Organic Chemistry at Polymer Surfaces To Promote Adhesion to Gold and Copper: Surface-Modified Polybutadiene Having Functional Groups Containing Sulfur

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The photolytic addition of thiols or thiolacetic acid to olefinic groups at the surfaces of syndiotactic 1,2-polybutadiene (PBD) provided polymer surfaces bearing sulfide or thioacetate groups. Ethanolysis cleaved these thioacetate groups to give the corresponding thiols. The product surfaces have been characterized by attenuated total reflectance infrared (ATR-IR) spectroscopy, X-ray photoelectron spectroscopy (XPS), and contact angles of water. Evaporated films of copper and of gold adhered to surfaces of sulfur-functionalized polymers but not to the unfunctionalized polymers in tape-peel tests. Quantitative adhesion experiments were performed using a 180° peel test with these surface-modified derivatives of PBD (and with the unmodified polymer) heated under pressure against copper foil substrates, and the limiting values of peel strength in these systems were related to the identity of the interfacial functionality in an understandable way. The rate in growth of adhesion was not limited by thermal reconstruction of the polymer surface. Mechanical studies of modified and unmodified samples of PBD indicated that the observed differences in adhesion are not due to changes in the bulk properties of the polymer.

Introduction

The science of adhesion addresses a complex combination of issues relating to the chemistry and physics of interfaces and the materials that comprise them.[1–4] The work presented in this paper focused on a narrow section of these issues: the role of interfacial functional groups on the adhesion of a polymer to a metal.[5] We have investigated the adhesion of a series of surface-modified derivatives of polybutadiene when heated against gold and against copper. By varying the interfacial functionality but leaving the bulk composition of the sample unchanged, contributions to adhesion from bulk properties should remain constant from sample to sample. On the background of this contribution from the bulk, the influence of the interfacial functionality should be apparent. Drawing inferences in complex systems, by comparing a closely related series of samples that differ primarily in a single variable, is a central theme in physical organic chemistry. This approach has been applied very successfully to the wettability of solid surfaces by liquids (a subset of adhesion).[5–12,20]

We have also investigated a simple, molecular, model system, which allowed detailed analysis of the polymer/metal interface not practical for the polymeric system. In these experiments, we replaced the surface-modified polymer with a solution of molecules bearing similar functional groups to those present on the surface of the polymer. This model system allowed chemical analysis, X-ray photoelectron spectroscopy (XPS), not easily applied to the "buried" polymer/metal interfaces studied in this work.

Our choice of systems—a polymer bearing a sulfur-containing functionality at its surface against gold or copper—was intended to take advantage of the strong chemisorption of thiols and disulfides at the surface of these metals that has been used in the formation of self-assembled organic monolayers,[7–12] adhesion of

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evaporated films of gold to surface-modified inorganic substrates and to organic–inorganic composite substrates,[13–16] and adsorption of sulfur-containing polymers from solution onto gold.[17–19] We have studied three types of sulfur-containing functionality: thioacetate, thiol (or disulfide), and dialkyl sulfide. Our studies have focused primarily on syndiotactic 1,2-polybutadiene (PBD), a polymer whose surface chemistry we have previously explored.[20] Methods used by others to improve the adhesion of polymers to substrates of copper or of gold have focused primarily on mechanical interlocking and/or covalent bonding involving a coupling agent or adhesive at the polymer/metal interface.[21–23] In addition, pretreatment of the surface of the polymer[22] or of the metal[23]—to roughen, chemically modify, or clean them—is typically required to improve adhesion.

A central problem faced in the rational design of adhesion between polymers and metals is the fact that almost all metals form stable, native oxides under ambient conditions.[24] The presence of oxide(s) implies the possibility of redox chemistry at interfaces that include them, especially those against oxidizable polymers. This possibility provides potential mechanisms for degradation of the polymer, corrosion of the metal, and formation of "weak boundary layers"[2,4,25] between the two bulk phases. Copper is an interesting and important example of such a metal, and its adhesion to polymers is of great interest, for instance in protective coatings for microcircuitry.[26]

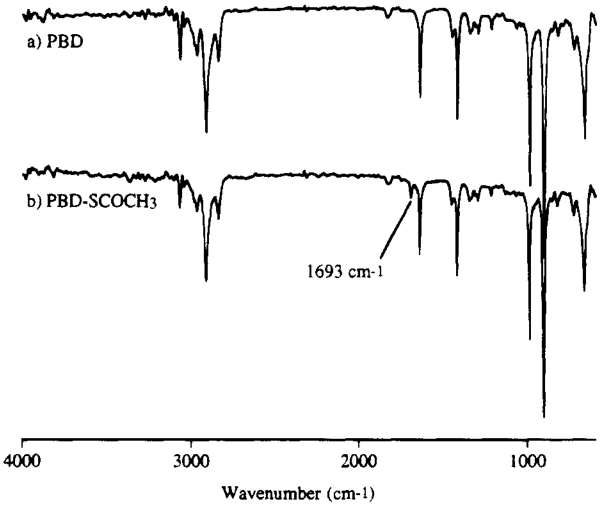

Figure 1. ATR-IR spectra of (a) unmodified PBD and (b) PBD–$SCOCH_3$.

At the beginning of this work, we recognized three processes that could be involved in the development of adhesion between the surface-modified polymers and copper surfaces. First, since the surfaces of both the polymer and copper are rough on the ~100-nm scale of length, we expected the viscous flow of the polymer to increase the degree of atomic contact at the polymer/copper interface. For the quantitative adhesion studies, the surface-modified polymer was heated against the copper foil under pressure to promote this flow. Second, thermal reconstruction of the interfacial region of the polymer could bring sulfur-containing functional groups, initially beneath the surface of the polymer, into contact with the copper surface. The thermal reconstruction of functional polymer surfaces is well-established.[6] Third, chemical reaction between these functional groups and the native copper oxide could produce strong, covalent, copper-thiolate bonds[9] at the polymer/copper interface.

Finally, we examined whether the mechanical properties of the surface-modified polymers differed from

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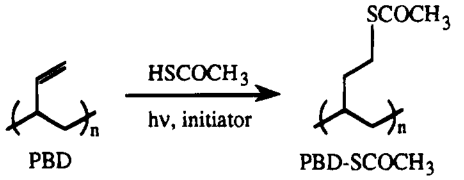
those of the unmodified polymer. Since the initial surface modification described in this paper required ultraviolet photolysis,[20] it is possible that the polymer could degrade or become cross-linked during that process. Degradation or an increase in the amount of cross-linking could affect the adhesion tests by changing the ability of the polymer to dissipate energy viscoelastically. We measured two mechanical properties useful in the characterization of elastomers: the apparent modulus (the ratio of stress to strain for small extensions) and the stress–relaxation of samples at a given strain.

Results and Discussion

The free-radical addition of thiolacetic acid to the alkenyl groups at the surface of PBD, catalyzed by ultraviolet light in the presence of an initiator (eq 1),[20,27,28] provided surface-bound thioacetate groups. The attenuated total reflectance infrared (ATR-IR) spectrum of the product surface displayed the expected carbonyl stretching band at 1693 cm^{-1} for PBD–$SCOCH_3$ (Figure 1). Equation 1 shows the expected regiochemistry of the thioacetate; formation of the secondary thioacetate is also possible, though unlikely.[27,29]



(1)

The ATR-IR spectra of PBD samples that had been exposed to the thiolacetic acid solution in the absence of UV light contained no carbonyl band near 1693 cm^{-1}. This absence indicated that little or no thiolacetic acid absorbed into the polymer during the photolytic functionalization. Preliminary adhesion experiments involving heating the samples against copper, however, produced a purple discoloration of the copper *outside* the area in contact with the polymer. A drop of the thiolacetic acid solution, used in the photolysis reactions, placed between an unmodified polymer film and copper also caused a similar discoloration of the copper. These control experiments indicated that some thiolacetic acid had, in fact, absorbed into the polymer film, though at a concentration below the threshold detected by ATR-IR. This discoloration could be avoided by heating the surface-modified polymer against hot water or ethanol prior to the adhesion experiments. We inferred, therefore, that this annealing step removed any absorbed thiolacetic acid. The amount of thiolacetic acid desorbed in this step was quantified by thiolate–disulfide interchange with 5,5′-dithiobis(2-nitrobenzoic acid) (Ellman's reagent) and spectrophotometric detection of the product chromophore.[30] In these experiments, 15–18 nmol of thiolacetic acid were desorbed per cm^2 of polymer.

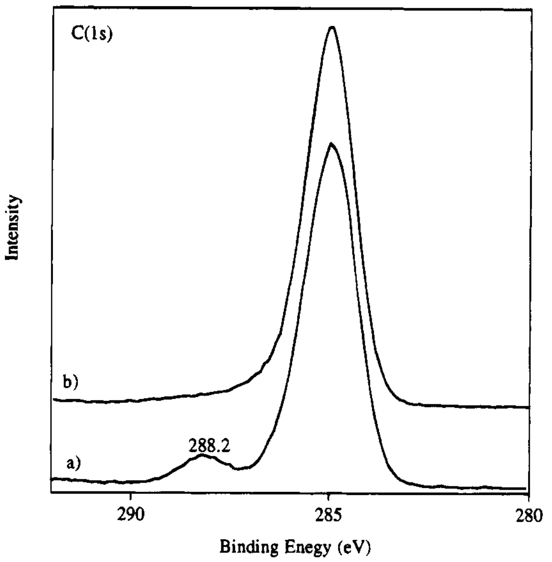


Figure 2. High-resolution XPS spectra of the C(1s) region of (a) PBD–$SCOCH_3$ after heating on water for 1 h at 50 °C and (b) PBD–SH derived from the ethanolysis of the thioacetate. The absence of an oxidized C(1s) peak at a binding energy of 288.2 eV, characteristic of the thioacetate group, indicates that the ethanolysis reaction was complete. The binding energy of the main C(1s) peak in each spectrum has been corrected for charge compensation and set to 285.0 eV.

X-ray photoelectron spectroscopy (XPS) of PBD–$SCOCH_3$ confirmed the presence of thioacetate groups. A high-resolution spectrum of the C(1s) region displayed a peak at a binding energy of 288.2 eV, consistent with the reported value for the carbonyl carbon of a thioacetate group (Figure 2).[14] The expected atomic ratios of carbon (total):oxygen:sulfur for a quantitative reaction were 6:1:1, and the experimentally determined ratios were 11.5:1.0:1.1. The yield of this reaction, taken as the average of those yields calculated using the molar ratios of total carbon:oxygen and total carbon:sulfur, is 45% in that portion of the polymer sensed by XPS under our experimental conditions.[31] The expected ratios of *carbonyl* carbon:oxygen:sulfur were 1:1:1, and the experimentally determined ratios were 1.0:1.2:1.4. The apparent deficiency in the amount of carbonyl carbon, relative to oxygen and sulfur, may be due to the difficulty in accurately fitting the small peak at 288.2 eV in the presence of the larger C(1s) peaks in the spectrum.

During the course of the reaction, the advancing and receding contact angles of water decreased from 98° and 75° for unmodified PBD to 80° and 55° for PBD–$SCOCH_3$. For comparison, the advancing contact angle of water was reported as 78–80° for alkylsiloxane monolayers formed by adsorption of $Cl_3Si(CH_2)_{11}SCOCH_3$ onto a silicon wafer[14] and 78–83° for similar monolayers on surface-oxidized poly(dimethylsilox-

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(31) After curve-fitting, ratios of peak areas (total carbon/oxygen and total carbon/sulfur) were used to calculate the yield of reaction, assuming the presence of only unreacted and product repeat units. The reported yield is the average of yields calculated separately based on each of the ratios. This procedure is described more fully elsewhere.[20]

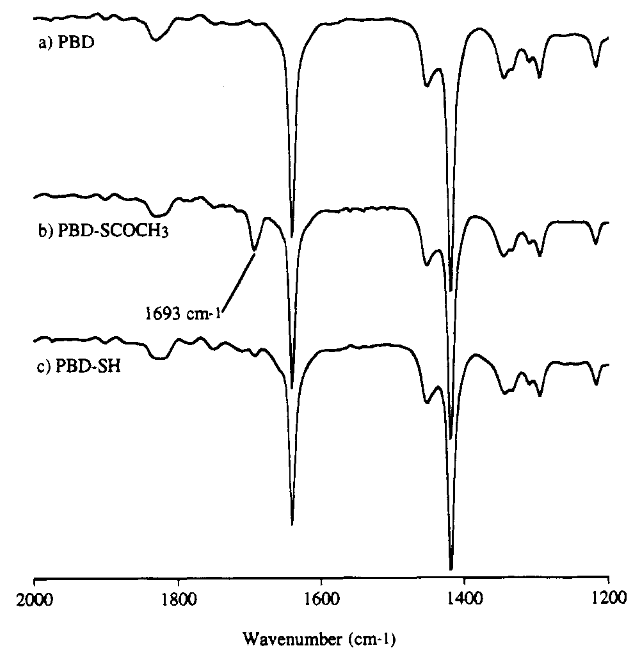
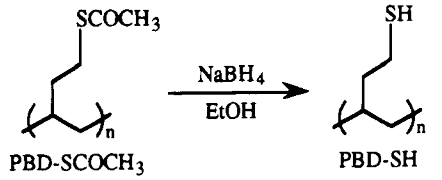


Figure 3. ATR-IR spectra of (a) PBD, (b) PBD$-$SCOCH$_3$, and (c) the product of PBD$-$SCOCH$_3$ treated with ethanolic sodium borohydride at 50 °C for 2 h.

ane).[15] The similarities in wettability by water are consistent with, though do not demand, similarities in structure at these interfaces.

Treatment of PBD$-$SCOCH$_3$ with ethanolic sodium borohydride for 2 h caused the carbonyl band in the ATR-IR spectra to diminish (Figure 3) to no more than ~7% of its original intensity. Our hope was that the sodium borohydride would both act as a base to facilitate ethanolysis and minimize oxidation of the thiols by adventitious oxidants (e.g., O$_2$) during the reaction. The decrease in the carbonyl band is consistent with the formation of the thiol, PBD$-$SH (eq 2), though oxidation



(2)

of the thiol by atmospheric oxygen may occur *after* isolation of the product surfaces. In fact, the XPS spectrum of PBD$-$SH that had been stored overnight against water in air showed a new peak on the high binding energy side of the main S(2p) resonance, indicating possible oxidation of sulfur. The binding energy of the new photoemission (approximately 168.0 and 169.2 eV for the S(2p$_{3/2}$) and S(2p$_{1/2}$) components) suggests the presence of sulfonate groups.[9,32,33] In contrast, samples of PBD$-$SH that had been floated on water in air for only 5 min, prior to XPS analysis, showed much less intensity under the high-binding-energy doublet (Figure 4). Although oxidation of thiols to disulfides probably also occurs in these samples to some extent,[34] we would not expect to be able to resolve them by XPS.[8,14,19] The high-resolution XPS spectrum of the C(1s) region of PBD$-$SH showed no oxidized carbon peak at 288.2 eV (Figure 2), again consistent with the conversion of PBD$-$SCOCH$_3$ to PBD$-$SH. The advancing contact angle of water on PBD$-$SH was indistinguishable from that on PBD$-$SCOCH$_3$, though the receding angle was lower (46°).

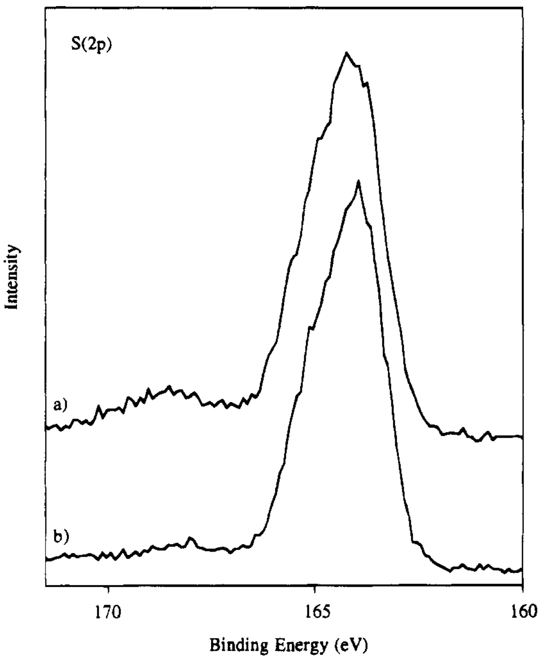


Figure 4. High-resolution XPS spectra of the S(2p) region of PBD$-$SH: (a) stored overnight against water, in air, and (b) stored for only 5 min against water, in air, prior to XPS analysis. The broad peak at the high binding-energy side of the main S(2p) resonance suggests the susceptibility of thiol groups at the surface of PBD$-$SH to oxidation upon storing against water, in air, for extended times.

Samples of PBD$-$SH also contained a significant amount of oxygen. The atomic ratio of sulfur:oxygen was 1.0:0.8 for a sample stored on water in air for 5 min and 1.0:0.9 for one stored overnight. We can identify from the survey XPS spectra (0.8 eV resolution) two contaminants as possible sources of oxygen on these surfaces. Small peaks due to silicon are present and at a binding energy (Si 2p, 102 eV) consistent with alkylsiloxane, perhaps polymer derived from the octadecyltrichlorosilane used to silanize some of our glassware. We also noted a small amount of nitrogen in these spectra at a binding energy (N 1s, 400 eV) consistent with amides, presumably proteins. Assuming that the oxidized sulfur (vide supra) is due to sulfonate, and that the contaminants have stoichiometries of 1:1.5 for Si:O and 1:1 for N:O, we can account for approximately 51% of the oxygen sensed by XPS. Our inability to account for the remaining oxygen signal may reflect the difficulty in accurately fitting the small peak due to oxidized sulfur in Figure 4a, or it may reflect localization of the contaminants at the surface and thereby enhancement of their XPS signals relative to those of sulfur.

Adhesion Studies

In initial adhesion experiments, we formed thin, conformal coatings of gold and of copper on the modified

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polymer surfaces by slow evaporation of the metal. We expected this method to provide a high degree of atomic contact at the new polymer/metal interface. We evaluated the adhesion at these interfaces using a tape-peel test: First, the metal film was gently scratched with a spatula to provide a locus of fracture, and tape was applied to the metal film using finger-pressure to ensure intimate contact. After peeling the tape from the polymer/metal sample, the adhesive side of the tape was examined visually for the presence or absence of metal. The absence of metal on the tape signified a passed adhesion test, and any metal on the tape signified a failed test.

Approximately 25–70 nm of gold were thermally evaporated, at a rate of 1–6 Å/s and a background pressure of (3.0–6.0) × 10^{-6} Torr, onto surfaces of PBD, PBD–$SCOCH_3$, and PBD–SH. Similarly, ca. 40 nm of copper was thermally evaporated, at a rate of 1–6 Å/s and a background pressure of (2.8–8.5) × 10^{-6} Torr, onto other samples of the same surfaces. All of the resulting interfaces of both gold and copper against *sulfur-functionalized* PBD passed manual peel tests with duct tape; that is, fracture appeared (visually) to occur at the tape/metal interface. The samples having interfaces of metal against the *unfunctionalized* PBD failed the peel tests, and fracture appeared (visually) to occur at the polymer/metal interface.

To quantify the strength of adhesion at the interfaces of metal against sulfur-functionalized PBD, we extended these studies by heating the modified surfaces against preformed gold and copper substrates under pressure. The gold substrate was formed by evaporating a film of the metal onto a glass microscope slide that had been treated with $HSCH_2CH_2CH_2Si(OCH_3)_3$ to promote adhesion at the gold/glass interface.[16] The polymers PBD, PBD–$SCOCH_3$, and PBD–SH were pressed with a pressure of 13 ± 2 kPa against the gold substrate and heated at 80 °C. After 18 h, the samples were removed from the oven and allowed to cool to room temperature. The PBD sample peeled easily from the gold, and adhesive failure appeared (visually) to occur at the polymer/gold interface. The PBD–$SCOCH_3$ and PBD–SH samples, however, showed strong adhesion to the gold films, indicated by failure that appeared (visually) to occur at the gold/*glass* interface. In each case, this transfer of gold to the polymer created a new polymer/gold interface, which itself then passed manual *tape*-peel tests. Adhesive failure at the gold/glass interface indicated that a bulk–metal substrate would be required to make quantitative measurements of adhesion at the polymer/metal interface.

We used copper instead of gold for these experiments, since it is readily available and inexpensive. Strips of copper foil were vigorously rubbed with a Kimwipe and soapy water, rinsed thoroughly with deionized water, and blown dry with nitrogen. High-resolution XPS spectra of the Cu(2p), O(1s), and Cu $L_3M_{4,5}M_{4,5}$ Auger regions on the cleaned copper indicated that the native oxide was predominantly Cu_2O, and that a thin layer of $Cu(OH)_2$ existed at the outermost surface of the foil.[35–40] A later section in this paper describes the characterization of the copper foil surface by XPS. In the discussion of adhesion studies that follows, the reader should interpret references to "copper" as implicitly including the presence of this native oxide.

In preliminary, *qualitative* peel tests, samples of PBD, PBD–$SCOCH_3$, and PBD–SH were pressed (13 ± 2 kPa) against the cleaned copper and heated at 80 °C for 18 h. The resulting PBD/copper and PBD–SH/copper interfaces failed easily, while PBD–$SCOCH_3$ adhered strongly to the copper foil. By "strong", we mean that peeling caused either severe distortion (necking) or breakage of the polymer. Samples of PBD–$SCH_2CO_2CH_3$ and PBD–SCH_2CO_2H,[20] formed by photolytic addition of the corresponding thiols to PBD, also showed strong adhesion to copper under similar conditions.

Quantitative measurements for the PBD–$SCOCH_3$/copper, PBD–SCH_2CO_2H/copper, PBD–$SCH_2CO_2CH_3$/copper, and PBD–SH/copper systems were performed to determine the maximum yield strength of adhesion, as a function of time of heating at 80 °C under a pressure of 13 ± 2 kPa. In addition to these sulfur-containing surfaces, PBD and PBD–diol (formed by oxidation with cold, dilute $KMnO_4$) were also pressed/heated against copper, and the resulting adhesion was measured. These systems provided useful comparisons, since they represent low and (relatively) high surface free energy surfaces that do not contain sulfur.[41] Peel tests using an Instron 1011 tensile tester and a 180° geometry were performed with a peel rate of 10 mm/min (Figures 5 and 6).[42] We interpret these values of maximum yield strength only in a comparative (rather than absolute) sense, since stronger adhesion at the polymer/copper interface leads to a greater dissipation of energy viscoelastically and plastically within the polymer, and the adhesion depended on the particular lot from which the copper was purchased. Hence, we interpret these data only to rank the interfacial strengths of the various samples relative to one another, and we used a single lot of copper in these experiments. For the PBD/copper, PBD–SH/copper, PBD–diol/copper, PBD–SCH_2CO_2H/copper, and PBD–$SCH_2CO_2CH_3$/copper samples, failure appeared (visually) to occur at the polymer/copper interface for all heating times. For the PBD–$SCOCH_3$/copper samples, however, failure appeared (visually) to occur *co*hesively within the polymer in some places after as little as 2.5 h of heating, and this mode of failure appeared to dominate after 12 h of heating.

As expected, the PBD–$SCOCH_3$/copper interface developed a much higher yield strength than did the unmodified PBD/copper interface. Since PBD–$SCOCH_3$ failed *co*hesively within the polymer, the measured yield

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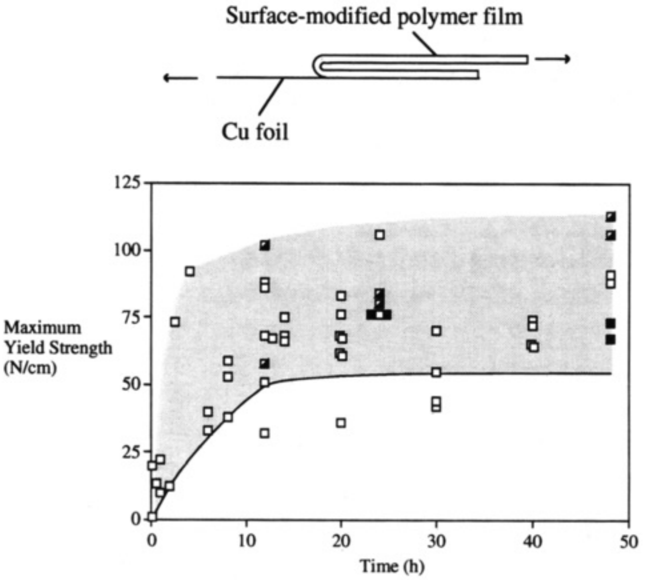

Figure 5. Maximum yield strength versus annealing time at 80 °C under pressure, prior to peel testing, for the $\mathrm{PBD{-}SCOCH_3}$/copper system (□). Peel tests were performed using an Instron 1011 tensile tester, a 180° geometry, and a peel rate of 10 mm/min. Four $\mathrm{PBD{-}SCOCH_3}$/copper samples (■) were subjected to boiling tap water for 1 h, prior to peel-testing. Other $\mathrm{PBD{-}SCOCH_3}$/copper samples (◪) contained $\mathrm{PBD{-}SCOCH_3}$ strips that had been heated in stirred ethanol for 2 h at 50 °C under nitrogen, prior to placement against copper.

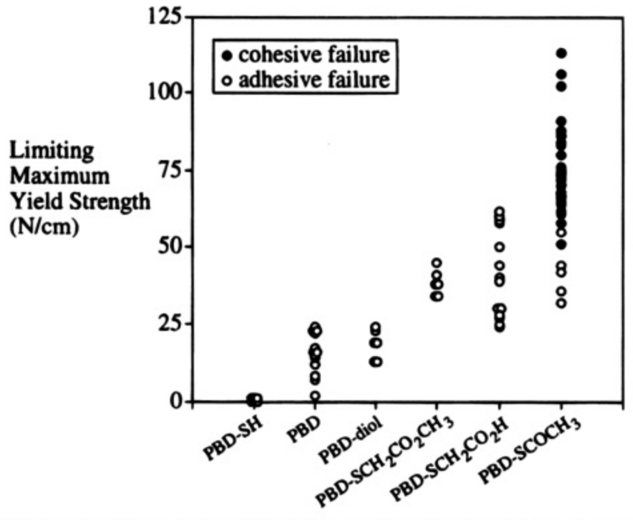

Figure 6. Range of limiting values of maximum yield strength for the functionalized and unfunctionalized PBD surfaces that were pressed and heated against copper at 80 °C.

strength represents a lower limit on the actual strength of the polymer/metal interface. This mode of failure, we believe, also gives rise to the observed variability in the maximum yield strength in this system, because the measured strength at failure may be determined by bulk properties and defects of the polymer and not by interfacial forces. The PBD−diol/copper interface failed at a yield strength similar to that of PBD/copper, despite the higher surface free energy of the polymeric component.

The sulfide $\mathrm{PBD{-}SCH_2CO_2H}$[20] adhered to copper almost as strongly as did $\mathrm{PBD{-}SCOCH_3}$. This result was not surprising, since dialkyl sulfides have been reported to chemisorb to gold, leading to formation of self-assembled monolayers or polymer adsorption from solution.[17] The presence of the carboxylic acid group, however, may have been important in this adhesion. To test this hypothesis, we examined a closely related surface, the methyl ester $\mathrm{PBD{-}SCH_2CO_2CH_3}$,[43] and found that its adhesion to copper was similar to that of the carboxylic acid surface (Figure 6). The similarity in adhesion of these two surfaces to copper indicates that the carboxylic acid group of $\mathrm{PBD{-}SCH_2CO_2H}$ is probably not critical to its adhesion to copper. Advancing and receding contact angles of water were 63° and 0° on $\mathrm{PBD{-}SCH_2CO_2H}$,[20] and 81° and 34° on $\mathrm{PBD{-}SCH_2CO_2CH_3}$. An ATR-IR spectrum of $\mathrm{PBD{-}SCH_2CO_2H}$ that had been pressed and heated against copper at 80 °C for 4 h and then peeled showed no additional peaks that could be ascribed to copper carboxylate species.

A particularly striking result reported in Figure 6 was the apparent lack of adhesion for the PBD−SH/copper system. These data were surprising, since alkanethiols are known to form self-assembled monolayers on copper.[9,10] We note, however, that highly oxidized copper has been reported to complicate or inhibit these adsorptions.[9] In addition, PBD−SH is susceptible to oxidation to form disulfides[27,34] and sulfonates,[9,27,44] especially at elevated temperatures in the presence of oxygen. The storage time for samples of PBD−SH, prior to being pressed/heated against copper, was minimized (~10 min−3 h) to limit the amount of atmospheric oxidation. The presence of disulfides would cross-link the interfacial region, which could inhibit the flow of the polymer at 80 °C, thus preventing it from conforming to the contours of the copper surface. Such cross-linking could also introduce a stress at the polymer/copper interface. Scanning electron micrographs of surfaces of PBD−SH that had been pressed/heated against copper (for as little as 10 min), however, showed replication of the features on the surface of the copper, indicating that polymeric flow was not inhibited, at least on the ~100 nm scale of length. The formation of sulfonates would increase the surface free energy of the polymer and might therefore increase its adhesion. Alternatively, oxidation of thiol groups by the copper oxides to sulfonates could lead to formation of a weak boundary layer[2,4,25] containing copper sulfonate species.

A control experiment ruled out the possibility that heating in ethanol (conditions used in the synthesis of PBD−SH) was responsible for its lack of adhesion to copper, for instance by facilitating migration of chemically modified chains into the bulk of the polymer and away from the surface. Six strips of $\mathrm{PBD{-}SCOCH_3}$ were treated with ethanol at 50 °C for 2 h while stirring under nitrogen, without sodium borohydride, to simulate conditions used in the conversion of $\mathrm{PBD{-}SCOCH_3}$ to PBD−SH. Pairs of these samples were then pressed/heated against copper at 80 °C for 12, 24, and 48 h and then evaluated with the Instron peel test. Cohesive failure was observed for all samples, and the observed maximum yield strengths were within the range ex-

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pected for this system (Figure 5). We conclude, therefore, that heating in ethanol was not responsible for the lack of adhesion of PBD–SH to copper.

In the hope of elucidating the reason(s) for the lack of adhesion in the PBD–SH/copper system, we examined the fractured surfaces spectroscopically. An ATR-IR spectrum of PBD–SH that had been pressed and heated against copper at 80 °C for 24 h displayed no new peaks attributable to disulfides or oxidized sulfur (e.g., sulfonates). The XPS survey spectrum (0.25 eV resolution) of PBD–SH that had been pressed and heated against copper at 80 °C for 48 h, however, showed a large amount of oxidized sulfur ($S(2p_{3/2})$ and $S(2p_{1/2})$ peaks at 167.8 and 169.1 eV), very similar to that found for PBD–SH that had been stored overnight on water. The spectrum also showed $Cu(2p_{3/2})$ and $Cu(2p_{1/2})$ peaks at approximately 934.3 and 954.2 eV with satellites at approximately 942.3 and 962.7 eV, all due to oxidized copper (Cu^{2+}). The survey spectrum of the copper foil showed the presence of Cu^0, Cu_2O, and $Cu(OH)_2$ but no sulfur. From these data, we conclude that the interface fractured in large part within the copper oxide. This mode of failure and the low adhesion ($\leq$1 N/cm) of the PBD–SH/copper system indicate the formation of a weak boundary layer,[2,4,25] perhaps including copper sulfonate species at the PBD–SH/copper(oxide) interface. The presence of an oxide is clearly responsible for the striking difference between copper foil and the evaporated metal in adhesion to PBD–SH.

To test the adhesive stability of the PBD–$SCOCH_3$/copper system, samples of the laminated structure were immersed in hot water prior to peel testing. In these experiments, two strips of PBD–$SCOCH_3$ were pressed/heated against copper at 80 °C for 24 h; another pair of samples were treated in the same way for 48 h. The binder clips that supplied pressure to the samples were then removed, and all of the samples were placed into boiling tap water for 1 h. A gradual tarnishing of the copper developed during this time. The samples were cooled by immersion in room-temperature tap water for 10 min and then peeled to measure the adhesion. Both sets of samples had maximum yield strengths in the range found for samples not heated in water (Figure 5). This treatment thus had little or no effect on the adhesive strength of the PBD–$SCOCH_3$/copper interface.

Rate of Development of Adhesion at the PBD–$SCOCH_3$/Copper Interface

The data in Figures 5 and 6 show that the PBD–$SCOCH_3$/copper system reached a limiting value of yield strength only after several hours; the other systems behaved similarly. There are at least three processes that could limit the rate in growth of adhesion in these systems: (i) thermal reconstruction of the polymer surface involving migration of functional groups to and from the polymer/copper interface; (ii) viscous flow of the polymer into the crevices in the copper surface to increase the degree of atomic contact between the surfaces; (iii) chemical reaction between those functional groups at the surface of the polymer and the native copper oxide. We have addressed each of these possibilities experimentally.

Since the presence of thioacetate groups in the interfacial region of PBD–$SCOCH_3$ promoted its strong adhesion to copper, the speed with which those groups could move to and from the surface of the polymer was an important parameter in understanding the kinetics of growth in adhesion. The thermal reconstruction of polymer surfaces is known to involve both conformational changes at the interface and slower diffusion of polymer chains in the interfacial region, processes that usually lower the interfacial free energy of the system.[6] We monitored the changes at the surface of PBD–$SCOCH_3$ that occur on heating in air by measuring contact angles of water. As expected, the surface became more hydrophobic upon heating in air at 80 °C. In fact, within 1 min, the advancing contact angle of water rose from 80° to 98°, the same as that on unmodified PBD. Since this process required only seconds and strong adhesion required hours to develop, it is clear that thermal reconstruction does not limit the rate at which adhesion grows in this system.

We assessed the kinetics of viscous flow of the polymer by observing, using scanning electron microscopy (SEM), the polymeric replicas of the copper surface taken from polymer/copper samples that had been pressed/heated for various amounts of time. Since PBD–$SCOCH_3$ adhered strongly to copper, the polymeric replica could not be separated from the foil without severely distorting or tearing the polymer. As a model, we observed SEM images of unmodified PBD and PBD–SH pressed/heated against copper at 80 °C as a function of time. These micrographs showed that within 10 min, the polymeric replicas became very similar in topography to the copper surface at the scale of length observed ($\geq$100 nm). While this process is slower than that of thermal reconstruction of the surface of PBD–$SCOCH_3$, it is much faster than the growth of adhesion. We note, however, that changes in topography on this scale of length may not accurately reflect changes at the angstrom level, the scale of length directly relevant to the degree of atomic contact between the surfaces.

We have investigated the chemistry that may occur at the PBD–$SCOCH_3$/copper interface by examining the interaction of a model compound, 1-octyl thioacetate (OTA), with the surface of copper. A 0.1 M solution of OTA in methanol was dripped onto a sample (~1 cm^2) of unmodified PBD, and the solvent was allowed to evaporate leaving behind residual OTA. This process was repeated until ~1 mg of OTA had been deposited. This sample was pressed and heated against copper foil (~1 cm^2) for 13 h at 80 °C. The polymer sample was then peeled from the copper; it did not adhere strongly. A slight purple discoloration was evident on the copper surface that was in contact with the polymer sample, and rinsing with methanol did not remove the discoloration.

High-resolution XPS analysis of this copper surface (Figure 7) revealed three spin–orbit doublets in the S(2p) region at 162.2 and 163.2 eV, at 163.9 and 165.0 eV, and at 167.2 and 168.4 eV (referenced to the main C(1s) peak, set at 285.0 eV), indicating the presence of three oxidation states of sulfur. The largest $S(2p_{3/2})$ peak (162.2 eV) is close in binding energy to that reported for self-assembled monolayers of alkyl thiolates (162.1 eV) on copper and may indicate the presence of a copper thiolate species.[9] We believe that the small difference in binding energy (0.1 eV) is due, in part, to a difference in referencing. The peak at 163.2 eV is the

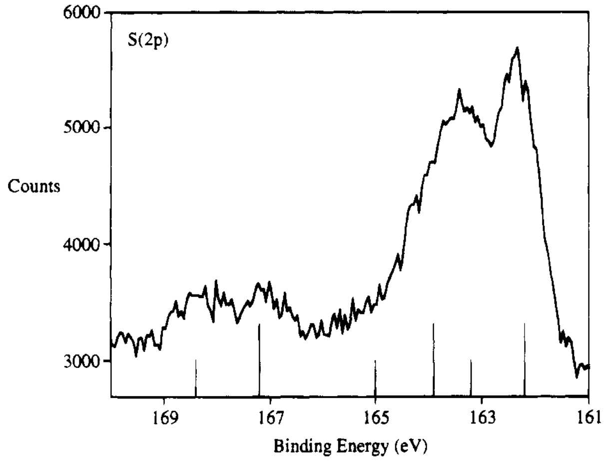

Figure 7. High-resolution XPS spectrum of the S(2p) region of copper foil heated against PBD/OTA at 80 °C. This spectrum was collected with a shallow takeoff angle (15°) to maximize the sensitivity to species at the outermost portion of the solid. The three pairs of peaks are referenced to the main C(1s) peak, set at 285.0 eV, and appear at 162.2 and 163.2 eV, at 163.9 and 165.0 eV, and at 167.2 and 168.4 eV. The vertical lines represent the curve-fitted positions of the three spin–orbit doublets corresponding to the $S(2p_{3/2})$ and $S(2p_{1/2})$ components of each species.

corresponding $S(2p_{1/2})$ resonance. The doublet at 163.9 and 165.0 eV in the copper/OTA sample suggests formation of octyl disulfide from cleaved OTA. Octanethiol is also a possible source of this spin–orbit doublet, though we would expect this compound to have been rinsed away in methanol or removed in vacuo in the XPS chamber. The doublet at 167.2 and 168.4 eV for the copper/OTA sample suggests the presence of sulfonate groups.[9,32,33] High-resolution XPS spectrum of the same surface in the C(1s) region contained a peak characteristic of a carboxyl carbon (binding energy 288.7 eV), indicating that acetate derived from OTA was also present on the surface.

Photoemission spectra from polymer samples that had not been heated against copper provided useful comparisons. For instance, high-resolution XPS spectra of the S(2p) region of PBD–SH (Figure 4b) contained $S(2p_{3/2})$ and $S(2p_{1/2})$ components at 163.8 and 165.0 eV. These components are similar to those suggested above for the formation of octyl disulfide and may suggest the susceptibilty of PBD–SH in forming the disulfide. High-resolution XPS spectra of the S(2p) region of PBD–$SCOCH_3$ contained $S(2p_{3/2})$ and $S(2p_{1/2})$ components at 161.3 and 162.5 eV. The absence of peaks in this region for the Cu/OTA sample indicated that any unreacted OTA was removed by rinsing or by vacuum. Overall, these data suggest that cleavage of the sulfur–acyl bond of OTA and thus of PBD–$SCOCH_3$ by analogy to form copper–thiolate moieties is likely under the conditions used in our adhesion experiments.

Mechanical Studies: Comparison of PBD and PBD–$SCOCH_3$

One assumption in this work is that the viscoelastic properties of the bulk polymer do not change as a result of surface modification. To test this hypothesis, we compared the mechanical properties of PBD–$SCOCH_3$ and unmodified PBD. Two conveniently measured, bulk properties of particular interest are the apparent modulus and the rate of decrease of the stress, at a given strain, as the samples relaxes. The apparent modulus is the ratio of stress to strain (i.e., force per unit area to extension) measured as the sample is stretched (tensile mode), and is approximated in the regime of small (1–3%) extensions, as shown in Figure 8. Interpretation of the modulus is complicated for elastomers, since these materials typically exhibit nonlinear stress–strain curves, even for small extensions. Consequently, the reported tensile moduli should be interpreted as only an approximate measure of the polymer's initial response to an applied strain. The apparent moduli of PBD and PBD–$SCOCH_3$ were 60 ± 1 and 49 ± 2 MPa.

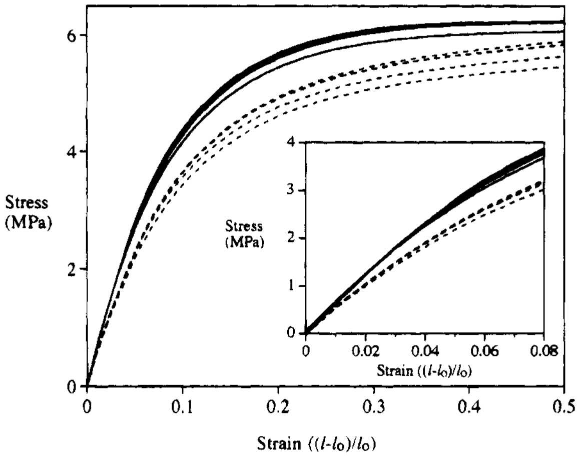

Figure 8. Stress versus strain curves for PBD (solid lines) and PBD–$SCOCH_3$ (dashed lines). The apparent modulus was approximated in the range of 0.01–0.03 extension, shown expanded in the inset. The symbols used to define strain are the gauge length of the sample after extension (l) and the original gauge length of the sample before extension (l_0).

While these data initially appeared to indicate a change in modulus resulting from surface modification, control experiments showed that the modulus depended on the thermal history of the samples. Hence, heating unmodified PBD against water at 50 °C for 1 h (conditions used to extract small amounts of free thiol from PBD–$SCOCH_3$) lowered its modulus to 53 ± 2 MPa. This change in modulus had no effect on the maximum yield strength measured in peel tests with annealed PBD against copper. Analogously, the modulus of a sample of PBD–$SCOCH_3$ increased to 53 MPa upon storage for 4 days, and to 56 ± 2 MPa upon storage for 30 days at room temperature (after the 50 °C extraction step). These results indicate that the thermal history, probably due to changes in the degree of crystallinity, is important in determining the modulus of these materials. Nonetheless, these changes in modulus did not appear to affect the measured maximum yield strengths in our peel tests.

The second bulk-polymer property that we used to characterize our elastomers was the rate at which the polymer relaxed after application of a strain. We measured these rates for unmodified PBD and PBD–$SCOCH_3$ by rapidly stretching the polymer to a given extension (strain) and measuring the force per unit area (stress $\sigma(t)$) while maintaining that static extension over time. These "step strain–stress relaxation" experiments[45] were repeated for five different extensions, and the resulting data for one of these extensions are reported in Figure 9. The average (10 samples for PBD; 4 samples for PBD–$SCOCH_3$) normalized stress, f_σ =

Table 1. Binding Energies (eV) of Photoelectrons from the Soap-Cleaned Copper Surface Taken at Takeoff Angles of 15° and 90° (Assignments and Relative Area Percentages Are Listed for Each Principal Photoelectron Peak)

takeoff angle	Cu(2p$_{3/2}$)		O(1s)			Cu L$_3$M$_{4,5}$M$_{4,5}$ Auger		
90°	Cu^0 or Cu$_2$O	932.6 (1.0)[a]	Cu$_2$O	530.4 (0.8)	63%	Cu^0	565.5	6%
			Cu(OH)$_2$	531.4 (1.3)	26%	Cu^0	567.1	5%
			O$^-$	532.5 (1.6)	10%	Cu^0	568.2	38%
						Cu$_2$O	569.9	51%
15°	Cu^0 or Cu$_2$O	932.5 (1.0)	Cu$_2$O	530.3 (0.8)	47%	Cu^0	565.3	3%
			Cu(OH)$_2$	531.3 (1.5)	39%	Cu^0	567.0	3%
			O$^-$	532.5 (1.8)	13%	Cu^0	568.1	28%
						Cu$_2$O	570.0	66%

[a] The value in parentheses is the full width (eV) at half-maximum of the principal photoelectron peak.

Table 2. Binding Energies (eV) for Photoelectrons from Copper and Several of Its Oxides

	region			
	Cu(2p$_{3/2}$)	O(1s)	Cu L$_3$M$_{4,5}$M$_{4,5}$ Auger	ref
Cu metal	932.5 ± 0.15 (1.1)[a]		567.6	36, 37
			~565.1	36, 37
Cu$_2$O	932.5 ± 0.2 (1.2)	530.5 ± 0.2 (1.2)	569.9	36, 37
CuO	933.8 ± 0.2 (2.9)	529.6 ± 0.15 (1.3)	568.4	36, 37
Cu(OH)$_2$	934.4 ± 0.2 (2.6)	530.9 ± 0.2 (1.8)		36
Cu(OH)$_2$ + Cu$_2$O			570.3	37
Cu$_2$O lattice oxygen (O^{2-})		530.4		38
surface hydroxide ion (Cu(OH)$_2$)		531.4		38
strongly chemisorbed oxygen (O$^-$)		532.2		38
Cu$_2$O lattice oxygen (O^{2-})		530.4		39
surface hydroxide ion (Cu(OH)$_2$)		531.1		39
strongly chemisorbed oxygen (O$^-$)		532.4		39

[a] The value in parentheses is the full width (eV) at half-maximum of the principal photoelectron peak.

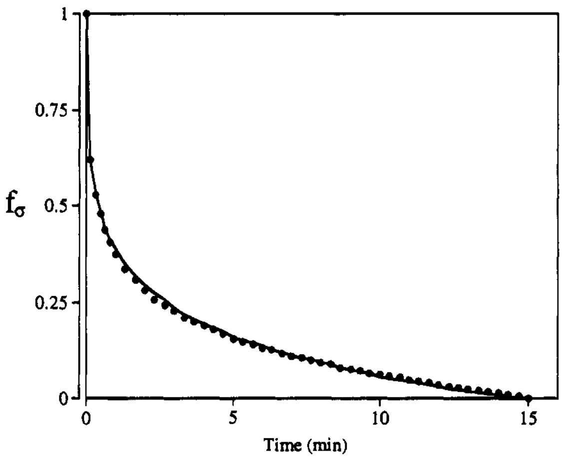

Figure 9. Normalized stress f_σ versus relaxation time for a stress–relaxation experiment performed under ambient conditions for PBD (line) and PBD–SCOCH$_3$ (●). The PBD curve is the average of 10 samples, and the PBD–SCOCH$_3$ curve is the average of four samples, stressed to an extension of ~1–2% of the initial gauge length (101.6 mm). The size of the data points represents approximately the range of scatter of the four curves. Data was collected at a rate of 5 points/s. For clarity, only every 100th point is plotted, except at times below 1 min, where every 50th point is plotted.

$(\sigma(t) - \sigma_{\min})/(\sigma_{\max} - \sigma_{\min})$, is plotted in this figure to normalize the curves to the same initial and final stresses. At the other extensions, the data for PBD and PBD–SCOCH$_3$ were even more similar than those shown in Figure 9. The small differences in stress relaxation are within the experimental error of these measurements and indicate that surface modification does not change the dynamical stress–relaxation of the bulk polymer.

Characterization of the Surface of the Copper Foil Used in the Adhesion Experiments

We collected high-resolution XPS spectra of the soap-cleaned copper surface at takeoff angles of 15 and 90°. A summary of binding energies and relative areas of the observed peaks are reported in Table 1. These binding energies were referenced to the C(1s) peak at a binding energy of 284.9 eV and with a full width at half-maximum of 1.1 eV. Table 2 summarizes binding energies for copper and its various oxides that have been reported in the literature.

From the high-resolution spectra taken at a 90° takeoff angle, the atomic composition of the copper surface was 47% copper, 22% oxygen, and 30% (adventitious) carbon. The single Cu(2p$_{3/2}$) peak at 932.6 eV in our spectrum is consistent with the presence of Cu metal and Cu$_2$O and/or CuO$_{0.67}$, but not CuO.[35–40] McIntyre reported prominent, well-defined satellite peaks due to ligand–metal electron transfer at binding energies higher by approximately 7.8 and 10.2 eV for CuO and 6.2 and 9.0 eV for Cu(OH)$_2$ than the main Cu(2p$_{3/2}$) resonance.[36] No satellite peaks were observed in our spectra. The O(1s) peak at 530.4 eV in our spectrum is consistent with Cu$_2$O as the native oxide, and that at 531.4 eV suggests the presence of a smaller amount of Cu(OH)$_2$.[36–39] The O(1s) peak at 532.5 eV indicates the presence of some strongly chemisorbed oxygen as well.[38,39] The absence of a Cu(2p$_{3/2}$) peak due to Cu(OH)$_2$ and of satellite structures indicates that this oxide is present in only low concentration. The Auger peaks at 565.5, 567.1, and 568.2 eV are characteristic of metallic copper.[35] The Auger peak at 569.9 eV is again consistent with Cu$_2$O as the predominant native oxide.[36,37] The spectra taken at a takeoff angle of 15° were very similar

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to those spectra taken at 90°. Furthermore, the enhancement of the peak at 531.3 eV at the shallower takeoff angle indicated that this species is located at the outermost portion of the surface.

Conclusions

The photolytic addition of thiols to the carbon–carbon double bonds at the surface of PBD provided a convenient method for preparing substrates for studying the effect of sulfur-containing functional groups on the adhesion of this polymer to metals. Qualitative tape-peel tests indicated that the presence of thioacetate or thiol groups enhanced its adhesion to evaporated films of gold and copper. We also performed quantitative peel tests to study the adhesion of surface-modified PBD to copper foil. Analysis of the surface of the foil by XPS revealed the predominant native oxide to be Cu_2O. The presence of this oxide, as expected, modified the adhesion to the polymers by introducing possibilities for chemical reactions with the polymer surface.

The thioacetate groups at the surface of PBD–$SCOCH_3$ greatly enhanced its adhesion, relative to unmodified PBD, to copper foil. In fact, when the PBD–$SCOCH_3$/copper laminate was pressed and heated for at least 12 h, cohesive failure within the polymer usually resulted during peel tests. We believe that this cohesive failure reflected strong bonding, covalent and/or dative, between polymer-bound sulfur atoms and the copper surface. Analysis by XPS of copper treated with a model nonpolymeric, alkyl thioacetate revealed the formation of copper thiolate species, indicating that covalent chemisorption may occur in the polymeric system. The addition of sulfides to the polymer surface (PBD–SCH_2CO_2H and PBD–$SCH_2CO_2CH_3$) also significantly increased the adhesion, relative to unmodified PBD, to copper foil. Oxidation of the surface of PBD with cold, dilute $KMnO_4$, a treatment that produces primarily 1,2-diols, had little effect on its adhesion. Although alkanethiols form self-assembled monolayers on copper, the adhesion of PBD–SH to the copper foil was negligible, weaker even than for unmodified PBD. Photoelectron spectroscopy indicated that this failure was likely due to oxidation of thiol to sulfonate and formation of an interfacial weak boundary layer containing copper(II). The presence of a native oxide thus caused a dramatic decrease in adhesion of the copper foil to PBD–SH, relative to that of evaporated copper to the same surface.

We examined three processes that could affect the kinetics of the development of adhesion in the PBD–$SCOCH_3$/copper system: (i) thermal reconstruction of the surface of PBD–$SCOCH_3$ to bring thioacetate groups to the polymer/copper interface; (ii) viscous flow of the polymer into the crevices (~100 nm) at the surface of the copper to increase the degree of atomic contact necessary for adhesion; (iii) chemical reaction of these thioacetate groups with the native oxide(s) of copper. Since the surface reconstruction of PBD–$SCOCH_3$ at 80 °C is fast relative to the growth in its adhesion to copper, it cannot limit the rate of this growth. The viscous flow of the polymer necessary to replicate features on the copper surface with sizes greater than ~100 nm is also fast relative to the growth in adhesion in this system. It is possible, however, that flow of the polymer in crevices smaller than ~100 nm could determine the rate of growth in adhesion. The XPS spectra of a copper surface that had been treated with 1-octyl thioacetate—a model for our surface-modified polymer—indicated that cleavage of the thioacetate to give copper–thiolate species was occurring, though we did not measure the rate of this reaction.

Studies of the mechanical properties of PBD–$SCOCH_3$ and unmodified PBD ruled out changes in these properties as a major source of differences between these polymers in the adhesion measurements. There was a small difference between the apparent moduli of these polymers that was likely due to a difference in their degrees of crystallinity. This difference, however, did not affect their adhesion to copper. The relaxation of these two polymers after an applied stress, a property more directly related to our peel tests, was indistinguishable.

These studies demonstrate the usefulness of organic chemistry at polymer surfaces in controlling adhesion to metals. In particular, reactivity at the interfaces of PBD with reagent solutions offers a versatile method for producing systems for studying the relations between molecular structure at a disordered organic surface and its adhesion to substrates of interest.

Experimental Section

General Methods. Thiolacetic acid (Sigma), methyl thioglycolate (Aldrich), benzophenone (99%, Aldrich), sodium borohydride (98%, Ventron, Alfa division), 5,5′-dithiobis(2-nitrobenzoic acid) (Ellman's reagent, 99%, Aldrich), ethylenediaminetetraacetic acid disodium salt dihydrate (99%, Sigma), ethanol (absolute, Midwest Grain), HCl (37%, Mallinckrodt), 1-bromooctane (99%, Aldrich), sodium metal (99%, Aldrich), anhydrous ether (99+%, Aldrich), and argon and nitrogen gas (Airco, 4.8 grade) were used without further purification. Sodium phosphate, methanol, $KMnO_4$, and NaOH were certified ACS grade (Fisher) and used as received. Deionized water (purified to a resistivity of 16–18 MΩ cm) was obtained from a triple-stage, Milli-Q-Filtering system (Millipore). Gold wire (0.5 mm diameter, 99.999%, AEsar/Johnson Matthey or Aldrich), and copper wire (0.5 mm diameter, 99.999%, Aldrich) were used as received. The surface of the copper foil (0.127 mm thick, 99+%, Aldrich) was cleaned with soapy water prior to use (see Quantitative Adhesion Experiments section).

Poly(butadiene, 1,2-syndiotactic) (Polysciences) was received as pellets and melted into a film (~1 mm thick) against a silanized glass petri dish at 130–140 °C for 12–20 h.[20] The side of the PBD film heated against the glass was used in these experiments.

Samples of PBD–diol were prepared by oxidation with cold, dilute $KMnO_4$ as reported elsewhere.[20] The advancing and receding contact angles of water measured on this surface were 79° and 0°. This advancing contact angle of water differs from that reported (68°) and may be due to incomplete reaction or to the fact that for the data reported here, we functionalized the side of the film that was heated against the silanized glass when the film was prepared (i.e., melted).

Visible spectra were obtained with a Milton Roy Spectronic 20 UV–vis spectrophotometer (spectral slit width of 2 nm) equipped with a grating monochromator, a photomultiplier tube detector, and a tungsten-halogen light source.

1-Octyl Thioacetate (OTA). The preparation of 1-octyl thioacetate (OTA) was a modified version of a procedure reported for the preparation of 1-undecanethiol from the alkyl bromide and sodium thioacetate.[11] In our case, of course, the alkyl thioacetate was not hydrolyzed. This modified procedure afforded a purified product of 1-octyl thioacetate ($C_8H_{17}SCOCH_3$): ^1H NMR ($CDCl_3$) δ 2.86 (t, 2 H), 2.31 (s, 3 H), 1.26 (m, 12 H), 0.87 (t, 3H).

PBD–$SCOCH_3$. Polymer strips were cut to dimensions of ~9 × 25 mm and added to a Pyrex tube containing 15 mL of ethanol, 2 drops of thiolacetic acid (~30 mg or 0.02 M solution), and a few crystals of benzophenone (≤10 mg). The tube was exposed to ultraviolet light in a Rayonet RPR-100 photochemical reactor (350 nm; ~24 W at the center of the chamber) for 30 min. The polymer strips were then sequentially rinsed with ethanol and then with water. To remove absorbed thiolacetic acid, the functionalized polymer strips were heated on water or in ethanol (~15 mL) at 50 °C for 1 h with one change of water or ethanol after 30 min. Attenuated total reflectance infrared spectroscopy showed that the carbonyl stretching band decreased by only ~13% in intensity upon heating in water, indicating that little hydrolysis had occurred. This treatment did not change the advancing contact angle of water, but the receding angle increased slightly, from 55° to 62°. Furthermore, heating PBD−$SCOCH_3$ in ethanol at 50 °C for 2 h had no effect on its adhesion to copper.

PBD−SCH_2CO_2H and PBD−$SCH_2CO_2CH_3$. The carboxylic acid and methyl ester surfaces were prepared using a method reported elsewhere for the preparation of PBD−SCH_2CO_2H.[20] After the photolysis, PBD−$SCH_2CO_2CH_3$ was rinsed with methanol then heated in 50 °C methanol for 1 h to remove any absorbed methyl thioglycolate. The ATR-IR spectrum of PBD−$SCH_2CO_2CH_3$ displayed a peak at 1737 cm^{-1}, characteristic of the methyl ester of a carboxylic acid.

PBD−SH. A sample of PBD−$SCOCH_3$ was added to a stirred slurry of 2 g of sodium borohydride in 100 mL of ethanol at 50 °C, while sparging with nitrogen or argon. Samples were immersed in this solution for 2 h. The product surfaces were removed, rinsed with ethanol, rinsed with water, and then floated on 0.1 M HCl for 10 min to ensure protonation of the thiolate to the corresponding thiol. The samples were then rinsed in water and dried with a stream of nitrogen, and contact angles of water were measured. The functionalized polymer films were stored against room temperature water until needed for ATR-IR or XPS measurements. XPS experiments showed that PBD−SH was susceptible to oxidation if floated on water at room temperature overnight in air. When PBD−SH was floated on room temperature water for only 5 min, however, oxidation occurred to a much smaller extent. If this ethanolysis reaction was performed immediately following the synthesis of the thioester, the sample was *not* heated on water or ethanol to remove absorbed thiolacetic acid, since the ethanolysis also appeared to remove it (as expected).

Spectrophotometric Determination of Absorbed Thiolacetic Acid in PBD−$SCOCH_3$. A PBD film was cut into 9 × 20 mm pieces and weighed. Three of these samples were converted to PBD−$SCOCH_3$, rinsed with ethanol and with water, and dried with a stream of nitrogen. To extract any absorbed thiolacetic acid, the samples were then heated at 50 °C for 1 h under nitrogen against a deoxygenated aqueous buffer (0.050 M Na_2HPO_4; 1.0×10^{-6} M EDTA; pH 7.0, adjusted by addition of HCl). After removing the polymer, 1.0 mL aliquots of the solution were analyzed by thiol−disulfide interchange reaction with 5,5′-dithiobis(2-nitrobenzoic acid) (Ellman's reagent) and spectrophotometric quantification of the product chromophore.[30]

The UV−vis spectrometer was set to read zero absorbance with a cuvette (1.0 cm path length) containing 1.0 mL of a 1.0×10^{-4} M solution of the aromatic disulfide in the buffer described above in the sample beam. To this disulfide was added 1.0 mL of the thiolacetic acid extract, and the resulting solution was mixed by repeatedly withdrawing and expelling the solution with a disposable glass pipet. The absorbance was recorded as a function of time until a limiting value was reached. The amount of thiolacetic acid extracted from these samples was 15−18 nmol/cm^2 of PBD−$SCOCH_3$.

In control experiments, no thiolacetic acid was detected in extracts from unmodified PBD. Also, a calibration plot derived from solutions of thiolacetic acid with known concentrations showed the linear dependence of absorbance upon concentration expected from Beer's law over a range of concentrations (3.4×10^{-7}−1.1×10^{-5} M) that contained those in the experiments as described above (~3×10^{-6} M).

Contact Angles. All surfaces were rinsed with water and dried with a stream of nitrogen, prior to these measurements. Advancing and receding contact angles of water were measured using a Ramé-Hart Model 100-00 115 contact angle goniometer by measuring the tangent to the water drop, close to where the drop met the surface. All measurements were taken under ambient conditions within 5−15 s after application of the drop. Reported values are the average of eight measurements, taken on four ~1 μL drops at different locations on the surface; contact angle measurements were taken using both sides of the drop. Advancing contact angles were obtained by adding water until the drop edge advanced across the surface. Once the edge stopped moving, angles were measured with the needle still in the drop. Receding water contact angles were obtained in a similar way, though after removing water until the drop edge receded across the surface.

Metal Evaporations. Metal evaporations onto polymer and glass substrates were performed using a Denton Vacuum DV-502 evaporator equipped with a Sycon Instruments STM-100 thickness/rate monitor. Evaporations were performed at rates of 1−6 Å/s and at background pressures of $(3.0-6.0) \times 10^{-6}$ Torr for gold and $(2.8-8.5) \times 10^{-6}$ Torr for copper. The final thicknesses were ~25−70 nm for gold and ~40 nm for copper.

Attenuated Total Reflectance Infrared (ATR-IR) Spectroscopy. Samples were dried in vacuo (0.05−0.10 Torr) for approximately 10 min, prior to ATR-IR analysis, to remove absorbed water. Spectra were obtained using a Mattson Polaris FT-100 infrared spectrometer (1024 or 2048 scans at 2 or 4 cm^{-1} resolution) purged with dry air. A germanium crystal (25 × 10 × 3 mm; incident beam 45° from the plane of the sample) was used as an internal reflectance element, and polymer samples were placed on both sides of the crystal. Assuming an index of refraction of ~1.5 for our samples,[46] the sampling depth for our polymer samples was approximately 0.1−1 μm (a function of the incident IR frequency).[47] The number of internal reflections within the Ge crystal was about 8.

X-ray Photoelectron Spectroscopy (XPS). Spectra were obtained using a Scienta Instrument Model ESCA-300 spectrometer with a monochromatized Al Kα X-ray source (1486.6 eV) operating at a background pressure of 10^{-6}−10^{-7} Pa. High-resolution spectra of the polymer samples were obtained by collecting three scans at a 45° takeoff angle (α, defined as the angle between the detector and the surface of the sample) with a pass energy of 150 eV, a slit width of 0.8 mm, and a resolution of 0.05 or 0.1 eV. A specially designed sample holder was used to minimize surface charging,[20] though we still required the use of a flood gun to neutralize residual charging. High-resolution spectra of the copper samples were obtained by collecting five scans at a 15° or 90° takeoff angle (α) with a pass energy of 150 eV, a slit width of 0.5 mm, and a resolution of 0.05 eV. Unless otherwise reported, all spectra were referenced to the main C(1s) peak, set at a binding energy of 285.0 eV. High-resolution spectra were curve-fitted for quantification, using a linear background subtraction, and according to a published procedure.[32] The survey spectrum of the polymer sample was obtained at a 45° takeoff angle with a pass energy of 300 eV, a slit width of 0.8 mm, and a resolution of 0.25 eV. The survey spectrum of the copper sample was obtained at a 45° takeoff angle with a pass energy of 150 eV, a slit width of 0.5 mm, and a resolution of 0.25 eV. Using 4 nm as the approximate attenuation length (λ) of photoelectrons in PBD, approximately 95% of the photoemission ($3\lambda \sin \alpha$) originated within the outermost 8 nm of our polymeric samples. Using 3 nm as the approximate attenuation length (λ) of photoelectrons in copper, approximately 95% of the photoemission ($3\lambda \sin \alpha$) originated within the outermost 9, 6, and 2 nm of our samples for takeoff angles (α) of 90°, 45°, and 15°. This estimate of λ followed a procedure described in the literature and applies specifically to C(1s) photoelectrons.[48]

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(47) Harrick, N. J. *Internal Reflection Spectroscopy*; Interscience: New York, 1967; Chapter 2.

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Tape-Peel Tests. An evaporated metal film on a polymeric substrate was gently scratched with a spatula to provide a locus of fracture, and then tape was applied to the film using finger pressure to ensure intimate contact. Manual tape tests were performed using duct tape (ServiStar, professional grade) at a slow peel rate (~300 mm/min). Duct tape was necessary for the peel tests, since transparent tape did not adhere strongly enough to distinguish between the modified and unmodified samples.

Quantitative Adhesion Experiments. A film of PBD was melted in a large (27.5 cm × 17.5 cm) glass tray that had been silanized with octadecyltrichlorosilane. Strips were then cut (~1 mm × 1 cm × ~13 cm) and converted to PBD−SCOCH$_3$, PBD−SCH$_2$CO$_2$H, PBD−SCH$_2$CO$_2$CH$_3$, PBD−SH, or PBD−diol. The polymer strips were floated on room temperature water until needed (1−50 h). For strips of PBD−SH, this time was minimized (~10 min−3 h) to limit atmospheric oxidation. Copper foil was cut (1 cm × ~7.5 cm) and cleaned by rubbing vigorously with a Kimwipe and soapy (Liqui-Nox) water, rinsed thoroughly with water, and dried with a stream of nitrogen. This cleaning procedure was repeated two additional times. Functionalized or unfunctionalized strips of PBD were placed in contact with the cleaned copper surface, except at one end (~1−2 cm) where the two surfaces were separated by Teflon tape to provide places to be gripped by the Instron. These samples were clamped between two glass microscope slides with a medium (1.25 in. wide) binder clip. The samples were then heated in an oven at 80 °C for various lengths of time. The binder clip provided a pressure of 13 ± 2 kPa: the force exerted by the clip was determined using Instron (180° geometry) measurements at a 3 mm separation, approximately the same separation present when the polymer/copper samples were clamped between two glass slides. The reported pressure is the average of seven force-measurements divided by the area of the glass microscope slide.

After heating, the samples were removed from the oven and stored at room temperature clamped between the binder clips for no more than 24 h. Samples of PBD−SH/copper were stored, still clamped, under argon to minimize possible oxidation by oxygen. Previous experiments showed that films of PBD−SCOCH$_3$ clamped to copper foil *at room temperature* for 48 h do not adhere. Peel tests (180° geometry) using an Instron 1011 tensile tester, equipped with a 500 N load transducer, were performed at a peel rate of 10 mm/min immediately following the annealing of those samples heated for the longest time (48 h).[42] Plots of peel force versus displacement were usually nonuniform, presumably due to nonuniform contact across the entire sample. The *maximum* values of force, taken from these plots, were reported. Control experiments showed that the observed values of yield strength in the PBD−SCOCH$_3$/copper system depended on the particular lot of copper purchased. As a result, all the quantitative adhesion experiments were performed using the same lot of copper.

Apparent Modulus Experiments. Strips of PBD were cut (~15−20 cm × 1.9 cm × ~1 mm) and some converted to PBD−SCOCH$_3$. Immediately prior to the experiment, the strips were cut to a standard "dogbone" shape with a cutting die to a gauge length (l_0) of 101.6 mm and a gauge width of 12.7 mm. These dogbone samples were similar in design to that described in ASTM D 2707-85, which prescribed a gauge length of 75.0 mm. Samples of PBD and of PBD−SCOCH$_3$ were pulled at a rate of 100 mm/min and force data collected at a rate of 5 points/s during the extension. These tests were performed without an extensometer. Values of force were converted to stress by dividing by the cross-sectional area of the polymer sample (gauge width multiplied by the average of five measurements of the strip thickness measured within the gauge length to ±0.01 mm accuracy). Plots of stress versus strain ($(l - l_0)/l_0$) were generated, and the apparent modulus (slope) was estimated in the region of 1−3% extension. The reported values are the average measured on five or six samples.

Stress−Relaxation Experiments.[45] Strips of PBD were cut (~15−20 cm × 1.9 cm × ~1 mm) and some converted to PBD−SCOCH$_3$. Immediately prior to the experiment, the strips were cut to a standard "dogbone" shape with a cutting die to a gauge length (l_0) of 101.6 mm and a gauge width of 12.7 mm. Using the Instron, each sample was pulled at a rate of 100 mm/min to an extension of ~1−2%. This extension corresponded to an initial load of ~15 N. The force necessary to maintain this static extension was then measured at a rate of five data points/s for 15 min. Meanwhile the fractional change in extension ($(l - l_0)/l_0$) was measured. After termination of data collection, the sample was manually relaxed to ~0 N (for ~5 min), as the software parameters were modified to stress to the next load. This procedure was repeated using extensions of 2−4, 4−6, 6−9, and 10−13%, corresponding to initial loads of approximately 25, 35, 45, and 55 N. Values of force were converted to stress by dividing the force by the cross-sectional area of the polymer sample (gauge width multiplied by the average of five measurements of the strip thickness measured within the gauge length to ±0.01 mm accuracy). Plots of the normalized stress f_σ versus time were generated and compared for PBD and PBD−SCOCH$_3$.

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