cm^{-1} due to the carbonyl of PP-COOH. Protonation[33] does not provide any significant changes in the ATR IR spectrum, indicating that the esters are predominantly acetates (PP-$OCOCH_3$).

The XPS spectrum indicates a slight oxidation (Figures 3b and 4): the maximum O:C ratio is 1:12 which corresponds to one oxygen per four PP repeat units. The fact that a portion of this oxygen is present as hydroxyl groups is indicated by their reaction with heptafluorobutyryl chloride (Figures 3c and 5e). The low receding contact angles and large contact angle hysteresis (Table I) are consistent with a slight oxidation and suggest that the O:C stoichiometry determined by XPS is a reasonable description of the contact angle sampling region.[34]

The kinetics of the reactions that produce PP-[O] are autoinhibitive when monitored by UV–vis or XPS (Figures 2 and 4), suggesting that the reactions selectively occur at sites accessible to the oxidizing solution (the surface) and then cease. Angle-resolved XPS analysis indicates that reaction in the outer 10 Å is complete before the reaction in the outer 40 Å. Gravimetric analysis (a qualification of the quantitative significance of these data is stated above) (Figure 6) indicates that after an initial gain, mass is gradually lost upon reaction. Two alternative explanations for this mass loss are (1) the oxidation reaction, in addition to introducing functionality, is cleaving chains and low molecular weight fragments are ablated and (2) the functionalized product (PP-[O]) slowly dissolves into the oxidizing solution. We favor the second explanation because of the absence of a significant quantity of carboxylic acids, which would be present if chains were cleaved. Storing the oxidized film in reaction solvent causes the O:C ratio, observed by XPS, to decrease by

30–40%; this also supports the second explanation. Scheme I is a graphic representation of the oxidation reaction.

The relative extents of reaction in the outer 10 Å and outer 40 Å (as determined by XPS—Figure 4) and the fact that the increase in the amount of oxidized product in the outer 40 Å levels off at the same rate that the increase in the amount of oxidized product in the entire film levels off (as determined by UV–vis—Figure 2) indicate that the thickness of the modified layer is on the order of the XPS sampling depth. Gravimetric data qualitatively substantiate this value (a 5-μg mass loss corresponds to a ca. 100-Å thick PP layer), and we place our estimate at a 100-Å thick modified layer. This value is at the limits of SEM resolution and is consistent with our observations of no topographical changes.

Hydroboration reduces the carbonyl functionality and a portion of the olefins[29] as evidenced by ATR IR (Figure 5c) and breaks up the conjugation as evidence by UV–vis (Figure 1b) and visual inspection (the yellow tint disappears). The density of hydroxyl groups on PP-OH is about double that on PP-[O]: the yield of the heptafluorobutyryl chloride labeling reaction is doubled (Table II).

Summary and Conclusions

Oxidation of PP film with $CrO_3/AcOH/Ac_2O$ at room temperature introduces hydroxyl, ester (PP-$OCOCH_3$), ketone, and olefin functionality to the outermost 100 Å of the film surface. Concomitant with this modification is the dissolution of the modified polymer; the modified layer remains ca. 100 Å thick. The carbonyls and a portion of the olefins in this modified layer can be reduced with borane to increase the density of hydroxyl groups. There is no change in surface topography with either the oxidation or the reduction. The hydroxyl groups are esterified with heptafluorobutyryl chloride, and the wetting properties of the surface change due to this transformation.

Acknowledgment. We are grateful to the University of Massachusetts NSF Materials Research Laboratory and Hercules Inc. for financial support. Electron microscopy was carried out by Mr. Louis Raboin using a University of Massachusetts NSF Materials Research Laboratory electron microscope. T.J.M. acknowledges the support of the National Science Foundation in the form of a Presidential Young Investigator Award.

Registry No. PP, 25085-53-4; $ClCOC_3F_7$, 375-16-6.

References and Notes

(1) Baum, B.; Parker, C.; Deanin, R. In *Plastics Polymer Science and Technology*; Baijal, M. D., Ed.; Wiley-Interscience: New York, 1982.

(2) Briggs, D.; Kendall, C. R.; Blythe, A. R.; Wooten, A. B. *Polymer* **1983**, *24*, 47.

(3) Steinhauser, H.; Ellinghorst, G. *Angew. Makromol. Chem.* **1984**, *120*, 177.

(4) Brewis, D. M.; Briggs, D. *Polymer* **1981**, *22*, 7.

(5) Blais, P.; Carlsson, D. J.; Csullog, G. W.; Wiles, D. M. *J. Colloid Interface Sci.* **1974**, *47*, 636.

(6) Briggs, D.; Brewis, D. M.; Konieczo, M. B. *J. Mater. Sci.* **1976**, *11*, 1270.

(7) Shah, C. D.; Jain, D. K. *Text. Res. J.* **1984**, *54*, 742.

(8) Harttig, H.; Huttinger, K. J. *J. Colloid Interface Sci.* **1983**, *93*, 63.

(9) Nakagawa, T.; Yamada, S. *J. Appl. Polym. Sci.* **1972**, *16*, 1997.

(10) Narebska, A.; Bukowska, Z. *Makromol. Chem.* **1985**, *186*, 1411.

(11) Krisyuk, B. E.; Popov, A. A.; Zaikov, G. Y. *Polym. Sci. USSR (Engl. Transl.)* **1980**, *24*, 389.

(12) Citovicky, P.; Mikulasova, D.; Chrastova, V.; Mejzlik, J.; Majar, J. *Angew. Makromol. Chem.* **1983**, *117*, 131.

(13) Harley, F. R.; Murray, S. G.; Nicholson, P. N. *J. Polym. Sci., Polym. Chem. Ed.* **1982**, *20*, 2395.

(14) Hartley, F. R.; McCaffrey, D. J. A.; Murray, S. G.; Nicholson, P. N. *J. Organomet. Chem.* **1981**, *206*, 347.

(15) Busfield, W. K. *Eur. Polym. J.* **1981**, *17*, 333.

(16) Jellinek, H. H. G.; Wei, Y. C. *J. Polym. Sci., Polym. Chem. Ed.* **1986**, *24*, 389.

(17) Gaylord, N. G.; Mishra, M. K. *J. Polym. Sci., Polym. Lett. Ed.* **1983**, *21*, 23.

(18) Dias, A. J.; McCarthy, T. J. *Macromolecules* **1987**, *20*, 2068. This paper reports the independent introductions of carboxylic acid, aldehyde, and alcohol functionality to the surface of poly(chlorotrifluoroethylene).

(19) Lee, K.-W.; McCarthy, T. J. *Macromolecules* **1987**, *20*, 1437. This paper reports chemical transformations of surface hydroxyl groups on poly(chlorotrifluoroethylene).

(20) Costello, C. A.; McCarthy, T. J. *Macromolecules* **1987**, *20*, 2819. This paper reports the introduction of alcohol, amine, and carboxylic acid functionality to the surface of poly(tetrafluoroethylene).

(21) Dias, A. J.; McCarthy, T. J. *Macromolecules* **1984**, *17*, 2529. This paper reports the surface-selective dehydrofluorination of poly(vinylidene fluoride). We have extended this chemistry to introduce amine and hydroxyl functionality: Brennan, J. V., unpublished results.

(22) Shilov, A. E. *Activation of Saturated Hydrocarbons by Transition Metal Complexes*; D. Riedel Publishing Co.: Holland, 1984.

(23) Wiberg, K. B.; Foster, G. *J. Am. Chem. Soc.* **1961**, *83*, 423.

(24) Rocek, J. *Tetrahedron Lett.* **1962**, 135.

(25) The absorbance band of the product is broad and is flat between 260 and 275 nm.

(26) The hydroxyl band is difficult to observe as it is broad and has a relatively low extinction coefficient. We have introduced hydroxyl groups to the surface of poly(chlorotrifluoroethylene) (PCTFE) and can control the modification depth. The hydroxyl band is clearly observed in samples with modified layers of 1500 Å thickness and is not observed in samples with modified layers of 100 Å or less.[35]

(27) Nuzzo, R. E.; Smolinsky, G. *Macromolecules* **1984**, *17*, 1013. These authors report the reduction of plasma-induced functionality to hydroxyl groups on a polyethylene surface.

(28) Working up the hydroboration with basic peroxide introduces additional hydroxyl groups. Atomic ratios (from XPS, 15° takeoff angle) (O:C) are 8:92 (acetic acid) and 11:89 (basic peroxide).

(29) Hydroboration for 24 h reduces most of the olefins but there is an accompanying mass loss with this prolonged treatment.

(30) Holmes-Farley, S. R.; Reamey, R. H.; McCarthy, T. J.; Deutch, J.; Whitesides, G. M. *Langmuir* **1985**, *1*, 725. These authors report that a carboxylic acid on the surface of polyethylene ($\nu_{C=O}$ = 1710 cm^{-1}) is rapidly deprotonated by aqueous base.

(31) Similar experiments were carried out by using trichloroacetyl isocyanate. The XPS spectrum exhibits N_{1s} (404 eV) and Cl_{2p} (205 eV) photoelectron lines. The ATR IR spectrum exhibits two weak carbonyl bands at 1804 and 1748 cm^{-1} (PCTFE-$OCONHCOCCl_3$ has two carbonyl bands at 1796 and 1746 cm^{-1}).[35] This conversion requires a very long reaction, and we have not brought it to completion.

(32) The ester carbonyl band of PCTFE-$OCOC_3F_7$ appears at 1782 cm^{-1} (Lee, K.-W., unpublished result).

(33) We acknowledge a reviewer for suggesting this experiment.

(34) Johnson, R. E.; Dettre, R. In *Surface and Colloid Science*; Matijevic, E., Ed.; Wiley: New York, 1980.

(35) Lee, K.-W.; McCarthy, T. J., submitted for publication.