Chemical Surface Modification of Poly(ethylene terephthalate)

Wei Chen and Thomas J. McCarthy*

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

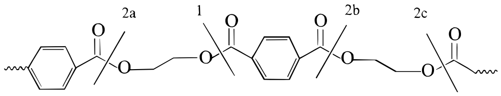
Received July 15, 1997; Revised Manuscript Received March 9, 1998

ABSTRACT: Reactions of semicrystalline poly(ethylene terephthalate) (PET) film with ester-selective reagents at the film−solution interface can be controlled to produce modified film samples containing a thin (less than ~ 40 Å) surface layer of the reagent-induced functionality. Hydrolysis of PET yields a surface mixture of alcohol and carboxylic acid groups. Reduction with lithium aluminum hydride and transesterification with ethylene glycol (glycolysis) both produce surfaces with alcohol functionality (PET−OH^R and PET−OH^G, respectively). Each of these modification reactions involves chain cleavage and can lead to significant sample degradation (reactive dissolution); for each modification reaction, conditions were optimized to maximize conversion and minimize degradation. The reactivity of surface alcohols (PET−OH) was assessed for samples prepared by both reduction and glycolysis, and a comparative analysis was made: the presence of benzylic alcohols in reduced samples and their absence in glycolyzed samples as well as the difference in surface alcohol concentration between the two surfaces (the surface density of alcohols is higher on PET−OH^G than on PET−OH^R by a factor of ~2) affect the reactivity. Reaction with thionyl chloride produces a surface mixture containing alkyl chloride (PET−Cl and sulfite (PET−(O)$_2$SO) functionality. Reactions with acid chlorides yield esters (PET−OC(O)R) and reactions with isocyanates yield urethanes (PET−OC(O)NHR). Reactions with diisocyanates produce surface mixtures containing diurethane and half urethane/half isocyanate functionality (PET−(OC(O)NH)$_2$R/−OC(O)-NHRNCO); the composition of these mixtures depends on both the method of PET−OH preparation and the diisocyanate structure. Reactions were monitored and products were characterized by gravimetric analysis, contact angle, XPS, ATR IR, and SEM. Reaction yields were assessed by quantitative XPS analysis and were generally >70%.

Introduction

Chemistry at polymer surfaces and interfaces is central to many polymer materials applications.[1,2] We have been developing synthetic routes to chemically modify polymer surfaces with the objective of preparing substrates with controllable surface chemical structures so that we can rationally address the control of macroscopic surface properties (adsorption, adhesion, wettability, and friction). We have focused on chemically resistant polymer film samples as substrates and have devised methods to introduce versatile organic functional groups at their surfaces. A surface-functionalized film sample of this type can be converted to a spectrum of samples having the same inert interior and the same concentration of surface functionality, but different surface-chemical structures. These spectra of samples permit correlations between microscopic surface structure and macroscopic surface properties. We have focused primarily on fluoropolymers, including poly(tetrafluoroethylene) (PTFE),[3,4] poly(tetrafluoroethylene-*co*-hexafluoropropylene) (FEP),[5,6] poly(chlorotrifluoroethylene) (PCTFE)[6−13] and poly(vinylidene fluoride) (PVF$_2$),[6,14,15] but have also studied nonfluorinated chemically resistant polymers including polypropylene[16] and poly(ether ether ketone) (PEEK).[17] The advantages of these materials as substrates for surface chemistry have been discussed in these papers. More recently, we have turned our attention to the surface modification of less chemically resistant (more reactive) polymers and report here studies on the chemical surface modification of poly(ethylene terephthalate) (PET). PET is widely used in various forms for a large variety of applications;[18] it has good mechanical strength, toughness, fatigue resistance at elevated temperatures, and a high crystalline melting temperature (270 °C). That it can be (and is being) recycled is an advantage. Its intrinsic low surface energy results, however, in poor adhesion, wettability, and biocompatibility—it is an ideal candidate for chemical surface modification.

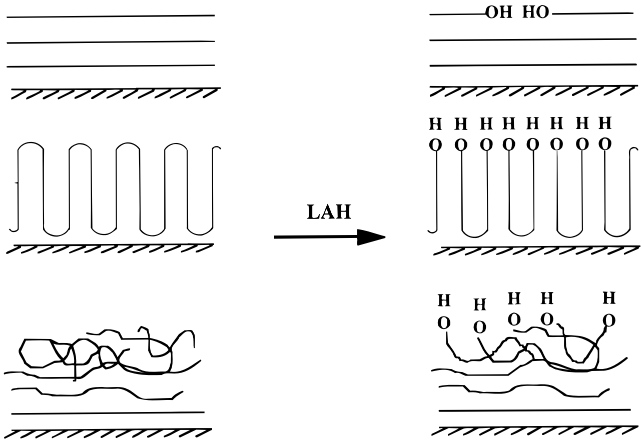
Scheme 1. Sequential Hydrolytic Cleavage Sites on PET



In some senses it is more straightforward to modify a reactive polymer than a chemically resistant one: the ester moiety in PET clearly suggests more chemical strategies than do the perfluoroalkane chains in PTFE. There are, however, equally challenging issues to address in preparing modified substrates that are suitable for further chemical modification; we point out five of these general issues for reactive substrates as they apply to PET: (1) Modification of PET through ester reactivity involves chain cleavage that leads to surface functionality at new chain ends but also causes the degradation of the polymer sample. Reaction conditions have to be tuned to optimize functional group concentration and minimize degradation. (2) The sequence of ester cleavage reactions on PET can determine the relative concentration of surface functionality. In hydrolysis of PET (Scheme 1), for example, the first reaction yields one alcohol and one carboxylic acid. If the modification reaction involves only initial chain cleavage events, then the surface will contain an equal concentration of alcohols and carboxylic acids. If, however, the reaction proceeds near the initial hydrolysis sites, the relative surface functional group concen-

S0024-9297(97)01060-7 CCC: $15.00

Scheme 2. Conformations of PET Surface Chains



trations will depend on the relative rates of different hydrolyses. The second reaction near an initial hydrolysis site can yield (Scheme 1) two carboxylic acids (2a), two alcohols (2b), or one alcohol and one acid (2c). (3) The surface functional group density will depend on the morphology of the polymer near the surface, and, in particular, on the orientation of chains relative to the plane of the surface. This is described pictorially (using the reduction of PET to alcohols as an example) in Scheme 2: If chains are oriented more perpendicular to the plane of the surface, then surface functional group density will be higher than if chains are oriented more parallel. If the chain orientation varies with depth, surface functional group composition will change with extent of reaction due to the change in chain orientation. (4) The surface-functionalized PET samples prepared by initial modification reactions will still contain reactive ester functionality. Conditions for subsequent functional group transformations have to be selective against ester chemistry. (5) Surface functional groups on PET may react differently because of structural differences. For example, an alcohol-containing PET surface prepared by reduction will contain both hydroxyethyl groups and benzylic alcohols as reactive species, and these may react at different rates or yield different products with some reagents.

These issues were the focus of this study. Our initial objectives were to prepare and study the reactivities of alcohol-functionalized PET surfaces prepared by three routes (reduction, transesterification with ethylene glycol—glycolysis, and hydrolysis followed by selective reduction of the carboxylic acid), acid-functionalized surfaces prepared by hydrolysis followed by reaction with succinic anhydride, and mixed surfaces prepared by hydrolysis. We were not successful in preparing a surface containing only carboxylic acids or in selectively reducing acids on the polyester surface. We report here the control of functionality and degradation with hydrolysis conditions and the preparation and reactivity of alcohol-functionalized PET surfaces prepared by two different routes: reduction with lithium aluminum hydride and transesterification with ethylene glycol. There are several reports of chemical surface modification of PET by hydrolysis[19−21] and reduction.[21,22] PET has also been surface modified by other techniques including plasma,[23] corona discharge,[24] ion beam treatment,[25] laser treatment,[26] photoinitiated graft polymerization,[27] aminolysis,[21,28] entrapment of poly(ethylene oxide),[29] and activation of alcohol chain ends with *p*-toluenesulfonyl chloride and subsequent chemistry.[30,31] The chemical reactions of PET with regard to chemical recycling have been reviewed.[32]

Experimental Section

Materials. PET film (Du Pont Mylar, 5 mil) was cleaned by rinsing with distilled water and methanol and then in refluxing hexane for 2 h. All reagents were obtained from Aldrich. Tetrahydrofuran was distilled from sodium benzophenone dianion; pyridine and hexadecane were distilled from calcium hydride at reduced pressure. Anhydrous ethylene glycol was further dried under vacuum (0.02 mm, room temperature, >1 h) after the addition of ~1% benzene. House-purified water (reverse osmosis) was purified using a Millipore Milli-Q system that involves reverse osmosis, ion-exchange, and filtration steps. Thionyl chloride was purified by distillation; heptafluorobutyryl chloride and acetyl chloride were purified by freeze−pump−thaw cycles and then trap-to-trap distillation; stearoyl chloride was distilled at reduced pressure. Dibutyltin dilaurate, 1 M borane in THF, 1,1′-carbonyldiimidazole, 1,6-diisocyanatohexane, 1 M lithium aluminum hydride in THF, lithium diisopropylamide, phenyl isocyanate, potassium *tert*-butoxide, succinic anhydride, tolylene-2,4-diisocyanate, and trichloroacetyl isocyanate were used as received. Air-sensitive materials were stored under dry nitrogen. All reactions except hydrolyses were carried out under dry nitrogen in Schlenk flasks; reagents were transferred via either cannula or syringe; reactions with films were not stirred.

Methods. X-ray photoelectron spectra (XPS) were obtained with a Perkin-Elmer-Physical Electronics 5100 with Al Kα excitation (400 W, 15.0 kV). Spectra were taken at two different takeoff angles, 15 and 75° (between the plane of the surface and the entrance lens of the detector optics). Contact angle measurements were made with a Ramè-Hart telescopic goniometer and a Gilmont syringe with a 24-gauge flat-tipped needle. Probe fluids were water, purified as described above, and hexadecane. Dynamic advancing (θ_A) and receding angles (θ_R) were recorded while the probe fluid was added to and withdrawn from the drop, respectively. The values reported are averages of five measurements made on different areas of the film sample surface. Attenuated total reflectance infrared (ATR IR) spectra were obtained under dry air using an IBM 38 FTIR spectrometer and a germanium internal reflection element (45°). Scanning electron microscopy (SEM) was performed using a JEOL 100CX STEM. Gravimetric measurements were made with a Sartorius 1612MP-1 analytical balance.

Hydrolysis of PET (PET−OH/-COOH).[19−21] A cleaned PET film sample (1 × 5 cm) was introduced to a flask containing 25 mL of 1 M NaOH that had been equilibrated to the desired temperature in a constant-temperature bath for at least 1 h. After the desired reaction time, the film sample was removed with tweezers and rinsed sequentially with 0.1 M HCl, two aliquots of water, methanol, and hexane, and then dried at reduced pressure (0.02 mm, room temperature, 24 h).

Reduction of PET (PET−OH^R).[21,22] To a nitrogen-purged Schlenk tube containing a cleaned PET film sample was added 25 mL of THF. After 4.5 h at room temperature, the solvent was removed and the film was dried (0.02 mm, room temp., 24 h). A THF solution (25 mL) of $LiAlH_4$ (at the desired concentration) was added. After the desired reaction time at the desired reaction temperature, the film was washed sequentially with THF (two aliquots), water, 0.1 M HCl, water (two aliquots), methanol, and hexane and then dried (0.02 mm, room temperature, 24 h).

Glycolysis of PET (PET−OH^G).[33] To a nitrogen-purged Schlenk tube containing a cleaned PET film sample was introduced 25 mL of 0.60 M potassium *tert*-butoxide in ethylene glycol. After the desired reaction time at room temperature, the film was rinsed sequentially with ethylene glycol (two aliquots), water, 0.1 M HCl, water (two aliquots), methanol, and hexane and then dried (0.02 mm, room temperature, 24 h).

Labeling Reactions. (1) −OH groups (PET−OC(O)-C_3F_7). To a nitrogen-purged Schlenk tube containing the film under study was added a solution of heptafluorobutyryl chloride (1.556 g, 6.69 mmol) in THF (25 mL). After reaction for 2 h at room temperature, the film was removed, rinsed sequentially with THF (three aliquots), methanol, and hexane, and then dried (0.02 mm, room temperature, 24 h).

(2) −COOH groups (PET-C(O)$C_3H_3N_2$). To a nitrogen-purged Schlenk tube with a film already labeled with heptafluorobutyryl chloride was introduced a solution of 1,1′-carbonyldiimidazole (0.5 g, 3.08 mmol) in THF (25 mL). After 4 h at room temperature, the film was rinsed sequentially with THF (four aliquots) and hexane and dried (0.02 mm, room temperature, 24 h).

Reaction of PET−OH with Thionyl Chloride (PET−Cl/O_2SO). PET−OH film samples were allowed to react under nitrogen with thionyl chloride (1.631 g, 13.7 mmol) in THF (25 mL) at room temperature for 24 h. The film samples were rinsed with THF (four aliquots) and then dried (0.02 mm, room temperature, 24 h).

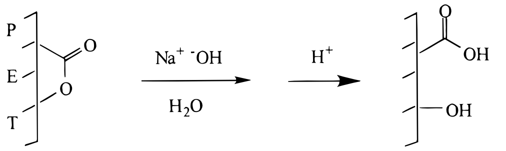
Reaction of PET−OH with Acid Chlorides (Acetyl Chloride, Stearoyl Chloride) (PET−OC(O)R). To a nitrogen-purged Schlenk tube containing PET−OH film samples was added THF (25 mL) via cannula, and then the acid chloride (6−14 mmol) followed by 0.10 mL of pyridine was introduced via syringe. The reactions were allowed to proceed at room temperature for 24 h. The films were rinsed sequentially with THF (three aliquots), methanol, and hexane and then dried (0.02 mm, room temperature, 24 h).

Reaction of PET−OH with Isocyanates (Phenyl Isocyanate, Trichloroacetyl Isocyanate, 1,6-Diisocyanatohexane, Tolylene-2,4-Diisocyanate) (PET−OC(O)NHR−NCO/$(OC(O)NH)_2R$). PET−OH film samples were allowed to react under nitrogen with isocyanate (6−9 mmol) and 0.10 mL of dibutyltin dilaurate in THF (25 mL) at room temperature for 24 h. The film samples were rinsed sequentially with THF (three aliquots) and hexane and then dried (0.02 mm, room temperature, 24 h).

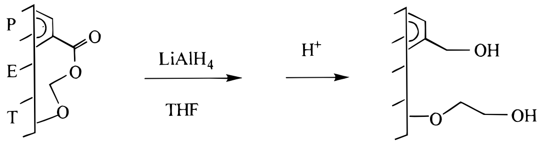
Results and Discussion

Commercial PET film samples were cut to appropriate size, cleaned with water, methanol, and then refluxing hexane, and dried to constant mass. Tared samples lost ~0.18% mass over 24 h at reduced pressure and room temperature, and no further mass loss was observed upon additional drying. After this procedure, PET surfaces exhibit advancing/receding contact angles (θ_A/θ_R) of 77/55° and are free of impurities as assessed by both ATR IR and XPS analyses. SEM analysis indicates the presence of ~0.1 μm diameter filler particles spaced by ~1 μm that are present in the commercial samples as antiblocking agents. These are subsurface as they are not detected by XPS, and the surface roughness that they impart does not affect the contact angle analysis. We have carried out a series of reactions on PET film samples, each of which involves exposing the film samples to reactive solutions in Schlenk tubes for various lengths of time at a controlled temperature; the reactions were not stirred. For each reported reaction, a number of experiments were performed to maximize conversion. In cases where careful kinetics are not reported, the conditions given represented those that gave the highest reproducible yields. The initial modification reactions were directed at the ester functionality to yield alcohol and alcohol/carboxylic acid functionalized surfaces (eqs 1−3).

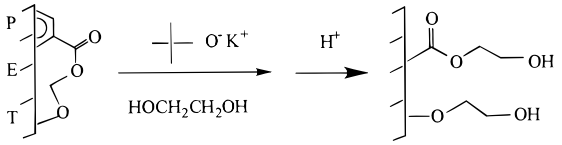
The surface concentration of functionality was assessed by XPS labeling reactions that are specific for alcohol and carboxylic acid groups. The reactivity of the alcohol functionality on different modified substrates was then assessed by converting PET−OH film samples to a range of samples using reagents that do not react with PET in control experiments. The resulting samples thus have different surface-chemical structures but identical interiors. Each of the reactions was monitored by contact angle, XPS, ATR IR, and gravimetric analysis.



(1)



(2)



(3)

Hydrolysis of PET (PET−OH/COOH). A range of hydrolysis conditions was surveyed in preliminary experiments that were monitored by gravimetric analysis and contact angle. Acid-catalyzed hydrolysis conditions that were studied include 1 M HCl at elevated temperatures (73, 100 °C), *p*-toluenesulfonic acid in water (60, 100 °C) and *p*-toluenesulfonic acid in acetone/water mixtures at 70 °C. Base-catalyzed hydrolysis studies used sodium hydroxide in various concentrations (0.2−4 M) in water and water/methanol mixtures at various temperatures. The base-catalyzed reactions were clearly more effective than those catalyzed by acid and were chosen for further study. Wettability improved significantly with no measurable mass loss in base-catalyzed reactions, but this was not the case for acid-catalyzed reactions. One of our objectives (described above−Scheme 1) was to control the alcohol:carboxylic acid ratio and we suspected that acid vs base catalysis may be one method to do this. We abandoned acid catalysis, however, due to the corrosive behavior of the reactions that gave poorer yields of surface functionality. We note that the addition of methanol to base-catalyzed reactions significantly increases the rate of reactions but does not improve wettability over aqueous sodium hydroxide solutions.

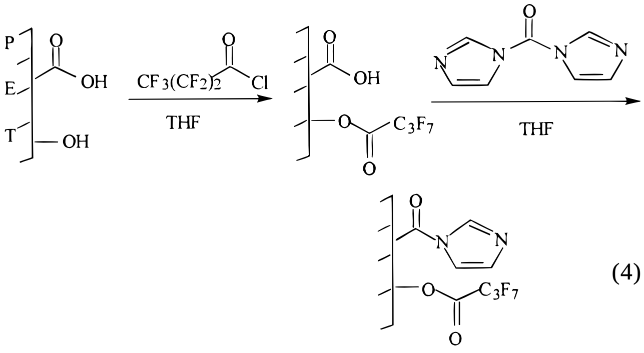
Reaction kinetics for hydrolysis of PET in 1 M aqueous NaOH at 25, 40, 60, 65, and 70 °C were determined using both contact angle and gravimetric analysis of the film samples. At each temperature, the water contact angles of the hydrolyzed surfaces decreased and reached constant values before any degradation was detectable by gravimetric analysis. Longer reaction times resulted in surfaces of identical wettability, but mass loss of the film samples became measurable. These observations agree with previous findings.[19−21] The disappearance of filler particles from the surface was also observed at longer reaction times. Hydrolyzed film samples (PET−OH/-COOH) for further study were prepared at each temperature using a reaction time that gave leveled contact angles and no measurable mass loss. Reaction times of 4 h and 30, 16, 16, and 8 min were chosen for hydrolysis temperatures at 25, 40, 60, 65, and 70 °C, respectively. Water contact angles of each of these PET−OH/−COOH

Table 1. Advancing and Receding Contact Angles (deg) (Water) for PET Derivatives

film sample	θ_A	θ_R
PET	77	55
$\mathrm{PET{-}OH/COOH}$	62	16
$\mathrm{PET{-}OH^{R}}$	72	32
$\mathrm{PET{-}OH^{G}}$	63	25
$\mathrm{PET{-}Cl/PET{-}O_2SO^{R}}$	78	44
$\mathrm{PET{-}Cl/PET{-}O_2SO^{G}}$	69	32
$\mathrm{PET{-}OC(O)C_3F_7{}^{R}}$	83	54
$\mathrm{PET{-}OC(O)C_3F_7{}^{G}}$	106	46
$\mathrm{PET{-}OC(O)CH_3{}^{R}}$	77	43
$\mathrm{PET{-}OC(O)CH_3{}^{G}}$	73	32
$\mathrm{PET{-}OC(O)(CH_2)_{16}CH_3{}^{R}}$	88	54
$\mathrm{PET{-}OC(O)(CH_2)_{16}CH_3{}^{G}}$	101	52
$\mathrm{PET{-}OC(O)NHPh^{R}}$	81	43
$\mathrm{PET{-}OC(O)NHPh^{G}}$	82	28
$\mathrm{PET{-}OC(O)NHCCl_3{}^{R}}$	79	34
$\mathrm{PET{-}OC(O)NHCCl_3{}^{G}}$	75	21
$\mathrm{PET{-}OC(O)NH(CH_2)_6NCO/(OC(O)NH)_2(CH_2)_6{}^{R}}$	73	41
$\mathrm{PET{-}OC(O)NH(CH_2)_6NCO/(OC(O)NH)_2(CH_2)_6{}^{G}}$	76	34
$\mathrm{PET{-}OC(O)NHPh(CH_3)NCO/(OC(O)NH)_2PhCH_3{}^{R}}$	84	42
$\mathrm{PET{-}OC(O)NHPh(CH_3)NCO/(OC(O)NH)_2PhCH_3{}^{G}}$	80	29

surfaces were indistinguishable ($\theta_A/\theta_R = 62 \pm 2°/16 \pm 1°$). The contact angle data for all of the surfaces described in this paper are in Table 1. We note that the contact angles observed for acid-catalyzed hydrolysis were $\theta_A/\theta_R = 69 \pm 3°/40 \pm 3°$.

The rationale for choosing a range of hydrolysis temperatures was that the total surface functional group density and the ratio of −OH and −COOH groups may be a function of hydrolysis temperature. Different activation energies for cleavage at different sites (Scheme 1) would result in a temperature-dependent surface composition. Surface functional group densities were determined by an XPS labeling scheme that distinguishes between alcohols and carboxylic acids (eq 4).



(4)

Heptafluorobutyryl chloride reacts selectively with alcohols in the presence of carboxylic acids and 1,1′-carbonyldiimidazole reacts with carboxylic acids.[34] These reactions introduce fluorine and nitrogen that can be quantified by XPS to determine the relative number of alcohol and carboxylic acid functional groups as well as the total functional group density relative to PET repeat units in the XPS sampling depth. The atomic composition of the PET repeat unit is $C_{10}O_4$ (XPS does not detect hydrogen); if n and m are the number of −OH and −COOH groups per PET repeat unit, respectively, the labeled surfaces have atomic compositions of $(C_{10}O_4)(C_4F_7O_2)_n(C_3N_2O)_m$. The values for n and m can be directly determined from the XPS data. The 15° takeoff angle data (that assess the composition of the outermost ~10 Å of the samples[35]) indicate that the surfaces contain ~0.1 −OH groups per PET repeat unit and ~0.06 −COOH groups per repeat unit within the XPS sampling region. These data, along with the total surface functional group concentrations, are plotted vs hydrolysis temperature in Figure 1. The 75° takeoff angle data, that assess the outer ~40 Å of the samples,[25] indicate ~0.06 −OH and ~0.04 −COOH groups per repeat unit. Both fluorine and nitrogen atomic composition data at both 15 and 75° takeoff angles show no dependence on hydrolysis temperature. The takeoff angle dependence indicates that the thickness of the modified layers (depth of the hydrolysis reactions) is less than 40 Å and, in particular, that the functional group density is higher in the outermost 10 Å than in the region beneath this. This is consistent with the gravimetric analysis and also the fact that no changes in ATR IR spectra are observed for these reactions. The lack of changes in the infrared spectra indicate a modification depth of less than 200 Å (we would expect to see changes if the depth were greater than this value because the sampling depth[36] under the condition employed is ~0.2−0.5 μm for 3000−1500 cm^{-1}). These labeling reactions were the only chemistry of PET−OH/COOH studied in any detail. The synthesis of a pure carboxylic acid surface from PET−OH/COOH was attempted using base-catalyzed esterification of the alcohol functionality with succinic anhydride. Carboxylic acid concentration increased, but conditions were not found that did not cause a reaction with virgin PET in control experiments.

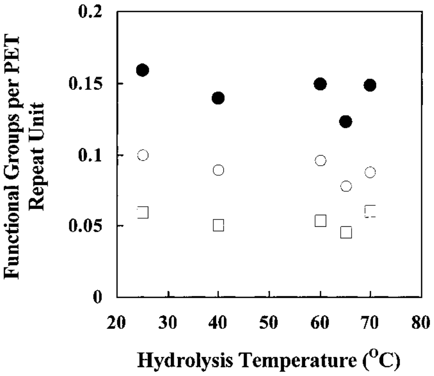


Figure 1. Number of functional groups per PET repeat unit as a function of hydrolysis temperature, determined from XPS analysis of labeled PET−OH/COOH surfaces: alcohols (○), carboxylic acids (□), total functional groups (●).

The functional group concentrations determined by XPS, expressed as ratios to PET repeat units in Figure 1, can be used to estimate surface densities (functional groups/cm^2). There are 4.2×10^{14} PET repeat units/cm^2 in the outermost 10 Å of virgin PET (assuming a density of 1.375). The ratios determined from the 15° takeoff angle XPS data thus indicate that there are ~4 × 10^{13} alcohols/cm^2 and ~2.5 × 10^{13} carboxylic acids/cm^2. We emphasize that these numbers are only estimates and are calculated only for comparison with data described below. The alcohol:carboxylic acid ratio (4:2.5) is likely biased high and should not be construed to indicate that hydrolysis at particular sites is favored: the perfluoroalkyl groups likely stratify above the acyl imidazolide groups to lower surface energy. We conclude that base-catalyzed hydrolysis consistently yields surface mixtures of alcohols and carboxylic acids and that the surface density and relative numbers of −OH and −COOH groups have no dependence on the hydrolysis temperature in the range studied.

Reduction of PET (PET−OH^{R}). Initial experiments to screen conditions for reducing PET to an

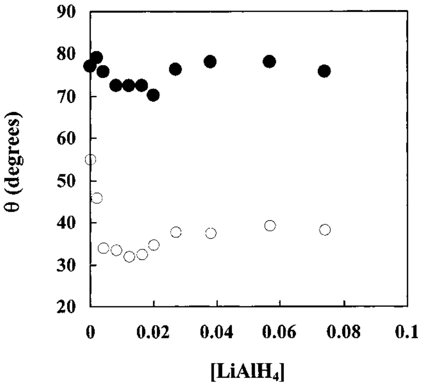


Figure 2. Water contact angle of PET−OH^R surfaces as a function of reducing agent ($LiAlH_4$) concentration: θ_A(●); θ_R(○).

alcohol-containing surface (PET−OH^R) used lithium aluminum hydride and bis(2-methoxyethoxy)aluminum hydride in THF and toluene solutions; contact angle and XPS analysis of heptafluorobutyryl chloride labeled samples were used to assess conversions. THF solutions of $LiAlH_4$ were chosen for further studies, as they gave the most consistent results. During the course of these studies we noted that if the PET samples were soaked in THF prior to exposure to the reducing agent, then the yield of surface alcohols was improved significantly. We believe that the solvent anneals the surface and changes the average chain orientation to render the increased yields; this is described in Scheme 2 above and below to a further extent. The PET used for all of the experiments described below as substrates for reduction was solvent-annealed for 4.5 h in THF at room temperature prior to reaction. These conditions were chosen somewhat arbitrarily and a careful study was not made to optimize yield.

Three reaction parameters were studied to optimize the yield of surface alcohol functionality: reducing agent concentration, reaction time, and reaction temperature. These variables are not independent, and they were optimized sequentially to maximize alcohol density on the modified surface. For the first parameter studied, $LiAlH_4$ concentration, the reaction time and temperature were kept constant, at 30 min and 25 °C. Water contact angles of the reduced surfaces are shown as a function of reducing agent concentration in Figure 2. The U-shaped curves observed in both the advancing and receding angle data were confusing, but reproducible. The initial increase in wettability with increasing reagent concentration to a maximum is expected for reaction at a solution−solid interface, but the subsequent drop in wettability upon further increase of the reducing agent concentration puzzled us for sometime. A plausible explanation follows: In virgin PET the chains tend to be parallel to the surface due to the processing conditions (biaxial orientation). With this initial chain conformation, small chain segments produced during reduction leave the surface and dissolve in the solution. This leads to surfaces with low alcohol density as was observed in PET samples that were reduced prior to annealing in THF (see Scheme 2). At the other extreme, if all the chains near the interface were perpendicular to the surface, a high alcohol density surface would result from reduction. We believe that the solvent annealing allows chains near the surface to relax and adopt a more random conformation, that is between these two extremes. Accordingly, reduction of solvent-annealed PET gives higher alcohol density than that of unannealed PET. The increase in contact angle observed with increasing reducing agent concentration can be ascribed to the removal of this randomized layer and exposure of parallel oriented chains. The same type of behavior (a maximum in alcohol concentration) is observed with the variables of temperature and reaction time (discussed below).

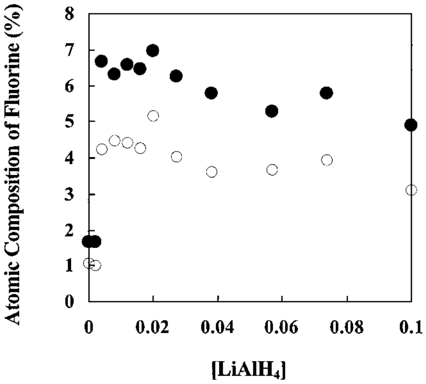


Figure 3. XPS fluorine atomic concentration of PET−OH^R as a function of reducing agent concentration after labeling with heptafluorobutyryl chloride: 15° takeoff angle data (●); 75° takeoff angle data (○).

The reduced film samples were labeled with heptafluorobutyryl chloride and 1,1′-carbonyldiimidazole for XPS analysis to quantify the number of −OH and −COOH groups on the surface. No nitrogen was detected indicating the absence of carboxylic acids. Figure 3 shows plots of fluorine content of PET−OH^R vs $LiAlH_4$ concentration. Both the 15 and 75° takeoff angle data show maximum modification in the same concentration region as contact angle analysis indicates maximum wettability. That the fluorine content observed at 15° is considerably higher than that observed at 75° indicates that the reduction is surface-selective. No mass loss was observed at any of the concentrations studied; this confirms the surface selectivity and also indicates that the region of the surface that is reoriented during the solvent annealing is very thin. SEM indicates that the filler particles are not disturbed by this procedure.

We chose the midpoint of the maximum modification region, $[LiAlH_4] = 0.012$ M, as the concentration to use for studying reaction time (at 25 °C); the reaction time was varied from 5 to 60 min. Water contact angles of different film samples were insensitive to the variation of reaction time in the range studied. XPS indicated, based on fluorine content of heptafluorobutyryl chloride labeled samples that the surface alcohol concentration increased over the first ~30 min of reaction and decreased subsequently. The fluorine atomic concentration for a 30 min reacted sample was 6.6%/4.4% (15/75° takeoff angle).

The effect of reaction temperature was studied with $LiAlH_4$ concentration and reaction time at the determined optimum values, 0.012 M and 30 min. Reactions were carried out at 0, 25, 35, and 45 °C. The contact angles of film samples were again not sensitive to the variation of reaction temperature. XPS analysis of labeled samples indicated a maximum in alcohol concentration for the sample prepared at 35 °C; the fluorine atomic concentration for this sample was 6.8%/4.4% (15/75° takeoff angle). This alcohol concentration is essentially identical to that of samples prepared at 25 °C

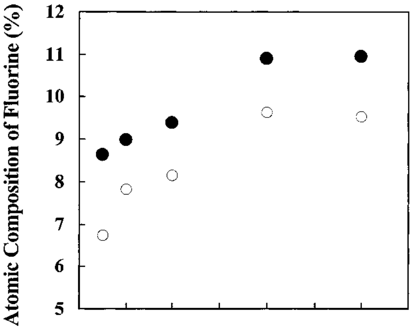


Figure 4. Kinetics of PET−OH^G formation as assessed by XPS fluorine concentration of heptafluorobutyryl chloride labeled samples: 15° takeoff angle data (●); 75° takeoff angle data (○).

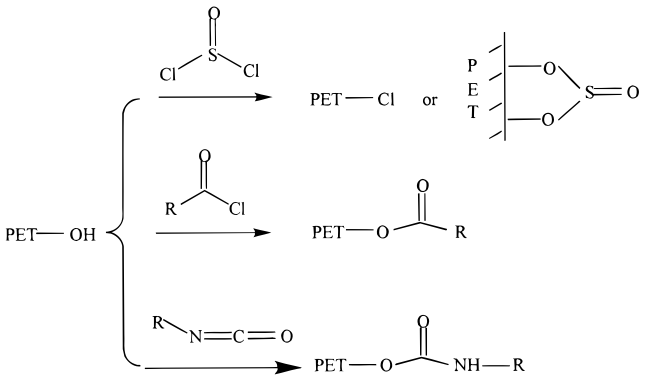
so we chose 25 °C (for experimental simplicity), 0.012 M LiAlH$_4$, and 30 min as the conditions for further studies. The 15° takeoff angle data indicate that the surfaces prepared under these conditions contain ∼0.15 −OH groups per PET repeat unit. This corresponds, using the assumptions discussed above, to ∼6.3×10^{13} alcohols/cm^2. The PET−OH^R surface thus has approximately the same density of alcohol functionality as the total functional group density of PET−OH/COOH.

Glycolysis of PET (PET−OH^G). Transesterification using ethylene glycol was the other method used to prepare alcohol-functionalized PET. We realized from the reduction studies just discussed that the reaction parameters (reagent concentration, reaction time, and reaction temperature) that affect the extent of modification are dependent variables and arbitrarily chose a fixed reagent concentration and a fixed reaction temperature and optimized the reaction by studying the kinetics under these conditions. Glycolysis was carried out in 0.60 M potassium *tert*-butoxide in ethylene glycol at room temperature. The water contact angles decreased upon reaction from θ_A/θ_R = 77/55° to θ_A/θ_R = 63/30° over the first 30 min of reaction. The advancing contact angle remained at 63° until 6 h reaction time (the longest time studied), while the receding contact angle decreased further to 25° after 4 h reaction, where it remained until 6 h reaction time. Gravimetric analysis of glycolyzed film samples indicated no detectable mass loss upon reaction; the scatter in the data suggested a slight mass gain, if anything. SEM indicates that the filler particles are still present after this procedure. Glycolyzed film samples were labeled with heptafluorobutyryl chloride (for −OH groups) and 1,1′-carbonyldiimidazole (for −COOH groups). No nitrogen was detected, indicating that no carboxylic acids are present. Figure 4 shows the XPS results (fluorine content vs reaction time) for this series of labeled samples. The results mirror the contact angle data, indicating that the alcohol density levels after 4 h of reaction. Both the XPS and contact angle data suggest that the reaction may stop after ∼4 h, but this may not be the case. The glycolysis may continue and degrade the sample leaving a steady state concentration of alcohols. The gravimetric data (no mass loss) suggests that under these conditions, degradation is negligible and a thin modified layer is formed. The takeoff angle dependence of the fluorine content (Figure 4) as well as the ATR IR spectra (only PET absorbances) support this conclusion. The 15° takeoff angle data indicate PET−OH^G prepared under these conditions (4 h, 0.60 M potassium *tert*-butoxide, 25 °C) contains ∼0.27 surface alcohol groups per PET repeat unit. From this ratio a surface alcohol density of ∼1.3×10^{14} alcohols/cm^2 is calculated using the assumptions described above. The PET−OH^G surface contains about twice the alcohol concentration as the PET−OH^R surface and twice the total functional group density of PET−OH/COOH surfaces.

Table 2. XPS Atomic Composition Data (15° Takeoff Angle) for PET Derivatives

film sample	% C	% O	% N	%Cl	%S or % F
PET	71.50	28.50			
PET−OH/PET−COOH	69.90	30.10			
PET−OH^R	70.68	29.32			
PET−OH^G	69.10	30.90			
PET−Cl/PET−O$_2$SO^R	69.56	30.02		0.26	0.16^S
PET−Cl/PET−O$_2$SO^G	68.27	31.22		0.16	0.35^S
PET−OC(O)C$_3$F$_7^R$	66.47	26.96			6.57^F
PET−OC(O)C$_3$F$_7^G$	62.43	26.69			10.88^F
PET−OC(O)CH$_3^R$	68.08	31.92			
PET−OC(O)CH$_3^G$	67.93	32.07			
PET−OC(O)(CH$_2$)$_{16}$CH$_3^R$	70.84	29.16			
PET−OC(O)(CH$_2$)$_{16}$CH$_3^G$	73.51	26.49			
PET−OC(O)NHPh^R	69.03	30.18	0.79		
PET−OC(O)NHPh^G	68.23	30.48	1.29		
PET−OC(O)NHCCl$_3^R$	67.04	30.44	0.92	1.60	
PET−OC(O)NHCCl$_3^G$	63.15	31.66	1.57	3.61	
PET−OC(O)NH(CH$_2$)$_6$NCO/ (OC(O)NH)$_2$(CH$_2$)$_6^R$	67.87	31.04	1.08		
PET−OC(O)NH(CH$_2$)$_6$NCO/ (OC(O)NH)$_2$(CH$_2$)$_6^G$	67.53	30.59	1.88		
PET−OC(O)NHPh(CH$_3$)NCO/ (OC(O)NH)$_2$PhCH$_3^R$	67.70	31.10	1.20		
PET−OC(O)NHPh(CH$_3$)NCO/ (OC(O)NH)$_2$PhCH$_3^G$	67.23	30.38	2.39		

PET−OH Chemistry. The reactivity of surface alcohols was assessed using two film samples, PET−OH^R and PET−OH^G, prepared using the optimized conditions described above. These two surfaces differ chemically in two respects: (1) the PET−OH^R surface contains both hydroxyethyl groups and benzylic alcohols, and the PET−OH^G surface contains only hydroxyethyl groups; (2) the density of alcohols on the PET−OH^G surface is about twice as high as on PET−OH^R. Reactions with thionyl chloride, acid chlorides and isocyanates were studied (eq 5). The water contact angle and XPS atomic composition data (15° takeoff angle) for all of the PET derivatives are given in Tables 1 and 2, respectively. We assessed the reactivity of the surface alcohols in general and the differences in



(5)

reactivity of the two alcohol surfaces. The XPS spectra of all surfaces exhibited a takeoff angle (15 and 75°) dependence indicating that unreacted PET is present in the outer ~40 Å of film samples. The 15° data reported here are more representative of the composition of the portions of the samples that have been modified.

Reactions of PET−OH with Thionyl Chloride. Both PET−OH^R and PET−OH^G were allowed to react with thionyl chloride. After the reactions, contact angles of the film samples increased (Table 1), and both sulfur and chlorine were observed by XPS (Table 2), indicating the formation of both alkyl chloride and sulfite functionality (PET−Cl/O_2SO). We have studied this reaction previously with two different alcohol surfaces, PEEK−OH[17] and PCTFE−OH.[9] In the case of PEEK−OH, only PEEK−Cl is formed and in the case of PCTFE−OH, only the sulfite forms. We ascribe this reactivity difference to three factors: surface alcohol concentration, functional group flexibility, and chemical structure. PEEK−OH contains a relatively low concentration of secondary doubly benzylic alcohols attached directly to the PEEK backbone; each of these factors favors alkyl chloride formation rather than sulfite formation; we suspect that this reaction proceeds by an S_N1 mechanism. On the other hand, the PCTFE−OH structure contains a high concentration of primary alcohols attached to the polymer chain by a flexible three-methylene spacer, favoring sulfite formation.

The presence of both sulfur and chlorine in the reaction products of PET−OH^R and PET−OH^G indicates competition between alkyl chloride and sulfite formation. The relative amount of sulfur and chlorine is, however, different on the two PET−OH-derived surfaces (Table 2), indicating different reactivities: chlorine is present in higher concentration than sulfur on PET−OH^R, and the ratio is the reverse on PET−OH^G. This difference in reactivities can be ascribed to the different alcohol structures and densities on the two surfaces. PET−OH^R contains both a lower alcohol concentration (more greatly spaced) as well as benzylic alcohols favoring alkyl chloride formation, and PET−OH^G contains a more dense array of primary alkyl groups favoring the sulfite. The reaction yields were determined by labeling unreacted alcohols with heptafluorobutyryl chloride after the reactions. The 15° takeoff angle XPS data indicate yields (based on fluorine atomic composition) of 69.4% for PET−OH^R and 59.2% for PET−OH^G.

Reactions of PET−OH with Acid Chlorides (PET−OC(O)R). We have used heptafluorobutyryl chloride extensively as a labeling reagent for surface alcohols both in this study and several others. The kinetics of this reaction was studied with PET−OH^G and indicates that esterification is rapid. After 10 min of reaction with 1.556 g (6.69 mmol) of heptafluorobutyryl chloride in 25 mL of THF at room temperature, PET−OH^G (now PET−OC(O)$C_3F_7{}^G$) exhibits water contact angles of θ_A/θ_R = 106/46° and XPS data indistinguishable from those for samples reacted for longer times (up to 4 h). We assume that this reaction is quantitative (reaction times of 2 h were used for all labeling studies), and the reaction yields and compositions indicated in this paper are based on this assumption. We note that the advancing contact angle of PET−OC(O)$C_3F_7{}^R$ is significantly lower than that of PET−OC(O)$C_3F_7{}^G$ indicating the expected lower concentration of perfluoropropyl groups.

PET−OH^R and PET−OH^G were allowed to react with acetyl chloride, and unreacted −OH groups were labeled with heptafluorobutyryl chloride to determine yields. Without the addition of pyridine to the reactions, the yields were ~60% after 24 h. The lower reaction rates of acetyl chloride compared to heptafluorobutyryl chloride are due to electronic differences. With pyridine catalysis, acetyl chloride reacts rapidly. From labeling studies, there were essentially no residual alcohol groups on PET−OH surfaces after reactions. Yields calculated from XPS data are ~100% for both PET−OH^R and PET−OH^G surfaces.

Reactions with stearoyl chloride were even slower than with acetyl chloride due to sterics. Yields were ~20% after 24 h without pyridine. With the presence of pyridine, the yields improved significantly to 93.0% for PET−OH^R and 90.8% for PET−OH^G. Longer reaction times did not improve the yields. Water contact angles of the ester surfaces were high (Table 1), especially the stearate surface derived from PET−OH^G (with higher ester group density). There is, however, no change in hexadecane contact angles of the film samples after the reaction (θ_A/θ_R = ~10/0°). If the closely packed long hydrocarbon chains crystallized on the surface, we would expect to see an increase in hexadecane contact angle; this is the case for the reaction of stearoyl chloride with PCTFE−OH.[37] The low hexadecane contact angles indicate relatively low −OH density on both PET−OH surfaces resulting in loosely packed hydrocarbon chains that do not crystallize.

Reactivity of PET−OH surfaces toward the three acid chlorides studied are in the order of heptafluorobutyryl chloride ≫ acetyl chloride > stearoyl chloride due to electronic and steric reasons. Reaction yields reached >90% in all cases. Both PET−OH^R and PET−OH^G surfaces show similar reactivity (nucleophilicity) in these reactions.

Reactions of PET−OH with Isocyanates. PET−OH samples were reacted with both monoisocyanates (trichloroacetyl isocyanate and phenyl isocyanate) and diisocyanates (1,6-diisocyanatohexane, HDI, and tolylene-2,4-diisocyanate, TDI) using dibutyltin dilaurate catalysis. For the reactions with monoisocyanates, reaction yields could be calculated directly by XPS (nitrogen content) analysis of the urethane surfaces. For the reactions with phenyl isocyanate, yields were 84.2% for PET−OH^R and 83.0% for PET−OH^G (15° takeoff angle data). Yields for the reactions with trichloroacetyl isocyanate were ~100% for both PET−OH film samples. The higher reaction yields may be due to sterics or the higher reactivity of trichloroacetyl isocyanate (kinetics were not determined). We note (Table 2) that the chlorine atomic concentration is low relative to nitrogen (there should be three Cl atoms per N) on the PET−OC(O)NHCOCCl_3 surfaces. This is due to the fact that chlorine is lost as a result of X-ray damage; no special precautions (reduced X-ray power or minimized acquisition time) were taken in analysis.

The situation is more complicated with reactions of diisocyanates. The diisocyanates, R$(NCO)_2$, can couple with two adjacent −OH groups to form PET−(OC(O)-NH)$_2$R or react with only one alcohol to form PET−OC-(O)NHRNCO. The ratios of these two products can be determined using XPS (nitrogen content) in conjunction with the labeling of unreacted alcohols with heptafluorobutyryl chloride to determine overall reaction yield. For the reaction with HDI, reaction yields were calculated to be 79.7% for PET−OH^R and 75.6% for PET−OH^G (15° takeoff angle data). Yields of reactions with TDI were calculated to be 84.5% for PET−OH^R and 80.3% for PET−OH^G. The ratio of surface alcohols on PET−OH^R that react with HDI and form diurethane (coupled product) to surface alcohols that react with a single site on the diisocyanate (to form a half urethane/half isocyanate moiety) is 73:37. The same ratio for reaction of PET−OH^R with TDI is 49:51. The results for PET−OH^G, expressed as the same ratio, are 27:73 for HDI and 8:92 for TDI. The result that HDI reacts bifunctionally to a greater extent than TDI with both surfaces is readily explained: The two isocyanate groups on the former have the same reactivity while those on the latter have different reactivities, and furthermore, the former is more flexible. The observation that alcohol groups on PET−OH^R are more likely to form diurethane than those on PET−OH^G is counter to what we expected from relative surface alcohol concentrations and is difficult to explain. Perhaps the partitioning of the diisocyanates between bulk solution and the solution/solid interface is different for the two PET−OH surfaces and there are higher local concentrations of diisocyanates at the PET−OH^R surface. We cannot offer a clearer explanation.

Summary and Conclusions

Alcohol functionality can be introduced to the surface of PET using either reduction or glycolysis, both of which cleave the PET chain. The surface density of alcohols is higher on PET−OH samples prepared by glycolysis than on those prepared by reduction by a factor of ∼2. The concentration of alcohols on reduced surfaces is increased by solvent annealing of the PET film prior to reduction; we believe that this is due to a reorientation of chains near the surface. Both of these modified surfaces (PET−OH^R and PET−OH^G) and hydrolyzed PET (PET−OH/COOH) can be prepared using conditions that minimize sample degradation. Conditions that optimize surface functional group concentration were determined. PET−OH^R and PET−OH^G samples react with alcohol-selective reagents (thionyl chloride, acid chlorides, and isocyanates), and their reactivities differ due to their chemical differences and their different surface alcohol densities.

Acknowledgment. We thank the Office of Naval Research for financial support. Use of the NSF-sponsored Materials Research Science and Engineering Center central facilities is acknowledged as well.

References and Notes

(1) Clark, D. T.; Feast, W. J. *Polymer Surfaces*; Wiley-Interscience: New York, 1978.
(2) Feast, W. J.; Munro, H. S.; Richards, R. W. Polymer Surfaces and Interfaces; John Wiley and Sons: New York, 1993.
(3) Costello, C. A.; McCarthy, T. J. *Macromolecules* **1987**, *20*, 2819.
(4) Costello, C. A.; McCarthy, T. J. *Macromolecules* **1990**, *23*, 2648.
(5) Bening, R. C.; McCarthy, T. J. *Macromolecules* **1990**, *23*, 2648.
(6) Shoichet, M. S.; McCarthy, T. J. *Macromolecules* **1991**, *24*, 982.
(7) Dias, A. J.; McCarthy, T. J. *Macromolecules* **1985**, *18*, 1826.
(8) Dias, A. J.; McCarthy, T. J. *Macromolecules* **1987**, *20*, 2068.
(9) Lee, K.-W.; McCarthy, T. J. *Macromolecules* **1988**, *21*, 2318.
(10) Lee, K.-W.; McCarthy, T. J. *Macromolecules* **1988**, *21*, 3353.
(11) Kolb, B. U.; Patton, P. A.; McCarthy, T. J. *Macromolecules* **1990**, *23*, 366.
(12) Cross, E. M.; McCarthy, T. J. *Macromolecules* **1990**, *23*, 3916.
(13) Bee, T. G.; McCarthy, T. J. *Macromolecules* **1992**, *25*, 2093.
(14) Dias, A. J.; McCarthy, T. J. *Macromolecules* **1984**, *17*, 2529.
(15) Iyengar, D. R.; Brennan, J. V.; McCarthy, T. J. *Macromolecules* **1991**, *24*, 5886.
(16) Lee, K.-W.; McCarthy, T. J. *Macromolecules* **1988**, *21*, 309.
(17) Franchina, N. L.; McCarthy, T. J. *Macromolecules* **1991**, *24*, 3045.
(18) Werner, E.; Janocha, S.; Hopper, M. J.; Mackenzie, K. J. *Enclycolpedia of Polymer Science and Engineering*, 2nd, ed.; Mark, H. F., Bikales, N. M., Overberger, C. G., Mengers, G., Kroschwitz, J. I., Eds.; John Wiley and Sons: New York, 1989; Vol. 12, p 193.
(19) Kumar, D. J.; Srivastava, H. C. *J. Appl. Polym. Sci.* **1987**, *33*, 455.
(20) Solbrig, C. M.; Obendorf, S. K. *J. Appl. Polym. Sci.: Appl. Polym. Symp.* **1991**, *47*, 437.
(21) Bùi, L. N.; Thompson, M.; McKeown, N. B.; Romaschin, A. D.; Kalman, P. G. *Analyst* **1993**, *118*, 463.
(22) Collin, R. J. US Pat. 2,955,954, 1964.
(23) Wang, J.; Feng, D.; Wang, H.; Rembold, M.; Fritz, T. *J. Appl. Polym. Sci.* **1993**, *50*, 585.
(24) Strobel, M.; Lyons, C. S.; Strobel, J. M.; Kapaun, R. S. *J. Adhes. Sci. Technol.* **1992**, *6*, 429.
(25) Bertrand, P.; DePuydt, Y.; Beuken, J. M.; Lutgen, P.; Feyder, G. *Nucl. Instrum. Methods Phys. Res., Sect. B.* **1987**, *B19-20*, 887.
(26) Arenolz, E.; Heitz, J.; Wagner, M.; Baeuerle, D.; Hibst, H.; Hagemeyer, A. *Appl. Surf. Sci.* **1993**, *69*, 16.
(27) Yao, Z. P.; Rånby, B. *J. Appl. Polym. Sci.* **1990**, *41*, 1459.
(28) Avny, Y.; Reubenfeld, L. *J. Appl. Polym. Sci.* **1986**, *32*, 4009.
(29) Desai, N. P.; Hubbell, J. A. *Macromolecules* **1992**, *25*, 226.
(30) Mougenot, P.; Marchand-Brynaert, J. *Macromolecules* **1996**, *29*, 3552.
(31) Mougenot, P.; Koch, M.; Dupont, I.; Schneider, Y.-J.; Marchand- Brynaert, J. *J. Coll. Interfac. Sci.* **1996**, *177*, 162.
(32) Paszun, D. and Spychaj, T. *Ind. Eng. Chem. Res.* **1997**, *36*, 6, 1373.
(33) Baliga, S.; Wong, W. T. *J. Polym. Sci.: Polym. Chem. Ed.* **1989**, *27*, 2071.
(34) Carbonyl diimidazole reacts with alcohols as well as carboxylic acids; thus, the labeling reaction with heptafluorobutyryl chloride was carried out first. That heptafluorobutyryl chloride does not react with carboxylic acids (to form anhydrides) under these conditions was determined using PMP−COOH (poly(4-methyl-1-pentene) containing surface carboxylic acids).[38]
(35) The values are calculated using 14 Å as the mean free path of C_{1s} electrons ejected using Al Kα irradiation. This value was measured in poly(*p*-xylylene): Clark, D. T.; Thomas, H. R. *J. Polym. Sci.: Polym. Chem. Ed.* **1977**, *15*, 2843.
(36) Harrick, N. J. *Internal Reflection Spectroscopy*; Wiley Interscience: New York, 1967.
(37) Bee, T. G. Ph.D. Dissertation, University of Massachusetts, 993.
(38) Leväsalmi, J.-M.; McCarthy, T. J. *Macromolecules* **1997**, *30*, 1752.

MA9710601