Integration of Bulk and Interfacial Properties in a Polymeric System. 2. Rubber Elasticity at Polyisoprene/Water Interfaces

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ABSTRACT: After oxidation of the surface of cross-linked *cis*-1,4-polyisoprene with aqueous permanganate, the composition of its interface with water depended on temperature. The polymer remained hydrophilic against cool water but became more hydrophobic against hot water. These changes depended upon the amount of cross-linking and on the amount of surface oxidation. They were also reversible when cycled between high and low temperature, and this reversibility disappeared only gradually over many cycles. The system independence of this behavior provided an important test of our hypothesis that the surface dynamics of elastomers can involve a competition between enthalpically favorable solvation of hydrophilic functional groups at the polymer/water interface and entropically unfavorable chain extension.

Introduction

The relationship between bulk polymeric properties and interfacial composition and dynamics (reconstruction) has been a focus of attention in our research group because these connections offer opportunities for designing "smart", responsive systems.[1–4] In particular, we have proposed a model for understanding the role of cross-linking on interfacial dynamics and thermodynamics. Of greatest interest to us has been the role of rubber elasticity in producing coupled bulk and interfacial behavior in systems having intermediate (what we have called "regime II") levels of cross-linking.[1–3,5] We proposed that in this regime of cross-linking the composition of a polymer/water interface may be determined by a competition between enthalpically favorable solvation of hydrophilic functional groups and entropically unfavorable chain extension (i.e., rubber elasticity) necessary to bring the groups into contact with the water.[6] As a result, reconstruction of this interface may produce a hydrophilic polymer surface at room temperature and a hydrophobic surface at higher temperature.[7–9]

We observed this type of behavior for surface-modified films of both 1,4-polybutadiene (1,4-PBD) and 1,2-polybutadiene (1,2-PBD). In both cases, these changes were reversible when the polymer/water interfaces were cycled between high and low temperature, and for 1,4-PBD, the reversibility was persistent, damping out only gradually over many cycles of heating and cooling.[1] These studies demonstrated the usefulness of a chemically cross-linked, amorphous elastomer as a model system for testing our proposal.

Our hypothesis regarding the influence of rubber elasticity on interfacial dynamics is not specific to a single polymer or to isomers of a single polymer (e.g., 1,4-PBD and 1,2-PBD); rather, this behavior should be general to other elastomers as well. Hence, our goal in the work presented here was to test that hypothesis by examining a different elastomer, cross-linked *cis*-1,4-polyisoprene (PI). The particular polymer chosen had a molecular weight (M_w) of 800 000 g/mol and contained 97% cis-repeat units. It was attractive for this study because it was amorphous and had a low glass-transition temperature of approximately −60 to −50 °C. As a result, it reconstructed over convenient time scales at

temperatures between room temperature and 80 °C, the practical working range with water. In addition, polyisoprene is an important commercial polymer, especially in applications as an elastomeric composite material requiring contact against other substrates (e.g., in tires, drive belts, and bushings).[10]

As with PBD, the level of cross-linking of polyisoprene could be varied systematically by either radical cross-linking with an organic peroxide or vulcanization with sulfur. Chemical modification of its surface was also straightforward, by oxidation with aqueous permanganate. To produce samples that show temperature-actuated behavior, we used the same synthetic strategy that we applied successfully in the 1,4-PBD case. We reasoned that surface modification of a hydrophobic polymer, such as PBD or PI, on an aqueous solution should produce derivatized chains in *extended* conformations, due to "pinning" of the newly formed functional groups at the polymer/solution interface.[1] This system allowed us to relate the magnitude of "regime II" behavior with both the molecular weight between cross-links and the degree of surface modification.

Experimental Section

General. Dicumyl peroxide (98%; Aldrich), zinc oxide powder (95%; Aldrich), stearic acid (95%; Aldrich), 2-mercaptobenzothiazole (96%; Aldrich), sublimed sulfur (99+ %; Fisher), toluene (99%; E.M. Science), potassium permanganate (99+%; Fisher), potassium carbonate (99+%, Fisher), sodium bisulfite (A.C.S. reagent; Aldrich), and hydrochloric acid (36.5%, Mallinckrodt) were used as received.

Differential scanning calorimetry (DSC) was accomplished using a DSC-2920 modulated DSC (TA Instruments) with a standard cell under a nitrogen atmosphere. The sample size was in the range 10−20 mg, and the range of temperatures examined was −90 to 250 °C, with a ramp rate of 5 °C/min and temperature modulation of ±0.5 °C/min.

Dynamic mechanical testing for evaluation of the dynamic storage modulus (in the rubbery plateau region of the dynamic viscoelastic behavior) of the un-cross-linked, amorphous polymer was performed using a Rheometric dynamic analyzer (RDA-II).[11] This modulus was used to estimate the entanglement modulus, which was then used to calculate the average molecular weight between entanglements.

For X-ray photoelectron spectroscopic (XPS) analysis, samples were mounted on aluminum stubs and spectra obtained with
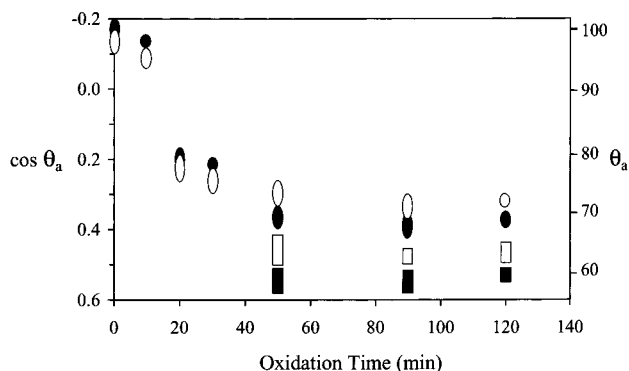
a Scienta ESCA300 spectrometer with monochromatized X-rays from an Al Kα source (1486.6 eV), as described previously.[1,2,4] The survey spectra were collected with a pass energy of 300 eV. The takeoff angle between the detector and the surface of the samples was ~15° or 90°, as noted. All spectra were referenced to the C(1s) peak set at 285.0 eV.

Cross-Linking and Film Formation. Five grams of synthetic *cis*-1,4-polyisoprene (M_w = 800 000 g/mol; 97% cis; Aldrich) was dissolved in ~100 mL of toluene and stirred overnight. For free-radical cross-linking, dicumyl peroxide (DCP) was separately predissolved in 10 mL of toluene and then added to the polymer solution and stirred for an additional 4 h. For sulfur cross-linking, stearic acid (0.05 g) and sulfur were predissolved in 10 mL of toluene and then added to the polymer solution with 0.25 g of zinc oxide (activator) and 0.05 g of 2-mercaptobenzothiazole (accelerator) and stirred for 4 h. The particular amount of DCP and sulfur used in each experiment is indicated in the corresponding figure captions. The polymer was then dried of solvent under vacuum to constant mass. These compound mixtures were stored at 4 °C until pressing, normally within 24 h.

Two polished aluminum plates (10 × 10 cm²) were cleaned by soaking in toluene for 30 min and wiping with cotton balls. A cardboard frame with a thickness of ~1 mm was cut to the dimensions of the plates and a window (~5 × 5 cm²) cut in the frame to serve as a mold. A tetrahedron press set at 2.0 klb of force was used to cure the polymer films at 150 °C for 84 min for the DCP cross-linking (8 half-lives)[12] and 65 min for the sulfur cross-linking. In separate experiments, we found 65 min to be sufficient to reach a limiting value of molecular weight between cross-links (M_c) for the sulfur vulcanization of PI. After cooling to room temperature (at a rate of ~12 °C/min for both types of cross-linking), the films were peeled from the aluminum plates using tweezers and cut into small pieces (~0.7 × 2.0 cm²). Each one of these pieces was swollen in a separate vial with 20 mL of toluene for at least 36 h to extract any unbound polymer chains that were not part of the cross-linked network and to measure the M_c. The optimum swelling time was determined by following the loss of mass by the swelled samples until it reached a constant value. Swelling for 36 h was generally sufficient to reach a constant mass for the cross-linked films. These samples were then dried in a vacuum at room temperature to constant mass.

Surface Oxidation of *cis*-1,4-Polyisoprene. Sample surfaces were oxidized with an aqueous solution of KMnO₄ (0.045 M) and K₂CO₃ (0.017 M), as described previously.[1]

Contact Angle Measurements. All advancing contact angles (θ_a) of water (pH 1 or 13) were taken at room temperature and ambient humidity using a Rame-Hart model 100 contact angle goniometer. Before determining θ_a on samples that had been heated against water, they were immediately cooled in room temperature water for 3 min to slow the surface reconstruction during the measurements. Each of the reported values of θ_a is an average of at least eight different measurements taken within 10–20 s of applying the drop of water.

Analysis of Oxidation Products by Infrared Spectroscopy. Both sides of an unextracted DCP-cross-linked PI film (M_c = 20 000 g/mol) with dimensions of ~1 × 3 cm² were oxidized by dipping into an aqueous solution of KMnO₄/K₂CO₃ for 50 min (vide supra). The oxidized film was then swollen in 15 mL of toluene for 36 h to extract those chains not attached to the network. The solvent was removed from the extract under vacuum at room temperature until ~0.5 mL remained. The concentrated extract was cast as a thin film on both sides of a 50 mm × 20 mm × 2 mm (60° angle of incidence) KRS-5 crystal, and the solvent was allowed to dry. Attenuated total reflectance infrared (ATR-IR) spectra were then collected using a Perkin-Elmer 1650 spectrometer. For comparison, a film that had not been oxidized was treated and analyzed in the same way.

Results and Discussion

Cross-Linking and Surface Oxidation. Cross-linked polyisoprene (PI) films were formed by curing for

Figure 1. Average molecular weight between cross-links (M_c) for cured *cis*-1,4-polyisoprene films as a function of the amount of cross-linking agent added (phr = parts per hundred of rubber), determined by the swelling method: (a) DCP-cross-linked and (b) sulfur-cross-linked.

eight half-lives with dicumyl peroxide (DCP) or vulcanization with sulfur, using zinc oxide and stearic acid as activators and 2-mercaptobenzothiazole as an accelerator.[13] After cross-linking, the films were swollen with toluene to remove any chains that were not bound to the network[14] and to measure the average molecular weight between cross-links (M_c) using the Flory–Rehner equation.[15] As shown in Figure 1, adjusting the amount of DCP or sulfur[16] added to the PI allowed systematic variation of the M_c. Both plots show a steep initial decline of about an order of magnitude in M_c, followed by a more gradual decrease, as the amount of cross-linking agent was increased. The resulting range of values of M_c was 104 000–3200 g/mol for DCP-cross-linked PI and 94 000–2300 g/mol for sulfur-vulcanized PI.

We expected the surface of cross-linked PI to react with basic, aqueous KMnO₄ (0.045 M) to produce a range of oxidized functional groups, including carboxylic acids, methyl ketones, and diols, thus providing a hydrophilic surface (eq 1).[1–3,17]

$$\text{[structure]} \xrightarrow[\text{RT}]{\text{KMnO}_4 / \text{K}_2\text{CO}_3} \text{[structures]} \quad (1)$$

Consistent with this expectation, the advancing contact angle (θ_a) of water (pH 1) on representative DCP-cross-linked (0.5 phr; M_c = 13 700 g/mol) and sulfur-

Figure 2. Advancing contact angles (θ_a) of water (pH 1, ovals) on the surface of cross-linked PI as a function of oxidation time on aqueous permanganate. The open symbols represent DCP-cross-linked samples (M_c = 13 700 g/mol, DCP 0.5 phr), and the filled symbols represent sulfur-cross-linked samples (M_c = 11 000 g/mol, sulfur 2.0 phr). The rectangular symbols at longer oxidation times represent contact angles on these surfaces using water at pH 13. The height of each symbol indicates the range of values within one standard deviation of the average.

vulcanized (2.0 phr; M_c = 11 000 g/mol) samples decreased from 97° to 74° (DCP) and from 100° to 68° (sulfur) during the first 50 min of treatment (Figure 2). We chose 50 min oxidations for all of the samples prepared for this study because continued treatment for 2 h did not significantly lower the contact angle further. We note that any chain scission as a result of this treatment would produce functional chain ends that would also contribute to the changes in interfacial behavior in this system.

Carboxylic acids at surfaces are known to be titrable using contact angles of water at different pHs, due to the greater hydrophilicity of ionized carboxylate groups relative to the uncharged parent acids.[18] Thus, the lower contact angles of basic water (pH 13) on the oxidized surfaces (Figure 2), 64° (DCP) and 58° (sulfur), were consistent with the presence of ionizable carboxylic acid groups.[1,2] Infrared spectra of DCP-cross-linked PI film (M_c = 20 000 g/mol) that had been oxidized in this way were inconclusive. Spectroscopic evidence for the formation of carboxylic acid groups, however, was provided by a separate experiment. Permanganate oxidation of a DCP-cross-linked PI film *that had not been swollen in toluene to extract unbound chains* allowed the oxidized free chains to be extracted and preconcentrated for infrared analysis. An unoxidized sample was also extracted and analyzed for comparison. The appearance of a new carbonyl stretching band at 1718 cm^{-1} (Figure 3) in the spectrum of the oxidized sample was consistent with the presence of carboxylic acids and/or ketones.[19]

X-ray photoelectron spectra of DCP-cross-linked films (M_c = 20 000 g/mol) before and after permanganate oxidation also provided evidence of surface oxidation. Survey spectra at a shallow takeoff angle (~15°, Figure 4a) revealed much more oxygen in the oxidized interphase (37.0 atom %) than in the unoxidized one (14.6 atom %). Survey spectra at a high takeoff angle (~90°, Figure 4b) also revealed an increase in the amount of oxygen, from 9.4 to 27.0 atom %, upon oxidation but showed less oxygen overall. The angular dependence of the oxygen photoemission indicates that most of the surface oxidation occurred within the XPS interphase (top 50–100 Å).

Temperature-Dependent Reconstruction of Surface-Oxidized PI against Water. Surface-oxidized
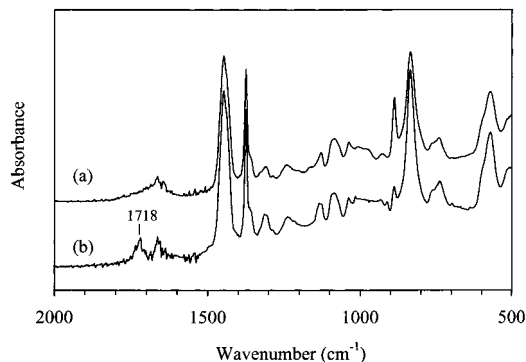
Figure 3. Attenuated total reflectance infrared spectra of (a) extracted unmodified *cis*-1,4-polyisoprene and (b) extracted oxidized *cis*-1,4-polyisoprene after 50 min in an aqueous solution of KMnO$_4$/K$_2$CO$_3$.
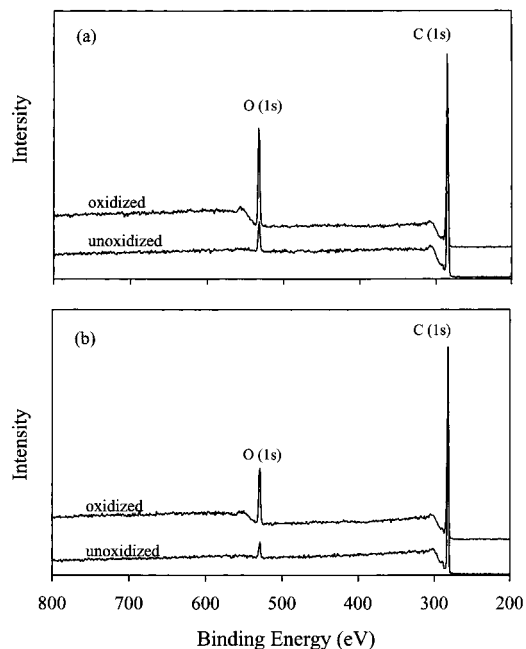
Figure 4. Survey XPS spectra of DCP-cross-linked PI (M_c = 20 000 g/mol), before and after surface oxidation: (a) 15° takeoff angle and (b) 90° takeoff angle.

samples of DCP-cross-linked (0.2 phr; M_c = 21 800 g/mol) and sulfur-cross-linked (1.5 phr; M_c = 23 000 g/mol) PI films having approximately the same M_c were allowed to equilibrate against water at various temperatures. The heated samples were then cooled to room temperature, and advancing contact angles of water were measured to assess the reconstruction of the surfaces (Figure 5). The surfaces of both types of sample were inert at room temperature (RT) and remained hydrophilic. As the temperature of the water was increased, however, the surfaces became increasingly hydro*phobic*.[20] This behavior mirrors that of surface-modified 1,4-PBD and is consistent with our hypothesis regarding the importance of entropy and rubber elasticity (temperature-dependent restoring force) in this "regime II" reconstruction behavior. The magnitude of the change in wettability, expressed as the difference in the values of cos θ_a before and after heating against water at various temperatures (Δ cos θ_a), tended to be larger for the samples cross-linked with sulfur than for those cross-linked with DCP, due primarily to the greater hydrophilicity of those surfaces after oxidation. The kinetics of reconstruction for both types of sample
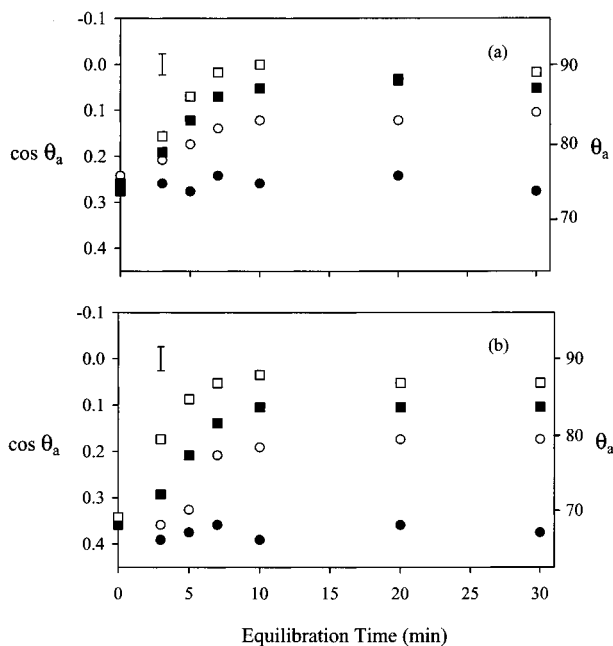
Figure 5. Advancing contact angles of water (pH 1) on surface-oxidized samples as a function of time against water at various temperatures: (a) DCP-cross-linked films (M_c = 21 800 g/mol, DCP 0.2 phr) and (b) sulfur-cross-linked films (M_c = 23 000 g/mol, sulfur 1.5 phr). The symbols indicate the different temperatures: room temperature (●), 60 °C (○), 70 °C (■), and 80 °C (□). The error bar in each plot indicates 2 times the largest standard deviation for any of the points, in $\cos \theta_a$.
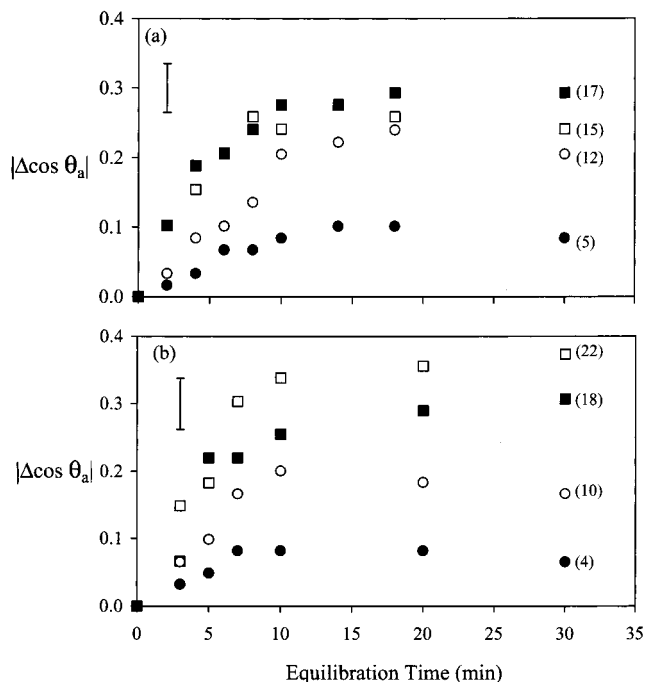

Figure 6. Kinetics of the change in $|\Delta \cos \theta_a|$ (H$_2$O, pH 1) on surface-modified PI as a function of time against water at 80 °C: (a) DCP-cross-linked films with M_c = 5400 g/mol (●), M_c = 8200 g/mol (○), M_c = 65 000 g/mol (■), M_c = 104 000 g/mol (□) and (b) sulfur-cross-linked films with M_c = 2400 g/mol (●), M_c = 7600 g/mol (○), M_c = 23 000 g/mol (■), M_c = 94 000 g/mol (□). The error bar in each plot indicates 2 times the largest standard deviation for any of the points, in $\cos \theta_a$, and the numbers in parentheses give the corresponding change in the advancing contact angle.

was fast above room temperature, requiring no more than 10 min to reach a steady-state composition.
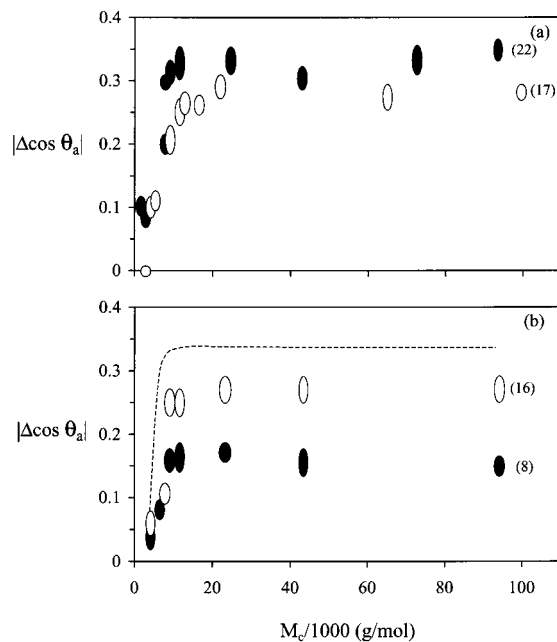
Figure 7. Limiting change in $|\Delta \cos \theta_a|$ (H$_2$O, pH 1) on surface-modified PI before and after heating against water as a function of molecular weight between cross-links (M_c): (a) equilibration of DCP-cross-linked (open) and sulfur-cross-linked (filled) films against water at 80 °C and (b) sulfur-cross-linked films heated against water at 60 °C (filled) or at 70 °C (open). The dashed line shows the data for samples heated on water at 80 °C, for comparison. The height of each data point indicates values within one standard deviation of the average, and the numbers in parentheses give the corresponding change in the advancing contact angle.

To test our hypothesis that regime II behavior should characterize *lightly* cross-linked elastomers, in this case PI, we systematically varied M_c with each type of cross-linking and measured the resulting magnitudes of $\Delta \cos \theta_a$. The surfaces of appropriately cross-linked films were oxidized for 50 min on basic, aqueous KMnO$_4$ to produce samples for these experiments. The films were then equilibrated against water at 80 °C, and the wettability of their surfaces was monitored as a function of time. The reconstructions were fast (Figure 6), with all of the samples reaching steady-state values of contact angle within approximately 10−20 min. The kinetics were, nonetheless, slower than found for 1,4-PBD, which equilibrated at these temperatures within 5−10 min.[1] This difference likely reflects the steric hindrance of isoprenyl methyl groups that could inhibit chain diffusion, relative to 1,4-PBD.[21,22] The rates of local motion of PI chains are known to be slower than those of 1,4-PBD by about an order of magnitude.[21]

As expected, at high levels of cross-linking (small M_c), the magnitude of the change in wettability ($|\Delta \cos \theta_a|$) was small (Figures 6 and 7a), indicating that the interfacial chains were too constrained to allow significant chain extension and hence elasticity. As the amount of cross-linking was reduced (increasing M_c), $|\Delta \cos \theta_a|$ rose sharply (Figure 7a), eventually reaching a plateau for values of M_c greater than or equal to the chain entanglement length (M_e) for this polymer, approximately 9000 g/mol. These results are consistent with those found for 1,4-PBD, with the initial rise indicating the onset of regime II behavior. The plateau suggests that chain entanglement places a lower limit on the amount of effective (chemical and physical) cross-linking in the interfacial region of these samples.[23]
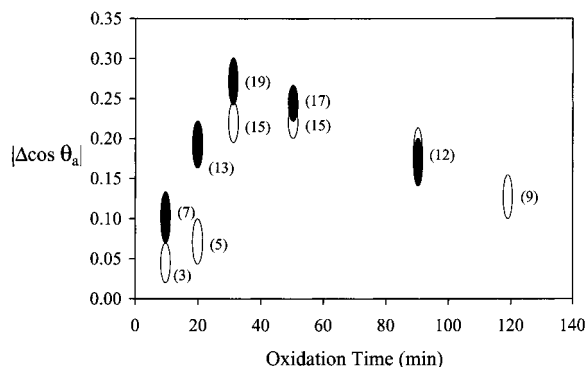
Figure 8. Limiting change in $|\Delta \cos \theta_a|$ (H$_2$O, pH 1) on surface-modified PI before and after heating against 80 °C water as a function of the oxidation time used to prepare the samples: the open symbols represent DCP-cross-linked films ($M_c = 13\,700$ g/mol, DCP 0.5 phr), and the filled symbols represent sulfur-cross-linked films ($M_c = 11\,000$ g/mol, sulfur 2.0 phr). The height of each data point indicates values within one standard deviation of the average, and the numbers in parentheses give the corresponding change in the advancing contact angle.

An alternative explanation for the plateau could be that the surface becomes saturated with hydrophobic groups at 80 °C, which could limit the increase in the value of $|\Delta \cos \theta_a|$. We ruled out this possibility for 1,4-PBD by demonstrating a similar, but lower, plateau for samples equilibrated at lower temperature. Likewise for PI (Figure 7b), the reconstruction of samples equilibrated at 60 or 70 °C also plateaued at about the same value of M_c as found at 80 °C, but at smaller values of $|\Delta \cos \theta_a|$.

At the outset of this work, we recognized the importance of the degree of surface oxidation on the magnitude of $\Delta \cos \theta_a$. Although a 50 min oxidation produced a limiting hydrophilicity in this system (Figure 2), its connection to the magnitude of $\Delta \cos \theta_a$ remained to be demonstrated. A priori, we expected a plot of $|\Delta \cos \theta_a|$ vs degree of surface oxidation to display a maximum. If the surface were under-functionalized, it would never be sufficiently hydrophilic to allow a large change in cos θ_a with temperature. If the surface were over-functionalized, the oxidized repeat units might be sufficiently abundant in the interfacial region that chain extension would not be necessary to bring them into contact with the water at the interface. Indeed, as with the 1,2-PBD-ox and 1,4-PBD-ox systems, the cross-linked PI films reached a maximum in the magnitude of $\Delta \cos \theta_a$ at approximately 30–50 min of oxidation on aqueous permanganate (Figure 8).[24]

Reversibility of Reconstruction in these Samples. Cycling the surface-oxidized PI films against water at 80 °C and at room temperature resulted in a well-defined oscillation of the wettability of the surfaces (Figure 9), hydrophobic at high temperature and hydrophilic at room temperature. Thermograms obtained using differential scanning calorimetry contained no evidence of a melting transition (T_m) and no significant change in the glass transition temperature (T_g, Table 1) as a result of the treatments indicated in Figure 9.

As expected from the data in Figure 7a, the size of the changes in cos θ_a in these cycling experiments varied with M_c, and the most lightly cross-linked films generally showed the largest changes. For both types of sample, however, these changes gradually decayed, over ∼15 cycles for the DCP-cross-linked samples and over 6–8 cycles for the sulfur-cross-linked samples. Two
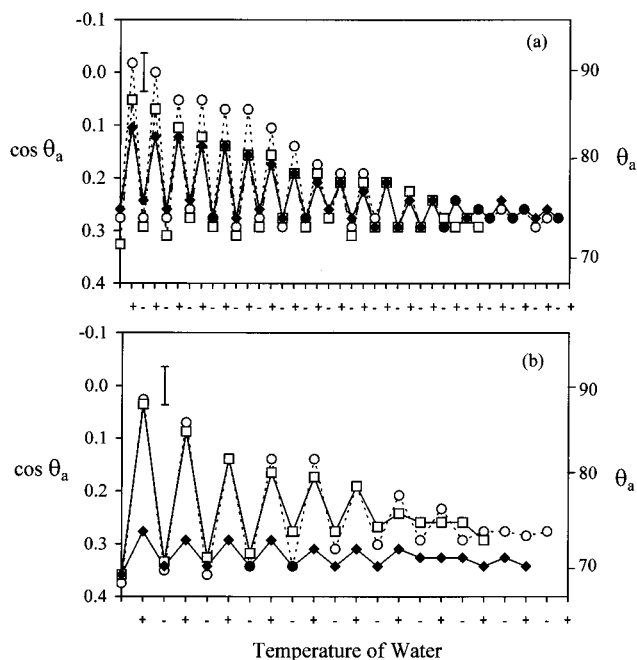

Figure 9. Advancing contact angles of water (pH 1) on surface-modified PI films upon cycling between water at 80 °C (+) and room temperature (−): (a) DCP-cross-linked films $M_c = 65\,000$ g/mol (○), $M_c = 11\,700$ g/mol (□), $M_c = 5400$ g/mol (♦), and (b) sulfur-cross-linked films $M_c = 75\,000$ g/mol (○), $M_c = 11\,000$ g/mol (□), $M_c = 3200$ g/mol (♦). The error bar in each plot indicates 2 times the largest standard deviation for any of the points, in cos θ_a.

Table 1. Glass Transition Temperature (in °C) of DCP- and Sulfer-Cross-Linked PI Films

	DCP-cross-linking			S-cross-linking		
M_c (g/mol)	65 000	13 700	5400	75 000	11 000	3200
before equilibration	−65	−65	−54	−64	−59	−48
after equilibration	−64	−64	−55	−64	−57	−49

features of these data are striking, when compared to the results of our previous study on 1,4-PBD. First, the persistence of the oscillations reported here is much greater, by almost a factor of 2, than for 1,4-PBD. We attribute this difference to the steric influence of the isoprenyl methyl groups in hindering alignment of polymer chains in the low-temperature (i.e., chain-extended) configuration, a mechanism known to reduce elasticity.[21,22,25] Extensive studies of the possible cause(s) of the damping of oscillation will be the focus of a subsequent publication. The second difference between these results and those of our previous study is that the most highly sulfur-cross-linked PI film remained hydrophilic throughout the cycling experiment, whereas the corresponding 1,4-PBD film became hydrophobic in the first cycle and then remained so throughout the experiment. We had attributed this 1,4-PBD behavior to bond interchange reactions of the polysulfide bridges,[26] especially at elevated temperature, which could effectively move branch points and trap the polymer interface in the hydrophobic (high-T) configuration. If this hypothesis were correct, then we would expect the isoprenyl methyl groups to hinder this process as well.

Conclusions

Our studies of the temperature-dependent reconstruction of surface-modified elastomers against water have

revealed close analogies between cross-linked *cis*-1,4-polyisoprene and 1,4-polybutadiene. Surface-modified samples of both PI and 1,4-PBD films reconstructed reversibly against water to produce a hydrophobic surface at high temperature and a hydrophilic surface at room temperature. This reversibility was persistent in both polymers and damped out only gradually as samples were cycled repeatedly between water at high and low temperature. This common behavior is consistent with our hypothesis that lightly cross-linked elastomers can display surface dynamics (and thermodynamics) that reflect the entropic changes associated with rubber elasticity. Specifically, chains near the surface must extend out of random-coil conformations to accommodate hydrogen-bonding at the polymer/water interface. These changes reflect changes in the relative surface concentrations of hydrophobic and hydrophilic functional groups, and the mobility of the chain segments carrying those groups depends on the molecular weight between cross-links (up the chain-entanglement length). Consequently, for both polymers, the magnitude of effect of rubber elasticity on surface composition was small for high levels of cross-linking and increased at lower levels of cross-linking. These changes also depended on, but were not specific to, the particular method of cross-linking used, with radical cross-linking generally giving more persistent reversibility. The degree of surface functionalization is also an important experimental parameter for both polymers, with maximum temperature dependence characterizing surfaces with an intermediate level of surface oxidation. These results confirm the correlation of interfacial and bulk mechanical properties in elastomers and the importance of thinking of a polymer and its surface as an integrated system.

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(5) To summarize, we proposed that in regime I (un-cross-linked) systems interfacial dynamics would be unimpeded by cross-linking and would tend toward a "classical" minimization of interfacial free energy, in regime II (lightly cross-linked) systems, interfacial dynamics would be coupled to the extension of chains out of random-coil conformation (i.e., rubber elasticity), and in regime III (heavily cross-linked) systems motion of chain segments in the interfacial region would be highly constrained. See refs 1−3.

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