J. Am. Chem. Soc. **2001,** *123,* 12927−12928

Coupled, Consecutive Reconstructions at a Polymer/Air Interface

Stephen J. Grunzinger and Gregory S. Ferguson*

Departments of Chemistry and
Material Science & Engineering
Lehigh University
Bethlehem, Pennsylvania 18015

Received June 29, 2001

The interfacial properties of polymers—such as adhesion, friction, and biocompatibility—may be enhanced by surface modification using plasma or solution-phase methods, though the resulting surfaces are known to reconstruct, or reorganize, to minimize interfacial free energy.[1−8] As a consequence, the stability of polymer surfaces can be strongly affected by contacting phases. For example, surfaces generally tend to be populated by hydrophilic functional groups when against water, if possible, and hydrophobic groups when against air. Recent reports, however, have described polymeric surfaces that behave differently. For example, the surface of sulfonated polyethylene becomes more hydrophilic in a vacuum than in water, and permanganate-oxidized elastomers are more hydrophobic against water at elevated temperatures than at lower temperatures.[9−12] Herein, we present a polymeric system that spontaneously becomes more hydrophilic in air when cooled from an elevated temperature and then proceeds to a more hydrophobic state. Rationalizing these changes requires an extension of the conventional two-state model used to describe most reconstruction behavior over the past several decades.

The surfaces of polyisoprene (PI) films, cross-linked with dicumylperoxide, were chemically modified using a three-step plasma oxidation. Samples were first treated for 5 s with a water-vapor (0.2 Torr) plasma produced in a 250-mL round-bottom flask with a Tesla coil. As a result of this treatment, the advancing contact angle of water (θ_a) on this surface fell from 100° (unmodified surface) to 80−85°, consistent with the introduction of oxidized functionality. The samples were then heated in a sealed tube under N_2 at 60 °C for 3 h to allow partial reconstruction, resulting in an increase in θ_a to 89−93°, consistent with an increase in the number of unmodified polymer chains at the surface. The samples were then treated a second time with a water-vapor plasma, though at a higher pressure (0.6 Torr). After this treatment, the contact angle of water on the surface had decreased further, to 70−75°, consistent with further oxidation beyond that achieved in the first treatment. This three-step procedure increased the amount of polar functionality in the interfacial region, as well as the subsequent change in contact angle (vide infra), relative to a single plasma treatment.[13]

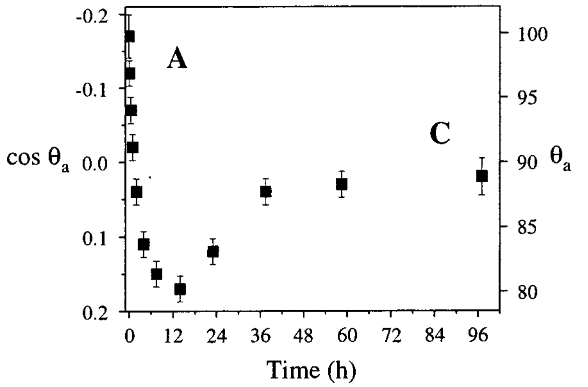

Figure 1. Advancing contact angles of water on plasma-oxidized PI upon cooling in air from 60 °C to room temperature. Contact angles were taken using buffered water (pH 7), and error bars indicate one standard deviation above and below the average.

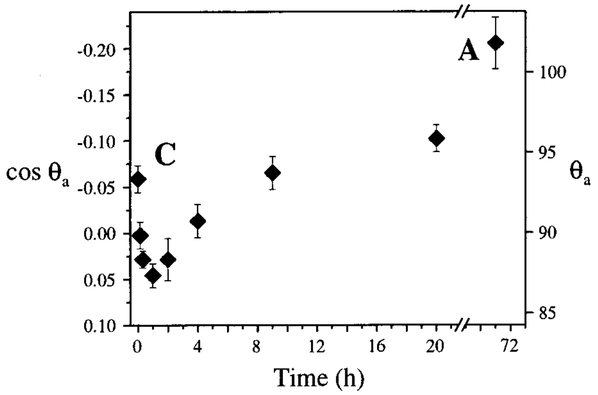

Figure 2. Advancing contact angles of water on plasma-oxidized PI initially in the room-temperature final state (state C) upon heating in air at 60 °C. Each point represents a separate sample, contact angles were taken using buffered water (pH 7), and error bars indicate one standard deviation above and below the average.

These surface-modified samples reconstructed in air at 60 °C for 72 h and reached a steady-state contact angle of ∼100°, indistinguishable from that on unmodified PI. Upon cooling to room temperature *in air*, the surface then became more hydro*philic* over the next few hours, in contrast to the behavior of most other systems. Even more surprising, θ_a reached a minimum of ∼80° before increasing again to almost 90° (Figure 1). This final state of the polymer was then stable for long periods of time. Behavior similar to that in Figure 1 was also found for samples that had been swollen in toluene to extract any soluble oligomers that may have formed during plasma treatment. This behavior was reversible: heating samples in this final state at 60 °C caused an initial *de*crease in θ_a, followed by an increase to >95° (Figure 2). As shown in Figure 3, this behavior was also persistent for seven cycles of heating (60 °C, 72 h) and cooling (room temperature), with an average initial drop in θ_a of ∼18°. The eventual loss of reversibility was likely due to degradation of the polymer films, as they were significantly yellowed after eight cycles.

Most reconstructions of polymer surfaces can be adequately described as a simple reversible rearrangement ($A \leftrightarrows B$), for example a hydrophobic surface becoming hydrophilic against water and hydrophobic against air. Such a two-state model is clearly not adequate to describe the behavior in Figures 1−3. A reversible three-state model ($A \leftrightarrows B \leftrightarrows C$), however, is consistent with these data, where state A is the initial hydrophobic

---

(1) Ferguson, G. S.; Whitesides, G. M. In *Modern Approaches to Wettability*; Schrader, M. E., Loeb, G. I., Eds.; Plenum Press: New York, 1992.

(2) Bergbreiter, D. E. *Prog. Polym. Sci.* **1994**, *19*, 529.

(3) *Polymer Surfaces and Interfaces*; Mittal, K. L., Lee, K. W., Eds.; VSP: Utrecht, The Netherlands, 1997.

(4) *Chemically Modified Surfaces*; Mottola, H. A., Steinmetz, J. R., Eds.; Elsevier: New York, 1992.

(5) Wheale, S. H.; Badyal, J. P. S. In *Interfacial Science*; Roberts, M. W., Eds.; Blackwell Science: Malsen, MA, 1997.

(6) Elbert, D. L.; Hubbell, J. A. *Annu. Rev. Mater. Sci.* **1996**, *26*, 365.

(7) Loh, I. H.; Sheu, M. S. *Mater. Res. Soc. Symp. Proc.* **1996**, *414*, 43.

(8) Egitto, F. D.; Matienzo, L. J. *J. Res. Dev.* **1994**, *38*, 423.

(9) Kabza, K.; Bergbreiter, D. E. *J. Am. Chem. Soc.* **1991**, *113*, 1447.

(10) Carey, D. H.; Grunzinger, S. J.; Ferguson, G. S. *Macromolecules* **2000**, *33*, 8802.

(11) Khongtong, S.; Ferguson, G. S. *J. Am. Chem. Soc.* **2001**, *123*, 3588.

(12) Bergbreiter, D. E.; Kabza, K. J. *J. Am. Chem. Soc.* **1991**, *113*, 1447.

(13) All contact angles were measured at room temperature in air using a Rame-Hart (Model 100-00 115) goiniometer as described previously.[10,11]

10.1021/ja0165279 CCC: $20.00

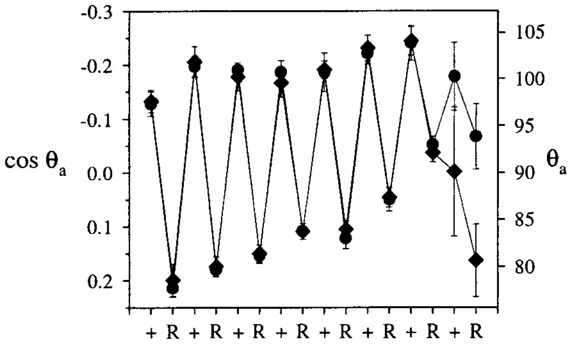

Figure 3. Advancing contact angles of water on plasma-oxidized PI film (two independent samples) upon cycling between hot (60 °C, +) and cool (room temperature, R) air. The room-temperature values correspond to the *minimum* contact angles measured in each cycle. Contact angles were taken using buffered water (pH 7), and error bars indicate one standard deviation above and below the average.

configuration of the polymer surface, state B is a hydrophilic intermediate configuration, and state C is the final room-temperature configuration.[14] In the forward direction, the initial decrease in θ_a is consistent with the migration of oxidized functional groups to the surface. As the system approaches state B, however, the $B \rightarrow C$ process also becomes important and eventually leads to a reversal in the wettability of the surface. It is important to recognize that this reversal in θ_a does not correspond to a simple reversal in the $A \rightarrow B$ process, but rather, must arise due to a second process. If this conclusion were not the case, θ_a would have changed from ~100° (A) to ~89° (C) directly, without becoming hydrophilic in the interim. The distinct initial dip in θ_a during the reverse process (Figure 2) confirms state B as an intermediate between states A and C. This analysis and the conclusion, we believe, are phenomenological. Extending this description to provide a plausible physical model for the identities of states A, B, and C required chemical analysis of the interfacial region.

X-ray photoelectron spectra (90° takeoff angle) of unmodified and freshly modified PI samples contained photoemission due to only carbon and oxygen. The spectrum of unmodified PI contained only a trace amount of oxygen, likely due to autoxidation in air or to a byproduct of the dicumylperoxide used in the cross-linking reaction. High-resolution spectra in the C1s region revealed that the main peak of the modified PI had shifted to higher binding energy and had become asymmetric, with significant new photoemission to the high binding energy side of the peak. In addition, the π-to-π^* shake-up satellite present in the spectrum of unmodified PI was absent in that of the oxidized surface, indicating that the carbon−carbon double bonds near the surface had been consumed during the plasma treatment. This loss of sp^2-hybridized carbon atoms, in turn, is also consistent with the shift of the main C1s peak to higher binding energy.[15] The new photoemission to the high binding energy side of the main C1s peak comprised ~16% of the total carbon photoemission and could be fit with three peaks at 286.5 eV (C—O), 287.8 (C═O) eV, and 289.2 eV (O—C═O), in a ratio of 9:5:1.[15] A spectrum in the same region at a shallow takeoff angle (15°) indicated a higher concentration of oxidized material near the surface, as expected. These data are consistent with additional cross-linking occurring during the plasma treatment, as not all of the sp^2-hybridized carbons consumed during the plasma treatment can be accounted for by oxidation alone.

On the basis of these data, we speculate that the $A \leftrightarrows B \leftrightarrows C$ equilibrium involves reversible association of polar groups in the interfacial region, analogous to the bulk behavior of ionomeric polymers.[16] In ionomers, charged groups do not associate at elevated temperatures, due to entropically driven coiling of the polymer chains. By analogy, in state A, many of the polar groups added by plasma oxidation may migrate away from the interface as the chains that carry them explore the available conformation space. At lower temperatures, the entropic loss due to chain extension is smaller, and the charged groups in ionomers can associate. By analogy, in state B, aggregation of polar groups (perhaps by hydrogen bonding) may occur at the surface. This hypothesis leads to the following question: Why does aggregation occur at the surface rather than in the bulk? The answer to this question, however, is straightforward: it is plausible to assume that some of the added hydrophilic groups near the surface of our samples are adjacent to added cross-link points and are thus unable to migrate into the bulk. As a result, when the temperature is decreased and the polymer chains can extend out of random coil conformations, the polar groups tend to aggregate at the surface, thus making it hydrophilic against air, state B. Finally, a slower second reconstruction ensues, presumably involving migration of hydrophobic chains from the bulk to cover the polar aggregates at the surface and thereby decrease the wettability and produce state C. Alternative explanations involving a bulk thermal transition were ruled out by the absence of thermal transitions of any kind between room temperature and 60 °C by differential scanning calorimetry.

In summary, we have developed a polymeric surface that first increases in wettability after cooling from an elevated temperature and then decreases in wettability. These changes are consistent with a reversible, consecutive three-state model. We speculate that reversible association of polar groups near the surface causes the decrease in contact angle upon cooling. Ongoing studies are aimed at testing this proposed physical model, as well as determining the kinetic parameters (rate constants and activation energies) involved.

Acknowledgment. We gratefully acknowledge the support for these studies from the Office of Naval Research (ONR). We also acknowledge Lehigh University for supporting the SCIENTA ESCA 300 laboratory and Dr. Alfred C. Miller for technical assistance.

Supporting Information Available: Experimental details (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

JA0165279

---

[14] For examples of analogous consecutive, reversible chemical reactions, see: Richard, J. P.; Amyes, T. L.; Lin, S.-S.; O'Donoghue, A. C.; Toteva, M. M.; Tsuji, T.; Williams, K. B. In *Advances in Physical Organic Chemistry*; Tidwell, T. T., Ed.; Academic Press: San Diego, 2000; Vol. 35, pp 67−115.

[15] Peak assignments were made with reference to: Beamson, G.; Briggs, D. *High-Resolution XPS of Organic Polymers, The Scienta ESCA300 Database*; John Wiley and Sons: New York, 1992.

[16] *Ionomers Characterization, Theory, and Application*; Schlick, S., Ed.; CRC Press: Boca Raton, FL, 1996.