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A Smart Surface: Entropic Control of Composition at a Polymer/Water Interface

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A critical feature of many polymer surfaces is the tendency for chains and pendent functional groups to reorient in order to decrease the interfacial free energy of the system.[1−4] This process, “thermal reconstruction”, changes the composition of the surface and is thus important in determining the interfacial properties of polymeric systems. While synthetic organic chemistry allows control of molecular structure at polymer surfaces, reconstruction often determines whether that structure remains at a surface of interest. The relative concentrations of polar and nonpolar groups in the outermost portion of a polymer, at equilibrium, are generally determined by enthalpic forces—e.g., hydrogen bonding, Lewis acid−base interactions, van der Waals forces—between the polymer and any contacting phase.[5−7] This communication presents a system for which *entropy* plays a central role in determining the composition of the polymer surface when it is in contact with water.

Several studies of polymer surface dynamics have appeared that report the use of solid/liquid contact angles as a convenient, qualitative measure of the relative populations of polar and nonpolar groups within the outermost 5−10 Å of the solid.[8,9] Equilibration of a polymer surface containing polar and nonpolar groups against water usually results in an increase in the surface concentration of polar functional groups in contact with the water. This type of behavior has been demonstrated for a wide range of polymers at and above room temperature.[1,10−12] In this communication, we report the thermal reconstruction of a surface-modified polymer in contact with water, for which the hydrophilicity *varies reversibly* with temperature.[13−15] This reversible, temperature-dependent behavior establishes this system as a “smart” polymeric material that responds to changes in the temperature of its aqueous environment.[16]

A film of syndiotactic 1,2-polybutadiene (PBD) was formed by melting in air at 135−140 °C for 10−11 h.[17] Its surface was oxidized using an aqueous solution of $KMnO_4$ (0.045 M) and K_2CO_3 (0.017 M) at room temperature for 10 min; subsequently rinsed successively with aqueous $NaHSO_3$ (0.05 M), deionized water, aqueous HCl (0.1 M), and deionized water; and then dried with a stream of nitrogen. Samples were treated with this oxidation-rinsing procedure a total of three times. This treatment produced a mixture of polar functional groups at the surface of the polymer (denoted PBD-ox), which we characterized using a combination of surface chemical and spectroscopic techniques. The advancing contact angle (θ_a) of water (pH 1) on PBD-ox was 58° and showed a dependence on the pH of the contacting drop (pH 13, $\theta_a = 47°$), indicating that one constituent of the oxidized functionality was carboxylic acid groups.[18,19] The receding contact angle of water (pH 1) on this surface was 0°. For comparison, the advancing and receding contact angles on unmodified PBD were 95° and 82°. X-ray photoelectron spectroscopy (XPS) indicated the presence of hydroxyl, ketone and/or aldehyde, and carboxylic acid groups.

When heated against water, the surface of PBD-ox became more hydro*phobic* (Figure 1a), a result apparently contrary to that expected based on the tendency of systems to minimize interfacial free energy. The advancing contact angle of water (pH 1) for this system, in fact, increased with increasing temperature of the water against which it was equilibrated. For three separate samples of PBD-ox that had been heated against deionized water at 80−85 °C, θ_a increased by 15−20°. To ensure that reconstruction against air did not significantly influence our results, we took the following steps: after removal of these samples from the hot water, they were cooled to room temperature by immediate immersion in running water, floated on water for 3 min, and then dried with a stream of nitrogen. Since the kinetics of reconstruction at room temperature are slow for this system ($t_{1/2} \sim 30$ min),[20] this protocol trapped the polymer surface in a high-temperature configuration for analysis at room temperature. The difference in kinetics of reconstruction at room temperature versus higher temperatures simplified the interpretation of the wettability data, as the contact angles did not change significantly over the time necessary to make the measurements (1 min) at room temperature. A second experiment confirmed that the trapped configuration corresponded to a minimum in free energy for the system: two separate samples of PBD-ox were pre-equilibrated against water at temperatures above and below a central temperature of interest (60 °C). A surface that had been pre-equilibrated against water at 85 °C was initially hydrophobic, and one pre-equilibrated against water at 21 °C was hydrophilic. Figure 1b shows the kinetics of reconstruction upon equilibration of these two samples at 60 °C. In both cases, the advancing contact angle converged to the same value within experimental error, indicating that the final state of the two samples was the same.

The temperature dependence of the contact angle indicates that a delicate balance between enthalpy and entropy determines the concentrations of hydrophilic and hydrophobic groups present at the polymer/water interface.[21,22] Indeed, as the temperature of the water increased, the polymer surface became more hydro*phobic*—a result opposite to that expected on enthalpic grounds! In an experiment designed to determine the extent of reversibility in this system, a sample of PBD-ox was equilibrated alternately against water at 80 °C and then at 43 °C, for 15 min at each temperature. Figure 2 shows the change in the advancing contact angle of water (pH 1) as a result of

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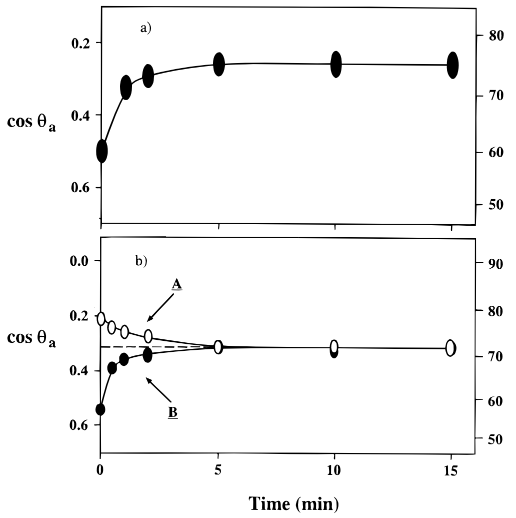

Figure 1. (a) The thermal reconstruction of PBD-ox was characterized by measuring advancing contact angles of water (pH 1) as a function of time the sample was heated against deionized water at 83 °C. (b**)** The change in the advancing contact angle of water (pH 1) was monitored as a function of time for two samples of PBD-ox heated against deionized water at 60 °C. Sample **A** (open ovals) was pre-equilibrated at 85 °C and was initially more hydrophobic than the final product surface. Sample **B** (black ovals) was pre-equilibrated at 21 °C and was initially more hydrophilic than the final product surface. All contact angles were measured at room temperature.

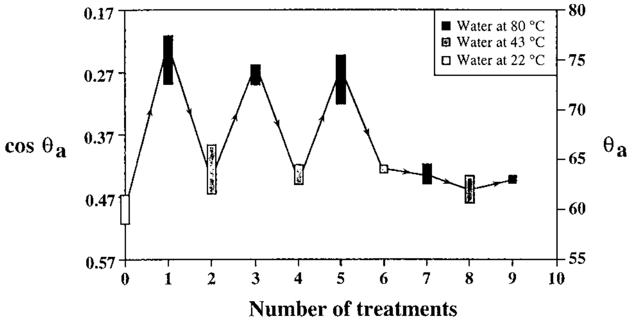

Figure 2. The range in advancing contact angles of water (pH 1) on two separate samples of PBD-ox that were heated sequentially against water at 80 and 43 °C. After three such complete cycles, the wettability of these samples became independent of the temperature.

these treatments. Over the first six treatments (three complete cycles), the surface responded reversibly to changes in temperature. Beyond this point, however, the hydrophilicity of the surface ceased to depend on the temperature. These results suggested that the type of equilibration shown in Figure 1 (parts a and b) leaves the interface in a *local* minimum of free energy. The loss of reversibility indicates that the system eventually relaxes to a more stable state. An additional experiment confirmed this hypothesis. A sample of PBD-ox was heated against water at 80 °C for an extended period and its contact angle of water monitored. After an initial period (0−25 min) during which the system appeared to reach equilibrium as in Figure 1a, a slower reconstruction began, which ultimately rendered the surface hydrophilic ($\theta_a \approx 61°$ after 2 h). Nonetheless, the behavior displayed in Figure 1 is both reproducible and reversible (for a few cycles of temperature).

We believe that the unusual behavior of this system may result from entropic forces associated with rubber elasticity. Since the interfacial region of PBD-ox contains a small number of polar groups relative to the number of nonpolar groups, the migration of the polar groups to the polymer/water interface likely requires extension of polymer chains out of their entropically preferred, random-coil conformations. At elevated temperatures, however, entropy causes these chains to recoil and thereby rebury the polar groups. The relationship between entropy and conformational extension of polymer chains in the rubber elasticity of lightly cross-linked elastomers is well established, and also lies at the center of current theory regarding the morphology of ionomeric polymers.[23] This explanation presumes the presence of light cross-linking—either chemical or physical—in the interfacial region of the polymer.[24]

A possible alternative explanation for the unusual entropic control of the wettability in this system is that it arises from a reversible chemical reaction between the surface and water. This explanation is not consistent with the behavior of the cross-linked samples of PBD-ox, which should display similar reactivity to the parent surface, and thus would have shown similar temperature-dependent behavior. A second alternative explanation is that this behavior arises from an interfacial example of a lower critical temperature of solution (LCTS). A LCTS is a temperature below which a particular polymer and solvent are miscible and above which they are not. Several interesting examples of polymers with a LCTS have recently been reported.[25−27] In fact in one case, the presence of a LCTS gave rise to changes in wettability of a surface to which the polymer was grafted.[27] The entropic effect reported in this communication appears different from those associated with a LCTS, however: our contact angles were measured *at room temperature,* not at the elevated temperatures where such an effect might be expected.[28] In addition, the behavior displayed in Figure 2 (e.g., the loss of reversibility) would not be expected, even if the kinetics of LCTS-related swelling were slow.

Chemical modification of the surfaces of solids and the control it provides over macroscopic properties such as wetting,[1] adhesion,[29] and biocompatability[2] provide fascinating new challenges in synthetic and physical organic chemistry. The behavior described in this paper opens intriguing possibilities for designing “smart” polymer surfaces that respond in a well-defined and reversible way to changes in their environment (e.g., temperature). This work also significantly extends our understanding of the reconstruction of polymer surfaces by demonstrating the possibility of metastable states whose interfacial composition is determined, in part, by entropy. The entropically controlled reconstruction described here is *not* characteristic of all surface-modified derivatives of PBD, and depends upon the interfacial reaction used to modify its surface. Ongoing studies in our group aim at establishing the underlying molecular mechanisms that produce this behavior in this system and at developing other model systems, with well-defined levels of cross-linking, that also show it.

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Supporting Information Available: X-ray photoelectron spectroscopic data for PBD-ox, including a high-resolution spectrum of the C 1s region, are provided (3 pages). See any current masthead page for ordering and Internet access instructions.

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