

Temperature-Actuated Changes in Wettability at Elastomer/Water Interfaces

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Surface modification of 1,4-polybutadiene and *cis*-1,4-polyisoprene to introduce polar functional groups provided surfaces that reconstructed reversibly against water as a function of temperature. These surfaces became hydrophobic in contact with hot water, but their original hydrophilicity returned upon equilibration against cold water. Repeated cycling between hot and cold water, however, led to a damping of this reversibility. A series of parallel experiments on both the interfacial and bulk behavior of these elastomers strongly indicated that this damping was due to the alignment of extended interfacial chains during temperature cycling and to a decay of the restoring force on the interfacial chains under extension. These studies thus demonstrate that the interfacial behavior of elastomers can display close analogies to the bulk viscoelastic properties of the solid.

Introduction

The use of analogy is often the first recourse of scientists in rationalizing new or surprising results. There is good reason for this approach: analogy offers a wealth of potential connections to established principles. The degree to which analogies work—the degree to which well-understood phenomena can be used to predict or explain poorly understood ones—however depends on the strength of the coupling between them. We have begun to examine the strength of analogies between well-understood mechanical behavior and less-well-understood interfacial behavior of elastomers, and the emerging evidence is compelling.

Our research group has previously reported that oxidation of the surface of lightly cross-linked 1,4-polybutadiene (1,4-PBD) and synthetic *cis*-1,4-polyisoprene (PI) can be used to produce polymer/water and polymer/metal interfaces that respond reversibly to changes in temperature.^{1,2} The design of these systems involves introducing a competition between surface activity and rubber elasticity: enthalpically favorable interactions (e.g., hydrogen bonding, Lewis acid–base, and dipole–dipole) at the interface are balanced by entropically unfavorable polymer-chain extension (i.e., rubber elasticity) necessary to bring surface-active functional groups to the interface. As a direct result of this competition, the elastomers were hydrophilic when equilibrated against water at room temperature and became hydrophobic when equilibrated against water at elevated temperature. Likewise, these elastomers adhered strongly to aluminum (oxide) at room temperature and weakly at elevated temperature.

These surface reconstructions were reversible at both the polymer/water and polymer/aluminum interfaces, though the reversibility at the water interface damped out as the number of temperature cycles increased. For both 1,4-PBD and PI, damping was more rapid for samples cross-linked with sulfur than for those cross-linked with dicumyl peroxide (DCP). To account for this difference in

cross-linking method, we have suggested that, during hot water equilibration of the sulfur-cross-linked polymers, bond interchange between polysulfide bridges in the sulfur-cross-linked network could lead to the relocation of branch points,^{3,4} thereby trapping chain segments in their high-temperature configuration.¹ This hypothesis, however, is not relevant to the damping observed in DCP-cross-linked samples, whose branch points consist of inert carbon–carbon linkages.⁴

This paper presents studies of possible mechanisms leading to damping of reversibility in these “entropic reconstructions”, for both 1,4-PBD and PI cross-linked with DCP. We focused on two possible sources of the damping behavior during the cycling experiments: (i) increases in chemical cross-linking during the cycling experiments and (ii) gradual changes in the viscoelastic properties of interfacial chains during repeated cycling. An increase in chemical cross-linking in the polymers, for example, by autoxidation in air-saturated water or by postcuring, could limit the mobility of chain segments in the interfacial region and consequently dampen the temperature-dependent response.^{5,6} On the other hand, viscoelastic changes in the polymer interphase, due either to the development of tensile set or relaxation of the entropic restoring force (stress relaxation)^{7,8} when interfacial chains are in extended conformations at low temperature,¹ could gradually pin polar functional groups at the interface and reduce the magnitude of the temperature-dependent response.

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Experimental Section

General Methods. Toluene (99%; E.M. Science), hydrochloric acid (36.5%; Mallinckrodt), potassium permanganate (99+%; Fisher), sodium bisulfite (A.C.S. reagent; 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. Solid additives used in the sulfur-cross-linking reactions were ground using a mortar and pestle prior to use.

Differential scanning calorimetry (DSC) was done using a DSC-2920 modulated differential scanning calorimeter (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 from –120 to 280 °C, with a ramp rate of 5 °C/min and temperature modulation of ± 0.5 °C/min.

Cross-Linking and Film Formation. For 1,4-polybutadiene, 5 g of the polymer ($M_w = 420\,000$ g/mol; 36% cis, 55% trans, and 9% 1,2; Aldrich) was dissolved in 50 mL of toluene and stirred overnight. For free-radical cross-linking of this polymer, dicumyl peroxide (DCP) was separately predissolved in 10 mL of toluene, then added to the polymer solution, and stirred for an additional 2 h. For sulfur cross-linking, stearic acid (0.05 g) and sulfur 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), and stirred for 2 h.

For synthetic *cis*-1,4-polyisoprene, 5 g of the polymer ($M_w = 800\,000$ g/mol; 97% cis; Aldrich) was dissolved in ~ 100 mL of toluene and stirred overnight. For free-radical cross-linking of this polymer, dicumyl peroxide (DCP) was separately predissolved in 10 mL of toluene, 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, 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 or sulfur used in each preparation depended on the desired molecular weight between cross-links and has been discussed elsewhere.¹

Two polished aluminum plates (10×10 cm²) were cleaned by soaking them in toluene for 30 min and wiping them with cotton balls. A cardboard frame with a thickness of ~ 1 mm was cut to the dimensions of the plates, and a window ($\sim 5 \times 5$ cm²) was 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 (eight half-lives)¹² or 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 ($\sim 0.7 \times 2.0$ 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 value. The optimum swelling time was determined by following the loss of mass by the swelled samples until a constant value was reached. 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. Surfaces of samples ($\sim 0.7 \times 2.0$ cm²) were oxidized with an aqueous solution of KMnO_4 (0.045 M) and K_2CO_3 (0.017 M) for 50 min, as described previously.¹

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Measurement of Contact Angles. All advancing contact angles (θ_a values) of water (pH 1) were measured at room temperature and ambient humidity using a Rame-Hart Model 100 contact angle goniometer. Before determining θ_a on heated samples, they were first immediately cooled in room-temperature water for 3 min and then under a stream of room-temperature nitrogen for 1 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.

Temperature-Cycling Experiments. Surface-modified 1,4-PBD and PI samples were equilibrated against hot and room-temperature water that had been deaerated by sparging with nitrogen to minimize any autoxidation, unless otherwise stated. Equilibration times at 80 °C were 5 min for 1,4-PBD films and 10 min for PI films, unless otherwise stated. The equilibration times against room-temperature water for 1,4-PBD and PI films were 18 and 24 h, respectively, unless otherwise stated. These equilibration times against hot and room-temperature water were found previously to be sufficient for the full surface reconstruction for each polymer.¹

Tensile-Set Measurements. Strips of polymer were cut to dimensions of $80 \times 10 \times 1$ mm³. Two marks with a 50.0-mm separation were drawn near the middle of the specimens at each end. The specimens were then gripped at each end into an Instron 5567 tensile tester and adjusted symmetrically. The samples were stretched to a specific elongation (12%) at a rate of 500 mm/min and held at that elongation for 10 min. They were then released quickly from that extension without snapping and allowed to recover for 10 min before the distance between two marks was again measured using a microcaliper.

Stress-Relaxation Tests. Strips of polymers with the same dimensions as those used for the tensile-set experiments were prepared. The Instron 5567 tensile tester was used to stretch the samples to 10 or 20% elongation at a rate of 500 mm/min. The decay of restoring force in the samples at the specific extension was then followed for 60 min. The Instron Series IX software was used to control the test and to collect the data.

Results and Discussion

Increase in Chemical Cross-Linking during Temperature Cycling? The solid lines in Figure 1 connect data points showing that a gradual decrease in the magnitude of the *change* in wettability, as well as an increase in the hydrophilicity of the 80 °C state, accompanies temperature cycling of these polymers against water.¹ We examined the possibility that this damping of the oscillations could be due to an increase in the level of cross-linking during the temperature cycling. An increase in chemical cross-linking could occur by autoxidation in air-saturated water or by reaction of any residual cross-linking agents as the samples are heated.^{9,10} To test the autoxidation hypothesis, separate samples of the polymers were cycled between room temperature and 80 °C against air-saturated and deaerated water. Surface-modified films of 1,4-PBD ($M_c \approx 30\,000$ g/mol) and PI ($M_c \approx 28\,000$ g/mol),¹¹ cross-linked with DCP, showed only slight differences in damping when equilibrated against the two types of water (Figure 1).

To test the postcuring hypothesis, we used differential scanning calorimetry (DSC) to detect any shift in the glass-transition temperature, which might be expected to accompany an increase in cross-linking. As shown in Figure 2, thermograms of damped samples of surface-modified 1,4-PBD ($M_c \approx 30\,000$ g/mol, DCP; $M_c \approx 10\,000$ g/mol, sulfur) and PI ($M_c \approx 28\,000$ g/mol, DCP; $M_c \approx 11\,000$ g/mol, sulfur) did not show any significant change in the glass-transition temperatures (Table 1), compared to undamped samples tested prior to temperature cycling. In separate experiments, isothermal DSC thermograms over 60 min at 80 and 100 °C for 1,4-PBD and PI films were featureless for both types of cross-linking. These

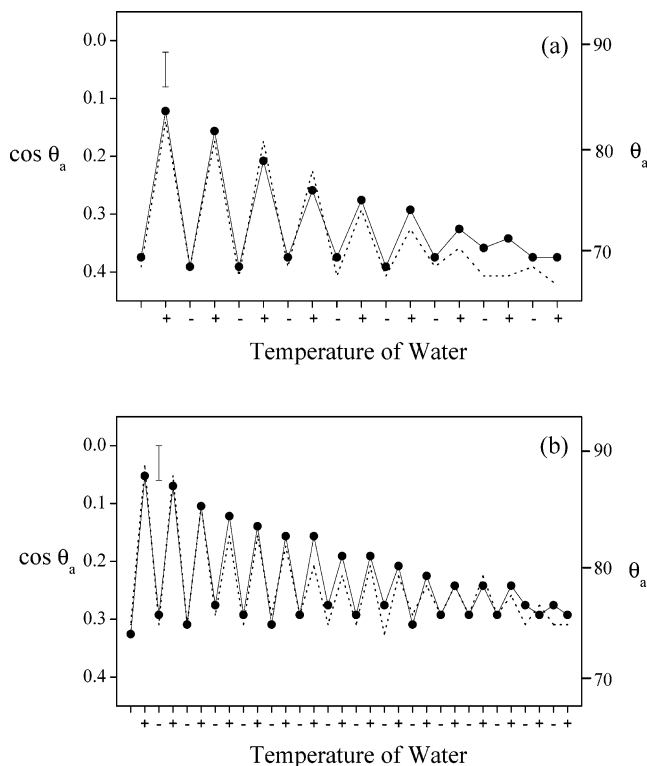


Figure 1. Advancing contact angles of water (pH 1) on surface-modified films during cycling between deaerated water at 80 °C (+) and room temperature (-): (a) DCP-cross-linked 1,4-PBD ($M_c \approx 30\,000$ g/mol); (b) DCP-cross-linked PI ($M_c \approx 28\,000$ g/mol). The dashed lines show the data for the same samples equilibrated against air-saturated water for comparison. The error in each plot indicates twice the largest standard deviation for any of the points, in $\cos \theta_a$.

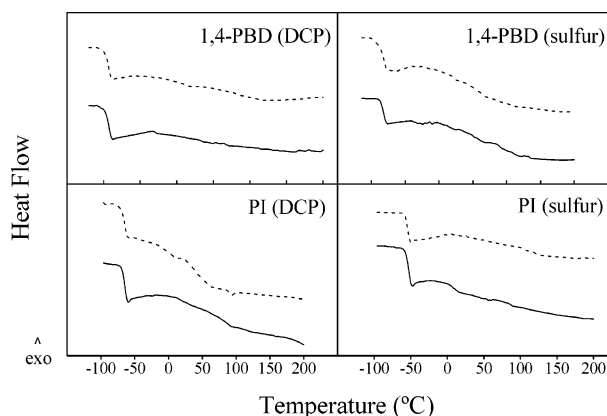


Figure 2. Differential scanning calorimetry thermograms for the damped samples of 1,4-PBD and PI cross-linked with DCP or with sulfur. The dashed lines represent data for undamped samples for comparison.

Table 1. Glass-Transition Temperatures (in °C) of Both Undamped and Damped 1,4-PBD and PI Films

	1,4-PBD		PI	
	DCP-cross-linked	S-cross-linked	DCP-cross-linked	S-cross-linked
undamped samples	-92	-83	-65	-59
damped samples	-92	-83	-64	-57

results indicated that no significant cross-linking occurred in these samples during annealing at these temperatures. Taken together, all of these experiments effectively ruled out the hypothesis that damping in these systems is due

to the addition of cross-linking during the temperature-cycling experiments.

Viscoelastic Changes Arising from Interfacial Strain? Our other hypothesis regarding the source of damping of entropic oscillations was that, by analogy to the bulk behavior of polymers, tensile strain can lead to viscoelastic changes such as “tensile set”. This term refers to the incomplete recovery of polymers to their initial length after having been elongated by a tensile force and is known to be time- and temperature-dependent.⁷ For such elongated polymers, there is evidence that segmental alignment of the extended chains in the direction of the tensile force is responsible for this tensile-set behavior.¹² Tensile set can easily be measured using eq 1, where L is the distance between benchmarks after 10 min of recovery following elongation and L_0 is the original distance between the benchmarks.¹³

$$\text{tensile set (\%)} = 100[L - L_0]/L_0 \quad (1)$$

By analogy, chains in the stressed state at the polymer/water interface (low temperature)¹ would have extended conformations, and the elongated chains might tend to align with one another and lead to the formation of ordered, metastable domains. Initial alignment could produce nucleation sites for packing of other elongated chains in order to increase the van der Waals interaction between them.¹⁴ As a result, the net alignment of interfacial chains could increase as the numbers of temperature cycles is increased, as illustrated in Figure 3. Such formation of ordered domains could gradually stiffen the interfacial region and lead to the damping effect. This hypothesis is consistent with the observed gradual increase in hydrophilicity of the surface as the elasticity dampens (Figure 1), indicating that polar groups are gradually pinned at the interface during this process. In bulk systems, this type of alignment is generally thermodynamically unstable, and we expected that to be the case for the interfacial analogue as well. Thus, we expected that, if this hypothesis were correct, the elasticity of interfacial chains would be recoverable if the dampened samples were allowed to relax back to equilibrium.

To test this hypothesis, we conducted parallel strain-recovery experiments on both the bulk elastomers and their interfacial analogues. As a model study of the bulk polymer, we used small (12%) tensile extension for samples of both 1,4-PBD and PI and both types of cross-linking. After extension, the elastomers were released to allow the polymer chains to relax to their random-coil conformations (analogous to the relaxation of interfacial polymer chains when the surface was equilibrated against hot water). As expected, we found that tensile set in these samples gradually increased with an increasing number of stretch-release cycles (Figure 4).¹⁵ Values of tensile set for DCP- and sulfur-cross-linked 1,4-PBD had reached approximately 6.2 and 8.1%, respectively, after 10 cycles; those of PI gradually reached about 2.5 and 5.1%, respectively, during the same treatment. This development of tensile set is consistent with the progressive alignment of extended chains during the repeated tensile

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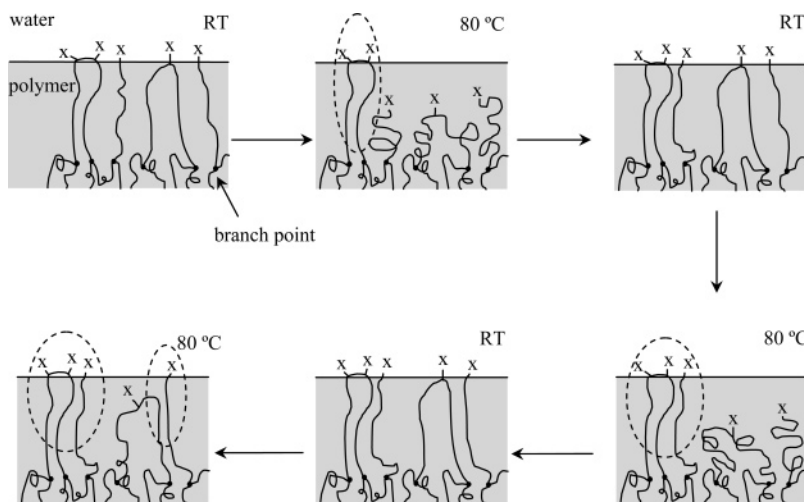


Figure 3. Stylized illustration of the gradual alignment of extended polymer chains at the polymer/water interface during temperature cycling. The dashed ovals identify aligned chains, which pin polar functional groups at the polymer/water interface.

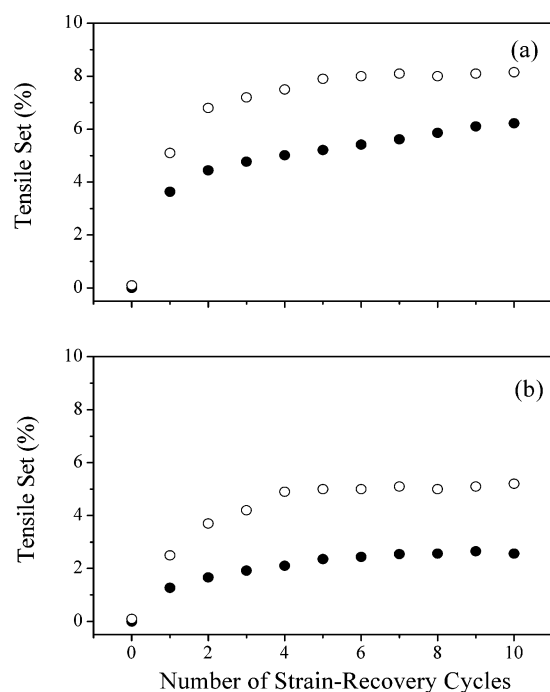


Figure 4. Average tensile set during strain-recovery cycling experiments, using 12% elongations for (a) 1,4-PBD (DCP, $M_c \approx 30\,000$ g/mol, ●; sulfur, $M_c \approx 31\,000$ g/mol, ○) and (b) PI (DCP, $M_c \approx 28\,000$ g/mol, ●; sulfur, $M_c \approx 28\,000$ g/mol, ○).

deformation.^{16,17} The tendency of sulfur-cross-linked samples to show greater tensile set for this treatment was expected, on the basis of the known lability of polysulfide bridges toward bond-interchange reactions in these systems.^{1-3,17-19} Furthermore, the larger magnitude of tensile set for 1,4-PBD, relative to that for PI, likely reflects the difference in steric hindrance along the backbones of these two polymers. As a result, we would expect the extended chains of 1,4-PBD to pack more easily than those of PI.²⁰

As expected, samples that had reached the plateau of tensile set relaxed at room temperature over ~ 24 h, once

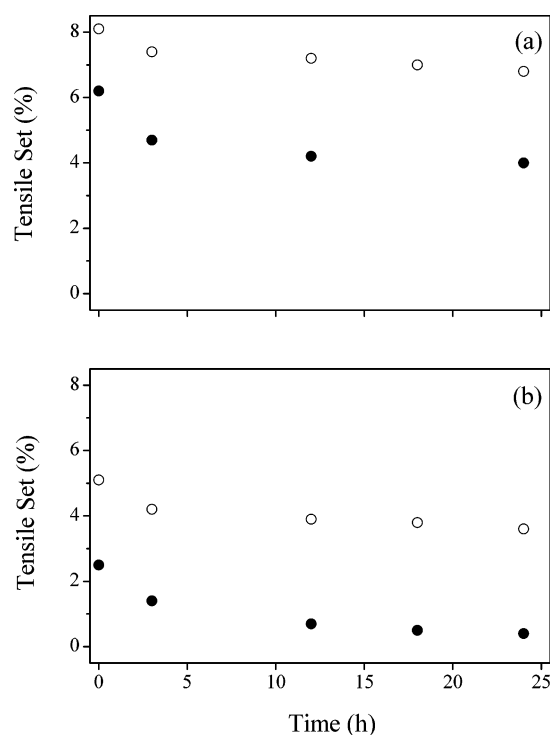


Figure 5. Relaxation of tensile set after the strain-recovery cycling experiments for (a) 1,4-PBD (DCP, $M_c \approx 30\,000$ g/mol, ●; sulfur, $M_c \approx 31\,000$ g/mol, ○) and (b) PI (DCP, $M_c \approx 28\,000$ g/mol, ●; sulfur, $M_c \approx 28\,000$ g/mol, ○).

the applied strain was released. The values of tensile set for the DCP-cross-linked polymers dropped significantly, from approximately 6.2 and 2.5% to approximately 4.0 and 0.5%, respectively (Figure 5). The values for the sulfur-cross-linked polymers, however, showed only a small recovery, from approximately 8.1 and 5.1% to approximately 7.0 and 3.5%, respectively (Figure 5), as expected. Again, the smaller recovery observed in sulfur-cross-linked sam-

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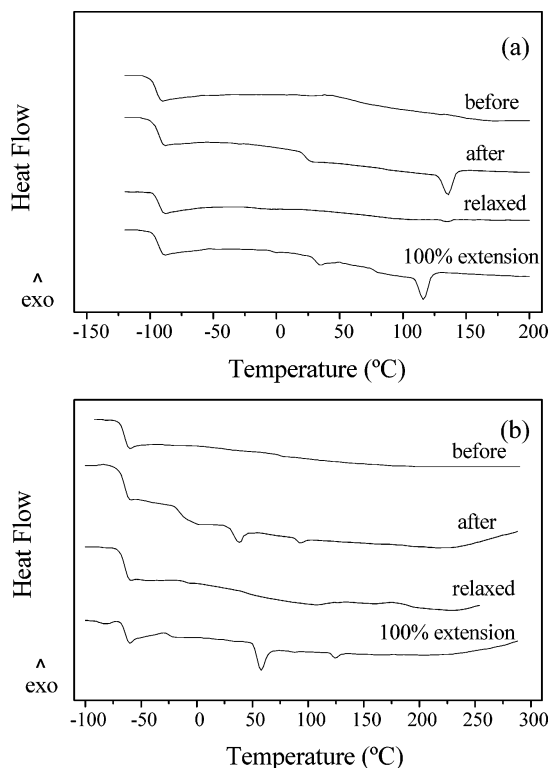


Figure 6. Differential scanning calorimetry thermograms of (a) 1,4-PBD ($M_c \approx 30\,000$ g/mol) and (b) PI ($M_c \approx 28\,000$ g/mol) before and after strain-recovery cycling experiments, as well as after storing at room temperature for 24 h. Thermograms of samples elongated to a 100% extension are added for comparison.

ples likely reflects bond-interchange reactions involving the polysulfide bridges during repeated deformation.^{1,17–19}

Differential scanning calorimetry of the DCP-cross-linked samples during the course of these strain-recovery experiments revealed the appearance of a new glass-transition temperature and endotherm(s) (Figure 6), indicating the formation of ordered domains induced by the repeated deformations.²¹ For comparison, we also collected thermograms of similar samples that had been elongated to a 100% extension and held at that length for 30 min. Thermograms of these samples also revealed the appearance of new glass transitions and endotherms. The changes observed in the thermograms of samples treated with repeated strain-recovery cycles disappeared after those samples were allowed to relax at room temperature for 24 h under no applied strain, consistent with loss of tensile set reported above. The new glass transitions and endotherms also disappeared in second scans of these samples. These results confirm the presence of chain alignment during repeated mechanical deformation and the loss of that alignment upon relaxation under unstressed conditions for extended periods of time. They also argue against the possibility that the development of tensile set observed during these strain-recovery experiments was due to plastic flow in the samples.⁷

To examine possible parallels between this behavior of the bulk elastomer and damping of the temperature-

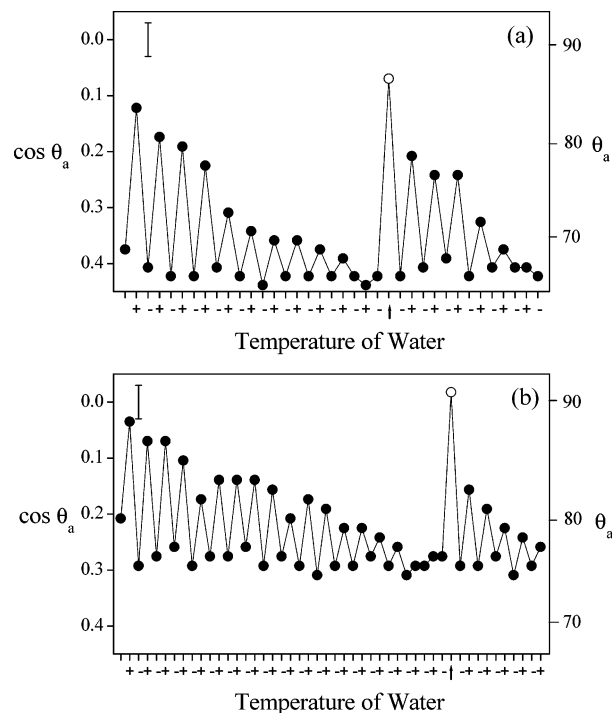


Figure 7. Advancing contact angles of water (pH 1) on surface-modified films during cycling between water at 80 °C (+) and room temperature (–): (a) DCP-cross-linked 1,4-PBD with $M_c \approx 30\,000$ g/mol; (b) DCP-cross-linked PI with $M_c \approx 28\,000$ g/mol. The symbol (†) represents an annealing step at 40 °C for 18 h under nitrogen. The error bar in each plot represents twice the largest standard deviation for any of the points, in $\cos \theta_a$.

actuated reconstruction at the polymer/water interfaces, surface-modified films of DCP-cross-linked 1,4-PBD and PI were cycled between 80 °C and room-temperature water until the oscillations in wettability completely damped out. Damping was approximately complete after 9 cycles for 1,4-PBD and 15 cycles for PI (Figure 7).²² We hypothesized that, in this state, the alignment of extended chains in the interphase inhibited the entropic recoiling of chains during equilibration against hot water (Figure 3). By analogy to the bulk stress-recovery cycling experiments (vide supra), we expected that the loss of reversibility could be recovered if the damped samples were allowed to relax. To this end, the damped samples were annealed under nitrogen at 40 °C for 18 h to allow the oriented portion of interfacial chains to relax and again achieve random-coil conformations. The slightly elevated temperature (40 °C) was used to accelerate the process. After annealing, the advancing contact angles of water on these surfaces had risen almost to values characteristic of the unmodified surface of each elastomer (Figure 7), 85–90° for unmodified DCP-cross-linked 1,4-PBD and 100–105° for unmodified DCP-cross-linked PI.

These results are consistent with our underlying hypothesis and indicate that the alignment of extended chains at the interface can, in large part, recover to random-coil conformations after annealing under these conditions. We infer that, as a result of this interfacial relaxation, the functional groups that had been pinned at the interface upon damping of the temperature-actuated oscillations can migrate into the subsurface region again. After this relaxation step, the samples were equilibrated again against room temperature water until the advancing

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(22) The samples were cycled between hot and room-temperature water until the variation in advancing contact angle decreased to within the experimental error of the measurement.

Table 2. Recovery of Temperature Actuation in Damped Samples upon Annealing for 18 h at Different Temperatures

	1,4-PBD			PI		
	-8 °C	25 °C	40 °C	-8 °C	25 °C	40 °C
$\Delta\theta_a$ in first cycle (after annealing)	2–3°	6–9°	10–15°	0°	4–6°	8–10°
number of cycles until complete damping	2	3–5	5	0	4–5	>5

contact angles reached a steady hydrophilic state, corresponding to extended interfacial polymer chains with polar groups at the interface. The temperature-cycling experiment was then restarted, and as shown in Figure 7, the temperature-actuated oscillations in wettability again resumed. Results for sulfur-cross-linked 1,4-PBD and PI also showed this trend, but smaller initial entropic effects and fewer oscillations were observed after annealing, as expected. The recovery of temperature actuation strongly supports the hypothesis that, analogous to the bulk viscoelastic changes evident in Figure 5, the interfacial chains can regain their elasticity upon relaxation and associated diminution in chain alignment.

Two other temperatures (-8 and 25 °C) were also examined for the relaxation of damped samples from temperature-cycling experiments. After annealing at these two temperatures for 18 h, we found that the advancing contact angles of these surfaces had risen to 70–75° for 1,4-PBD and 78–87° for PI. As expected, we observed a relatively smaller initial entropic effect and shorter entropic oscillations over the same time period as for the annealing experiments at 40 °C (Table 2), indicating the kinetic dependence of strain recovery on the annealing temperature.²³ These results are also consistent with chain relaxation in the interfacial region of damped samples during annealing. The greater magnitude of $\Delta\theta_a$ for 1,4-PBD than for PI at the same annealing temperature in Table 2 simply reflects the greater initial hydrophilicity of surface-modified 1,4-PBD, as mentioned elsewhere.¹

As a further test of the hypothesis that chain alignment is responsible for damping, we also swelled damped samples of DCP-cross-linked 1,4-PBD, using toluene as a solvent, for 30 h. We expected that swelling would destroy the alignment of polymer chains in the interphase of these samples and return them to random coils upon deswelling. The samples were deswollen and then dried under vacuum at room temperature until they reached a constant mass, a process that took ~18 h. The advancing contact angle of water on these surfaces after drying was ~75–78°. For comparison, the advancing contact angle of water on undamped samples treated in the same way (swelling/deswelling) was ~80–85°. The dry samples were then equilibrated against water at room temperature to maximize the number of polar groups at the interface and thus the hydrophilicity of the surface ($\theta_a = 67^\circ$). When equilibrated against 80 °C water, these samples did not show temperature-actuated changes in wettability. Instead, the surfaces remained hydrophilic ($\theta_a = 68^\circ$). This result suggests that the interfacial polymer chains can easily repack again into order domains upon deswelling because they were already in extended conformations in the swollen state.^{8,24} When these surfaces were subse-

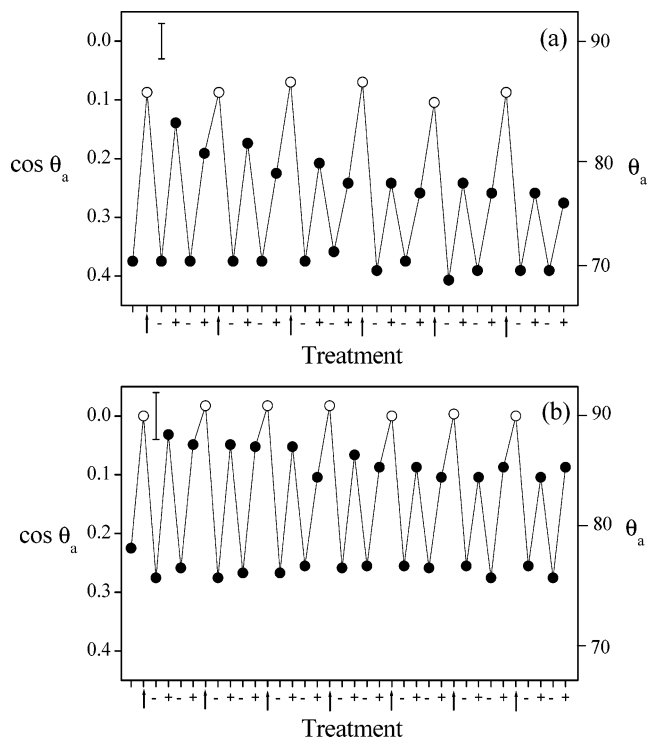


Figure 8. Advancing contact angles of water (pH 1) on surface-modified films upon cycling between water at 80 °C (+) and room temperature (-): (a) DCP-cross-linked 1,4-PBD with $M_c \approx 30\,000$ g/mol; (b) DCP-cross-linked PI with $M_c \approx 28\,000$ g/mol. The symbol (†) represent annealing steps at 40 °C for 18 h under nitrogen after every two cycles of temperature. The error bar in each plot indicates twice the largest standard deviation for any of the points, in $\cos \theta_a$.

quently annealed under nitrogen at 40 °C overnight and then equilibrated against water at room temperature, the entropic oscillations could be resumed ($\Delta\theta_a \sim 11^\circ$), as expected.

Inhibition of Chain Alignment by “Interrupted” Temperature Cycling. In a set of studies designed to test our hypothesis regarding the role of alignment of extended interfacial chains on the damping of temperature-actuated oscillations, we conducted temperature-cycling experiments with periodic interruptions to allow the samples to relax. Surface-modified films of both DCP-cross-linked 1,4-PBD and PI ($M_c = 30\,000$ and $28\,000$ g/mol, respectively) were examined in these experiments. The samples were initially cycled between water at 80 °C and room temperature for only two cycles. They were then annealed at 40 °C under nitrogen to allow any aligned interfacial chains, which we expected to be only partially established, to relax into random coils. As in the experiments described in the preceding section, the annealed samples were then equilibrated against water at room temperature to reintroduce polar groups at the interface and presumably extension of interfacial polymer chains, before restarting the cycling experiment between hot and cool water for another two cycles. Through six rounds of such treatments (i.e., 12 total cycles between hot and cool water), we observed little damping of entropic oscillations for both polymers (Figure 8). Results for sulfur-cross-linked samples of 1,4-PBD and PI ($M_c \approx 30\,000$ g/mol) treated in the same way showed faster damping of entropic oscillations than that found for the DCP-cross-linked systems, as expected. These results indicate that damping of the temperature-actuated oscillations can be avoided if the aligned chains are occasionally allowed to relax back to random-coil conformations.

(23) For other work reporting the dependence of strain recovery on temperature, see: Pegoretti, A.; Guardini, A.; Migliaresi, C.; Ricco, T. *Polymer* **2000**, *41*, 1857. Quinson, R.; Perez, J. *J. Mater. Sci.* **1996**, *31*, 4387. Maxwell, B. *Polym. Eng. Sci.* **1989**, *26*, 1405. Rizzo, G.; Spadaro, G. *Polym. Bull.* **1987**, *18*, 361.

(24) Patel, S. K.; Malone, S.; Cohen, C.; Gillmor, J. R.; Colby, R. H. *Macromolecules* **1992**, *25*, 5241.

Table 3. Number Temperature-Actuated Oscillations for Hot Water at Various Temperatures

	hot water temperature		
	40 °C	60 °C	80 °C
DCP-cross-linked 1,4-PBD	5	7	8
DCP-cross-linked PI	9	12	14

To examine this method of preventing chain alignment further, we conducted a set of temperature-cycling experiments using different temperatures (40, 60, and 80 °C) of the hot water. Surface-modified films of both 1,4-PBD and PI ($M_c \approx 30\,000$ g/mol) cross-linked with DCP were studied. We reasoned that higher temperatures would be more effective than lower temperatures at allowing relaxation (recoiling) of extended chains back into random-coil conformations. This expectation was based on the freely jointed chain (FJC) model, which predicts a greater elastic restoring force at higher temperature.²⁵ Samples were cycled between hot and room-temperature water until the temperature-actuated oscillations completely damped out. As shown in Table 3, higher temperatures induced more persistent oscillations in wettability. This result is consistent with our hypothesis regarding chain extension and with the applicability of models describing rubber elasticity, such as the FJC model, to these interfacial phenomena.

Stress Relaxation of Interfacial Chains. Stress relaxation is a general response of polymers under strain: over time, the restoring force (stress) within the polymer decreases as it relaxes.^{7,8} For surface-modified films of 1,4-PBD and PI equilibrated against room-temperature water during temperature-cycling experiments, we infer that interfacial chains are extended out of random-coil conformations in order to bring polar functional groups to the polymer/water interface. If this state were analogous to a bulk elastomer under strain, it should show signs of stress relaxation over time. Such stress relaxation would represent a decay in the restoring force for the extended interfacial chains, hence making it less able to compete with the enthalpic force tending to bring polar groups to the polymer/water interface, even at elevated temperature. As a result, we expected that the magnitude of the entropic effect ($\Delta \cos \theta$) should decrease with time if the sample were held in the strained state (i.e., against room-temperature water) over time.

To test this hypothesis, we monitored the magnitude of the temperature-actuated response for samples of surface-modified 1,4-PBD films having different values of M_c (DCP-cross-linked) that had been equilibrated against room-temperature water for various periods of time. As shown in Figure 9, the normalized values of $\Delta \cos \theta_a$ (i.e., the change in $\cos \theta_a$ with temperature) decreased substantially with time for all of the samples with an M_c value > 7700 g/mol. Moreover, the decay in the entropic effect was greater in the samples with higher values of M_c (i.e., lower amount of cross-linking). These results are consistent with the proposed analogy to bulk systems, as well as with our hypothesis that the restoring force—the source of the entropic effect—in the extended interfacial chains decreased over time during equilibration against water at room temperature.

To relate these results directly to stress relaxation in bulk samples, we performed stress-relaxation tests using bulk samples of DCP-cross-linked 1,4-PBD having various values of M_c . All samples were quickly stretched to a 10% elongation and held over time, analogous to the stretching of interfacial chains when surface-modified films were equilibrated against water at room temperature. Figure

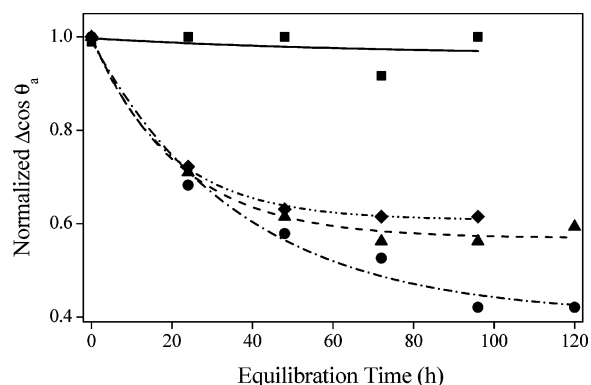


Figure 9. Decay of the temperature-actuated changes in wettability (normalized $\Delta \cos \theta_a$ upon heating against water at 80 °C) on surface-modified 1,4-PBD (DCP cross-linking) as a function of equilibration time against water at room temperature: (■) $M_c \approx 7700$ g/mol, (◆) $M_c \approx 11\,000$ g/mol, (▲) $M_c \approx 30\,000$ g/mol, (●) $M_c \approx 56\,000$ g/mol. Contact angles were measured with water at pH 1, and each data point represents a separate sample.

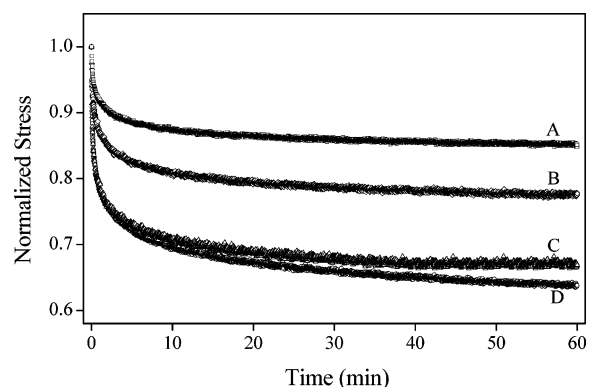


Figure 10. Decay of the restoring force (stress relaxation) in bulk samples of DCP-cross-linked 1,4-PBD as a function of time under 10% tensile elongations: (A) $M_c \approx 7700$ g/mol, (B) $M_c \approx 11\,000$ g/mol, (C) $M_c \approx 30\,000$ g/mol, (D) $M_c \approx 56\,000$ g/mol.

10 shows the stress relaxation of these bulk samples, reported as normalized stress. These results are analogous to those found for the interfacial chains (Figure 9): the restoring force decreased over time. In addition, the decay in restoring force of these samples was not only a function of time but also a function of M_c , with samples having larger values of M_c (lower amount of cross-linking) showing more and faster relaxation.²⁶ These results provide a compelling analogy to the decay of the restoring force in the extended interfacial chains during room-temperature equilibration as a source of damping of temperature-actuated oscillations.

For comparison, we also examined both interfacial and bulk stress relaxation for sulfur-cross-linked 1,4-PBD and for DCP-cross-linked PI. Figure 11 shows the magnitude of $\Delta \cos \theta$ for surface-modified samples had been equilibrated against room-temperature water for various periods of time and then heated against water at 80 °C. The decay of the temperature-actuated response for the sulfur-cross-linked 1,4-PBD was greater than that for DCP-cross-linked 1,4-PBD of similar M_c , again consistent with redistribution

(25) The relationship between temperature and restoring force in extended polymer chains was mentioned in our previous publications.¹

(26) For other work reporting the dependence of the decay in restoring force on levels of cross-linking, see: Ehabe, E. E.; Farid, S. A. *Eur. Polym. J.* **2001**, *37*, 329. Farris, R. J.; Vratsanos, M. S. *Int. J. Fract.* **1989**, *39*, 93. Arenz, R. J.; Landel, R. F. *J. Polym. Sci., Polym. Phys. Ed.* **1982**, *20*, 363. Tamura, S.; Murakami, K. *Polymer* **1980**, *21*, 1398. Tamura, S.; Murakami, K. *Polymer* **1976**, *17*, 325.

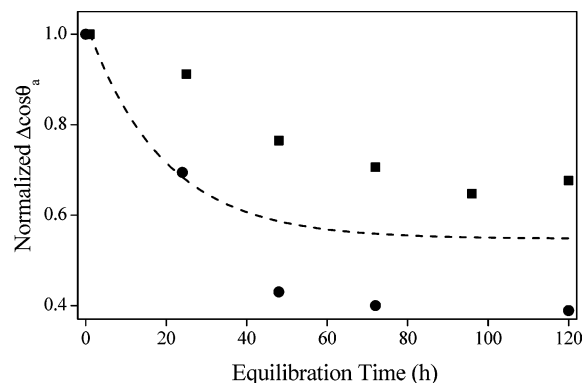


Figure 11. Magnitude of the temperature-actuated change in wettability upon heating against 80 °C water, expressed as normalized $\Delta\cos\theta_a$, on surface-modified polymers as a function of equilibration time against room-temperature water: (●) sulfur-cross-linked 1,4-PBD with $M_c \approx 30\,000$ g/mol; (■) DCP-cross-linked PI with $M_c \approx 28\,000$ g/mol. Contact angles were measured using water at pH 1, and each data point represents a separate sample. The dashed line shows the data for DCP-cross-linked 1,4-PBD ($M_c \approx 30\,000$ g/mol) for comparison.

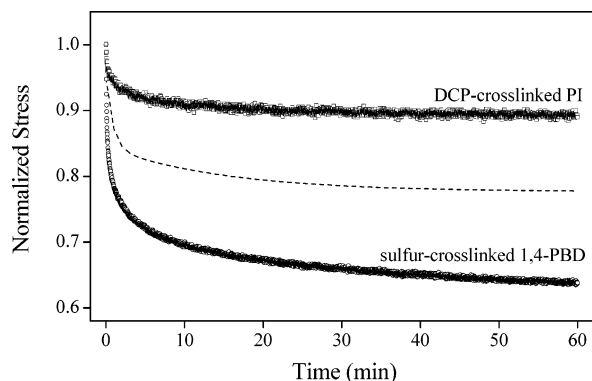


Figure 12. Decay of the restoring force (stress relaxation) in bulk samples of sulfur-cross-linked 1,4-PBD ($M_c \approx 30\,000$ g/mol) and DCP-cross-linked PI ($M_c \approx 28\,000$ g/mol) as a function of time under 10% tensile elongations. The dashed line shows the data for DCP-cross-linked 1,4-PBD ($M_c \approx 30\,000$ g/mol) for comparison.

of polysulfide cross-links.³ The decay of the entropic effect for the DCP-cross-linked 1,4-PBD was, however, greater than that for DCP-cross-linked PI, consistent with the damping results in Figure 1.

Analogous experiments performed on bulk samples (Figure 12) also showed the same trends. The greater decay in restoring force for a sulfur-cross-linked network observed here is consistent with work reported by other research groups,^{19,26} again presumably reflecting the known lability of polysulfide bridges. The data in Figures 11 and 12 show that the decay of the restoring force in both the interfacial and bulk chains of DCP-cross-linked PI was smaller than that of DCP-cross-linked 1,4-PBD. These results reflect the slower rate of chain motion in PI than in 1,4-PBD.²⁰ All of these trends in the decay of restoring forces are again consistent with a strong relationship between interfacial and bulk properties in these elastomers.

Recovery of the Restoring Force in Stress-Relaxed Interfacial Chains. As a further test of the hypothesis that the decay in temperature actuation with time against room-temperature water was due to the stress relaxation of extended interfacial chains, separate samples of surface-modified 1,4-PBD ($M_c \approx 56\,000$ g/mol, DCP-cross-linked) were equilibrated against room-temperature water for 24, 48, 72, 96, and 120 h. After each interval, the magnitude

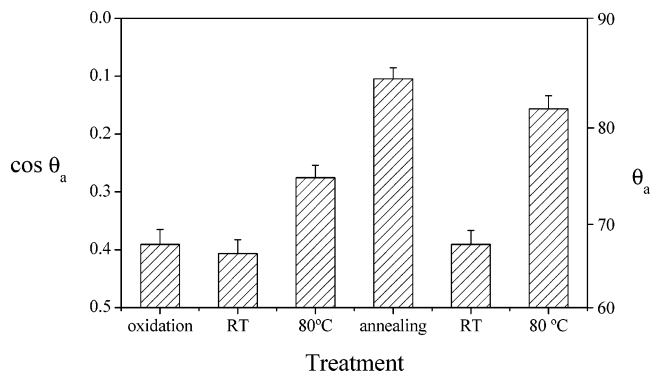


Figure 13. Advancing contact angles of water (pH 1) on the surface of a representative DCP-cross-linked 1,4-PBD film ($M_c \approx 56\,000$ g/mol) after oxidation, equilibration against water at room temperature (RT) for 120 h, equilibration against water at 80 °C, annealing at 40 °C under nitrogen, re-equilibration against water at room temperature, and re-equilibration against 80 °C water, respectively.

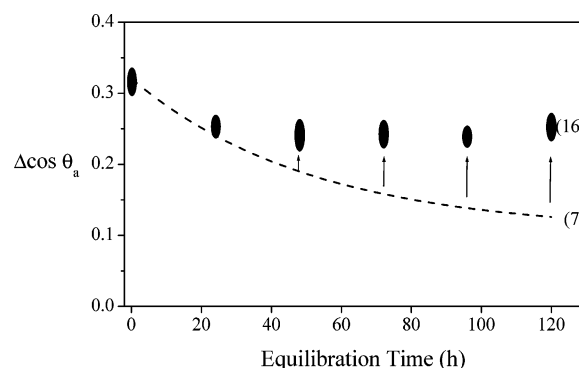


Figure 14. Magnitude of $\Delta\cos\theta_a$ on surface-modified 1,4-PBD (DCP, $M_c \approx 56\,000$ g/mol) after the sequence of treatments summarized in Figure 13 as a function of the initial equilibration time against water at room temperature. The numbers in parentheses give the corresponding change in θ_a . Contact angles were measured using water at pH 1, and the height of each data point indicates values within one standard deviation of the average. The dashed line shows the data for these samples in the stress-relaxed state (before annealing) for comparison.

of entropic reconstruction in each sample was monitored upon equilibration against 80 °C water. Then, each sample was annealed in nitrogen at 40 °C for ~ 24 h to allow the extended interfacial chains to recoil to the unstressed state (random coil). At this point, we expected the thermal/stress history of all of the samples to have been erased. The samples were then equilibrated against room-temperature water to reintroduce chain extension. As an example, Figure 13 shows the change in the contact angle on the surface of a representative sample (120-h equilibration against room-temperature water) over the course of this experiment. As expected, the magnitude of the temperature-actuated effect was reduced by equilibration in room-temperature water but returned after annealing in nitrogen. If our expectation were correct, the magnitude of the entropic effect after the second equilibration against 80 °C water for *all* of these samples should be about the same. As shown in Figure 14, after the second equilibration against 80 °C water, all of the films indeed showed approximately the same magnitude of temperature-actuated changes in wettability, $\Delta\theta_a \sim 16^\circ$. The values of $\Delta\cos\theta_a$ for the same samples prior to annealing are added to the figure for comparison.

In a related but separate set of experiments, we studied the behavior of bulk samples of DCP-cross-linked 1,4-PBD treated in an analogous way, using tensile elonga-

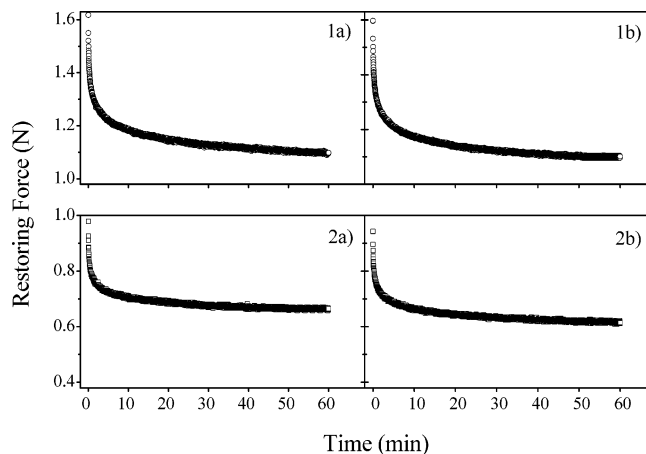


Figure 15. Stress relaxation in DCP-cross-linked 1,4-PBD ($M_c \approx 56\,000$ g/mol) as a function of time under tensile strain: (1a) 20% elongation, first run; (1b) 20% elongation, second run after an unstressed 60-min rest; (2a) 10% elongation, first run; (2b) 10% elongation, second run after an unstressed 60-min rest.

tions. Samples of film were quickly stretched to 10 or 20% elongation, and the decay of the resulting restoring force was followed for 60 min. The samples were then allowed to rest unstrained at room temperature for 60 min. The stress-relaxation test was then repeated, and again, the decay of the restoring force was monitored for another 60 min. The level of the initial restoring force in the second run was about the same as that in the first run. Moreover, the kinetics and magnitude of stress relaxation for both runs were about the same (Figure 15). These results confirmed that the stress-relaxed samples could regain their rubber elasticity after being allowed to rest unstrained, consistent with our proposed analogy between the decay of the restoring force in the extended interfacial chains (leading to damping of oscillations in wettability) and the bulk behavior of elastomers.

Conclusions

The experiments reported in this paper establish remarkably close analogies between the interfacial behavior and the bulk viscoelastic properties of chemically cross-linked elastomers. These analogies are evident in the following interpretations of the experimental results: when surface-modified films of 1,4-PBD and PI were cycled between hot and room-temperature water, the viscoelastic

properties of the interfacial region changed, leading to a damping of the temperature-actuated changes in wettability. Likewise, when bulk elastomers are repeatedly stretched and released, they develop tensile set, due to the alignment of elongated chains into ordered domains. We infer that, in the interfacial stressed state during temperature-cycling experiments, extended chains became more aligned as the number of temperature cycles increased. As a result, the elastic restoring force in these extended chains, which was responsible for making the surface hydrophobic at high temperature, decayed. In both the interfacial and bulk systems, this alignment of extended chains can relax to random-coil conformations upon annealing in the unstressed state. Thus, the damped interfacial system could be induced to show temperature-actuated oscillations again. In fact, periodic annealing during temperature-cycling experiments, using higher temperatures of the hot water, or extending of the equilibration time against hot water both tended to produce more persistent oscillations.

A second analogy involved stress relaxation *in the strained state*. The restoring force in bulk elastomers under strain gradually decreases, a phenomenon known as “stress relaxation”. Likewise, when the interfacial system was held in the strained (chain-extended) state against water at room temperature, the magnitude of the temperature-actuated effect due to rubber elasticity decreased. As with stress relaxation in the bulk, this process could be reversed by annealing, thus allowing the stress-relaxed interfacial chains to regain their ability to reconstruct entropically with almost the original magnitude. In sum, the results reported in this paper support our central hypothesis that, in these surface-modified elastomers, the migration of hydrogen-bonding groups to the polymer/water interface required polymer chains to extend out of random-coil conformations into more stretched conformations. They also illustrate the correlation of interfacial and bulk mechanical properties and the importance of treating a polymer and its surface as an integrated system.

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