

# Integration of Bulk and Interfacial Properties in a Polymeric System: Rubber Elasticity at a Polybutadiene/Water Interface

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**Abstract:** Oxidation of the surface of cross-linked 1,4-polybutadiene provided a hydrophilic substrate that reconstructed against hot water to become more hydrophobic. Subsequent equilibration against water at room temperature returned its original hydrophilicity. These temperature-dependent changes in the relative concentrations of hydrophobic and hydrophilic moieties at the polymer/water interface are interpreted as arising from the entropic influence of chain extension, associated with rubber elasticity. As expected, the magnitude of this effect depended on the cross-link density of the polymer and the degree of oxidation of the surface. The reversibility of the reconstruction when the water was cycled between high and low temperature damped out only gradually over many cycles.

## Introduction

Although the performance of polymers in many applications depends primarily on their bulk mechanical properties, the increased use of polymeric materials has also brought attention to the problems associated with their interfacial properties (e.g., adhesion, wettability, biocompatibility).<sup>1</sup> The relationship between the bulk mechanical properties of a polymer and the composition and dynamics at its surface (“reconstruction”) has been a focus of attention in our research group.<sup>2,3</sup> Specifically, we have used organic chemistry at polymer surfaces to provide the means for examining the role of rubber elasticity<sup>2</sup> and of glass-transition temperature<sup>3</sup> in determining the interfacial behavior of the polymer. This connection between the underlying architecture (and mechanical properties) of a polymer and its interfacial dynamics provides a rational basis for the design of “smart” surfaces that respond reversibly to external stimuli (e.g., changes in temperature).<sup>2,4</sup> Thus treating a polymer as an *integrated* system—comprising correlated bulk and interfacial properties—presents unique opportunities at the intersection of materials science and surface chemistry.

Previously, we reported evidence that changes in entropy strongly influence the reconstruction of surface-modified 1,2-

polybutadiene (PBD-ox) against water.<sup>2</sup> Unlike most other systems,<sup>3–6</sup> the reconstruction of PBD-ox produced a surface composition that depended on temperature. When heated against water, the surface became more hydrophobic with increasing temperature, contrary to expectations based on the influence of enthalpy on the interfacial free energy of this system. Our hypothesis regarding the source of this effect focuses on rubber elasticity, i.e., an entropic loss associated with the extension of polymer chains required to bring polar functional groups to the polymer/water interface.<sup>7</sup> This chain extension is required because branch points in the network inhibit the local mobility of segments attached to them. The temperature-dependent restoring force on a single polymer chain can be approximated, for example, using the Freely Jointed Chain (FJC) Model<sup>8</sup> (eq

$$F = \left[ \frac{3kT}{Nl^2} \right] r \quad (1)$$

1, where  $F$  is the restoring force,  $k$  is Boltzmann’s constant,  $T$  is temperature,  $N$  is the number of polymer segments,  $l$  is the polymer segment length, and  $r$  is end-to-end distance).<sup>9</sup> Hence we hypothesize that the composition at the polymer/water

(5) Whitesides, G. M.; Ferguson, G. S. *Chemtracts* **1988**, *1*, 171–187 and references therein.

(6) For additional recent work, see: Chen, W.; McCarthy, T. J. *Macromolecules* **1999**, *32*, 2342–2347. Wang, J.; Mao, G.; Ober, C. K.; Kramer, E. J. *Macromolecules* **1997**, *30*, 1906–1914. Tretinnikov, O. N.; Ikada, Y. *Langmuir* **1994**, *10*, 1606–1614. Xie, X.; Gengenbach, T. R.; Griesser, H. J. *J. Adhes. Sci. Technol.* **1992**, *6*, 1411–1431. Deng, Z.; Schreiber, H. P. *J. Adhes.* **1991**, *36*, 71–82.

(7) For other work proposing entropic influences at polymer surfaces, see: Griesser, H. L.; Dai, L.; Gengenbach, T. R.; Chatelier, R. C. *Polym. Prepr.* **1997**, *38*, 1081–1082. Walton, D. G.; Mayes, A. M. *Phys. Rev. E: Stat. Phys. Plasmas, Fluid, Relat. Interdiscip. Top.* **1996**, *54*, 2811–2815. Yethiraj, A. *Phys. Rev. Lett.* **1995**, *74*, 2018–2021. Sikka, M.; Singh, N.; Karim, A.; Bates, F.; Satija, S. K.; Majkrzak, C. F. *Phys. Rev. Lett.* **1993**, *70*, 307–310.

(8) Flory, P. J. *Statistical Mechanics of Chain Molecules*; Hanser Publishers: New York, 1989. Gent, A. N. In *Science and Technology of Rubber*; Eirich, F. R., Ed.; Academic Press: New York, 1978; pp 1–21.

(9) This equation results from truncation of the series expansion of the inverse Langevin function in the full FJC Model after the first term, and therefore should be useful only for small displacements.

(1) Valint, P. L.; Grobe, G. L.; McGee, J. A.; Ammon, D. A.; Rabke, C. E. In *Polymer Surfaces and Interfaces: Characterization, Modification and Application*; Mittal, K. L., Lee, K., Eds.; VSP: Zeist, The Netherlands, 1997; pp 71–82. Sheu, M.; Patch, G. M.; Loh, I.; Buretta, D. A. In *Polymer Surfaces and Interfaces: Characterization, Modification and Application*; Mittal, K. L., Lee, K., Eds.; VSP: Zeist, The Netherlands, 1997; pp 83–90. Peterson, B. L.; Pangborn, R. N. *J. Compos. Mater.* **1991**, *25*, 887–906. Ratner, B. D.; Horbett, T.; Hoffman, A. S.; Hauschka, S. P. *J. Biomed. Mater. Res.* **1975**, *9*, 407–422.

(2) Carey, D. H.; Ferguson, G. S. *J. Am. Chem. Soc.* **1996**, *118*, 9780–9781. Carey, D. H.; Grunzinger, S. J.; Ferguson, G. S. *Macromolecules* **2000**, *33*, 8802–8812.

(3) Rouse, J. H.; Ferguson, G. S. *Macromolecules* **1999**, *32*, 1665–1671.

(4) For reviews, see: Bergbreiter, D. E. In *Field Responsive Polymers: Electroresponsive, Photoresponsive and Responsive Polymers in Chemistry and Biology*; Khan, I. M., Harrison, J. S., Eds.; American Chemical Society: Washington, DC, 1999; pp 301–310. Ferguson, G. S.; Whitesides, G. M. In *Modern Approaches in Wettability: Theory and Applications*; Schrader, M. E., Leob, G. I., Eds.; Plenum: New York, 1992; pp 143–175.

interface is determined by an energetic balance between this entropically unfavorable chain extension out of random coils and the enthalpically favorable hydrogen bonding at the interface.

We previously proposed that there are three regimes of reconstruction behavior associated with different levels of cross-linking:<sup>2</sup> Regime I (un-cross-linked), characterized by interfacial dynamics unimpeded by cross-linking; Regime II (lightly cross-linked), influenced by coupling of interfacial dynamics to the extension of chains out of random-coil conformations (i.e., rubber elasticity); and Regime III (heavily cross-linked), characterized by limited motion of chain segments in the interfacial region. We also demonstrated that in addition to an intermediate level of cross-linking, an intermediate amount of surface modification was also necessary for PBD-ox to show Regime-II behavior. This requirement suggests that highly functionalized surfaces may not require chain extension to bring hydrophilic functional groups into contact with water. Surfaces with too few hydrophilic functional groups to affect wettability, in contrast, should remain hydrophobic against water.

Our hypothesis is not specific to the syndiotactic 1,2-PBD used to prepare PBD-ox and therefore implies that other systems should also show this type of behavior. In fact, a primary goal of the work presented here was to test this hypothesis by looking for other elastomers that display "Regime II" behavior. A second goal of the work presented here was to use an amorphous polymer with a well-defined level of chemical cross-linking, and thereby avoid the complexity of the PBD-ox system introduced by its partial crystallinity. The entropic reconstruction observed for PBD-ox was initially reversible, but it stopped after only a few cycles of heating and cooling. This loss of reversibility was accompanied by changes in the crystallinity in the polymer, which provided the physical cross-linking that produced rubber elasticity at its interface.<sup>2</sup> Using a chemically cross-linked amorphous polymer would not only simplify interpretation of the data, but if successful, it would also provide a system less likely to lose its reversibility when annealed.

In this paper, we report the successful preparation of a surface-modified 1,4-polybutadiene (PBD) whose surface reconstructs reversibly when heated and cooled against water. This polymer was chosen because it is amorphous, containing a random mixture of cis and trans repeat units ( $M_w = 420\,000$  g/mol; 36% cis, 55% trans, and 9%-1,2), and has a sufficiently low glass-transition temperature (approximately  $-80$  to  $-90$  °C) to allow reconstruction at temperatures between about 20 and 80 °C (the practical working range with water). Its carbon-carbon double bonds provided sites for convenient cross-linking and surface modification. Samples were prepared systematically with well-defined levels of cross-linking, using radical cross-linking or sulfur vulcanization. Surface oxidation then provided well-defined samples that showed Regime II reconstruction behavior against water. The magnitude of the changes in wettability with temperature varied with both the molecular weight between cross-links and the degree of surface modification.

## Experimental Section

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

For X-ray photoelectron spectroscopic (XPS) analysis, samples were mounted and spectra obtained with a Scienta ESCA300 spectrometer

with monochromatized X-rays from an Al  $K_{\alpha}$  source (1486.6 eV), as described previously,<sup>3,10,11</sup> with a takeoff angle between the detector and the surface of sample of 16.5°. Differential scanning calorimetry (DSC) was done by using a DSC-2920 Modulated DSC (TA Instruments) with a standard cell under a nitrogen atmosphere. The sample size was in the range of 10–20 mg, and the range of temperatures examined was  $-120$  to 150 °C, with a ramp rate of 5 °C/min and temperature modulation of  $\pm 0.5$  °C/100 s.

**Cross-linking and Film Formation.** Five grams of 1,4-polybutadiene ( $M_w = 420\,000$  g/mol; 36% cis, 55% trans, and 9% 1,2; Aldrich) were dissolved in 50 mL of toluene and stirred overnight. For free-radical cross-linking, the required amount of dicumyl peroxide (DCP)<sup>12</sup> was separately predissolved in 10 mL of toluene, then added to the polymer solution, which was stirred for an additional 2 h. For sulfur cross-linking, stearic acid (0.05 g) and the required amount of sulfur<sup>12</sup> were predissolved in 10 mL of toluene, then added to the polymer solution with 0.25 g of zinc oxide (activator) and 0.05 g of 2-mercaptobenzothiazole (accelerator) with stirring for 2 h. The solvent was then removed under vacuum until a stable weight was observed. These compound mixtures were stored at 4 °C until pressing, normally within 24 h.

Two polished aluminum plates ( $10 \times 10$  cm<sup>2</sup>) were cleaned by soaking in toluene for 30 min. A cardboard frame with a thickness of  $\sim 1$  mm was cut to the dimensions of the plates, and a hole ( $\sim 5 \times 5$  cm<sup>2</sup>) was cut in the frame to serve as a mold. A Tetrahedron Press set at 1.0 klb of force was used to cure the polymer films at 150 °C. The curing time was 84 min for the DCP cross-linking (8 half-lives)<sup>13</sup> and 45 min for the sulfur cross-linking. This curing time for the sulfur-cross-linked samples was found, in separate experiments, to be sufficient to reach a limiting value of molecular weight between cross-links ( $M_c$ ). The cooling rate was set at 280 °C/min for both types of cross-linking. The pressed films were peeled away from the aluminum plates with tweezers, then wrapped in aluminum foil and stored at 4 °C. Usually within 24 h, the films were cut into small pieces ( $\sim 0.7$  cm  $\times$  2.0 cm) and swelled individually in 20 mL of toluene for at least 36 h to extract any unbound polymer chains and to measure the  $M_c$ . The solvent was then removed under vacuum at room temperature until the sample reached a constant weight.

**Surface Oxidation of 1,4-Polybutadiene.** 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 1,4-PBD film at room temperature.<sup>2</sup> After oxidation for the chosen amount of time, the sample was rinsed with deionized water, floated on aqueous  $NaHSO_3$  (0.05 M) for 3 min, rinsed with deionized water, floated on aqueous HCl (0.1 M) for 3 min, rinsed with deionized water, and then blown dry with a stream of  $N_2$ .

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

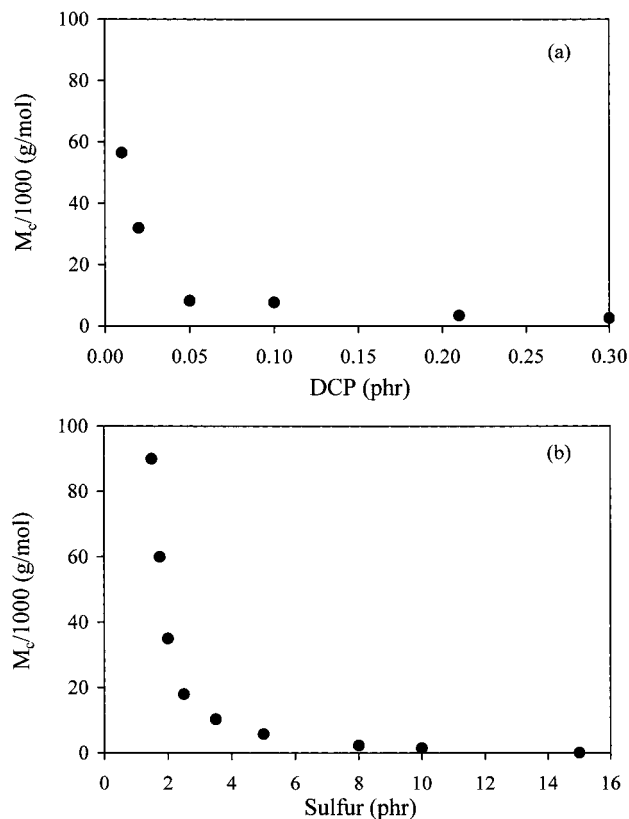
**Dynamic Mechanical Measurements.** Dynamic mechanical testing was performed with a Rheometric Dynamic Analyzer (RDA-II). Samples were cut to a standard rectangular geometry for torsional measurements with dimensions of about 30 mm  $\times$  10 mm  $\times$  1 mm. The entanglement modulus was measured at a frequency of 1.0 Hz while sweeping the temperature from  $-100$  to 200 °C with a ramp rate of 5 °C/min at a constant strain of 0.1%. Measurement of the entanglement modulus at 24 °C by sweeping the frequency from 0.05

(10) Carey, D. H.; Ferguson, G. S. *Macromolecules* **1994**, *27*, 7254–7266.

(11) Mumbauer, P. D.; Carey, D. H.; Ferguson, G. S. *Chem. Mater.* **1995**, *7*, 1303–1313.

(12) The amounts of DCP and sulfur used in each experiment were different and are given in the relevant figures.

(13) Brandrup, J.; Immergut, E. H.; Grulke, E. *Polymer Handbook*, 4th ed.; John Wiley & Sons: New York, 1999.



**Figure 1.** Average molecular weight between cross-links ( $M_c$ ) for cured 1,4-polybutadiene films, determined by the swelling method: (a) DCP cross-linked and (b) sulfur cross-linked.

to 60 Hz in log mode at a constant strain of 1.0% gave the same result. The instrument software was used to control the test and to analyze the data.

## Results and Discussion

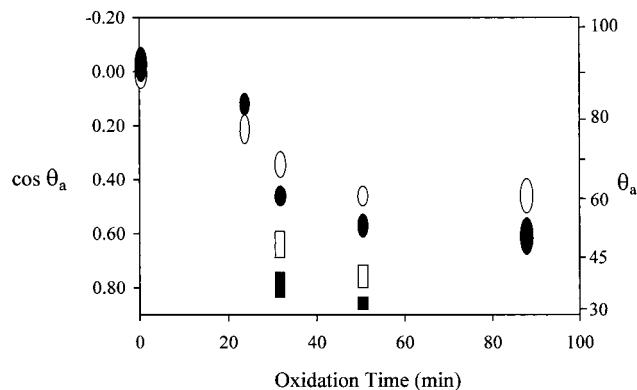
**Sample Preparation and Characterization.** Polymer films were formed by chemically cross-linking 1,4-PBD with either dicumyl peroxide (DCP) or sulfur. The DCP-cross-linked films were cured for eight half-lives at 150 °C. The sulfur-vulcanized films were cured with use of zinc oxide and stearic acid as activators and 2-mercaptobenzothiazole as an accelerator.<sup>14</sup> The amount of cross-linking in both cases was established by measuring the average molecular weight between cross-links ( $M_c$ ) using the swelling method, with toluene as a solvent and the Flory–Rehner equation to interpret the data.<sup>15</sup> Figure 1 shows the dependence of  $M_c$  on the nominal<sup>16</sup> concentration of cross-linking agent in the films for both curing systems. The value of  $M_c$  for the DCP-cross-linked films fell sharply from 58 000 to 8200 g/mol when the concentration of DCP was raised from 0.01 to 0.05 phr,<sup>17</sup> and then gradually fell further to approximately 2600 g/mol when the concentration of DCP was raised to 0.30 phr. Likewise, the  $M_c$  for the sulfur-cross-linked films initially fell from 90 000 to 5800 g/mol when the

(14) Coran, A. Y. In *Science and Technology of Rubber*; Eirich, F. R., Ed.; Academic Press: New York, 1978; pp 291–338. Hofmann, W. *Vulcanization and Vulcanizing Agents*; Maclaron and Sons: London, 1967.

(15) Sperling, L. H. *Introduction to Physical Polymer Science*, 2nd ed.; John Wiley & Sons: New York, 1992. Queslel, J. P.; Mark, J. E. *J. Chem. Phys.* **1985**, *82*, 3449–3452.

(16) It is possible that the actual concentrations of the cross-linking agents may be lower due to volatilization when the solvent was removed under vacuum.

(17) The acronym “phr” stands for parts per hundred of rubber (i.e., polymer) by weight. See: Alger, M. *Polymer Science Dictionary*, 2nd ed.; Chapman & Hall: New York, 1997; p 374.

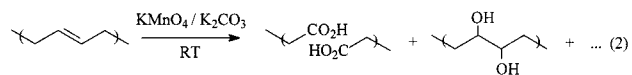


**Figure 2.** Change in advancing contact angles ( $\theta_a$ ) of water (pH 1, ovals) on the surface of cross-linked 1,4-PBD oxidized as a function of time on aqueous permanganate: unshaded symbols represent DCP-cross-linked 1,4-PBD ( $M_c = 8200$  g/mol, DCP 0.05 phr); and shaded symbols represent sulfur-cross-linked 1,4-PBD ( $M_c = 5800$  g/mol, sulfur 5.0 phr). The rectangular symbols represent contact angles on these surfaces using water at pH 13. The height of each symbol indicates values within one standard deviation of the average.

concentration of sulfur was raised from 1.5 to 5 phr, and then slowly dropped to 900 g/mol as the concentration of sulfur was raised to 15 phr. These methods provided the means to vary the amount of cross-linking systematically in the samples, and thereby allowed us to explore the dependence of reconstruction behavior on cross-link density.

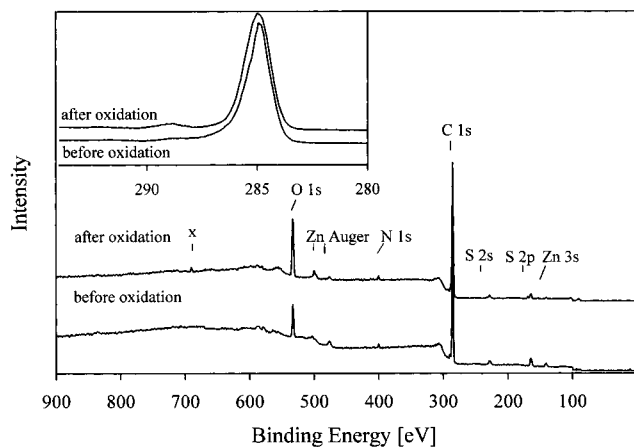
To ensure that the surface reconstruction monitored in these studies was not due to the migration (or “blooming”) to the surface of polymer chains that were not part of the cross-linked network, we extracted the unbound fraction by swelling the cross-linked films in toluene.<sup>18</sup> By following the weight loss during swelling of the sulfur-cross-linked samples with the lowest cross-link density ( $M_c = 90\,000$  g/mol) as well as another with a higher cross-link density ( $M_c = 5800$  g/mol), we found that 36 h of swelling was generally sufficient to extract the unbound fractions. This method was used to purify all samples from both cross-linking systems.

The surface of cross-linked 1,4-PBD was oxidized with an aqueous solution of  $\text{KMnO}_4$  (0.045 M) and  $\text{K}_2\text{CO}_3$  (0.017 M) to introduce carboxylic acid groups, and perhaps other oxidized functional groups, and thereby provide a hydrophilic surface for evaluation of interfacial mobility (eq 2).<sup>2</sup> As expected, the



advancing contact angle ( $\theta_a$ ) of water (pH 1) decreased as a function of the oxidation time for both types of cross-linked sample, consistent with the introduction of hydrophilic functionality. Figure 2 shows the advancing contact angles of water on representative DCP-cross-linked (0.05 phr;  $M_c = 8200$  g/mol) and sulfur-vulcanized (5 phr;  $M_c = 5800$  g/mol) samples that had been oxidized with this basic, aqueous permanganate at room temperature for various lengths of time. During the first 50 min of these treatments,  $\theta_a$  (pH 1) dropped from about 90° to 64° (DCP) or to 56° (sulfur). Treatment for 90 min produced little additional change in wettability; consequently, we used a 50-min oxidation for all of the samples prepared for this study. The contact angles of basic water (pH 13) on these surfaces fell more sharply, from about 90° to 42° (DCP) and to 31° (sulfur), than did those of acidic water, consistent with the presence of ionizable carboxylic acid groups after oxidation.<sup>5</sup>

(18) Llorente, M. A.; Mark, J. E. *Macromolecules* **1980**, *13*, 681–685.



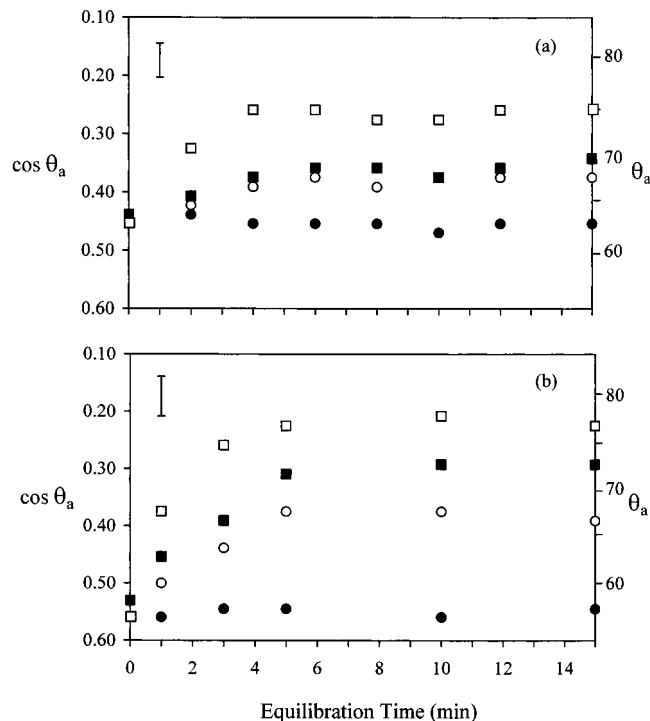
**Figure 3.** Survey XPS spectra ( $16.5^\circ$  takeoff angle) of sulfur-cross-linked 1,4-PBD ( $M_c = 5800$  g/mol, sulfur 5.0 phr) before and after surface oxidation. A high-resolution spectrum of the C 1s region on the oxidized film (inset) contained a peak at 289.4 eV assigned to carboxyl carbon atoms. The peak at 689.0 eV labeled with an "x" in the survey spectrum of the product indicates the presence of a small amount of adventitious fluorocarbon as a contaminant.<sup>20</sup> Spectra were referenced to the primary C1s peak, set at 285.0 eV.

X-ray photoelectron spectra of sulfur-cross-linked films also confirmed the oxidation and the presence of carboxylic acid groups on the chemically modified surface (Figure 3). Survey spectra ( $16.5^\circ$  takeoff angle) revealed an increase in the amount of oxygen, from 16 to 29 atom %, upon oxidation on permanganate for 50 min. Both survey spectra also contained elements (sulfur, zinc, and nitrogen) associated with film additives used in the vulcanization. The initial ratio of O:S (oxidized component, 168.7 eV, 23% of total sulfur):Zn:N was 8.2:0.5:1:0.5. Thus, about one-third of the oxygen present prior to oxidation could be accounted for by the presence of sulfur (sulfonate or sulfate) and ZnO. The increased C 1s photoemission at 289.4 eV in the high-resolution spectrum of the product (Figure 3, inset) is consistent with reported values for the carbonyl carbon of carboxylic acid groups.<sup>2,3,10,11,19,20</sup>

#### Reconstruction of the Oxidized Surfaces Against Water.

Representative oxidized samples of DCP- (0.05 phr;  $M_c = 8200$  g/mol) and sulfur-cross-linked (5 phr;  $M_c = 5800$  g/mol) films were allowed to equilibrate against water at room temperature, as well as at 40, 60, and 80 °C. After quickly cooling the heated samples to room temperature, the reconstruction of the surfaces was assessed by measuring advancing contact angles of water (Figure 4). Both types of sample remained hydrophilic at room temperature (RT), but became increasingly hydrophobic as the temperature of the water was increased, consistent with Regime II reconstruction behavior characterized by rubber elasticity. The kinetics of reconstruction in all cases was sufficiently fast above room temperature for these surfaces to reach a steady-state composition within about 5 min. The magnitude of the change in wettability ( $\Delta \cos \theta_a$ ) upon equilibration against high (80 °C) and low temperature (RT), however, differed for the samples cross-linked in different ways.<sup>21</sup>

To determine whether this difference in the magnitude of the entropic effect was due to the different chemistry used to cross-link the elastomers, or to the difference in  $M_c$  of the two



**Figure 4.** Advancing contact angles of water (pH 1) on surface-oxidized samples versus equilibration time against water at various temperatures: (a) DCP-cross-linked films ( $M_c = 8200$  g/mol, DCP 0.05 phr) and (b) sulfur-cross-linked films ( $M_c = 5800$  g/mol, sulfur 5.0 phr). The temperatures of the water correspond to the symbols as follows: room temperature (●), 40 °C (○), 60 °C (■), and 80 °C (□). The error bar in each plot indicates twice the largest standard deviation for any of the points, in  $\cos \theta_a$ .

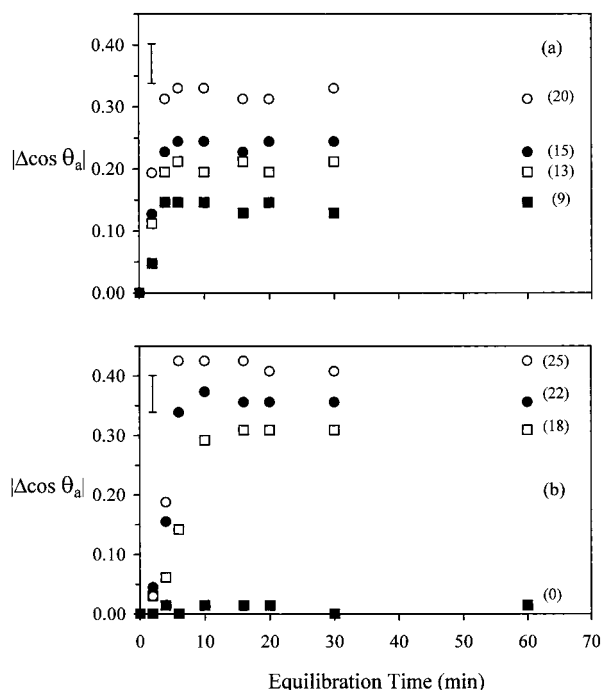
representative polymers chosen, we studied the role of cross-linking by systematically varying  $M_c$  for both types of film. After oxidation, these films were equilibrated against water at 80 °C and the reconstruction of their surfaces monitored as a function of time. All samples reached steady-state values of contact angle within 10 min (Figure 5), and then remained approximately unchanged after even 1 h of heating. Figure 6a shows the values of  $|\Delta \cos \theta_a|$  for samples equilibrated for 1 h as a function of  $M_c$ . As expected, the highly cross-linked samples showed only small values of  $|\Delta \cos \theta_a|$ . In both cross-linked systems, however, the magnitude of change in wettability ( $|\Delta \cos \theta_a|$ ) increased dramatically with increasing  $M_c$  up to a certain point and then reached an approximate plateau having a much smaller dependence on  $M_c$ . The difference between the highest values of  $M_c$  for the two systems in Figure 6a simply reflects our inability to form more-lightly cross-linked networks (with DCP) that were mechanically stable enough to remain intact during swelling and de-swelling. In addition, the higher values of  $|\Delta \cos \theta_a|$  in the sulfur-cross-linked samples are due primarily to the greater hydrophilicity of these surfaces after oxidation.

The initial rise in  $\Delta \cos \theta_a$  in Figure 6a is consistent with the anticipated transition from Regime III to Regime II reconstruction behavior as the level of cross-linking decreased. At low values of  $M_c$ , the polymer chains are presumably not sufficiently mobile to allow significant chain extension, and thus the entropic influence of rubber elasticity is small. Eventually for both systems, the magnitude of  $\Delta \cos \theta_a$  rose to an approximate plateau near the chain-entanglement length ( $M_c$ ) for this polymer, approximately 13 000 g/mol.<sup>22</sup> These results are consistent with chain entanglement providing a lower limiting amount of physical cross-linking that continues to require extension of chains near the surface out of random-coil

(19) Smith, L.; Doyle, C.; Gregonis, D. E.; Andrade, J. D. *J. Appl. Polym. Sci.* **1982**, *26*, 1269–1276.

(20) Beamson, G.; Briggs, D. *High-Resolution XPS of Organic Polymers, The Scienta ESCA300 Database*; John Wiley and Sons: New York, 1992.

(21) For comparison, reconstruction of this type of sample ( $M_c = 32\ 000$  or 10 300 g/mol) against hot air produced a more hydrophobic surface.

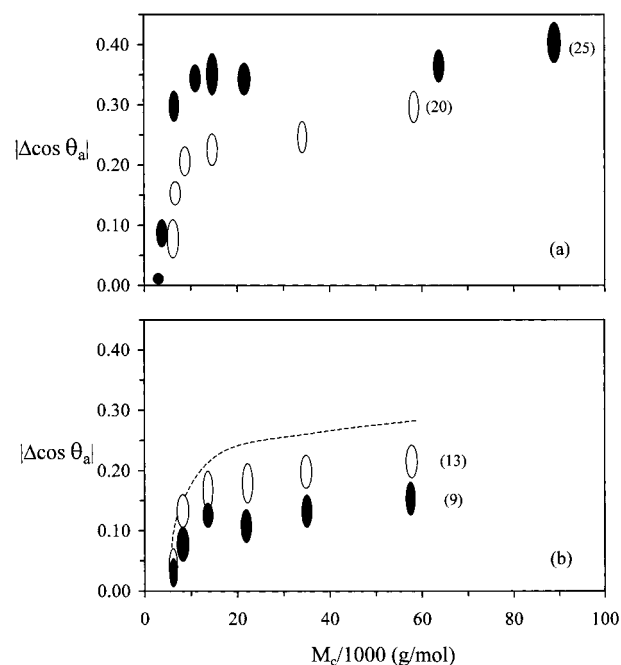


**Figure 5.** Magnitude of the change in  $\cos \theta_a$  ( $\text{H}_2\text{O}$ , pH 1) on surface-modified 1,4-PBD as a function of equilibration time against water at 80 °C: (a) DCP-cross-linked films with  $M_c = 58\,000$  g/mol (O),  $M_c = 32\,000$  g/mol (●),  $M_c = 8200$  g/mol (□), and  $M_c = 7700$  g/mol (■), and (b) sulfur-cross-linked films with  $M_c = 90\,000$  g/mol (O),  $M_c = 10\,300$  g/mol (●),  $M_c = 5800$  g/mol (□), and  $M_c = 2300$  g/mol (■). The error bar in each plot indicates twice 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.

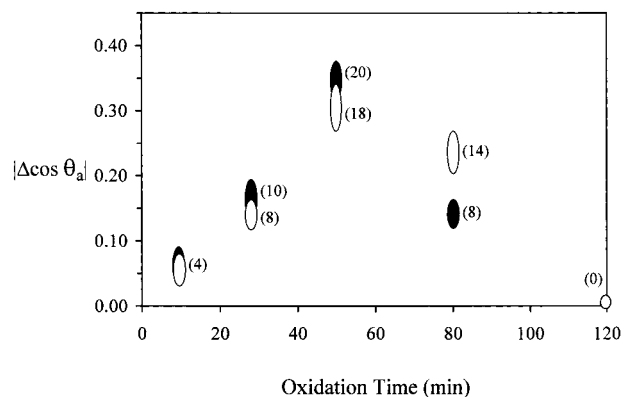
conformations (to accommodate hydrogen bonding at the polymer/water interface) at low levels of chemical cross-linking, i.e., when  $M_c$  is greater than  $M_e$ . To rule out the possibility that the plateau was due instead to a saturation of the surface with hydrophobic groups at 80 °C, thereby limiting the increase in  $|\Delta \cos \theta_a|$ , we also examined the reconstruction of the films against water at lower temperatures. Figure 6b shows that the magnitude of  $\Delta \cos \theta_a$  for samples equilibrated at 60 and 70 °C also plateaued at about the same value of  $M_c$  as found at 80 °C. The magnitudes of the change in  $\cos \theta_a$  at these temperatures were smaller than those at 80 °C, as expected.

The choice of a 50-min oxidation in these studies reflected the time necessary to reach a limiting wettability (vide supra), but was arbitrary with respect to the magnitude of the entropic effect. Since our previous studies of PBD-ox demonstrated that the degree of functionalization was important in determining the change in contact angle as a function of temperature,<sup>2</sup> we studied the influence of this parameter in these systems to maximize  $|\Delta \cos \theta_a|$ . Figure 7 shows that, like the PBD-ox system, the DCP- and sulfur-cross-linked polymers reach a maximum in the magnitude of  $\Delta \cos \theta_a$ , at approximately 50 min of oxidation on aqueous permanganate.

The correspondence of this maximum in  $|\Delta \cos \theta_a|$  with the time necessary to reach a limiting hydrophilicity during the



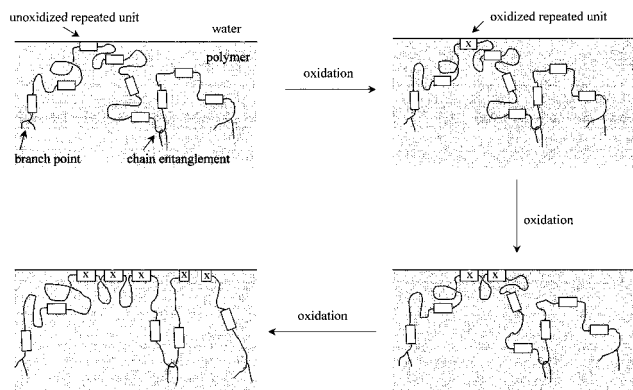
**Figure 6.** Magnitude of the limiting change in  $\cos \theta_a$  ( $\text{H}_2\text{O}$ , pH 1) on surface-modified 1,4-PBD before and after equilibration against heated water as a function of molecular weight between cross-links ( $M_c$ ): (a) equilibration of DCP-cross-linked (open) and sulfur-cross-linked (filled) films against water at 80 °C and (b) DCP-cross-linked films equilibrated against water at 60 °C (filled) or at 70 °C (open). The dashed line shows the data for 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.



**Figure 7.** Magnitude of the limiting change in  $\Delta \cos \theta_a$  ( $\text{H}_2\text{O}$ , pH 1) on surface-modified 1,4-PBD before and after equilibrating against 80 °C water as a function of oxidation time: the open symbols represent DCP-cross-linked films ( $M_c = 32\,000$  g/mol, DCP 0.02 phr) and the filled symbols represent sulfur-cross-linked films ( $M_c = 10\,300$  g/mol, sulfur 3.5 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.

surface modification may be fortuitous, or it may reflect the involvement of chain extension during the surface modification itself. The oxidation used to modify these surfaces occurs at or near the interface between the polymer and an aqueous solution. As a result, the product of oxidation at room temperature is the polymer surface in its room-temperature (i.e., chain-extended) configuration and having its highest concentration of hydrophilic functional groups at the polymer/water interface. We speculate that the mechanism leading to the chain-extended state during the oxidation involves “pinning” of newly formed hydrophilic

(22) The chain-entanglement length was calculated from the values of the entanglement modulus, estimated as the storage modulus in the rubbery plateau zone of the dynamic viscoelastic behavior (measured using the Rheometric Dynamic Analyzer), of the un-cross-linked amorphous polymer. See: Kramer, O.; Ferry, J. D. In *Science and Technology of Rubber*; Eirich, F. R., Ed.; Academic Press: New York, 1978; pp 179–200. Ferry, J. D. In *Deformation and Fracture of High Polymers*; Kausch, H. H., Hassell, J. A., Jaffee, R. I., Eds.; Plenum Press: New York, 1973; pp 27–40. Onogi, S.; Masuda, T.; Kitagawa, K. *Macromolecules* **1970**, *3*, 109–116.



**Figure 8.** Schematic illustration of a possible mechanism leading to chain extension during oxidation by pinning newly formed hydrophilic groups at the polymer/water interface.

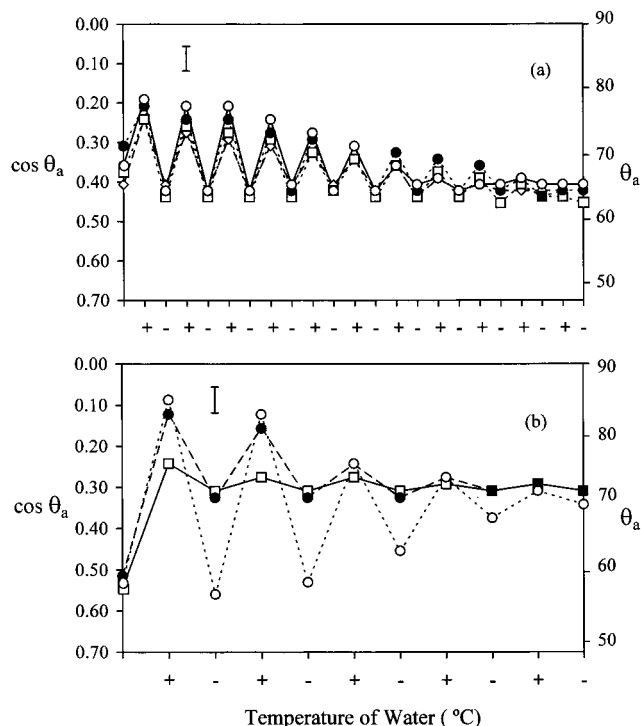
groups at the polymer/reagent interface, thereby increasing the probability of reaction (and concomitant pinning) of neighboring repeat units on the same chain(s) (Figure 8). Reaction beyond this point would likely result in functionalization more deeply into the interphase region or etching of the surface, either of which could diminish the requirement of chain extension as a condition for hydrophilicity at the surface and hence give rise to the maximum in Figure 7.

**Persistence of Regime-II Behavior in These Systems.** To test the hypothesis that the reversibility of entropic reconstruction should be more persistent for these chemically cross-linked systems than for PBD-ox, which lost its reversibility after three cycles of heating and cooling against water,<sup>2</sup> we equilibrated samples repeatedly against water at 80 °C and at room temperature. We conducted these experiments with both DCP- and sulfur-cross-linked samples and various levels of cross-linking to examine the dependence of reversibility on  $M_c$ . As expected, the surfaces became hydrophobic at 80 °C and hydrophilic again at room temperature (Figure 9). The exception in Figure 9 is the sulfur-cross-linked sample with an  $M_c$  of 5800 g/mol,<sup>23</sup> which became more hydrophobic when heated on water at 80 °C but then remained hydrophobic against water at room temperature. The tendency of the sulfur-cross-linked samples to become more hydrophobic during this cycling experiment may reflect the known lability of polysulfide bridges toward bond-interchange reactions in these systems, especially at elevated temperature.<sup>24</sup> Such interchange could relocate branch points, thereby trapping the polymer in its high-temperature configuration. The most lightly sulfur-cross-linked film had the largest entropic effect of any of the samples, with a value of  $|\Delta \cos \theta_a|$  in the first cycle of 0.42 ( $\Delta \theta_a = 25^\circ$ )! All of the DCP-cross-linked samples showed extended reversibility, relative to PBD-ox, with the initial magnitude of  $\Delta \cos \theta_a$  increasing with increasing  $M_c$ .

No evidence of crystallization (or recrystallization), which was associated with loss of reversibility in the 1,2-PBD system,<sup>2</sup> was found in the equilibrated films. Differential scanning calorimetry showed neither a melting transition ( $T_m$ ) nor a significant change in the glass transitions ( $T_g$ ) before and after the treatments summarized in Figure 9 (Table 1). These data suggest that more persistent temperature-dependent oscillations, relative to those of PBD-ox, can be achieved in these systems

(23) A sample of even lower  $M_c$  (2300 g/mol, Figure 5b) showed no entropic effect at all.

(24) Mochulsky, M.; Tobolsky, A. V. *Ind. Eng. Chem.* **1948**, *40*, 2155–2163. Stern, M. D.; Tobolsky, A. V. *J. Chem. Phys.* **1946**, *14*, 93–100. Chun, H.; Gent, A. N. *Rubber Chem. Technol.* **1996**, *69*, 577–590. Field, L. In *Organic Chemistry of Sulfur*; Oae, S., Ed.; Plenum Press: New York, 1977; pp 345–370.



**Figure 9.** Advancing contact angles of water (pH 1) on surface-modified 1,4-PBD films upon cycling between water at 80 °C (+) and water at room temperature (–): (a) DCP-cross-linked films with  $M_c = 32\,000$  g/mol (○),  $M_c = 7700$  g/mol (●),  $M_c = 3500$  g/mol (□), and  $M_c = 2600$  g/mol (◇), and (b) sulfur-cross-linked films with  $M_c = 90\,000$  g/mol (○),  $M_c = 10\,300$  g/mol (●), and  $M_c = 5800$  g/mol (□). The error bar in each plot indicates twice the largest standard deviation for any of the points, in  $\cos \theta_a$ .

**Table 1.** The Glass Transition Temperature (in °C) of DCP- and Sulfur-Cross-linked Films at Several  $M_c$  Values

	DCP-cross-linking at $M_c$ (g/mol) =			S-cross-linking at $M_c$ (g/mol) =		
	32 000	7700	2600	90 000	10 300	5800
before equilibration	–92	–90	–89	–90	–83	–80
after equilibration	–92	–91	–90	–90	–83	–79

with the presence of chemical cross-linking and the absence of crystallinity.

The magnitude of the oscillations in wettability that accompanied thermal cycling against water in these two cross-linking systems did, however, decrease with the number of treatments. The response of the DCP-cross-linked films damped out slowly, over about 7–9 cycles of heating and cooling. The response of the sulfur-cross-linked samples damped out more quickly, over 4–5 cycles. Possible causes of this damping include viscoelastic changes in the elastomer<sup>25</sup> resulting from the alignment and packing of extended polymer chains (during equilibration against water at room temperature) or to a change in the cross-link density due to post-curing. An alternative possibility is autoxidation of the polymer<sup>19</sup> that could shorten the polymer chains and increase the number of polar functional groups near the surface. These hypotheses will be the focus of a subsequent paper.

## Conclusion

The reconstruction of surface-modified 1,4-PBD against water produced a hydrophobic surface at high temperature and a

(25) Ward, I. M.; Hadley, D. W. *An Introduction to the Mechanical Properties of Solid Polymers*; John Wiley and Sons: New York, 1993.

hydrophilic surface at room temperature. These changes were reproducible and reversible, and this reversibility only gradually damped out when samples were cycled repeatedly between water at high and low temperature. This behavior is consistent with our central hypothesis that lightly cross-linked elastomers can display surface dynamics (and thermodynamics) that reflect the entropic changes associated with rubber elasticity. Also consistent with this hypothesis, we have demonstrated that the change in the relative surface concentrations of hydrophobic and hydrophilic functional groups depends on the molecular weight between cross-links (up to approximately the chain-entanglement length) and the degree of surface functionalization,

as well as on temperature. These results illustrate the correlation of interfacial and bulk mechanical properties and the importance of thinking of a polymer and its surface as an integrated system.

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