Synthesis and Characterization of Surface-Functionalized 1,2-Polybutadiene Bearing Hydroxyl or Carboxylic Acid Groups

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ABSTRACT: We have modified the surface of 1,2-polybutadiene (PBD), without severe etching, via oxidation with aqueous potassium permanganate. The primary functionality introduced, either hydroxyl or carboxylic acid groups, depends upon the concentration and temperature of the oxidizing solution. An alternative and more selective method for introducing hydroxyl or carboxylic acid moieties at this surface is the photolytic addition of 3-mercapto-1,2-propanediol or mercaptoacetic acid, using benzophenone as an initiator and light (350 nm). The surface-modified polymer films were characterized by X-ray photoelectron spectroscopy (XPS), attenuated total reflectance−infrared (ATR−IR) spectroscopy, scanning electron microscopy (SEM), and the measurement of solid/liquid contact angles. On the polymer surfaces containing carboxylic acid groups, contact angles varied with the pH of the contacting drop of water, consistent with the presence of ionizable functionality. Surfaces bearing 1,2-diol groups showed no spectroscopic evidence for carboxylic acid groups and had little or no dependence of contact angles on pH. Scanning electron microscopy revealed no gross topographical changes at the surface of PBD after any of these chemical derivatizations, except for samples treated for extended periods of time on a concentrated permanganate solution.

I. Introduction

The relations between molecular structure at a surface and macroscopic properties, such as wettability and adhesion, define the chemical basis for these important properties. The development of self-assembled monolayers, especially those formed by adsorption of alkanethiols on gold,[1] has allowed systematic control over surface structure in ordered systems and provided opportunities for inferring these relations. The surfaces of organic polymers are, in contrast, usually characterized more by disorder than by order, and the relations between molecular structure and macroscopic property are consequently more complex. Hydrocarbon polymers, in particular, are typically mixtures of amorphous and crystalline domains,[2] swellable by or soluble in a large variety of organic and inorganic liquids (e.g., solvents and reagents),[3] and composed of mobile chains that may undergo facile conformational changes or migrate to and from an interface of interest.[4,5]

In addition to their technological importance, the simplicity of hydrocarbon polymers attracted our interest in these studies. These polymers contain limited functionality and interact with contacting phases primarily via dispersion-type forces. As a result, their surfaces are hydrophobic and provide a background upon which to observe changes in wettability (and adhesion)[6,7] caused by the introduction of specific functional groups. Further, we felt that the choice of an *unsaturated*, hydrocarbon polymer would avoid the chemical resistance characteristic of such polymers as polyethylene, polypropylene, or most fluorinated polymers and would allow the controlled introduction of a high concentration of oxidized functionality at its surface.[2,8]

Chemical modification using reactions that are well-established in solution is a versatile method of manipulating the molecular structure at polymer surfaces.[2,9,10] Application of this method to hydrocarbon polymers requires a careful choice of solvents and reagents that neither swell nor dissolve the polymer to promote selective functionalization of the surface and not the bulk.[2] The most-studied surface of a hydrocarbon polymer is that of polyethylene (PE−H), and the studies of "polyethylene carboxylic acid" (PE−CO_2H) and its derivatives represent a paradigm in polymer surface chemistry.[2,4,11,12] Useful comparisons involving surface modifications of poly(chlorotrifluoroethylene) and related fluoropolymers have been provided by McCarthy and co-workers.[13−15] Organic synthesis at polyethylene surfaces has allowed systematic variation in structure and investigation of the influence of this structure on wettability.[4] A feature of these surfaces that complicates interpretation of the wetting data, however, is the etching that accompanies the initial oxidation of PE−H with chromic acid to give PE−CO_2H. This increased roughness of the functional surface contributes to the hydrophobicity of ester and amide derivatives (PE−CO_2R and PE−CONHR) and probably to the hydrophilicity of PE−CO_2H.[16]

Our goal in the research reported here was to functionalize, without etching, the surface of a hydrocarbon polymer. Our strategy was first to choose an appropriate polymer, one with reactive functionality (i.e., unsaturation) that could be chemically modified using organic reactions common to alkenes. The rubbery polymers, poly(1,3-dienes), are an important class that fit these criteria and attracted our interest. Since some synthetically useful reactions cleave carbon−carbon double bonds, a polymer with unsaturation primarily in side chains, and not in the backbone, would be preferable. Such a polymer would be less susceptible to chain scission and consequential etching of its surface. With these issues in mind, we chose to begin our studies with 1,2-polybutadiene (PBD).

The primary focus of this work was to develop methods for selectively oxidizing the vinyl groups at the surface of PBD. By analogy to solution-phase organic chemistry, we expected that oxidation with aqueous permanganate would provide routes to 1,2-diols or carboxylic acids, depending on the concentration and temperature of the oxidizing solution. A second synthetic route to surfaces bearing 1,2-diols or carboxylic

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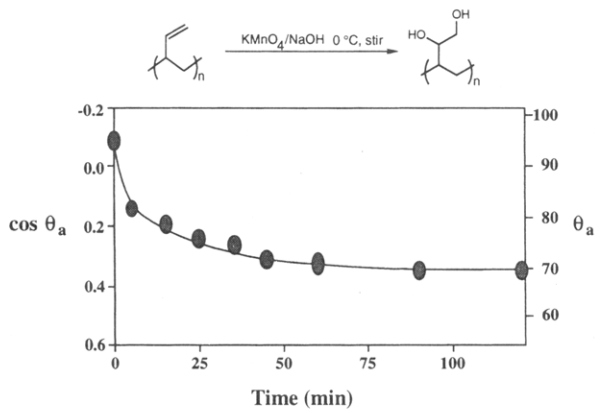

Figure 1. Contact angles of water (pH 1) on PBD as a function of time of treatment with an aqueous solution of $KMnO_4$ (6.9 mM) and NaOH (0.025 M) at 0 °C. Each point represents a separate sample treated for the reaction time indicated. These samples were floated on aqueous $NaHSO_3$ (0.05 M) and on aqueous HCl (0.1 M), then rinsed with deionized water, and dried prior to analysis.

acids, described in this paper for comparison, is the radical addition of 3-mercapto-1,2-propanediol ($HSCH_2CHOHCH_2OH$) or mercaptoacetic acid ($HSCH_2CO_2H$) to the interfacial vinyl groups of PBD.

At the outset of this work, we were confident that reactions of PBD with aqueous permanganate would yield oxidized surfaces. The selectivity with which these oxidations would occur was less certain, as was the related issue of yields that could be achieved without severely etching the polymer by oxidative cleavage of the carbon–carbon single bonds in the backbone of the polymer. Our approach therefore involved varying both the concentration and temperature of the oxidant solutions, monitoring changes in the surface-bound functional groups both spectroscopically and by measuring solid/liquid contact angles, and monitoring the surface topography by scanning electron microscopy (SEM).

II. Results

Preparation and Characterization of PBD–$CHOHCH_2OH$. We examined the oxidation of PBD using dilute aqueous solutions of potassium permanganate (6.9 mM) and sodium hydroxide (0.025 M) at 0 °C, conditions appropriate for conversion of vinyl groups to 1,2-diols.[17] The wettability of the surface by water was a convenient property for following the relative extent of reaction *at the surface* of the polymer.[16] The advancing and receding contact angles of water (θ_a and θ_r) on unmodified PBD are 95° and 82°, and, as expected, the surface became more hydrophilic upon oxidation. In these oxidations, the surface reached a limiting, advancing angle of water (pH 1) of 70° within 1.5 h. Figure 1 summarizes the changes in θ_a on PBD upon oxidation of its surface during this reaction, as a function of time. The receding angle of water (pH 1) fell to 0° within 35 min. We measured contact angles of water at pH 1 to avoid deprotonating any carboxylic acid groups that might be at the surface as a result of overoxidation. Deprotonation of such groups would lower the observed contact angle.[11]

Although the morphology of the surface of PBD–$CHOHCH_2OH$ appeared different than that of unmodified PBD by SEM, minimal etching appeared to occur during the chemical treatment of the surface (Figure 2). This result is consistent with the *addition* of hydroxyl groups to the vinyl carbons and with minimal side reactions to cleave carbon–carbon single bonds in the backbone of the polymer. As a result, we interpret the change in wettability, relative to the unmodified polymer, as resulting primarily from the added hydroxyl groups and not from changes in the roughness of the surface.

X-ray photoelectron spectroscopy (XPS) verified the addition of oxygen to the surface. Survey spectra of the oxidized product, and of the unmodified polymer for comparison, are shown in Figure 3. A high-resolution spectrum of the product in the C 1s region revealed a large peak due to unoxidized vinyl carbons and those carbons in the backbone of the polymer set at 285.0 eV and peaks due to oxidized carbon at 286.3 and 287.6 eV (Figure 3, inset). We tentatively assign the larger of the peaks at high binding energy (286.3 eV) to 1,2-diols[12,18,19] and the smaller peak to more highly oxidized derivatives, perhaps ketols.[17,18] The absence of a peak at a binding energy greater than 289.0 eV indicated that the surface contained few if any carboxylic acid groups.[18] Small amounts of oxygen and silicon were observed in the spectrum of the unmodified polymer, corresponding to 1% oxygen and 0.5% silicon on a molar basis.[20] Since the O:Si ratio was 2:1, we infer that the oxygen was associated with the silicon, and the binding energy of the Si 2p peak (102.5 eV) was consistent with the presence of silicate.[21] Its source may be the silanized glass Petri dish used for melting the polymer in the preparation of our films.

Angular-dependent XPS provided the atomic composition of the interfacial region of the modified polymer as a function of depth from the surface. We collected high-resolution spectra at three "take-off" angles (α) between the detector and the plane of the surface. At a shallow take-off angle of 20°, the ratio of carbon to oxygen was 9.1:1.0. This ratio represents the composition of approximately the outermost 4 nm of the polymer.[22] Spectra were also collected at higher take-off angles, 45° and 90°, which provided compositions of approximately the top 8 and 12 nm of polymer.[22] These data revealed higher carbon to oxygen ratios, 12.6:1.0 at 45° and 14.2:1.0 at 90°, indicating that most of the oxidized functionality resided in the outermost few nanometers of the polymer.

The molar ratio of 1,2-diols to more highly oxidized derivatives was higher at a take-off angle of 90° than at 45° or at 20° and may indicate a slight enrichment of the more highly oxidized groups within 4–8 nm of the surface. The ratio of area under the peaks at 286.3 and 287.6 eV was 5:1 at a take-off angle of 90°; it was 3:1 at 45° and 4:1 at 20°. We designate this material "PBD–$CHOHCH_2OH$" by analogy to other systems[11,14,23] and in order to emphasize the primary, oxidized functional groups at its surface.

The ATR–IR spectrum of PBD–$CHOHCH_2OH$ was especially sensitive to the spectroscopic parameters used in collecting the data. Its spectrum was similar to that of the unmodified polymer when a gain factor[24] of 2 was used. If this parameter was increased to 4, however, its spectrum contained a broad peak centered at 3418 cm^{-1} and a peak at 1736 cm^{-1} (Figure 4). We believe that the peak at 3418 cm^{-1} was due to an experimental artifact, as it also appeared in the spectrum of unmodified PBD,[25] though the peak observed in the carbonyl region may be due to a side product of this reaction.[17,26]

To verify the presence of hydroxyl groups, PBD–$CHOHCH_2OH$ was derivatized to the corresponding trifluoroacetate diester using a 5% (v/v) acetone solution of trifluoroacetic anhydride (tfa) for 15 min.[27] The

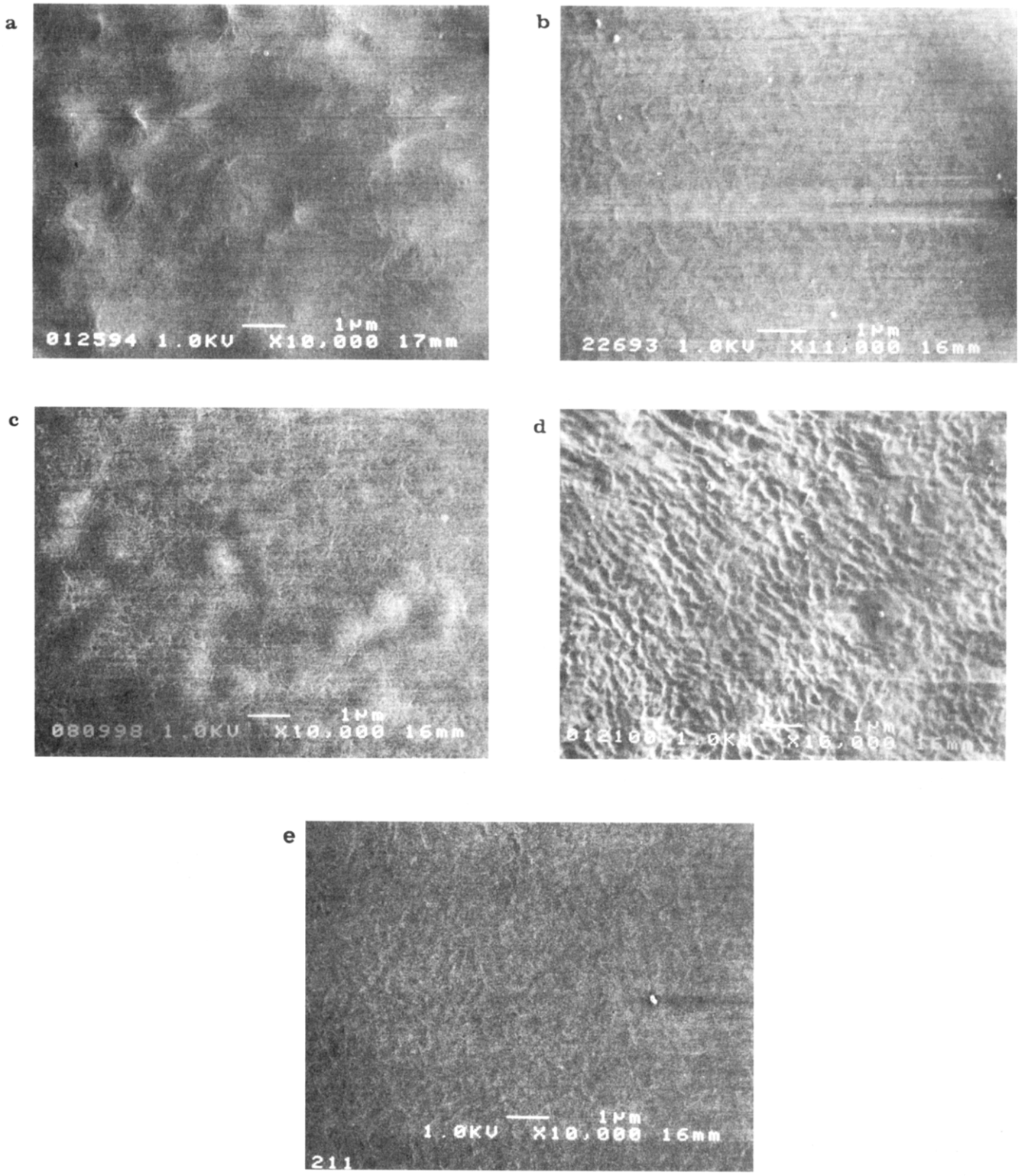

Figure 2. Scanning electron micrographs of (a) unmodified PBD, (b) PBD–$CHOHCH_2OH$, (c) PBD–CO_2H, (d) etched PBD–CO_2H, and (e) PBD–SCH_2CO_2H.

polymer sample was then soaked in acetone for 15 min to remove any absorbed tfa and dried under vacuum (~0.01 Torr) for 15 min. From an XPS survey spectrum at a 45° take-off angle, the O:F ratio of the derivatized surface was 1.0:1.1. This ratio was greater than that predicted based on the stoichiometry of the hypothetical diester (1.0:1.5) and indicates the presence of unreacted hydroxyl groups. A high-resolution spectrum of the C 1s region (inset, Figure 5) revealed four peaks on the high-binding-energy side of the main peak at 285.0 eV. The peak at 286.2 eV was assigned to the carbon atoms bound to unreacted hydroxyl groups,[18] that at 287.8 eV to carbon atoms bearing esterified oxygens, that at 290.7 eV to the carbonyl carbons of the ester, and that at 293.7 eV to the trifluoromethyl carbons.[18,27] To prove that fluorine in the derivatized sample was not simply due to absorbed tfa in the polymer, a sample of unmodified PBD was treated in the same manner as the PBD–$CHOHCH_2OH$. A survey spectrum of this control sample was similar to that of unmodified polymer and revealed no fluorine. An ATR–IR spectrum of the trifluoroacetylated surface contained a peak at 1791 cm^{-1} probably due to the carbonyl stretching mode of ester groups. A spectrum of unmodified PBD that had

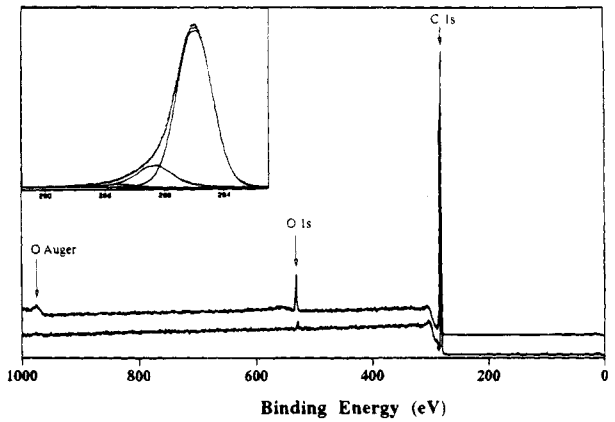

Figure 3. Survey XPS spectra at a 90° take-off angle of PBD–$CHOHCH_2OH$ (upper) and unmodified PBD (lower). The presence of small amounts of oxygen (532.6 eV) and silicon (153.0 and102.5 eV) in the unmodified spectrum was due to silicate and probably results from the method of film preparation. The binding energies were corrected for charge compensation by referencing to the main C 1s peak set at 285.0 eV. In the high-resolution spectrum of the C 1s region (inset), the peak at 286.3 eV is characteristic of alcohols and the very small peak at 287.6 eV is characteristic of more highly oxidized derivatives. The absence of a peak at a binding energy greater than 289.0 eV suggested that few, if any, carboxylic acid groups were present at the surface.

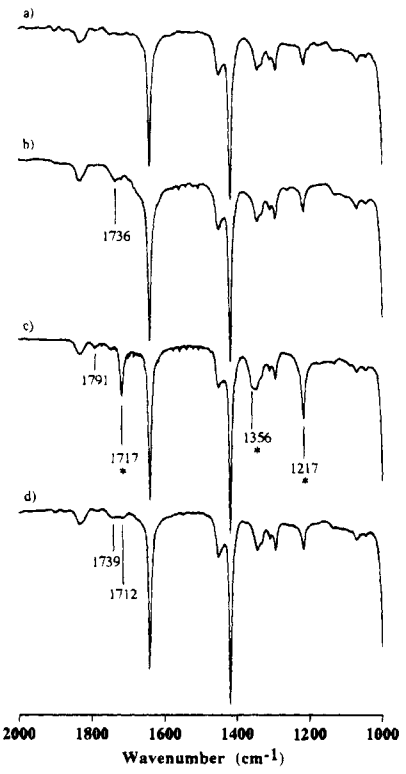

Figure 4. Attenuated total reflectance–infrared spectra of (a) unmodified PBD, (b) PBD–$CHOHCH_2OH$, (c) PBD–$CHOHCH_2OH$ after treatment with trifluoroacetic anhydride in acetone, and (d) PBD–$CHOHCH_2OH$ after treatment with acetic anhydride in pyridine. In spectrum c, peaks marked with asterisks were due to, or significantly enhanced by, acetone absorbed during the derivatization.

been soaked in acetone, however, showed a small peak at 1793 cm^{-1}, which could contribute to the absorbance in this region. Other peaks in the spectrum at 1717 and 1356 cm^{-1}, as well as the enhancement of the peak at 1217 cm^{-1}, were also due to acetone that had absorbed into the polymer during derivatization. The ATR–IR spectrum of a sample of PBD–$CHOHCH_2OH$ that had been treated with acetic anhydride in pyridine

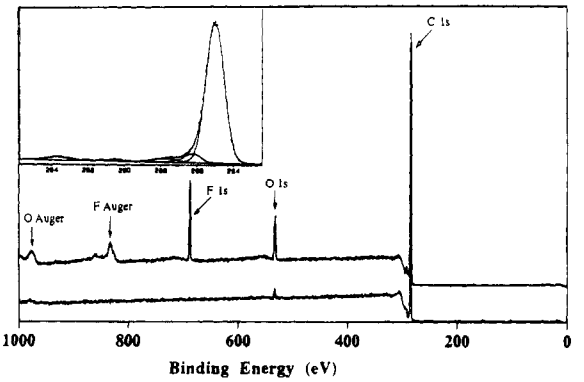

Figure 5. Survey XPS spectra at a 45° take-off angle of PBD–$CHOHCH_2OH$ after treatment with a 5% (v/v) solution of trifluoroacetic anhydride in acetone for 15 min (upper). For comparison, a sample of unmodified PBD was treated in the same way and analyzed (lower). Both samples were soaked in acetone to remove absorbed reagent and then dried *in vacuo* prior to analysis. The binding energies were corrected as in Figure 3. In the high-resolution spectrum of the C 1s region (inset), the peaks at binding energies of 287.8, 290.7, and 293.7 eV were characteristic of trifluoroacetate ester groups. The intensity to the left of the labeled fluorine Auger peak was the corresponding KL_1L_{23} Auger line of fluorine (862.7 eV).

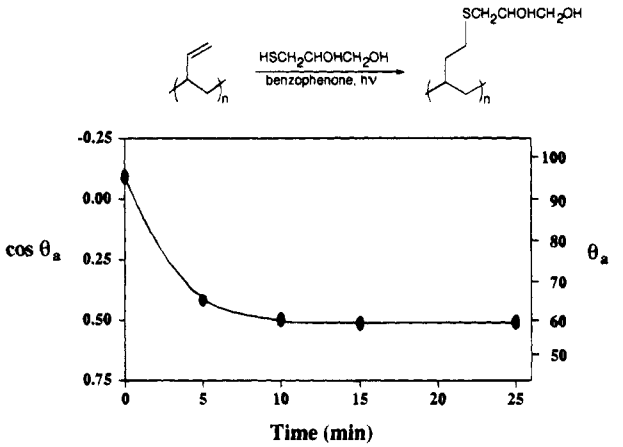

Figure 6. Contact angles of water (pH 1) on a single sample of PBD as a function of time irradiated (350 nm) in a solution of $HSCH_2CHOHCH_2OH$ (~0.08 M) in methanol, with benzophenone as an initiator. The sample was removed from the reagent solution, rinsed with ethanol and then deionized water, and blown dry with nitrogen prior to each set of measurements. The sample was returned to the solution, which was then sparged with argon for 3 min to remove oxygen.

failed to show a new carbonyl stretching band attributable to the corresponding acetates. The peak at 1739 cm^{-1} was most likely due an impurity[26] in the polymer, and the peak at 1712 cm^{-1} is assigned to absorbed acetic acid (Figure 4).

Preparation and Characterization of PBD–$SCH_2CHOHCH_2OH$. The photolytic addition of 3-mercapto-1,2-propanediol (~0.08 M in methanol), using benzophenone as an initiator, to the vinyl groups at the surface of PBD provided an alternative route to a surface bearing 1,2-diol groups.[28] This surface reached a limiting, advancing contact angle of water of 62° within 10 min of irradiation in a Rayonet reactor (350 nm) (Figure 6). The sample was rinsed with ethanol and deionized water and then heated on deionized water (50 °C) for 40 min to remove any absorbed thiol and methanol. After this treatment, the advancing contact angle of water was 60°, and a scanning electron micrograph showed that the product surface was smooth.

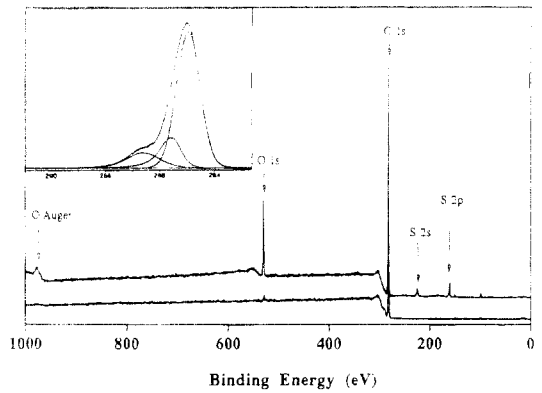

Figure 7. Survey XPS spectra at a 45° take-off angle of PBD–$SCH_2CHOHCH_2OH$ (upper) and unmodified PBD (lower). The binding energies were corrected as in Figure 3. A high-resolution spectrum of the C 1s region (inset) showed peaks at 285.6 and 286.6 eV, characteristic of carbon bound to sulfur and to hydroxyl groups.

A control experiment was performed to determine the quantity of 3-mercapto-1,2-propanediol absorbed in the polymer during the course of the reaction. Upon removal of a sample of PBD–$SCH_2CHOHCH_2OH$ from the reaction vessel in which it was prepared, it was rinsed with EtOH and deionized water and dried with a stream of nitrogen. It was then placed in a scintivial containing an aqueous buffer of Na_2HPO_4 (0.05 M)/EDTA (2×10^{-6} M) at pH 7 and 50 °C. After 40 min, the polymer sample was discarded and the buffer solution analyzed spectroscopically for the presence of 3-mercapto-1,2-propanediol using a derivative of Ellman's reagent.[29] In these experiments, the aliphatic thiolate was allowed to react with 5,5′-dithiobis(2-nitrobenzoic acid) to yield a mixed disulfide and 1 equiv of the chromophore 2-nitro-5-thiobenzoate ($\epsilon \approx 13\,700$ $cm^{-1}\,M^{-1}$).[30,31] The change in the absorption due to the formation of the dianion was monitored at a wavelength of 412 nm to determine the end point of the reaction. In three independent experiments (i.e., different samples of PBD–$SCH_2CHOHCH_2OH$), we found 8 nmol of desorbed 3-mercapto-1,2-propanediol per square centimeter of polymer. We thus routinely heated samples of PBD–$SCH_2CHOHCH_2OH$ against deionized water prior to spectroscopic analysis to remove the absorbed thiol.

The survey XPS spectrum of PBD–$SCH_2CHOHCH_2OH$ showed peaks due to oxygen and sulfur (Figure 7), consistent with the addition of the reagent thiol. A small amount of silicate impurity was present in the spectrum, as with the unmodified polymer. The S $2p_{3/2}$ peak appeared at 163.4 eV (high-resolution spectrum), a binding energy close to that expected for the dialkyl sulfide in the assumed structure of the product.[18,32] A new peak, not present in the spectrum of unmodified PBD, was present in the C 1s region at 286.6 eV, a binding energy that is consistent with the presence of 1,2-diol groups. This binding energy is very similar to that found for PBD–$CHOHCH_2OH$ and for the surfaces of other hydroxyl-containing polymers.[18] A second, new C 1s peak at 285.6 eV was consistent with the presence of carbon atoms bound to the sulfide sulfur atom.[18] We assume that the main C 1s peak (285.0 eV) includes the carbon atoms in the unmodified repeat units of the polymer and the backbone carbons of the modified repeat units.[33] From the high-resolution spectra in the C 1s, O 1s, and S 2p regions taken at a take-off angle of 45°, the carbon to oxygen to sulfur ratios were 18.2:2.4:1.0. From these ratios, we estimate the average yield of reaction (eq 1) as 30% *in that portion of polymer sensed by XPS under our experimental conditions (ca. 8 nm)*

$$I_C^{corr}/I_i^{corr} = n_C^{ave}/n_i^{ave} = (a\chi + 4(1-\chi))/b\chi \quad (1)$$

where I_i^{corr} = the integrated intensity of photoemission from the orbital of element i used for quantification, corrected using the individual sensitivity factor; n_i^{ave} = the average number of atoms i per repeat unit of the polymer within the XPS interphase; χ = the fraction of repeat units in the XPS interphase that have reacted; $1 - \chi$ = the fraction of unreacted repeat units of the polymer in the XPS interphase; a = the number of carbon atoms in a chemically modified repeat unit (i.e., 4 + the number of carbon atoms in the added thiol); b = the number of atoms i in a chemically modified repeat unit. The accuracy of the yield of the reaction depended upon two assumptions. First, the only source of heteroatoms was that of the thiol added to the polymer surface. Second, the calculated yields were not influenced by spurious artifacts, such as an inappropriate atomic sensitivity factor for sulfur[20] or anisotropy in the distribution of the added groups. Also, the S 2p region showed a spin-orbit doublet at higher binding energy (S $2p_{3/2}$ at 166.3 eV and S $2p_{1/2}$ at 167.4 eV) that contained ~11% of the photoemission intensity (*vide infra*, PBD–SCH_2CO_2H section). This intensity was included in the area ratios for the S 2p envelope and the yield reported. These yields assume no particular profile of concentration versus depth; rather, they are simple averages *over the portion of the polymer measured.*

The ATR–IR spectrum of PBD–$SCH_2CHOHCH_2OH$ was similar to those of PBD–$CHOHCH_2OH$ and unmodified PBD when the instrumental gain parameter was set at 2. As with PBD–$CHOHCH_2OH$, increasing the gain factor to 4 introduced an experimental artifact which appeared as a broad feature at 3369 cm^{-1} in the spectrum.[26] Using a different spectrometer, the spectrum of PBD–$SCH_2CHOHCH_2OH$ was similar to that of unmodified PBD even at a gain of 4, and a band in the hydroxyl stretching region was only observed when the spectrum of unmodified PBD was subtracted from that of the modified sample. The intensity of this peak was small and may have been due to adsorbed water from the air. We verified the presence of the hydroxyl groups in the interfacial region of PBD–$SCH_2CHOHCH_2OH$ by derivatizing them to their corresponding acetates.[34] A sample of PBD–$SCH_2CHOHCH_2OH$ was placed into a solution of acetic anhydride in pyridine for 1 h at room temperature. After then floating this sample on deionized water at room temperature overnight and heating it against deionized water at 50 °C for 5 h to remove any absorbed reagents or unbound byproducts, it was dried by vacuum (0.1–0.01 Torr) for 4 h. The ATR–IR spectrum of the resulting surface showed the appearance of a new peak at 1747 cm^{-1}, consistent with the presence of acetate groups (Figure 8). When the same treatment was performed using unmodified PBD (as a control), there was no spectroscopic evidence for the presence of acetate groups.

Preparation and Characterization of PBD–CO_2H. We have also examined the permanganate oxidation of the surface of PBD under conditions appropriate for the conversion of vinyl groups to carboxylic acids with one fewer carbon atom.[35] Our goal in this series of experiments was to introduce a high concentra-

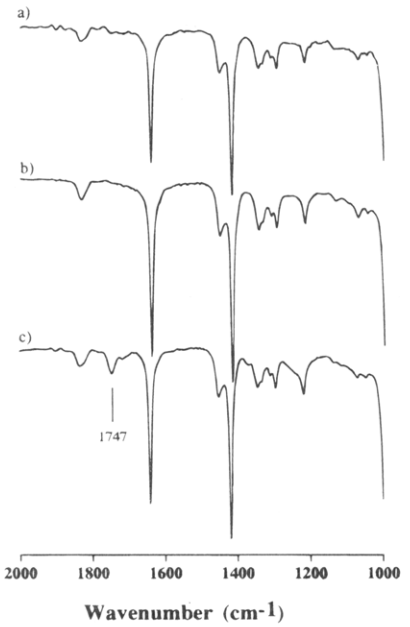

Figure 8. Attenuated total reflectance–infrared spectra of (a) unmodified PBD, (b) PBD–$SCH_2CHOHCH_2OH$, and (c) PBD–$SCH_2CHOAcCH_2OAc$.

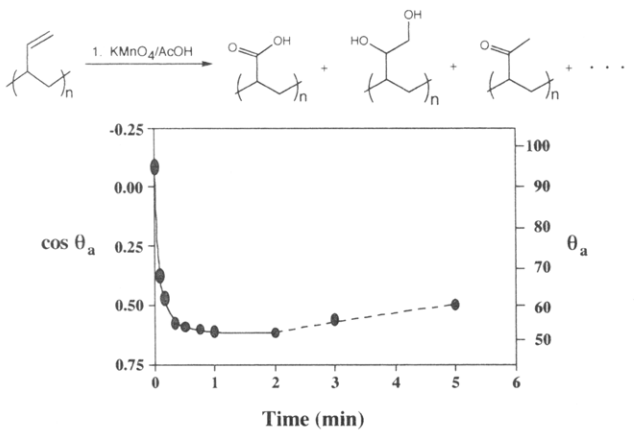

Figure 9. Contact angles of water (pH 1) on PBD as a function of time of treatment with an aqueous solution of $KMnO_4$ (0.45 M) and acetic acid (3 M). Each point represents a separate sample treated for the reaction time indicated. The samples were floated on aqueous $NaHSO_3$ (0.05 M) and on aqueous HCl (0.1 M), then rinsed with deionized water, and dried prior to analysis. After 2 min of reaction time, the advancing contact angles began to increase, possibly due to overoxidation of the sample surface.

tion of carboxylic acid groups at the surface, without etching. Krapcho et al. have shown that acetic acid suppresses overoxidation in these reactions;[35] however, treatment of the surface of PBD with a concentrated aqueous solution of $KMnO_4$ (0.45 M) and acetic acid (3 M) for 5 min afforded a highly oxidized surface comprising a mixture of products, though a low yield of carboxylic acid groups, as determined by XPS.[36] The change in the advancing contact angle of water (pH 1) as a function of time for this oxidation is shown in Figure 9. We measured contact angles using water at pH 1 to prevent the deprotonation of the carboxylic acid groups. Within 2 min on the oxidizing solution, θ_a had dropped from 95° to 52°. After 2 min, however, θ_a began to increase. In order to minimize both θ_a and any unnecessary etching of the surface, in subsequent experiments we limited the time of this reaction to 2 min.

Since 1,2-diols were possible side products of this reaction, we treated the oxidized surface with aqueous periodic acid (0.1 M) to cleave any of these groups to their corresponding aldehydes.[37] Treatment with aqueous periodic acid (0.1 M) for 10 min produced a surface with an advancing contact angle of water (pH 1) of 59°. A second oxidation with the original $KMnO_4$ solution was then intended to convert the aldehydes to carboxylic acids.[37,38] This treatment, for 5 s produced a surface with an advancing contact angle of water (pH 1) of 49°. If the sample was left for a longer time against the permanganate solution in this step, its surface began to etch as judged by SEM.

We expected that acetic acid, present in high concentration in the reagent solution, would absorb into the polymer during this synthesis. Since absorbed acetic acid could lower the contact angle of water (by desorbing into the contacting water drop) and interfere with the spectroscopic characterization of the surface, we performed control experiments to assess the possibility of its absorption. A sample of unmodified PBD was treated initially with aqueous acetic acid (3 M) at room temperature for 2 min. An ATR–IR spectrum of this material contained a small peak at 1716 cm^{-1}, characteristic of acetic acid. The sample was then treated with aqueous periodic acid (0.1 M) for 10 min, after which its ATR–IR spectrum was indistinguishable from that of unmodified PBD. The advancing contact angle of water (pH 1) on this surface was also the same as that of unmodified PBD. Finally, the sample was treated with aqueous acetic acid (3 M) for an additional 10 min and the ATR–IR spectrum of the resulting surface again revealed a small peak at 1716 cm^{-1}. The absorbed acetic acid could be removed, as judged by ATR–IR, by floating the surface against deionized water for 1 h at room temperature and then drying it under vacuum (~0.1–0.01 Torr) for 15 min. Samples of the polymer treated with aqueous $KMnO_4$/AcOH were thus treated in this way, prior to analysis. The advancing contact angle of water (pH 1) on PBD–CO_2H treated in this way was 58°. Scanning electron microscopy of this surface showed minimal etching as a result of the chemical derivatization (Figure 2).

We examined the surface of PBD–CO_2H spectroscopically. A survey XPS spectrum of this surface indicated extensive oxidation of the interfacial region of the polymer (Figure 10). It also contained small peaks due to sulfur at 169.1 eV (S 2p, spin-orbit components unresolved) and 232.0 eV (S 2s). These peaks were present in the XPS spectrum of PBD–CO_2H even after rinsing with and storing on deionized water for approximately 12 h. The most likely source of this contamination was the post-treatment of the sample with aqueous bisulfite (0.05 M) to rid the surface of oxides of manganese. The binding energy of the S 2p peak is consistent with the presence of sulfate[21,39] or with hydrosulfonates resulting from the addition of bisulfite across the carbon–carbon double bonds at the polymer surface.[38,40] Briggs and co-workers reported the binding energy of sulfonate groups at the surface of chromic acid-etched low-density polyethylene as 169.3 eV.[12] Examination of the survey spectrum revealed no evidence of alkali-metal ions or manganese that could serve as a counterion for the sulfate or sulfonate anion.

The high-resolution spectrum of the C 1s region (Figure 10, inset) revealed peaks at 289.4, 287.5, and 286.1 eV, in addition to the main C 1s peak at 285.0 eV. The peak at 289.4 eV is consistent with the

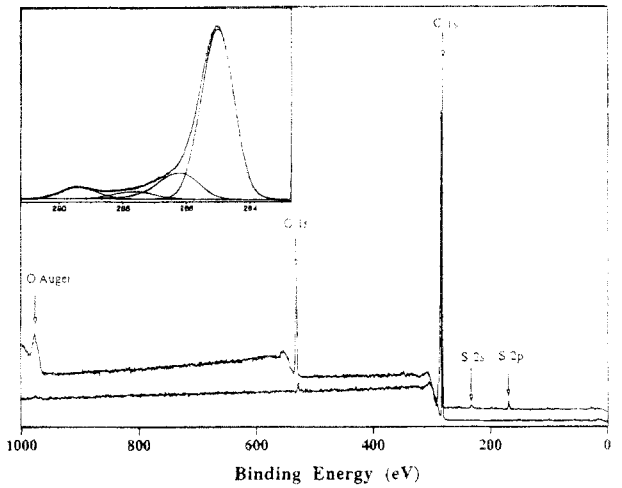

Figure 10. Survey XPS spectra at a 90° take-off angle of PBD−CO_2H (upper) and unmodified PBD (lower). The binding energies were corrected as in Figure 3. The small amount of sulfur in the modified film had a binding energy of 169.1 eV (S 2p), consistent with the presence of sulfate or sulfonate groups, probably resulting from the treatment with aqueous bisulfite to remove any deposited oxides of manganese. A high-resolution spectrum of the C 1s region (inset) showed a peak at 289.4 eV characteristic of carboxylic acid groups.

presence of carboxylic acids, that at 287.5 eV, of ketone- or aldehyde-containing functionality, and that at 286.1 eV, of alcohols or of carbons α to carboxylic acid groups.[18] The ratio of carbon to oxygen, calculated from the high-resolution spectra in those regions, was 4.4:1.0 at a take-off angle of 90°, 4.3:1.0 at 45°, and 5.1:1.0 at 20°. These data indicated a slightly higher concentration of oxidized functional groups just below the surface of the polymer. We caution that it is possible that roughness below the scale of length discernable in our scanning electron micrographs influenced these measurements, and the C:O ratio may actually be approximately constant throughout the top 4−12 nm of the polymer.[41] The ratios of area under the peaks at 289.4, 287.5, and 286.1 eV were 1:1:4 at take-off angles of 90° and 45° and 2:1:4 at 20°. The similarities in these ratios indicate that the relative yields of these products did not change dramatically as a function of depth into the polymer. There did, however, appear to be a higher concentration of carboxylic acid groups in the outermost 4 nm of the functionalized interphase, relative to deeper regions. The peak at 286.1 eV also included the α-carbons next to the carboxylic acid groups, so the concentration of hydroxyl groups was not as large as it would appear from these ratios. We designate this surface as "PBD−CO_2H" even though it clearly contains other oxidative products such as alcohols, aldehydes, and/or ketones.

The ATR−IR spectrum (Figure 11) of this surface showed a broad absorption at 1716 cm^{-1} due to the carboxylic acid groups in the oxidized repeat units of the polymer. The shoulder at 1734 cm^{-1} may represent another oxidative product of this reaction, e.g., aldehydes.[26] After treating the surface with aqueous NaOH (0.1 M) for 1 min, the peak at 1716 cm^{-1} disappeared and a new one appeared at 1574 cm^{-1}. This result is consistent with deprotonation of the carboxylic acid groups to give carboxylate anions,[11] and we assign this peak to the asymmetric stretching mode of that group.[42] A symmetric carboxylate stretching band was not observed and may have been obscured by the intense PBD band at 1417 cm^{-1}, which corresponds to the C−H, in-plane deformation of the vinyl group.[43]

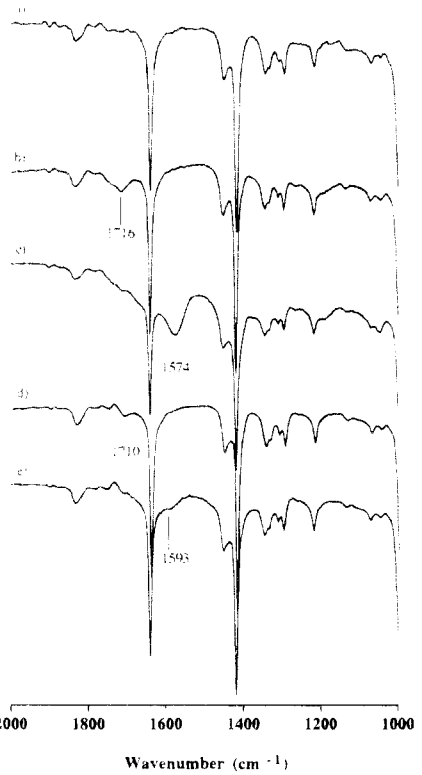

Figure 11. Attenuated total reflectance−infrared spectra of (a) unmodified PBD, (b) PBD−CO_2H, (c) PBD−CO_2H after 1 min on aqueous NaOH (0.1 M), (d) PBD−SCH_2CO_2H, and (e) PBD−SCH_2CO_2H after 1 min on aqueous NaOH (0.1 M).

Preparation and Characterization of Etched PBD−CO_2H. When PBD was left for 5 min or longer on the concentrated aqueous solution of $KMnO_4$ (0.45 M) and acetic acid (3 M) at room temperature, SEM revealed that its surface had begun to be pitted or etched and was rougher than unmodified PBD (Figure 2). For comparison to the unetched PBD−CO_2H, a PBD surface was treated sequentially with concentrated, acidic permanganate (0.45 M) for 5 min, aqueous periodic acid (0.1 M) for 10 min, and then the permanganate solution again for 2 min. The advancing contact angle of water (pH 1) on the product surface was 44°.

A high-resolution XPS spectrum of the C 1s region was collected for this sample, revealing peaks due to oxidized carbon at 289.3, 287.2, and 286.0 eV in addition to a large peak due to the unoxidized vinyl and backbone carbon atoms at 285.0 eV. Our peak assignments in this spectrum are the same as those in the spectrum of unetched PBD−CO_2H (Figure 10, inset). High-resolution XPS revealed a carbon to oxygen ratio of 4.0:1.0 at take-off angles of 90° and 45° and 4.5:1.0 at a take-off angle of 20°. We note, however, that roughness can affect angle-dependent XPS in assessing the profile of atomic concentration versus depth into the sample.[41] The ratios of area under the peaks at 289.3, 287.2, and 286.0 eV were 1:1:4 at take-off angles of 90° and 45° and 1:1:3 at 20°. The ratios at 90° and 45° were similar to those of its unetched analogue; the amount of carboxylic acid at 20°, however, was lower for this surface. The XPS survey spectrum of this sample also contained a S 2p peak (spin-orbit components unresolved) at 169.1 eV, a binding energy consistent with the presence of sulfate[21] or sulfonate[12] groups.

The ATR−IR spectrum of this etched surface showed a broad absorption at 1716 cm^{-1} due to carboxylic acid groups. After treating this surface with aqueous base, its spectrum changed similarly to that of its unetched

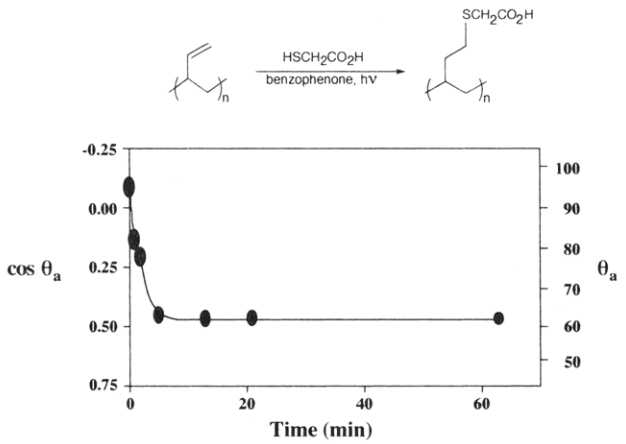

Figure 12. Contact angles of water (pH 1) on a single sample of PBD as a function of time irradiated (350 nm) in a solution of $HSCH_2CO_2H$ (~0.07 M) in methanol, with benzophenone as an initiator. The sample was removed from the reagent solution and rinsed with ethanol and then deionized water, and blown dry with nitrogen prior to each set of measurements. The sample was returned to the solution, which was then sparged with argon for 3 min to remove oxygen.

analogue: the peak at 1716 cm^{-1} disappeared, and a new one appeared at 1574 cm^{-1}. This result is consistent with the deprotonation of the carboxylic acid groups to give carboxylate anions,[11] and we assign this peak to the asymmetric stretching mode of that group.[42] Again, the symmetric carboxylate anion stretch was not observed. We designate this surface as "etched PBD–CO_2H".

For comparison, PBD–$CHOHCH_2OH$ was treated with aqueous periodic acid (0.1 M) for 10 min followed by treatment with concentrated, acidic permanganate (0.45 M) for 1 min. The sample was treated subsequently with aqueous bisulfite (0.05 M) and HCl (0.1 M) before floating on deionized water for 1 h at room temperature and then drying under vacuum (~0.1–0.01 Torr) for 20 min. This product surface was more hydrophilic than PBD–CO_2H but less hydrophilic than etched PBD–CO_2H: θ_a (pH 1) was 50°, and θ_a (pH 13) was 35°. A scanning electron micrograph revealed that the surface had become etched during the chemical modification.

Preparation and Characterization of PBD–SCH_2CO_2H. The photolytic addition of mercaptoacetic acid (~0.07 M in methanol), using benzophenone as an initiator, to the vinyl groups at the surface of PBD provided a second route to surface-bound carboxylic acids.[44] This surface reached a limiting, advancing contact angle of 62° within 10 min of irradiation in a Rayonet reactor (350 nm; Figure 12). A scanning electron micrograph of the product surface showed the presence of particulate matter, perhaps material derived from the reagents (e.g., disulfide) or of dust, which could be removed by rinsing the surface with absolute ethanol. After this treatment, SEM revealed that the product surface was smooth and similar to that of the unmodified polymer (Figure 2).

A control experiment was performed to determine the quantity of mercaptoacetic acid absorbed in the bulk of the polymer during the course of the reaction. Analogous to the experiments for the detection of 3-mercapto-1,2-propanediol desorbed from PBD–$SCH_2CHOHCH_2OH$, samples of PBD–SCH_2CO_2H were heated against Na_2HPO_4 (0.05 M)/EDTA (2×10^{-6} M) at 50 °C for 1 h. Each buffer solution was then analyzed for the presence of mercaptoacetic acid using 5,5′-dithiobis(2-nitrobenzoic acid).[29] In four independent experiments, the amount of thiol removed from a sample of PBD–SCH_2CO_2H treated in this way was 2–4 nmol of thiol/cm^2 of polymer.

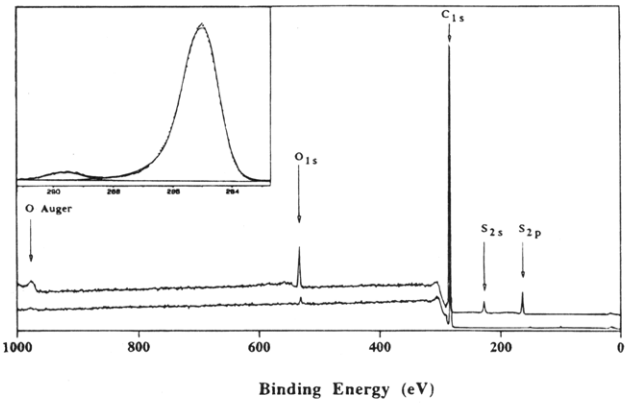

Figure 13. Survey XPS spectra at a 90° take-off angle of PBD–SCH_2CO_2H (upper) and unmodified PBD (lower). The binding energies were corrected as in Figure 3. A high-resolution spectrum of the C 1s region (inset) shows a peak at 289.5 eV characteristic of carboxylic acid groups.

A series of qualitative observations also indicated that absorption of small amounts of mercaptoacetic acid did occur under these reaction conditions. In the course of adhesion studies,[6] we noted that when PBD–SCH_2CO_2H (or unmodified polymer that was coated with a few milligrams of mercaptoacetic acid) was pressed against copper foil and heated in air at 80 °C for 11 h, the samples became discolored (orange–brown). The discoloration of the polymer samples was probably due to the formation of copper(I) thiolate species, which are known to decompose in air to give orange–brown residues.[45] Such species may form at the polymer/copper interface by reaction of absorbed mercaptoacetic acid with the native cuprous oxide. If, however, PBD–SCH_2CO_2H was heated against deionized water at ~50 °C for 1 h prior to pressing it against copper foil and heating, no discoloration of the polymer was noted.[46] Also, as expected, when a piece of unmodified PBD was pressed and heated against the copper foil, no discoloration occurred. After purification of PBD–SCH_2CO_2H by heating on water at ~50 °C for 1 h, a treatment that should also remove absorbed methanol, the advancing contact angle of water (pH 1) on this surface was 66°.

A survey XPS spectrum of purified PBD–SCH_2CO_2H revealed peaks due to oxygen and sulfur (Figure 13). The main S $2p_{3/2}$ peak appeared at 163.5 eV, a binding energy that was consistent with the dialkyl sulfide in the proposed structure of the product.[18,32] In addition to the main C 1s peak at 285.0 eV, a new peak at 289.5 eV was present, consistent with the presence of carboxylic acid groups.[12,18,19,32] We assume that the peak at 285.0 eV includes the carbon atoms in unmodified repeat units of the polymer and the backbone carbons of the modified repeat units.[33]

Using high-resolution XPS, we measured the relative atomic ratios for PBD–SCH_2CO_2H at three take-off angles. At a take-off angle of 20°, the C:O:S ratio was 15.8:1.8:1.0; at 45° it was 17.3:1.7:1.0; and at 90° it was 20.0:1.7:1.0. In each case, the O:S ratio was close to, but slightly less than, that expected from the stoichiometry of the added thiol (2:1). As with PBD–$SCH_2CHOHCH_2OH$, however, the high-resolution spectra of the S 2p region of PBD–SCH_2CO_2H revealed a spin-orbit doublet at 166.5 eV (S $2p_{3/2}$) and 167.6 eV (S $2p_{1/2}$), suggesting that ~9–14% of the sulfide sulfur atoms had

been oxidized. These binding energies are consistent with the presence of sulfoxide[21,47] or sulfone[21] species; however, the presence of such species, if derived from $HSCH_2CO_2H$, would increase the O:S ratio above 2:1, which was not observed. In a separate experiment, a sample of PBD−SCH_2CO_2H floated on aqueous HCl (0.1 *M*) for ~18 h prior to analysis and showed less apparent oxidation (~5−10%), but a *smaller* O:S ratio that varied with take-off angle (1.6:1.0 at 20°; 1.3:1.0 at 45°; and 1.2:1.0 at 90°).[48] These data are difficult to reconcile and may indicate that the surface was extremely sensitive to damage in the XPS experiment. If X-ray or electron beam (flood gun) damage was responsible for these results, it must have occurred very quickly, since reanalysis of the O 1s, S 2p, and C 1s regions of the original sample after 3 h of exposure to the X-ray source and flood gun revealed no significant changes.

The ratio of heteroatoms (O and S) to carbon increased with decreasing take-off angle, suggesting that the majority of added sulfide groups reside in the outermost portion of the polymer. The average yield of the photolytic addition to give PBD−SCH_2CO_2H, calculated using data for which the O:S ratio was constant to ±0.1 with take-off angle to avoid incorporation of experimental artifacts, was 24%. Our calculations assume that the O:S ratio of the modified polymer is that of the added thiol (eq 1) and represent only that portion of the polymer sensed by XPS. The high-binding-energy doublet in the sulfur 2p region (*vide supra*) contained ~9% of the total S 2p intensity at a take-off angle of 90°, ~11% at a take-off angle of 45°, and ~14% at a take-off angle of 20°. This intensity was included in the area ratios and yield reported.

The ATR−IR spectrum of PBD−SCH_2CO_2H showed a peak at 1710 cm^{-1}, characteristic of carboxylic acid groups, that was not present in the spectrum of unmodified PBD (Figure 11). After floating the sample on aqueous NaOH (0.1 M) for 1 min, its ATR−IR spectrum showed the disappearance of the peak at 1710 cm^{-1} and the appearance of a broad shoulder centered at about 1593 cm^{-1}. We attribute these changes to the deprotonation of the carboxylic acid groups by aqueous base to give carboxylate anions[11] and assign the peak at 1593 cm^{-1} to the asymmetric stretching mode of the carboxylate group.[42] As in the ATR−IR spectra of PBD−CO_2H, no band assignable to the corresponding symmetric mode was observed.

Contact Angle Titrations.[4,11] Variation in the wettability of a surface by water, as a function of the pH of the contacting drop, is evidence for the presence of ionizable functional groups in the interfacial region.[49] This experimental protocol is particularly useful for detecting the presence of carboxylic acids, i.e., groups with pK_a's well within the range of accessible pH in water. The surfaces of PBD−CO_2H (unetched and etched) and PBD−SCH_2CO_2H showed a dependence of θ_a on the pH of the contacting drop of water (Figure 14).[50] In each case, the value of θ_a was lowest at high pH, a result consistent with the greater hydrophilicity of the charged carboxylate anion relative to the uncharged acid.[51] Unmodified PBD, PBD−$CHOHCH_2OH$, and PBD−$SCH_2CHOHCH_2OH$, as expected, did not show a pH dependence in their contact angles of water.

The magnitude of the change in limiting contact angles at low and high pH, expressed as the difference of the cosines of the two angles (i.e., $\Delta \cos \theta_a$), is determined by at least two parameters: the number of ionizable groups (here, $-CO_2H$) within the interfacial region[52] and the ability of these groups to reorient with respect to the polymer/water interface upon changes in the pH of the contacting aqueous phase.[53] The values of $\Delta \cos \theta_a$ for PBD−CO_2H (unetched and etched) and PBD−SCH_2CO_2H and, for comparison, values reported by others for various surfaces are shown in Table 1. The absence of a pH dependence for contact angles of PBD−$CHOHCH_2OH$ and PBD−$SCH_2CHOHCH_2OH$ indicated that these surfaces did not contain ionizable functional groups, a conclusion consistent with the XPS and ATR−IR data. The larger value of $\Delta \cos \theta_a$ for unetched PBD−CO_2H, relative to etched PBD−CO_2H, was consistent with the higher relative concentration of carboxylic acid groups present at its surface, as shown by XPS.

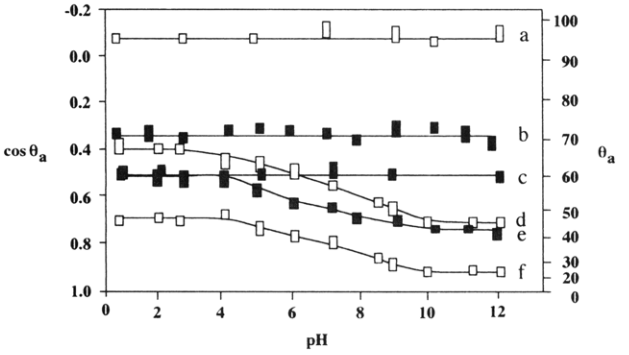

Figure 14. Contact angle titrations on the surfaces of (a) unmodified PBD, (b) PBD−$CHOHCH_2OH$, (c) PBD−$SCH_2CHOHCH_2OH$, (d) PBD−SCH_2CO_2H, (e) PBD−CO_2H, and (f) etched PBD−CO_2H.

Table 1. Advancing (θ_a) Contact Angles (deg) for Several Polymer Surfaces

product surface	pH 1	pH 12	Δ cos θ_a[a]	ref
PBD	95	97		[b]
PBD−$CHOHCH_2OH$	70	68		[b]
PBD−$SCH_2CHOHCH_2OH$	60	59		[b]
PE−CH_2OH	71	71		11
PVF_2−CH_2OH	77	80		15
PCTFE−OH	67			14
P−$PhCH_2OH$	46	48		23
PBD−CO_2H	58	36	0.28	[b]
etched PBD−CO_2H	44	24	0.19	[b]
PBD−SCH_2CO_2H	66	45	0.30	[b]
PE−CO_2H	55	22	0.35	11
PVF_2−CO_2H	75	68	0.12	15
P−$PhCO_2H$	70	25	0.56	23

[a] The magnitude of change in the cosines of the limiting contact angles at low and high pH. [b] Reported in this paper.

III. Discussion

Treating the surface of PBD with a dilute, basic permanganate solution produced PBD−$CHOHCH_2OH$, a surface containing 1,2-diol groups as the primary oxidized functionality. Analogous surfaces have been reported for other polymers, including surface-hydroxylated polyethylene (PE−CH_2OH)[11] and poly(vinylidene fluoride) (PVF_2−CH_2OH),[15] prepared by reducing the corresponding carboxylic acids (PE−CO_2H and PVF_2−CO_2H) with BH_3·THF. The surface of PBD−$CHOHCH_2OH$ was similar in hydrophilicity to PE−CH_2OH and slightly more hydrophilic than PVF_2−CH_2OH (Table 1). The surface of PBD−$CHOHCH_2OH$ was less hydrophilic, however, than poly[bis(4-methylphenoxy)phosphazene] alcohol (P−$PhCH_2OH$)[23] prepared by the $LiAlH_4$ reduction of the corresponding carboxylic acid surface. Surface-hydroxylated poly(chlorotrifluoroethylene) (PCTFE−OH),[14] formed by treatment of the

parent polymer with the lithiopropyl ethyl acetal of acetaldehyde followed by hydrolysis, has also been reported and has a hydrophilicity very similar to that of PBD–$CHOHCH_2OH$. Neither PBD–$CHOHCH_2OH$ nor any of these hydroxyl-containing surfaces showed a dependence of wettability on the pH of the water droplet on the surface.

The photolytic addition of 3-mercapto-1,2-propanediol produced PBD–$SCH_2CHOHCH_2OH$, a sulfide-containing analogue of PBD–$CHOHCH_2OH$. The surface of PBD–$SCH_2CHOHCH_2OH$ was more hydrophilic than that of PBD–$CHOHCH_2OH$, and its wettability also had no dependence on the pH of the water droplet (Figure 14). We believe that the difference in wettability between our two 1,2-diol-containing surfaces was due to a higher yield of hydroxyl groups on the surface of PBD–$SCH_2CHOHCH_2OH$ than on PBD–$CHOHCH_2OH$, as determined using the carbon to oxygen ratios measured by XPS with a take-off angle of 45°. An examination of Hansch π parameters indicated that the presence of the sulfide and added methylene group in PBD–$SCH_2CHOHCH_2OH$ would not enhance the hydrophilicity of that surface relative to PBD–$CHOHCH_2OH$.[4,51] In fact, they should make it more hydrophobic.

The *unetched* surface of PBD–CO_2H presented in this paper offers useful comparisons to polymer surfaces reported by others: PE–CO_2H, prepared by the oxidation of polyethylene with chromic acid;[11] PVF_2–CO_2H, prepared by base-induced elimination of the parent polymer, followed by oxidation with $KClO_3$ in sulfuric acid;[15] and P–$PhCO_2H$, prepared by permanganate oxidation of the parent poly[bis(4-methylphenoxy)phosphazene].[23] The magnitude of the change in the limiting values of $\cos\theta_a$ as a function of pH of the contacting drop ($\Delta\cos\theta_a$) was the greatest for P–$PhCO_2H$, followed by PE–CO_2H > PBD–SCH_2CO_2H > PBD–CO_2H > etched PBD–CO_2H > PVF_2–CO_2H (Table 1). One surface not included in Table 1, the anthranilate amide of PE–CO_2H, showed a $\Delta\cos\theta_a$ of 1.2. This tremendous change in θ_a with pH was attributed to the ability of this group to internally hydrogen-bond and present a very hydrophobic surface at low pH.[53]

The chemically-modified surfaces of PBD were not significantly rougher than the unmodified polymer, with the exception of etched PBD–CO_2H, as shown by SEM. For comparison, the surfaces of PE–CO_2H and P–$PhCO_2H$ were significantly rougher than that of PBD–CO_2H, and the roughness of the two fluoropolymers in Table 1 could be controlled, depending on the experimental conditions. Our goal was to retain smooth surfaces during surface modification, because roughness can strongly affect contact angle measurements. This phenomenon is described in a simple and approximate way by Wenzel's equation, which estimates the cosine of the intrinsic contact angle on a rough surface as the cosine of the observed angle divided by a roughness factor.[54] This factor is the ratio of actual surface area to projected surface area and compensates for the increase in the surface free energy of a system due to the increase in surface area. For surfaces that have an intrinsic contact angle less than 90°, for example, the surfaces in Table 1, this equation predicts that an increase in roughness upon modification would lower the observed contact angle. Surface roughness can also obviate the usefulness of angular-dependent XPS by altering the angles of electron escape, leading to "shading" portions of the surface.[41]

The primary disadvantage to using permanganate solutions to modify the surface of PBD was the lack of selectivity inherent in these oxidations. In the synthesis of PBD–$CHOHCH_2OH$, more highly oxidized byproducts were also produced. In the preparation of PBD–CO_2H with concentrated, acidic permanganate, other oxidative products, perhaps including 1,2-diols, ketones, and/or aldehydes, were also produced.[36] A second complication in using permanganate to produce PBD–CO_2H was the addition of oxidized sulfur, present as sulfate or sulfonate, that did not rinse away. This sulfur contamination probably resulted from several treatments of the surface with aqueous bisulfite that were necessary to remove any deposited oxides of manganese. The presence of these oxidized sulfur groups could affect the wettability of the surface and lower the contact angle of water. Since their concentration was low, however, their effect should be small.

Alternatively, the photolytic addition of 3-mercapto-1,2-propanediol or mercaptoacetic acid to the surface of PBD provided a synthetic route to a surface containing 1,2-diol or carboxylic acid groups without the introduction of side products. This method gave good yields, higher than those in the permanganate reactions, of the desired products. It is convenient, uses mild reagents and conditions, and provides a versatile route to functional surfaces.

IV. Conclusions

Treatment of PBD with aqueous permanganate yielded primarily either hydroxyl or more highly oxidized groups at the surface, depending on the temperature and concentration of the oxidizing solution. The use of cold, dilute permanganate (6.9 mM) under basic conditions gave a surface composed predominantly of 1,2-diol groups, though with some more highly oxidized byproduct(s). Treatment of PBD with an acidic solution of concentrated permanganate (0.45 M) for 2 min at room temperature and then aqueous periodic acid (0.1 M) for 10 min and a final treatment for 5 s with the original oxidizing solution yielded a mixture of oxidized functionality, including carboxylic acid groups that were identifiable by XPS and ATR–IR and gave rise to a pH-dependent contact angle of water.

An alternative and superior method for introducing 1,2-diols or carboxylic acids was the radical addition of 3-mercapto-1,2-propanediol or mercaptoacetic acid, initiated by benzophenone and light. We have used these reactions to functionalize the surface of PBD selectively and under mild conditions. The resulting surface-bound functional groups have been characterized spectroscopically (XPS and ATR–IR) and in their wettability by water.

We have demonstrated that all of these surfaces are not severely etched as a result of chemical derivatization, except for those treated with a concentrated, acidic permanganate (0.45 M) solution at room temperature for extended times. This feature of the syntheses is important, since changes in roughness upon chemical modification can influence measurements used to characterize organic surfaces. As for most surface-modified polymers, we expect the interfacial regions of these PBD derivatives to be susceptible to thermal reconstruction, via conformational changes or diffusion of polymer chains, that lowers their interfacial free energy. This dynamic behavior is currently a focus of our attention.

V. Experimental Section

General Methods. Methanol (ACS certified grade) and acetic acid (glacial; HPLC grade) were purchased from Fisher and used as received. Ethanol (absolute) was purchased from Midwest Grain Products Co. and used as received. Mercaptoacetic acid (95%; Aldrich) was purified prior to use by first drying it azeotropically with benzene (99+%; thiophene free, Aldrich, dried with CaH_2 under argon) and then by vacuum distillation. It was stored in a round-bottom flask, sealed under nitrogen, and covered with aluminum foil in a refrigerator. Hydrochloric acid (37% HCl; Mallinckrodt), potassium permanganate (certified ACS; Fisher), sodium bisulfite (ACS reagent; Aldrich), sodium phosphate (dibasic, anhydrous, certified ACS; Fisher), ethylenediaminetetraacetic acid (disodium salt, dihydrate, Sigma grade; Sigma), sodium hydroxide (certified ACS; Fisher), periodic acid (98%; Aldrich), 5,5'-dithiobis(2-nitrobenzoic acid) (99%; Aldrich), 3-mercapto-1,2-propanediol (95%; Aldrich), and benzophenone (99%, Aldrich) were used as received. Deionized water was obtained from a Milli-Q system and had a resistivity of 16–17 MΩ cm.

Advancing and receding contact angles were obtained using a Ramé-Hart Model 100–00 contact angle goniometer by estimating the tangent to the drop where it met the surface. A Gilmont syringe with a 22-gauge blunt-tip needle was used. Contact angles were measured within 10–20 s after the application of the ~1 μL drop under ambient conditions. All reported values were the average of at least eight measurements (4 drops, 2 sides each) taken at different areas on the polymer film surface.

Scanning electron micrographs were obtained on a JEOL 6300F at ≤1.0 kV with a tilt angle (the angle between the normal to the sample surface and electron beam source) of 0°. Most attenuated total reflectance–infrared (ATR–IR) spectra were obtained under dry and CO_2-free air using a Mattson Polaris FT-112 spectrometer with a liquid-nitrogen-cooled MCT detector and a 25 × 10 × 3 mm germanium (45° angle of incidence) crystal as the internal reflection element. Reported spectra are the accumulated average of 128 scans at 4 cm^{-1} resolution and a gain factor of 2, unless otherwise stated. A Perkin-Elmer 1750 spectrometer with a DTGS detector was used to collect ATR–IR spectra of unmodified PBD and PBD–$SCH_2CHOHCH_2OH$. Measurements with this instrument were made under a nitrogen atmosphere with a 50 × 20 × 1 mm silicon (45° angle of incidence) crystal as the internal reflection element. The spectra were an average of 256 scans at 4 cm^{-1} resolution and a gain factor of 4. Visible absorbance measurements were obtained at a wavelength of 412 nm using a Milton Roy Spectronic 1201 spectrometer.

X-ray Photoelectron Spectroscopy (XPS). Spectra were obtained using a Scienta ESCA300 (Uppsala, Sweden) spectrometer with monochromatized Al Kα X-rays from a rotating anode source. A pass energy of 300 eV was used to collect survey spectra, and a pass energy of 150 eV was used to collect the high-resolution spectra. The working pressure of the instrument was maintained at 10^{-8}–10^{-9} mbar. A slit width of 0.8 mm was used, and all spectra were referenced to the main C 1s peak, set at 285.0 eV.

Sample charging was minimized by mounting the polymer samples on a variable-height, custom-made stainless steel stub.[55] The face of the stub possessed an etched groove with dimensions 17 × 3 × 1 mm and was coated by the electrodeposition of gold using an electroplating solution of J N T Gold-Cote (J.N.T. Mfg. Co., Inc., Stormville, NY). The stub was biased at ~6.0 V to reduce the plating time, and a current of 100–500 mA was used. The polymer sample was mounted in the groove with a small strip of double-sided sticky tape by pressing the PBD sample at its ends. The surface of the polymer was approximately flush with the surface of the stub. Residual sample charging was compensated by exposing the sample to low-energy electrons (kinetic energy, 0.9 to 1.4 eV) using a Scienta flood gun that was aligned with the spot irradiated with X-rays on the sample surface. Minimum values of full width at half-maximum (fwhm) of the O 1s and C 1s peaks were taken as indicative of optimal charge neutralization. Once neutralization of the surface was optimized, the position of the sample was moved to a different spot on the sample to minimize X-ray-induced damage to the polymer before collecting the data.

The sample was positioned in the instrument while monitoring the photoelectron intensity at 84.0 eV (Au $4f_{7/2}$) to ensure that gold was not contributing to the spectrum. As the angle between the surface and detector (take-off angle) was varied, minor adjustments to the position of the sample were necessary. High-resolution spectra were collected in the desired regions of binding energy for more accurate quantification. Curve fitting was performed using the Scienta ESCA300 system software by describing each of the complex envelopes as a sum of Gaussian and Lorentzian functions.[56] A linear base line was defined. Curve fits were initiated using the method of Beamson and Briggs,[18] by choosing a model polymer structurally similar to the product surface and using published results for the number, position, and area ratio of the component peaks, the fwhm, and the asymmetry (A) and mixing (m) ratios. A good model polymer was not available for PBD–SCH_2CO_2H and PBD–$SCH_2CHOHCH_2OH$, and thus the structure of the added thiol group was used to set the number, position, and area ratios of the component peaks in the C 1s envelope. When the "goodness of fit" (χ^2) converged to a minimum value (generally ≤10), the constrained parameters were relaxed to refine the fit, except for the following cases: if the fwhm for the component peaks were greater than 1.5 eV, then this parameter was linked to that of the main C 1s peak (285.0 eV) to maintain acceptable values. The asymmetry and mixing ratios were also constrained to within reasonable limits of $A \leq 0.20$ and $m \geq 0.70$.[18] The line widths for the components of the C 1s envelope were in the range of 1.0–1.5 eV.

1,2-Polybutadiene. Poly(butadiene, 1,2-syndiotactic) (15–29% crystallinity) was purchased as pellets from Polysciences, Inc., who report its average molecular weight as 100 000 and density as 0.90 g/cm^3. We measured the T_g and T_m of the polymer as −9 and +129 °C, using a Mettler TC 10A differential scanning calorimeter. The PBD films were formed by melting pellets against a glass Petri dish that had been coated with a siloxane monolayer derived from octadecyltrichlorosilane (95%; Aldrich). The film was melted in an air-filled oven (Fisher Isotemp 500 Series) at 135–140 °C for 10–11 h. The resulting film was then peeled from the dish and stored on filter paper in the dark in a covered disposable Fisherbrand Petri dish. Chemical modifications were performed on the side of the polymer film that had been heated against air. We chose to work with this side because SEM revealed that it was smoother than the side heated against the glass, and XPS showed less surface contamination of oxygen and silicon than on the side heated against glass.

PBD–$CHOHCH_2OH$. A sample of PBD film (3 × 1 × 0.1 cm) was floated on a stirred aqueous solution of $KMnO_4$ (6.9 mM) and NaOH (0.025 M) at 0 °C for 1.5 h. The sample was rinsed with deionized water and then successively floated on aqueous $NaHSO_3$ (0.05 M) for 5–10 s, rinsed with deionized water, floated on aqueous HCl (0.1 M) for 5–10 s, and rinsed with deionized water. The surface was then blown dry with a stream of nitrogen.

PBD–$SCH_2CHOHCH_2OH$. In a Pyrex screw-top test tube, 15 mL of methanol and approximately 0.003 g of benzophenone were mixed. To this tube were added approximately 0.04 g of 3-mercapto-1,2-propanediol (~0.08 M), and a sample of PBD film (3 × 1 × 0.1 cm) was fully immersed in the solution. The solution was inverted several times and then sparged with argon (Airco, 4.8 grade) for 3 min to displace the oxygen, since oxygen is known to photochemically add to polymer surfaces.[57] The capped tube was exposed to light (350 nm) in a Rayonet RPR 100 photochemical reactor equipped with a water-cooled condenser that maintained the temperature of the sample at ~14 °C. Sixteen bulbs encircled the reaction cell holder at a radius of approximately 15 cm for a total of 24 W at the center of the reactor. After 10 min, the polymer sample was retrieved, rinsed with ethanol and deionized water, heated against deionized water at 50 °C for 40 min, and then blown dry with a stream of nitrogen.

PBD−CO_2H. An aqueous solution of $KMnO_4$ (0.45 M) and acetic acid (3 M) was formed by stirring the mixture vigorously at room temperature for 30 min. The solution was then gently stirred as a sample of PBD film (3 × 1 × 0.1 cm) was introduced. After 1 min on the oxidizing solution, the sample was treated with the following sequence of steps: rinsed with deionized water, floated on aqueous $NaHSO_3$ (0.05 M) for 5−10 s, rinsed with deionized water, floated on aqueous HCl (0.1 M) for 5−10 s, rinsed with deionized water, and then blown dry with a stream of nitrogen. The sample was then returned to the permanganate solution, and this procedure was repeated after 2 min of total time on the oxidizing solution. The sample was then floated on an aqueous solution of HIO_4 (0.1 M) for 10 min. It was rinsed with deionized water and blown dry with a stream of nitrogen before returning it to the original permanganate solution for an additional 5 s. The sample was rinsed with deionized water, floated on aqueous $NaHSO_3$ (0.05 M) for 5−10 s, rinsed with deionized water, floated on aqueous HCl (0.1 M) for 5−10 s, rinsed with deionized water, and then blown dry with a stream of nitrogen.[58] Finally, the sample was placed on room temperature water for 1 h and then dried under vacuum (≤0.1 Torr) for 15 min.

Etched PBD−CO_2H. The same reaction conditions described in the section for PBD−CO_2H were used to prepare etched PBD−CO_2H, with two modifications. First, the initial treatment with the permanganate solution was for 5 min, and the sample was floated on aqueous $NaHSO_3$ and HCl (as above) after 1, 2, and 5 min of the total reaction time. Second, the final treatment with the permanganate solution was for 2 min, and the sample was floated on aqueous $NaHSO_3$ and HCl after 1 and 2 min of the total reaction time.

PBD−SCH_2CO_2H. In a Pyrex screw-top test tube, 15 mL of methanol and approximately 0.003 g of benzophenone were mixed. To this tube were added approximately 0.09 g of mercaptoacetic acid (~0.07 M), and a sample of PBD film (3 × 1 × 0.1 cm) was fully immersed in the solution. The solution was inverted several times and then sparged with argon (Airco, 4.8 grade) for 3 min to displace oxygen.[57] The capped tube was exposed to light (350 nm) in a Rayonet RPR 100 photochemical reactor as described for PBD−$SCH_2CHOHCH_2OH$. After 10 min, the polymer sample was retrieved, rinsed with ethanol and deionized water, heated against deionized water at 50 °C for 1 h, and then blown dry with a stream of nitrogen.

Quantification of Desorbed Thiol. According to a published procedure,[30] 0.003 g of 5,5′-dithiobis(2-nitrobenzoic acid) (3×10^{-4} M) was added to 20 mL of a Na_2HPO_4 (0.05 M)/EDTA (2×10^{-6} M) buffer solution at pH 7.0. The deionized water used to prepare the buffer solution had been boiled for ~10−15 min and then bubbled with nitrogen as it cooled to room temperature, to remove oxygen. Samples of PBD (2 × 0.8 × 0.1 cm) were treated with the same reagents described for the surface photolytic addition of mercaptoacetic acid or 3-mercapto-1,2-propanediol. Upon removal from the reaction vessel, they were rinsed with EtOH, deionized water, and then dried with a stream of nitrogen. Each sample was then placed in a Fisherbrand scintivial containing 2 mL of a Na_2HPO_4 (0.05 M)/EDTA (2×10^{-6} M) buffer solution at pH 7.0 and heated to ~50 °C under an atmosphere of argon for 1 h (PBD−SCH_2CO_2H) or 40 min (PBD−$SCH_2CHOHCH_2OH$). After removing the samples from the vials, the buffer solutions were kept under argon until analyzed.

In a quartz cell of path length 1 cm, 1 mL of a buffer solution containing 5,5′-dithiobis(2-nitrobenzoic acid) was added and the absorbance set to zero. To the cell was then added 1 mL of the thiol solution (in the same buffer) to be analyzed. A calibration curve for each thiol was constructed using a series of thiol solutions of known concentration. The solution was mixed thoroughly using a Pasteur pipet. The increase in the absorbance was monitored as a function of time, until the absorbance became constant. For the samples desorbed from polymer, a quartz cell of path length 0.5 cm was used and 0.4 mL of the thiol/buffer solution was added to 0.4 mL of a buffer solution containing 5,5′-dithiobis(2-nitrobenzoic acid). The concentration of desorbed thiol was calculated using the linear equation derived from the calibration curves.

Polymer/Copper Foil Experiments.[6] Samples of PBD−SCH_2CO_2H and PBD−$SCH_2CHOHCH_2OH$ were placed, functionalized-side down, against a piece of copper foil (99.99+%; Aldrich) that had been cleaned with soapy water. A binder clip (ca. 13 kPa) was used to clamp the polymer/copper sandwich between glass slides, before placing the setup into an air-filled oven (Fisher Isotemp 500 Series) at 80 °C for 11 h. Teflon tape was placed between the polymer and the glass slide to prevent adhesion at that interface. Samples were removed from the oven, and both the polymer and the copper foil were examined visually for discoloration.

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