Entropically Influenced Reconstruction at the PBD-ox/Water Interface: The Role of Physical Cross-Linking and Rubber Elasticity

Deborah H. Carey, Stephen J. Grunzinger, and Gregory S. Ferguson*

Department of Chemistry, Lehigh University, Bethlehem, Pennsylvania 18015

Received February 1, 2000; Revised Manuscript Received July 27, 2000

ABSTRACT: Oxidation of the surface of syndiotactic 1,2-polybutadiene (PBD) films with aqueous $KMnO_4$/K_2CO_3 at room temperature produced PBD-ox, containing a range of oxidized functionality. When heated against water, the surface of PBD-ox became more hydrophobic, a result contrary to what would be expected if enthalpic forces dominated the reconstruction. Initially, the hydrophilicity of the surface varied reversibly as a function of temperature, reflecting reversible changes in the relative concentrations of hydrophilic and hydrophobic groups at the interface. Eventually, however, the surface remained hydrophilic against water, independent of temperature. The temperature dependence of this phenomenon suggests the importance of entropy in determining the state of minimum interfacial free energy in this system. This entropic effect is attributable to rubber elasticity arising from crystallinity in the polymer, and its loss is associated with a change in the amount and type of crystallinity.

Introduction

The interfaces of solids against liquids and gases offer useful model systems for studying interfacial properties relevant to the adhesion of solids to other solids.[1,2] When polymers are heated against liquids or gases, their surfaces usually reorganize (if possible) to minimize the interfacial free energy of the system. This type of behavior—thermal reconstruction—has been found in many polymeric systems.[3−18] The interfacial properties of polymers therefore depend on changes in interfacial composition that can result from conformational changes at the surface and on migration of chains carrying functional groups between the surface and bulk.[19] This statement is especially true for surface-modified polymers and for polymers containing additives such as slip agents, antistatic agents, antioxidants, or even low levels of surface-active impurities. It is also often true for those pure polymers whose structures contain more than one type of functional group.[9,10]

Most published accounts of dynamic behavior of surface-modified polymers are consistent with the minimization of interfacial free energy being the driving force toward initial reconstruction of the interfacial region. Equilibration of the surface of a polymer 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. Equilibration against air, inert gas, or vacuum usually has the opposite effect.[3,4,11,20,21] These results are consistent with the notion that enthalpy—via dispersion forces, hydrogen bonding, Lewis acid−base interactions, etc.—dominates the process. The kinetics of surface reconstruction depends on temperature, with the mobility of polymer chains in the interfacial region increasing with increasing temperature, especially at the onset of melting.[3,12−14]

We recently reported that oxidation of the surface of 1,2-polybutadiene with basic permanganate at room temperature produced PBD-ox, a surface for which the thermodynamics, not just kinetics, of reconstruction showed a pronounced dependence on temperature.[15] When PBD-ox was equilibrated against water, *the hydrophilicity of its surface changed as a function of temperature*.[11,14a,15−17,22] These changes in hydrophilicity were reversible and reflect changes in the relative concentrations of hydrophobic (hydrocarbon) moieties and hydrophilic (e.g., carboxylic acid, hydroxyl) functional groups in that part of the interfacial region that determines wettability by water. The direction of reconstruction in this system is the opposite of that expected on the basis of enthalpic considerations, such as hydrogen bonding between hydrophilic functionality at the surface and the contacting water, and leads directly to the conclusion that *entropy* is important in determining the equilibrium state resulting from surface reconstruction.[17] The enthalpic cost of hydrophilic groups moving away from the polymer/water interface may be reduced, however, if these groups take water of hydration with them into the subsurface region of the polymer. The kinetics of reconstruction of this surface is sufficiently slow at room temperature to allow its wettability to be measured conveniently after the polymer has cooled from a higher temperature of interest (vide infra).

Possible sources of this entropic effect include interfacial analogues of rubber elasticity associated with physical or chemical cross-linking, lower critical temperature of solution, or chemical equilibria. Results reported by us previously,[15] and in more detail here, argue against the latter two explanations and are consistent with rubber elasticity being the dominant source of the entropic driving force in this system. The hypothesis of a direct connection between cross-linking and chain dynamics in the interfacial region of polymers leads us to propose three experimentally distinguishable regimes of cross-linking arising from this connection. In un-cross-linked polymers (regime I), polymer chains are free to migrate to and from a polymer/water interface; as a result, the composition of the interface should be dominated by the tendency toward minimum interfacial free energy upon thermal reconstruction. Nonpolar surfaces should thus be stable against air or

10.1021/ma000189z CCC: $19.00 © 2000 American Chemical Society
Published on Web 10/21/2000

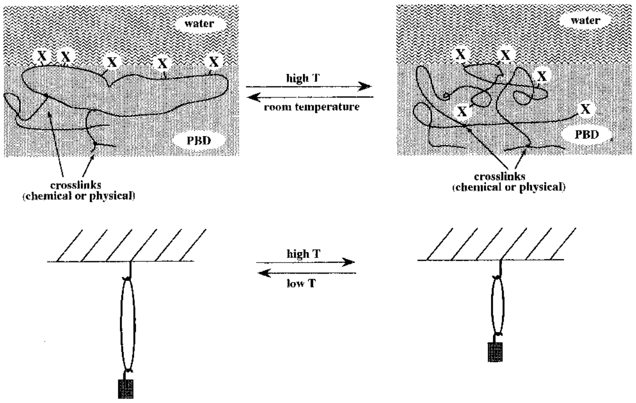


Figure 1. Stylized illustration of the proposed model for explaining the entropically controlled reconstruction of PBD-ox against water (top). A lack of mobility near branch points requires entropically unfavorable chain extension to bring hydrophilic ("X") groups into enthalpically favorable contact with the water. The resulting temperature-dependent behavior is analogous to that expected for a rubber band under constant stress (bottom).

vacuum, and hydrophilic surfaces should be stable against water. This type of behavior is by far the most common and has been reported by Whitesides[3,13] and others[14] for surface-modified polyethylene, by McCarthy for surface-modified poly(chlorotrifluoroethylene),[18] and by others for various polymers.[4−7]

In lightly cross-linked elastomers (regime II), rubber elasticity may compete with the tendency to minimize interfacial free energy and perhaps dominate the interfacial behavior at high temperatures. Rubber elasticity is generally considered a bulk property, though we believe that its relation to interfacial phenomena in these systems is straightforward. Segments of the polymer close to a branch point should be much less mobile than those remote from a branch point. As a result, the migration of functional groups attached to the mobile segments could require extension of chains out of their relaxed, random-coil conformations. This hypothesis is analogous to the thermodynamic changes that accompany small extensions of an elastomer: while stretching an elastomer can be enthalpically favorable,[23] an entropic restoring force determines the equilibrium extent of extension (Figure 1). In the interfacial case, however, there is a significant enthalpic driving force for bringing polar groups to the polymer/water interface: hydrogen bonding of those groups to water. Our hypothesis is also closely related to the multiplet-cluster theory describing the morphology of ionomeric polymers, where enthalpically favorable clustering of ions is opposed by an entropic stress from rubber elasticity.[24,25] The role of configurational entropy, and the extension of polymer chains, in the rubber elasticity of cross-linked elastomers is well-established.[26−30]

In addition to the degree of cross-linking, the degree of functionalization should also influence whether a polymer surface displays the reconstruction behavior described above for regime II polymers. For example, a surface that is highly functionalized may not require extension of chains out their random-coil conformations in order to fill the interfacial sites with polar groups. Thus, we expect that the novel behavior observed for PBD-ox will characterize polymers that are both lightly cross-linked *and* have an intermediate degree of functionalization.

At high levels of cross-linking (regime III), we expect "stable" interfaces against water and against air, as long as the bulk of the polymer is also highly cross-linked and does not contain free chains. A high density of cross-links should anchor all or most of the chains and prevent migration to and from the interfacial region. The thermally stable, hydrophilic surface of the latex film reported by Noda is an example of this type of behavior.[31]

This paper provides a full description of the entropically driven reconstruction of PBD-ox against water. In addition, it examines the source of the cross-linking in this system that gives rise to rubber elasticity, as well as how the amount of cross-linking affects the behavior.[8] Finally, it addresses the degree of functionalization as a factor determining the magnitude of the entropic effect for the proposed "regime II" behavior in this system.

Experimental Section

General. Hydrochloric acid (37% HCl, Mallinckrodt), potassium permanganate (Certified A.C.S., Fisher), sodium bisulfite (A.C.S. reagent, Aldrich), dicumyl peroxide (98%, Aldrich), sodium hydroxide (Certified A.C.S., Fisher), lithium aluminum hydride (95+%, Aldrich), chloroform (99.8%, Aldrich), and trifluoroacetic anhydride (99+%, Aldrich) were used as received. Potassium carbonate was purified by dissolving in boiling water, filtering to remove insoluble material, and recrystallizing upon cooling to below room temperature. Diethyl ether was distilled from sodium/benzophenone prior to use. Deionized water was obtained from a Milli-Q system and had a resistivity of 16−17 MΩ·cm. Advancing and receding contact angles of water 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 to deliver or remove the probe liquid for these measurements. Contact angles were measured within 5−10 s after the application of the ~1 μL drop under ambient conditions. All reported values are the average of at least eight measurements (four drops, two sides each) taken at different areas on the polymer surface. X-ray photoelectron spectroscopy (XPS) was obtained using the instrument and methods described previously.[32] 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 DTGS detector and a 25 × 10 × 3 mm germanium (45° angle of incidence) crystal as the internal reflection element. The reported spectra are the accumulated average of 128 scans at 4 cm^{-1} resolution and a gain factor of 2, unless otherwise noted. Differential scanning calorimetry (DSC) was performed using a Mettler model TC 10A and was run at a scan rate of 20 °C /min from −50 to 140 °C.

The dynamic mechanical analysis was performed using the Rheometrics RDA-II (Resource Series #41200806) interfaced to a personal computer. The polymer samples were cut to the dimensions of approximately 30 × 10 × 1 mm. A dynamic strain sweep was used to determine the limits of linear viscoelasticity by increasing the torsional angle incrementally at 24 °C and 1.0 Hz frequency from which the complex modulus (G^*) was measured.

Syndiotactic 1,2-Polybutadiene (PBD). Poly(butadiene, 1,2-syndiotactic) (15−29% crystallinity) was purchased as pellets from Polysciences, Inc., who reported its weight-average molecular weight as 100 000 g/mol and density as 0.90 g/cm^3. The PBD films were formed by melting pellets against a glass Petri dish that had been coated with a siloxane monolayer adsorbed from a methylene chloride solution of octadecyltrichlorosilane (95%, Aldrich). *No cross-linking agents were added.* The polymer was melted in an air-filled oven (Fisher Isotemp 500 series) at 135−140 °C for 10−11 h, and the resulting film was peeled from the dish and stored on filter paper in the dark in a covered disposable Fisherbrand Petri dish. The melting temperature range, measured by DSC, for PBD was 77−119 °C.

Cross-Linked PBD. In a 250 mL beaker covered with aluminum foil, ~200 mL of chloroform and 0.7 g of PBD were stirred overnight. The desired amount of dicumyl peroxide (DCP)[33] was then added, and the solution was stirred for 10−15 min before being poured into a crystallizing dish. The chloroform was removed using a vacuum desiccator and a water aspirator. Most of the solvent was removed within 5−6 h. The PBD was then cut into small pieces, placed in a round-bottom flask, and dried to constant weight on a vacuum line (0.01−0.03 Torr). The polymer was stored on weighing paper in a plastic Petri dish and covered with Al foil in a drawer until needed.

Two glass plates (10.1 cm × 10.2 cm × 0.5 cm) were silanized with octadecyltrichlorosilane and cleaned with ethanol and deionized water before pressing a film. A cardboard frame was cut with outer dimensions matching the glass plates and cavity dimensions of ~8 cm × 8 cm. The cavity was filled with the dry polymer/DCP mixture, the top glass plate was added, and a Tetrahedron press was used to cure the mixture at 135 °C and 800 lb of pressure for 5.2 h (5.7 half-lives).[34] The pressed films were peeled away from the glass plates using tweezers and placed in a plastic Petri dish lined with filter paper, and covered with Al foil in a drawer until used.

PBD-ox. An aqueous solution of $KMnO_4$ (0.045 M) and K_2CO_3 (0.017 M) was stirred vigorously at room temperature for 30 min before introducing a sample of PBD film (3 cm × 1 cm × 0.1 cm). It was possible that the $KMnO_4$ may not have all been dissolved after 30 min of stirring, but these results were reproducible. At 10 min intervals, 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. This procedure was repeated for a total of three times. At this point, the sample was considered “freshly prepared” (vide infra).

Chemical Derivatization of PBD-ox. To help characterize the surface chemistry of PBD-ox, a sample of this material was covered with a 1 M solution of $LiAlH_4$ in diethyl ether under nitrogen at room temperature for 1 min. The sample was rinsed with ethanol, deionized water, and then treated with aqueous HCl (0.1 M) for 1 h. The resulting sample of “PBD-OH” was then dried in air for 12 h. After this treatment, the surface of the sample had a cloudy appearance, possibly due to rapid deswelling of the interfacial region and/or to the presence of aluminum salts.

The surface of a sample of PBD-OH was covered with a diethyl ether solution of trifluoroacetic anhydride (5%, v/v) under nitrogen. After 1 min, the solvent had evaporated and the sample appeared dry (visually). It was then floated on deionized water at room temperature for 3 days, after which it was heated against deionized water at 65 °C for 8 h and dried under vacuum (0.005−0.01 Torr) for 1 h. In a control experiment, a sample of unmodified PBD was treated in the same way with trifluoroacetic anhydride. This sample was then floated against water at room temperature for 18 h and vacuum-dried at 0.01 Torr for 2 h.

Reconstruction of PBD-ox Against Hot Water. A sample of PBD-ox was heated against deionized water contained in a disposable scintillation vial (Fisherbrand) that was emersed in a constant temperature water bath (VWRbrand model 1146) at the desired temperature. Each time the sample was removed from the hot water, it was cooled by immediately rinsing with deionized water at room temperature and floating on deionized water at room temperature for 3 min. The sample was then dried with a stream of nitrogen prior to analysis. The kinetics of reconstruction and relevant control experiments are presented in the Results and Discussion section.

Photolytic Addition of Thiol Mixture to the Surface of PBD. The photolytic addition to the surface of PBD of a mixture of mercaptoacetic acid (0.07 M) and 3-mercapto-1,2-propanediol (0.08 M) in methanol was accomplished using a previously reported method.[32] The sample was then floated on deionized water at room temperature for 13 h to remove absorbed methanol and unreacted thiols from the polymer.

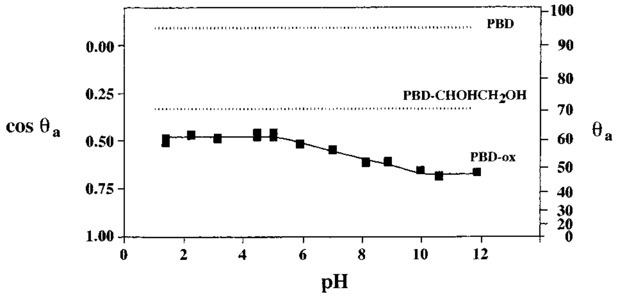


Figure 2. Contact angle titration on the surface of PBD-ox. The data were collected in random order of pH using three separate samples. The heights of the rectangles indicate one standard deviation above and below the mean of the contact angle measurements. The dashed lines show the pH-independent behavior of unmodified PBD and PBD-$CHOHCH_2OH$ (a PBD surface containing diol functionality),[32] for comparison.

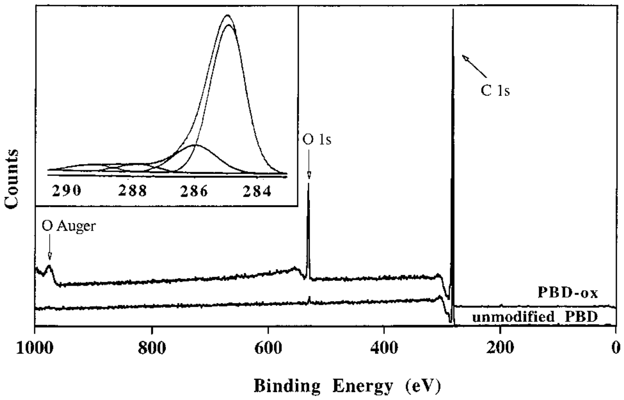


Figure 3. Survey XPS spectra at a 20° takeoff angle of PBD-ox (upper) and unmodified PBD (lower). The binding energies were corrected for charge compensation by referencing to the main C 1s peak set at 285.0 eV. In the high-resolution spectrum of the C 1s region (inset), a broad, unresolved envelope was fitted by three peaks at 286.0, 287.8, and 298.2 eV, in addition to the main peak at 285.0 eV.

Results and Discussion

Synthesis and Characterization of PBD-ox. The surface of PBD can be modified chemically using aqueous solutions of potassium permanganate with the type of functionality added to the surface depending, in part, on the concentration and pH of the oxidizing solution.[15,32] For example, treatment of PBD with a basic solution of $KMnO_4$ produced a mixture of polar functional groups at the surface (denoted PBD-ox), which we characterized by a combination of chemical and spectroscopic techniques. As a result of this oxidation, the advancing contact angle of water (pH 1) on the surface fell from 95° for the unmodified polymer to approximately 60° for PBD-ox. The advancing contact angle showed a dependence on the pH of the contacting water droplet (Figure 2), consistent with the presence of ionizable carboxylic acid groups at the polymer surface.[35] The receding contact angle of water (pH 1) on PBD-ox was close to 0°, compared to 82° for the unmodified polymer.

X-ray photoelectron spectroscopy at a 20° takeoff angle showed an increase in the amount of oxygen in the interfacial region, from 1% for the unmodified polymer to 12% for PBD-ox (Figure 3). A high-resolution spectrum of the C 1s region (Figure 3, inset) revealed a broad, unresolved envelope on the high-binding-energy side of the main peak set at 285.0 eV. We could fit this envelope with three peaks at 286.0, 287.8, and 289.3

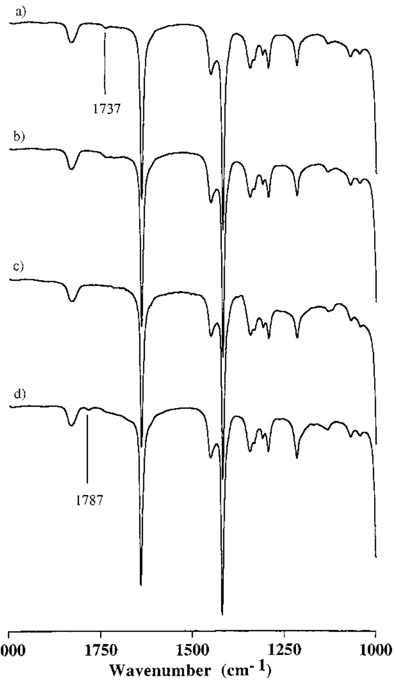


Figure 4. Attenuated total reflectance-infrared spectra of (a) unmodified PBD, (b) PBD-ox, (c) PBD-OH, and (d) sample c after treatment with a 5% (v/v) trifluoroacetic acid/ether solution. The small peak at 1737 cm^{-1} observed in spectra a and b was most likely due to an additive or end groups in the polymer that could be reduced or removed by treatment with $LiAlH_4$.

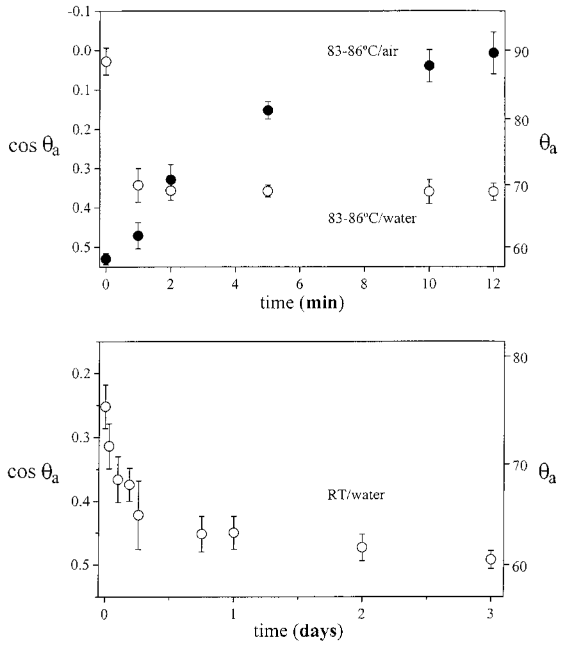


Figure 5. (a) Thermal reconstruction of PBD-ox, characterized by measuring the advancing contact angles of water at pH 1 as a function of time, initially heated in air at 83−86 °C (filled circles) and then heated against deionized water at the same temperature (open circles). (b) Reconstruction of a separate sample treated in the same manner and then allowed to equilibrate against deionized water at room temperature. The error bars indicate one standard deviation above and below the mean of the contact angle measurements.

eV, due to oxidized carbon. The peak at 286.0 eV, a binding energy consistent with carbon atoms bonded to hydroxyl groups, contains approximately 69% of the total intensity due to oxidized carbon. This peak may also include the intensity due to the α-carbons adjacent to carboxylic acid groups, so the actual concentration of hydroxyl-bearing carbons was probably less than 69%. The peak at 287.8 eV is assigned to carbonyl carbons in ketones and/or aldehydes and comprises 17% of the oxidized carbon. The peak at 289.3 eV, characteristic of carboxylic acid groups, contains the remaining 14%.

The attenuated total reflectance−infrared (ATR-IR) spectrum of PBD-ox showed two small, broad overlapping bands centered at 1702 and 1737 cm^{-1} (Figure 4b), indicating the presence of carbonyl-containing functionality. The higher frequency band was also present in the spectrum of unmodified PBD (Figure 4a), consistent with the presence of ester end groups or a polymer additive. The band at approximately 1702 cm^{-1}, which resulted from the permanganate oxidation, is consistent with the presence of carboxylic acid groups.

Chemical derivatization was used to characterize this surface further (eq 1).[36] The carbonyl-containing functional groups at the surface of PBD-ox were reduced with $LiAlH_4$ to

$$\text{PBD-ox} \xrightarrow{\text{LiAlH}_4} \text{PBD-OH} \xrightarrow{(\text{CF}_3\text{CO})_2\text{O}} \text{PBD-OCOCF}_3 \quad (1)$$

produce a hydroxylated surface (PBD-OH). An ATR-IR spectrum of PBD-OH showed no distinct peaks in the carbonyl region (Figure 4c). A spectrum of the carbonyl region of unmodified PBD that had been treated in the same way as PBD-ox, with the exception that the sample floated against aqueous HCl (1.0 M) for 7 h, was very similar to Figure 4c. Treatment of PBD-OH with trifluoroacetic anhydride resulted in trifluoroacetylation of the hydroxyl groups. An ATR-IR spectrum of the product contained a new peak at 1787 cm^{-1}, consistent with the presence of trifluoroacetate ester groups (Figure 4d),[37] and a small feature at about 1700 cm^{-1}. In an experiment designed to identify any peaks associated with simple absorption of reagent, a sample of unmodified PBD was treated in the same way with trifluoroacetic anhydride. The infrared spectrum then contained the small feature at approximately 1700 cm^{-1}, but no peak due to trifluoroacetate esters near 1787 cm^{-1}.

Initial Studies of the Reconstruction of PBD-ox Against Air and Water. Heating PBD-ox in air at 83−86 °C caused its surface to become hydrophobic, consistent with migration of the oxidized functionality away from the surface and minimization of interfacial free energy. The advancing contact angle of water reached an upper limit of near 90°, which was close to that of unmodified PBD (Figure 5). This behavior is similar to that observed for a variety of other surface-modified polymers and for unmodified polymers that contain both polar and nonpolar functional groups.[3,5,6,13,18,21] Figure 5 also shows the advancing contact angle of water (pH 1) on this reconstructed surface (open circles), during its subsequent equilibration against water at 83−86 °C and then at room temperature. Heating on water caused the advancing contact angle of water to decrease within 1 min to close to 70°, indicating an increase in the concentration of hydrophilic functional groups at the surface. Importantly, the contact angle did *not* reach the lower limit of about 60° found for freshly prepared PBD-ox. For two samples prepared on separate days, the drop in the advancing contact angle in this step varied by only 4°. When one of these samples was placed against

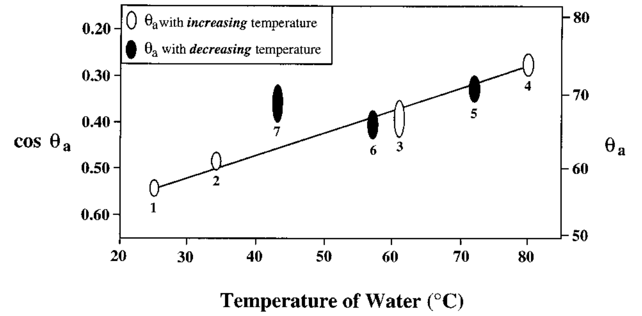


Figure 6. Contact angle of water (pH 1) on a sample of PBD-ox equilibrated against water at various temperatures. The numbers next to the ovals indicate the order in which the measurements were obtained, and the heights of the ovals indicate one standard deviation above and below the mean of the contact angle measurements.

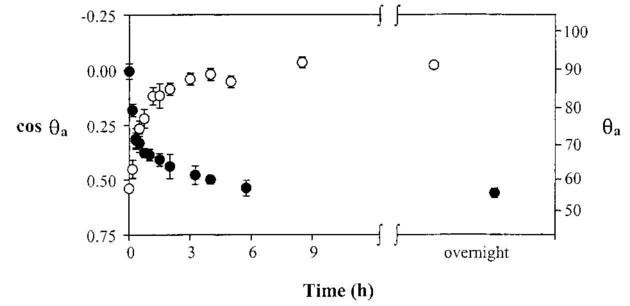


Figure 7. Advancing contact angles of water (pH 1) on a sample of PBD-ox equilibrated in air at room temperature under ambient laboratory conditions (open ovals) and then equilibrated against deionized water at room temperature (filled ovals). The error bars indicate one standard deviation above and below the mean of the contact angle measurements.

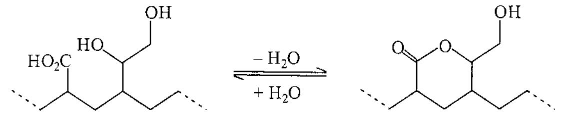
deionized water at room temperature over a period of days, however, its surface continued to reconstruct, eventually reaching the original hydrophilicity characteristic of PBD-ox ($\theta_a = 61°$).

These results indicated that the surface of PBD-ox that had been equilibrated against hot water was more hydrophobic than that equilibrated against water at a lower temperature and therefore implied a counterintuitive prediction: *heating freshly prepared (and hydrophilic) PBD-ox against water should make its surface more hydrophobic.* Indeed, we have shown previously that, upon heating freshly prepared PBD-ox against deionized water at 83 °C, the advancing contact angle of water (pH 1) on the surface increased from 58° to 75°.[15] This reconstruction of PBD-ox against water at elevated temperatures to produce a more hydrophobic surface appears contrary to expectations based on the tendency of systems to minimize their interfacial free energy. In a separate experiment, two samples of PBD-ox, equilibrated against water at different temperatures, were then heated against water at an intermediate temperature. The contact angles on the two samples converged within 5 min to a common, central value of 71°, indicating that the final states of the two samples were the same and correspond to a minimum in free energy for the system at this temperature.[15]

The advancing contact angle of water (pH 1) for this system depended on the temperature of the water against which it was equilibrated. Figure 6 shows the contact angle of water on a sample of PBD-ox equilibrated against water at various temperatures for 15 min each. These changes in hydrophilicity reflected changes in the relative concentrations of polar and nonpolar functional groups in that part of the interfacial region that determines wettability by water. The direction of the temperature dependence, i.e., hydrophilic (enthalpically preferred) at low temperature and hydrophobic (enthalpically disfavored) at high temperature, indicates that entropy plays a role in determining the relative concentrations of these hydrophilic and hydrophobic groups at the surface.

In these experiments, it was important to “trap” the surface of PBD-ox in its high-temperature configuration and to minimize the reconstruction of this surface against air as it emerged from the hot water. To ensure that such reconstruction of PBD-ox against air did not significantly influence our results as the sample emerged from the hot water, the surface of the polymer was cooled to room temperature by immediate immersion in running deionized water, followed by floating the sample against deionized water for 3 min at room temperature, and then drying with a stream of nitrogen. As a result, it was also important for us to determine the kinetics of reconstruction of PBD-ox in air and against water at room temperature (Figure 7). A sample of PBD-ox was allowed to equilibrate in air at 23 °C, and the advancing contact angles of water (pH 1) were measured as a function of time. After 10 min in air, θ_a (pH 1) had increased only slightly, from 57° to 60°. After an extended period in air (8.5 h), however, the contact angle had increased to 90°, a value close to that of unmodified PBD. Upon floating this sample on water at room temperature for 10 min, θ_a (pH 1) decreased from 90° to 80°. After several hours on room-temperature water, θ_a decreased further to 55°, the contact angle measurement observed for this sample. These results confirmed that the kinetics of reconstruction of PBD-ox at room temperature was slow enough to allow us to obtain reliable contact angle measurements.

In addition to our hypothesis that rubber elasticity plays an important role in the interfacial dynamics at PBD-ox/water interfaces, we have explored alternative explanations for the unusual entropic effect in this system. For example, a reversible chemical reaction at the PBD-ox/water interface could, in principle, give rise to these changes if its equilibrium constant depended strongly on temperature. One such reaction could be esterification or lactonization involving hydroxyl and carboxylic acid groups present at the interface (e.g., eq 2).



(2)

Lactonization, in particular, is often entropically favorable.[38,39] Our observation of similar entropic behavior for a different surface-modified PBD that did not contain a significant concentration of carboxylic acid groups (PBD-CHOHCH$_2$OH),[32] however, argues against such equilibria being the source of the entropic effect. As a further test of the esterification/lactonization hypothesis, we prepared a model surface that should contain both hydroxyl and carboxylic acid functional groups by the photolytic addition of a mixture of mercaptoacetic acid and 3-mercapto-1,2-propanediol to the vinyl groups at the surface of PBD.[32] The advancing contact angles of water at pH 1 and pH 12 for this sample were 70° and 46°, confirming the presence of

Table 1. Average Values of Complex Modulus (G^*) for Chemically Cross-Linked PBD

DCP (% w/w)	average G^* (Pa)
0.0	$(5.8 \pm 0.2) \times 10^7$
0.25	$(6.1 \pm 1) \times 10^7$
0.50	$(9.1 \pm 0.6) \times 10^7$
1.0	$(4.0 \pm 0.6) \times 10^8$

ionizable carboxylic acids at the surface.[35] These contact angle measurements were similar to those for PBD-SCH_2CO_2H ($\theta_{a(pH\ 1)} = 66°$; $\theta_{a(pH\ 12)} = 45°$).[32] The sample was floated against deionized water at room temperature for an additional 9 h before heating it against water at 80−83 °C for 10 min. The advancing contact angle of water at pH 1 did not change (71°), again indicating that esterification/lactonization was probably not responsible for the entropic effect.

A second, alternative explanation for the unusual entropic control of the wettability in PBD-ox is that it arises from an interfacial example of a lower critical temperature of solution (LCTS).[11,16,40,41] This entropically driven process can arise, for example, due to ordering of solvent molecules or to volume contraction upon mixing.[41] Several examples of interfacial analogues of this behavior have been reported.[11,16] In contrast to these examples, however, the surface of PBD-ox was cooled to room temperature *prior* to recording the contact angle measurements; thus under these experimental conditions, an LCTS should not be observed unless the kinetics of resolvation at room temperature are slow. Finally, one of the most convincing pieces of evidence that is inconsistent with both the chemical equilibria and LCTS hypotheses is the *loss* of the reversible entropic behavior by PBD-ox upon annealing or repeated thermal cycling against water (vide infra).

The Role of Cross-Linking. Our hypothesis that rubber elasticity influences the reconstruction of PBD-ox implies that the degree of cross-linking of the polymer should be an important parameter because it imposes the requirement that conformational extension of polymer chains be a necessary consequence of collective segment migration (as in Figure 1). We expect that physical cross-linking in this system arises primarily from its partial crystallinity,[42] though chain entanglement may also contribute. In addition, chemical cross-linking within the interfacial region, for example due to autoxidation in air, is also possible but much more difficult to detect. The amount of chemical cross-linking throughout the polymer, however, can easily be increased by curing it in the presence of a free radical initiator. We used this approach to test the hypothesis that the entropically driven reconstruction in this system should depend strongly on the degree of cross-linking, as described in the Introduction.

In these experiments, samples of PBD were cross-linked throughout the polymer by curing with dicumyl peroxide (DCP). Separate batches of PBD were prepared, nominally containing 0.25, 0.50, or 1.0% (w/w) of DCP initially.[43] After curing, the complex modulus, G^*, was measured for each cross-linked sample of PBD (done in triplicate), as well as for three separate samples of unmodified PBD for comparison. These data, reported in Table 1, are consistent with an increase in the amount of cross-linking (and thus increased G^*) with increasing concentration of DCP used in curing.

Table 2. Treatment Times for the Surface Oxidation of PBD Cross-Linked Using Dicumyl Peroxide and the Corresponding Advancing Contact Angles of Water (pH 1) on the Modified Surfaces

amount (%) of DCP used to cure the polymer (w/w)	treatment time with $KMnO_4$ (min)	θ_a (pH 1) on oxidized sample (deg)
0.25	20	57
0.50	10	61
1.0	5	56

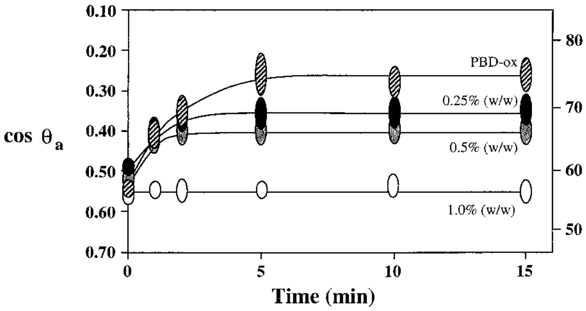


Figure 8. Comparison of the thermal reconstruction of PBD-ox against deionized water at 80 °C for samples that had been cross-linked with various amounts of dicumyl peroxide (DCP) prior to oxidation. The percentages given refer to the amount of DCP added to the polymer prior to curing and surface modification. The heights of the ovals indicate one standard deviation above and below the mean of the contact angle measurements.

An XPS spectrum (20° takeoff angle) of a freshly prepared and pressed PBD film cured with 0.25% DCP showed that the amount of oxygen on the surface was 3%. An ATR-IR spectrum of a cross-linked film pressed under the same conditions contained the usual peaks due to PBD, as well as three small peaks at 1373, 1261, and 801 cm^{-1}, consistent with the presence of cumyl alcohol, a byproduct of the cross-linking reaction.[33] For comparison, an XPS spectrum (20° takeoff angle) of a sample from the same cross-linked batch after 2 months showed that the amount of oxygen had increased to 5%, consistent with autoxidation of the polymer in air or with contamination.

Since the amount of oxygen at the surfaces of the cross-linked PBD films was different from that of unmodified PBD (as determined by XPS), the cross-linked films were oxidized for various times with aqueous permanganate to generate surfaces that had approximately the same initial advancing contact angle of water (pH 1) as PBD-ox (Table 2). These oxidized samples were then heated against water at 80−86 °C, and their wettability was monitored as a function of time (Figure 8). The magnitude of the change in contact angle diminished with increasing amount of cross-linking, consistent with a transition from regime II to regime III cross-linking. In fact, the θ_a of a cross-linked PBD film containing 1.0% DCP was stable against water. Since PBD-ox is prepared from film formed by melting alone, and not by pressing, we performed a control experiment to show that pressing did not affect the reconstruction of the cross-linked samples. A pressed PBD film containing no DCP and prepared in the same manner as the cross-linked samples was oxidized with aqueous, basic permanganate for 30 min. Its thermal reconstruction behavior against hot water was indistinguishable from that of PBD-ox prepared using films formed by melting.

The Role of Extent of Surface Functionalization. To test the hypothesis that the degree of functionalization is also an important parameter determining whether

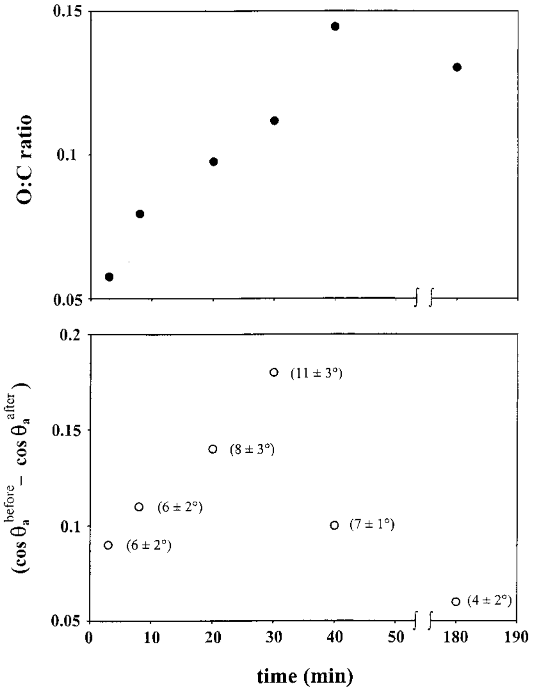


Figure 9. (a) Ratio of oxygen to carbon from high-resolution XPS spectra of the O 1s and C 1s regions (75° takeoff angle) for separate samples of PBD treated with an aqueous solution of $KMnO_4$ (0.045 M)/K_2CO_3 (0.017 M) at room temperature as a function of time. (b) Contact angles of water (pH 1) were recorded before and after heating the sample against water at 80 °C. The change in the wettability of each surface is expressed as the magnitude of the difference in cos θ_a before and after this treatment. The numbers in parentheses next to each point are the corresponding change in contact angle and the estimated error in the measurements (the root mean square of standard deviations before and after heating).

a polymer will display the reconstruction behavior shown by PBD-ox, we prepared several samples of PBD that had been modified to different extents. We expected that, for samples with low concentrations of oxidized functionality, the change in the wettability of the oxidized surface upon heating it against hot water would be small due to the low number of polar groups present in the interfacial region. For highly oxidized surfaces, we also anticipated a small entropic effect because the large number of polar functional groups could alleviate the need for chain extension.

In one set of experiments, we systematically varied the concentration of the oxidized functionality at the surface of PBD by treatment for various times on an aqueous permanganate solution (0.045 M). Figure 9a shows the ratio of oxygen to carbon at the surface of these samples, as determined by high-resolution XPS, and these data indicate that the oxygen content increased up to approximately 40 min of treatment. After 180 min of treatment, the oxygen-to-carbon ratio was slightly lower than for the 40 min sample, indicating that we had reached a maximum level of surface modification. Figure 9b shows the magnitude of the *increase* in contact angle of water when these samples were equilibrated against water at 80 °C for 5 min. The change in wettability reached a maximum for PBD-ox itself, corresponding to 30 min of treatment with the $KMnO_4$ solution, and then decreased for samples treated for longer times. The smaller changes for samples treated for less than 30 min may simply reflect the higher initial θ_a on the incompletely oxidized surfaces. These results are consistent with the hypothesis that an optimum extent of functionalization exists for which the entropic effect in this system is maximized.

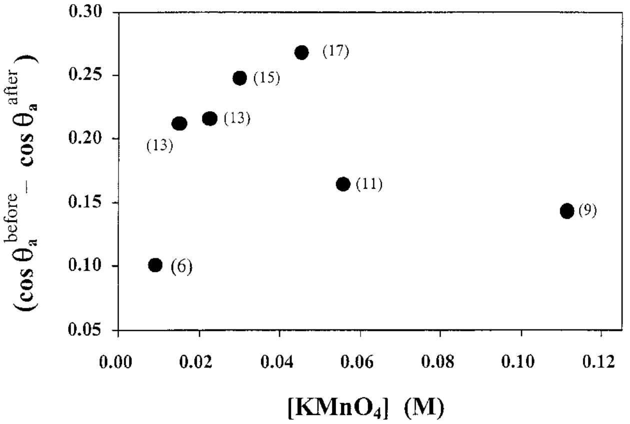


Figure 10. Change in the wettability, expressed as the magnitude of the change in cos θ_a, upon heating against water at 80 °C for samples of PBD-ox that had been treated with oxidizing solutions of various concentrations. The concentration of the original aqueous $KMnO_4$/K_2CO_3 solution was (0.045 M)/(0.017 M), and the concentration of K_2CO_3 was adjusted proportionally to the concentration of permanganate. The number in parentheses next to each point is the corresponding change in contact angle, and the estimated error in these measurements is ±2° (the root mean square of standard deviations before and after heating) in each case.

In a second set of experiments, we varied the concentration of oxidized functional groups at the surface of PBD by varying the concentration of the oxidizing solution in the range of 0.009−0.11 M. Aside from the difference in the concentration of the oxidizing solution, these samples were prepared in the same manner as PBD-ox. Each sample was then heated against water at 80 °C for 5 min, rinsed with deionized water, floated on deionized water at room temperature for 3 min, and dried with a stream of nitrogen before measuring contact angles. Figure 10 shows the magnitude of the increase in contact angle of water after this treatment. These results were also consistent with there being an optimum extent of functionalization for which the entropic effect in this system is maximized.

Heating PBD-ox Against Water for Extended Periods. The reconstruction of PBD-ox against water depended on the temperature of the water. As the temperature was increased, both the rate of reconstruction and the hydrophobicity of the final state of the surface increased. Figure 6 shows the final contact angles of water on a single sample of PBD-ox heated against water at various temperatures for 15 min. The position of point 7 in Figure 6 indicates a loss of the reversible temperature-dependent wettability of this surface after several heating treatments. To examine this loss of reversibility in more detail, we heated a sample of PBD-ox alternately against water at 80 and at 43 °C and monitored the changes in its wettability (Figure 11). The surface initially reconstructed reversibly, becoming more hydrophobic at 80 °C and more hydrophilic at 43 °C. After three complete cycles, however, its wettability became independent of the temperature of the water. Both experiments (reported in Figures 6 and 11) were repeated several times and were reproducible. For comparison, a PBD-ox sample that had been chemically cross-linked in the bulk with 0.25% DCP was also heated against water at 80 °C and then at 43 °C. The surface reconstructed reversibly for three complete cycles, though with a smaller change in

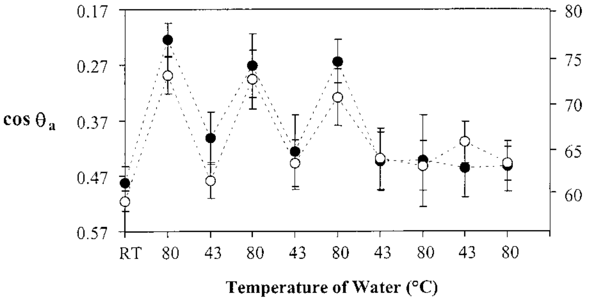


Figure 11. Contact angles of water (pH 1) for two separate samples of PBD-ox cycled repeatedly against deionized water at 80 and at 43 °C. The error bars one standard deviation above and below the mean of the contact angle measurements.

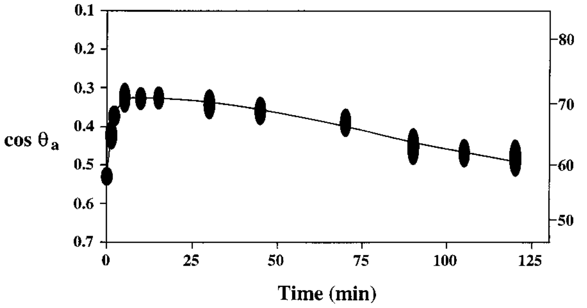


Figure 12. Contact angles of water (pH 1) on a sample of PBD-ox heated against deionized water at 80 °C over an extended time. The heights of the ovals indicate one standard deviation above and below the mean of the contact angle measurements.

contact angle ($\Delta\theta_a = 11°$) than PBD-ox, before its hydrophilicity became independent of the temperature. This result suggested that, in addition to physical cross-linking, chemical cross-linking also influenced the equilibrium state of the polymer against water. These results indicated that *the states of the PBD-ox/water interface responsible for the reversible behavior were metastable, corresponding to local, rather than global, minima of free energy* at these temperatures.

To confirm this conclusion about the thermodynamics of this system, we studied the wettability of PBD-ox as it was heated against water for an extended time (2 h, Figure 12). As expected, the advancing contact angle of water (pH 1) initially rose and appeared to reach equilibrium during the first 15 min. A slower reconstruction then commenced, eventually returning the sample close to its original hydrophilicity. A second sample of PBD-ox was heated continuously against deionized water at 80 °C for 2 h, after which time the θ_a did not appear to have changed within experimental error (64 ± 2°).

We have examined two hypotheses that could account for the loss of reversibility upon extended heating or cycling between hot and cool water. First, it is possible that the interfacial region of PBD-ox eventually became swollen with water, thus diminishing the need for entropically unfavorable chain extension for hydrophilic groups to contact the water phase. To test this hypothesis, we treated PBD-ox for three heating/cooling (80 °C/43 °C) cycles and then heated the sample in air at 95 °C for 5 min to remove water from the interfacial region. The advancing contact angle of water (pH 1) was 92° after this treatment but decreased to 63° after heating this sample against deionized water at 80 °C for 15 min. This sample was floated against water at room temperature for 1.5 days, after which the contact angle of water was 64°. When the sample was then heated against water at 80 °C for 15 min, the contact angle did not change. If the absorption of water in the interfacial region had been responsible for the loss of reversibility in the thermal reconstruction of PBD-ox, then removing the water from the interfacial region should have returned that behavior. We conclude, therefore, that absorption of water was probably not responsible for the loss of reversibility in this system.

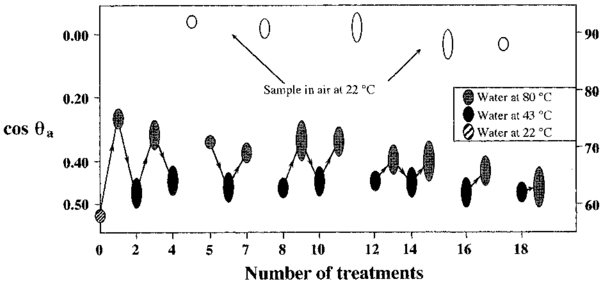


Figure 13. Contact angles of water (pH 1) on a single sample of PBD-ox that was cycled repeatedly between deionized water at 80 and 43 °C. Each time the sample emerged from the hot water, it was rinsed with deionized water, floated for 3 min on deionized water at room temperature, dried with a stream of nitrogen, and left in air under ambient conditions for 1−2 days (open ovals) before resuming the cycling against water at 80 and 43 °C. This procedure was repeated until the hydrophilicity of the surface became independent of the temperature of the water. The heights of the ovals indicate one standard deviation above and below the mean of the contact angle measurements.

A second hypothesis explaining the loss of reversibility of PBD-ox is that a change occurred in the amount or type of crystallinity (that can act as physical cross-links and thereby give rise to rubber elasticity) in the interfacial region as a result of cycling between high and low temperatures, i.e., that the reversible behavior could be annealed away. To test the hypothesis, we measured the wettability of a sample of PBD-ox after each step in the following control experiment (Figure 13): the sample was heated against water at 80 °C and then at 43 °C, for 15 min at each temperature. This procedure was then repeated to complete two heating/cooling cycles. The sample was then allowed to equilibrate at room temperature in air for 2 days so that it could reestablish an equilibrium amount of crystallinity. The sample was then heated against water for another 1.5 cycles (80 °C, then 43 °C, then 80 °C). Again, the sample was allowed to equilibrate at room temperature in air overnight before heating against water was continued. This type of "interrupted" temperature cycling was repeated several times. The results in Figure 13 show that allowing PBD-ox to reequilibrate at room temperature in air between heating cycles indeed prolonged the reversibility of the reconstruction behavior against water. In this case, the reversibility damped out gradually, rather than abruptly as in Figure 11. These results strongly suggest that the entropic effect in the reconstruction of PBD-ox is related to physical, rather than chemical, cross-linking and is associated with crystallinity (initially 15−29% in PBD) in the interfacial region.

In a separate experiment, we examined whether the metastable crystallinity responsible for the entropic reconstruction resulted from the way these films were prepared or whether it was an inherent property of the polymer itself. A sample of unmodified PBD was annealed against water at 85 °C for 2 h *prior* to oxidizing

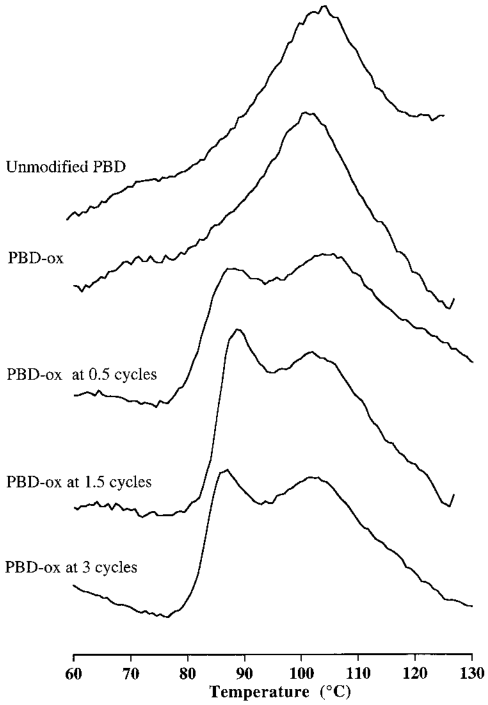


Figure 14. Differential scanning calorimetry scans of the melting temperature (T_m) region of unmodified PBD, PBD-ox, and PBD-ox cycled 0.5, 1.5, and 3 times between water at 80 and 43 °C.

it to produce PBD-ox. After oxidation, the sample was heated against deionized water at 80 °C, and the change in the advancing contact angle of water (pH 1) was monitored. After 15 min of heating against deionized water at 82 °C, the contact angle changed only slightly, from 57° to 61°. This experiment was repeated with the same result: the contact angle rose only from 61° to 64°. In another experiment, a sample of unmodified PBD was heated first against water at 85 °C for 2 h, and then heating in air at 83−86 °C for 2 h, before it was oxidized to PBD-ox. The results from this experiment, however, also showed only a small change in θ_a after heating PBD-ox against water at 80 °C for 15 min. This loss of entropic reconstruction behavior as a result of pre-annealing is consistent with the hypothesis that changes in the crystallinity at the interface caused by heating the film at 80 °C, which is near the onset of melting for the polymer (T_m range, 77−119 °C), are sufficient to produce a more stable configuration of the polymer from which the metastable states of interest are no longer accessible.

To obtain direct evidence for changes in crystallinity concomitant with annealing in this system, we used differential scanning calorimetry (DSC) to study PBD-ox before and after heating against deionized water (Figure 14). As expected, little if any change in the melting temperature (T_m) region accompanied the conversion of PBD to PBD-ox. Upon heating against water for only 20 min (0.5 heating/cooling cycle), however, this region changed dramatically, with a new T_m peak appearing at a lower temperature than the original T_m. This new peak intensified after 1.5 cycles but then remained unchanged after three complete cycles. A control experiment was performed to determine whether the appearance of the bimodal endotherm was specific to heating PBD-ox against water or rather was characteristic of the recrystallization of the bulk polymer upon heating and thus was independent of interfacial parameters. Two separate samples of unmodified PBD were used in this experiment: one sample was heated in air at 80 °C for 20 min, and the other sample was heated against deionized water at 80 °C for 20 min. A bimodal endotherm, similar to those in Figure 14, was observed in the DSC scans for each of these samples, indicating that these changes reflect the inherent behavior of the polymer itself.

Table 3. Average Values of Complex Modulus (G^*) for PBD-ox as a Function of Thermal Cycling

no. of cycles[a]	average G^* (Pa)
0	$(9.4 \pm 0.1) \times 10^7$
0.5	$(1.3 \pm 0.4) \times 10^8$
2	$(1.3 \pm 0.1) \times 10^8$
3	$(1.2 \pm 0.3) \times 10^8$

[a] One cycle involved heating PBD-ox against deionized water at 80 °C for 15 min, cooling to room temperature, heating against deionized water at 43 °C, and then cooling to room temperature.

The heat of fusion (calculated by the DSC instrument) of PBD-ox was 7.6 J/g; after equilibration against deionized water at 80 °C for 20 min and then cooling to room temperature, that value increased to 15.2 J/g. This increase in crystallinity of the polymer upon annealing should also increase the amount of physical cross-linking present.[43] To confirm this result and to complement the DSC data presented in Figure 14, we also measured G^* for four different samples of PBD-ox that had been treated with an increasing number of heating/cooling (80 °C/43 °C) cycles against water (Table 3). These results suggest that the overall amount of cross-linking of the polymer increased (thus producing an increased G^*) upon heating against water, consistent with the increase in crystallinity evident in the DSC data.

Conclusions

At present, there has been no systematic demonstration of the relationship between the various types of polymeric architecture and the thermal reconstruction of its surface. A clear understanding of how polymeric structure influences interfacial behavior, however, is necessary for the rational design of materials having both specific surface and bulk properties. We have worked toward this goal in this and previous studies.[12,15] In this paper, we examined the role of an important type of polymeric structure, cross-linking, on the interfacial dynamics of PBD. We expected that cross-linking would strongly modify the ability of functional groups to migrate into and out of the interfacial region and hypothesized the existence of three regimes of cross-linking (regimes I, II, and III) with characteristic types of reconstruction behavior.

The results reported here focus primarily on polymers having intermediate (regime II) levels of cross-linking and on the influence of rubber elasticity on their interfacial dynamics. The surface-modified polymer, PBD-ox, contains a limited number of polar groups relative to the number of nonpolar groups, and cross-linking (physical and perhaps chemical) tends to anchor segments of the polymer that lie near branch points. As a result, we believe that migration of polar groups to the polymer/water interface requires extension of the polymer chains out of entropically preferred, random-coil conformations. When the temperature is increased, however, the polymer chains recoil, pulling these polar groups away from the interface. This model is consistent with our observation that PBD-ox becomes hydrophobic when heated against hot water, as well as the other results reported here.

As a result of this entropic effect, the relative concentrations of polar and nonpolar groups at the interface of PBD-ox against water depended on temperature: the degree of hydrophobicity increased as the temperature of the water increased. This temperature-dependent reconstruction was reversible, but the number of cycles of heating and cooling giving reversible behavior depended on the thermal history of the sample and on the way that the experiment was run. When PBD-ox was heated against water for an extended period of time or cycled between hot and cool water repeatedly, it relaxed to an equilibrium state that was independent of temperature. Repetitive heating and cooling of the polymer film changed the amount and type of crystallinity, which was concomitant with the loss of reversibility. As a result, we believe that crystallites in the interfacial region of this polymer act as physical cross-links that produce the rubber elasticity responsible for this type of behavior. This loss of reversibility argues strongly against certain alternative explanations, involving chemical equilibria (e.g., reversible lactonization) or a lower critical temperature of solution, for the entropic effects in this system. Current studies underway in our group involve developing other polymeric systems for which rubber elasticity plays a significant role in determining the interfacial composition.

Acknowledgment. We gratefully acknowledge support for these studies from the Office of Naval Research (ONR). We also thank S. Khongtong, L. E. Stephans, and M. Uragami for helpful contributions and A. C. Miller for assistance with the XPS measurements. We acknowledge Lehigh University for its support of the Scienta ESCA facility.

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(22) We note that some reports describe contact angles measured on surfaces while they were held at temperatures that may allow simultaneously reconstruction at both the polymer/water and polymer/air interfaces, thus adding complexity to interpretations regarding composition near the three-phase contact line.

(23) We use enthalpy, instead of internal energy, to acknowledge the energetic contribution from small changes in volume upon extension. For the interfacial analogue, this choice is convenient because we consider the polymer/water interface as an inter*phase* with a small, but finite, volume and hence discuss changes in Gibbs (rather than Helmholtz) free energy.

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