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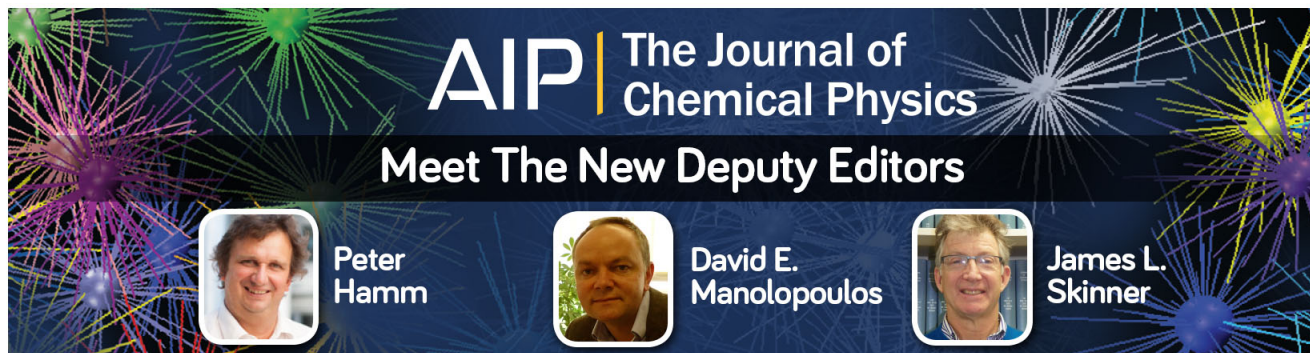
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Shape imprinting due to variable disulfide bonds in polyacrylamide gels

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Through the use of variable disulfide crosslinkers, we have created polyacrylamide gels whose shape can be altered after polymerization. *N,N'*-bisacryloylcystamine is incorporated as a crosslinker, along with a smaller amount of a permanent crosslinker. After polymerization, the disulfide bonds are cleaved into thiols through reduction. By reoxidizing the thiols with the gel held in a new macroscopic shape, a new set of disulfide bonds is formed, and the gel is forced to adopt the new shape. Retention of the new shape improves with greater distortion from the original shape, as well as with increased concentration of variable disulfide bonds. A simple theoretical model has been developed to explain these data, although the enigmatic kinetics of relaxation remain unexplained. © 2001 American Institute of Physics. [DOI: 10.1063/1.1369139]

I. INTRODUCTION

For some time now researchers have studied isotropic changes in the properties of gels.¹ They have been made to swell and shrink dramatically in response to a number of environmental variables, ranging from temperature² to metal ion concentration.³ In this experiment, we concentrated instead on a nonisotropic change. Through the use of variable crosslinkers, one can rearrange the polymers to give the gel a new equilibrium macroscopic shape. This is what we call “shape imprinting.” Figure 1 shows a gel that was synthesized as a rod but has since been bent into a spiral. This experiment differs from previous demonstrations of shape changing gels⁴ where monomer and crosslinker compositions, and thus the phase transition thresholds, are different in different regions of the gels.

Fundamentally the experiment involves five steps. First, a gel containing disulfide and nondisulfide crosslinkers is synthesized in some initial shape. Second, the disulfide bonds are cut through reduction into pairs of thiols. Third, the gel, which is now more flexible due to a smaller number of crosslinkers, is deformed into a new shape. In the fourth step, with the gel still held in its new shape, the disulfide bonds are reformed through oxidation. When the gel is let go in the fifth and final step, it retains the new shape. Due to the shape change, each thiol might not pick its original “partner,” but rather a new one which is closer to it in the new shape. The new disulfide bonds lock the polymer network into the new shape. The shape imprinting might not be perfect; some relaxation toward the initial shape may occur. Better shape imprinting results in closer retention of the new shape.

We observed the effect of two variables on shape imprinting: the concentration of variable crosslinkers, and the “degree of distortion” applied to the gel in step three. As one might expect, a greater number of variable crosslinkers (with permanent ones held at constant concentration) results

in better shape imprinting. Interesting, however, is the fact that increased distortion also causes better shape imprinting. Upon release, the gels exhibit strange relaxation kinetics: the gels relax partially in a few seconds, then undergo a motion back in the direction of the distortion for a few minutes, before relaxing once again to their final equilibrium within an hour. Once this equilibrium is reached, the new shape is quite stable and is retained indefinitely. In addition to reporting the experimental data, we discuss possible explanations for the observations, including a simple model that matches the results observed for the distortion dependence.

II. DESIGN OF THE EXPERIMENT

For quantitative measurements, we found twisting rectangular slabs of gel to be the most convenient geometry (Fig. 2). This technique allowed easy manipulation of the gels and measurement of their distortion in degrees of twisting per millimeter. The twisting is largely a shear deformation, and is uniform along the length of the slab.

Gel slabs having the same thickness and width, but different lengths L were twisted through a constant angle of 180° . In this way a range of angles per unit length was obtained. We will use θ to denote the twisting of a gel in degrees per millimeter. Initially a gel is at $\theta=0$. During reoxidation it is held at $\theta=\theta_i=180^\circ/L$, and upon release it relaxes to its new equilibrium shape with $\theta=\theta_{eq}$. Shape imprinting is quantified as the ratio θ_{eq}/θ_i . A gel exhibiting perfect shape imprinting would not spring back at all, giving a shape imprinting ratio of 1. If a gel exhibited no shape imprinting at all, the twisting process would have no effect, and the gel would return to its original shape to give a shape imprinting ratio of 0.

It should be noted that each set of data was collected from a series of gels (parallel construction), rather than by reusing a single one, since the shape imprinting process was found not to be completely reversible. Reduction after the shape change has taken place causes the gel to return to its

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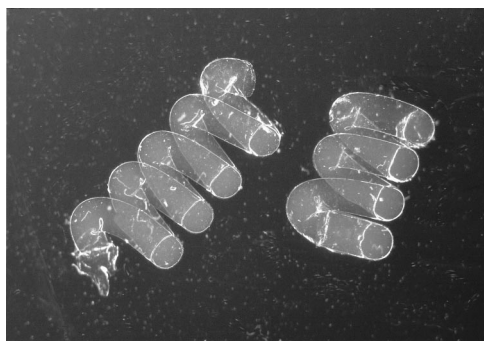


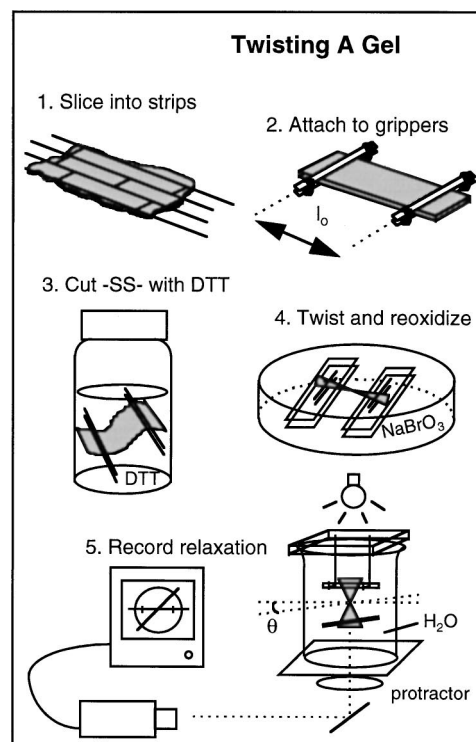
FIG. 1. This is a photograph of a gel (150 mM BAC/700 mM AAm/10 mM EGDMA) that was originally molded as rod. The $-SS-$ bonds were reduced by DTT, the gel was wrapped around a glass rod, and the $-SH$ groups were then reoxidized, imprinting the curly shape onto the polymer network. The gel shown is about 1 mm thick.

original shape, but the gel is brittle and unsuitable for further experiments.

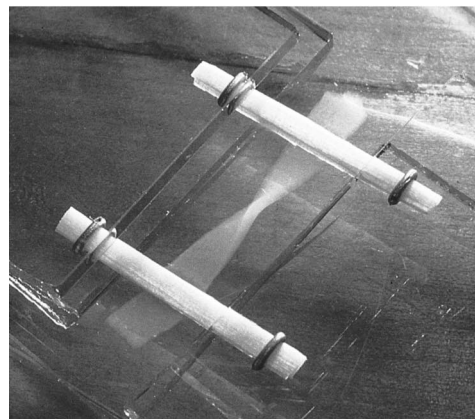
III. MATERIALS AND METHODS

The gels used in this experiment were formed by free radical polymerization. Acrylamide (AAm) was used as a backbone monomer, ethylene glycol dimethylacrylate (EGDMA) as a permanent crosslinker, 2,2'-azobisisobutyronitrile (AIBN) as an initiator, and *N,N'*-bisacryloylcystamine (BAC) as a source of disulfide linkages. The BAC molecule contains two vinyl groups that can be incorporated into the polymer network, linked by a chain containing a disulfide bond. Due to the low solubility of BAC in water, dimethyl sulfoxide (DMSO) was used as the solvent during gelation, which took place over 12–18 h (overnight) at 60 °C. The concentrations of EGDMA and AIBN were held at 10 mM and 0.10 wt%, respectively, while the concentrations of BAC and acrylamide varied. For the qualitative demonstrations (such as the gel in Fig. 1), 700 mM AAm and 150 mM BAC worked well. In the gels used in the quantitative experiments, the concentrations of AAm and BAC were varied together such that $[AAm] + 2 \times [BAC] = 900$ mM. This is so that in the reduced state, when each BAC monomer exists as two thiol-bearing residues, the density of crosslinks on the polymer chains is the same in all samples. For instance an acrylamide concentration of 700 mM corresponds to 100 mM BAC, while 800 mM AAm corresponds to 50 mM BAC. The concentrations used were 50 mM BAC/800 mM AAm, 75/750, 100/700, 125/650, and 150/600.

Before use, the gels were washed with water for several days to displace the DMSO. To reduce the disulfide bonds, the gels were immersed in a 100 mM solution of 1,4-dithiothreitol (DTT), a reagent routinely used to reduce disulfide bonds in proteins.^{5,6} A thin rod of gel will swell to about twice its original diameter as the disulfide bonds are cut, a process which takes about 48 h in the gels we used. The “cut” gel can be distorted into the desired new shape, and then transferred to a 2.0 wt% sodium bromate solution. In this solution the $-SH$ groups reoxidize to $-SS-$ in several hours, although in practice the gels were left in the sodium



(a)



(b)

FIG. 2. (a) A diagram of the process used for quantitative experiments. (b) A photograph of a gel at the reoxidation stage. The smooth twist of the slab is apparent. Once this stage is complete the plates are removed and the gel is transferred to the relaxation apparatus, where its relaxation kinetics and equilibrium are recorded.

bromate solution overnight. Once reoxidation is complete, the gel can be released, and its relaxation can be observed and measured.

The slab gels were molded between glass microscope slides spaced by another slide (thickness 1.0 mm). After washing, the slabs of gel were sliced into pieces with a uniform width of 2.5 mm [Fig. 2(a)]. The gel strips, of uniform width and thickness but varying length, were attached to grippers. These grippers, which allowed us to control the length of the gel used, to handle the gels without breaking them, to twist the gels, and later to measure their relaxation, consisted of two thin wood strips, one on either side of the gel, bound by small vinyl elastics. Other materials were tested but found to be unsatisfactory, and experiments con-

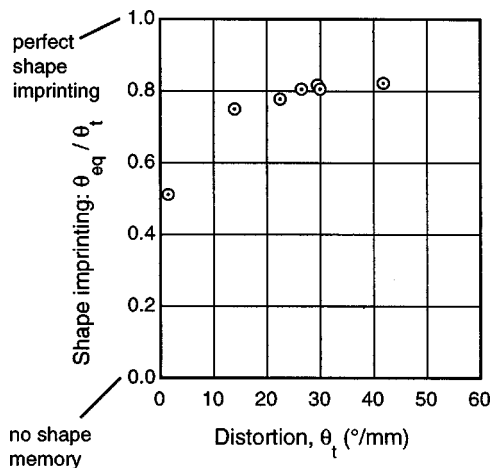


FIG. 3. Distortion dependence: the shape imprinting ratio vs distortion. In this series of normalized charts the vertical axis indicates the ratio of the equilibrium position of the gel to the amount of distortion applied. The twist deformation, measured in degrees per millimeter, was varied by applying a 180° twist to gels of various lengths. All gels contain 100 mM BAC, 700 mM AAm, and 10 mM EGDMA.

cluded that the materials did not affect the chemical reactions. The weight of the strips was controlled at 13 mg, their length at 22 mm. The length L of the gel between the grippers was measured.

After reduction, the gels were transferred to dishes of water where they were twisted 180° using the weight of thick glass slides to clamp the grippers [Fig. 2(b)]. Once the gels were twisted, sodium bromate was added, and 24 h was allowed for reoxidization. The slides were then removed and the gels were transferred to a beaker of water, where they were allowed to relax while suspended underwater by glass hooks. The angle between the grippers was observed from below using a videocamera [see Fig. 2(a)]. Dividing this angle by L gives θ in degrees per millimeter, allowing the shape imprinting ratio to be measured.

IV. RESULTS

Two primary sets of quantitative data were collected. A set of gels having equal concentrations of BAC (100 mM BAC, where 22.2% of monomers in the cut state have $-\text{SH}$) were twisted to varying degrees (Fig. 3), and their equilibrium shape imprinting ratios were determined. A second set of gels with varied concentrations of BAC were all twisted roughly $29^{\circ}/\text{mm}$ (Fig. 4) and their ratios likewise recorded. Precise repetition of the amount of twisting was difficult, as the length of the slabs to be twisted was hard to control (although measurement was accurate).

The data show that the shape imprinting ratio (θ_{eq}/θ_t) increases with increased distortion, to a maximum of about 0.82 for the 100 mM BAC gel for $\theta_t \geq 30^{\circ}/\text{mm}$. In the concentration-dependent study, we found that near-perfect shape imprinting was achieved at 150 mM BAC/600 mM AAm.

Toward the beginning of the project only equilibrium relaxation positions were recorded, but observation of the unusual relaxation kinetics prompted us to record more carefully the relaxation of the gels over time. The relaxation over

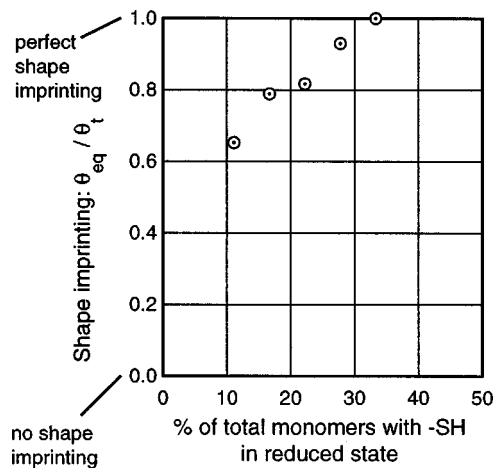


FIG. 4. Concentration dependence: the shape imprinting ratio as a function of the percentage of monomers with $-\text{SH}$ groups in the reduced state. In all cases the total concentration of monomers (besides EGDMA, the permanent crosslinker) in the pregel solution is 900 mM. We assume that each BAC molecule produces two $-\text{SH}$ monomers upon reduction. Thus the 100 mM BAC gel has 22.2% $-\text{SH}$ groups in the reduced state. All gels were twisted between 27 and $30^{\circ}/\text{mm}$, the spread due to the difficulty of setting up gels of exactly the same length.

time of several of the gels in Figs. 3 and 4 is plotted in Fig. 5. Note that one of the curves appears in both parts (a) and (b). After relaxing quickly in the first few seconds after release, the gels began retwisting: θ increased, in some cases surpassing θ_t , before decreasing again to come to equilibrium. Though it took many minutes to achieve equilibrium (θ_{eq}), the angle did not change after that. One gel was observed for over two weeks and showed no change. The kinetic data did not show a trend with respect to concentration or degree of distortion.

V. DISCUSSION

The experimental data show that increased distortion of the gel gives rise to better shape imprinting (Fig. 3). We believe that this occurs because as distortion is increased, it becomes more likely that $-\text{SH}$ groups will find new partners rather than returning to those they had in the original conformation. The number of crosslinks pulling the gel back to the original shape is decreased, and so the new shape is more thoroughly imprinted as distortion increases.

To further examine this distortion dependence, we used the following model. One recognizes that the shape imprinting observed when twisting the gel involves the relative motion of only the "tangential polymers," those which are primarily oriented tangentially to horizontal circles centered on the twisting axis (Fig. 6). We imagine the gel to be a stack of horizontal, rectangular plates separated by a uniform distance d . When the gel is twisted, tangential polymers at the same radius r in adjacent plates will slide past one another by a distance $r\Delta\theta$, where $\Delta\theta$ is the twisting angle between any two adjacent plates, dubbed the microscopic twist. If we know how these individual tangential polymers interact after reoxidation, we can integrate the force along the radius to get a torque, and set the torque to zero to find the equilibrium microscopic angle, $\Delta\theta_{eq}$. This will generate a shape imprint-

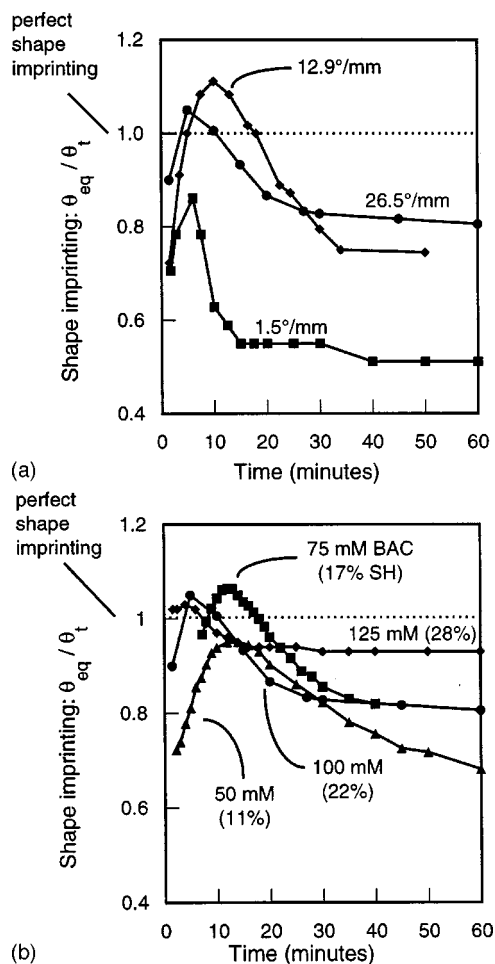


FIG. 5. The relaxation kinetics. These two charts plot the relaxation of several gels as a function of time. Zero on the time axis indicates the time of release from θ_t ; data collection starts a minute or two later, once the gel has been moved to the relaxation apparatus. (a) Relaxation kinetics of three gels of constant composition but various amounts of distortion, as in Fig. 3. (b) Relaxation kinetics of gels of similar distortion (about 29°/mm) and different concentrations of BAC, as in Fig. 4.

ing curve for the microscopic distortion, and by comparing this curve with the macroscopic version provided by the experiment, we can find d , since $d = \Delta\theta / \theta$. If this distance is on the order of the separation between polymers in the gel, we can feel confident that the model is consistent with the experimental data.

The first step is to model the interaction of two adjacent tangential polymers (Fig. 7). In Fig. 7, the $-SH$ group is depicted as being on the end of a polymer chain. In actuality each crosslinker lies in the midst of a chain of monomers, so that the “tails” in the picture would be loops, but this is of marginal importance to the model. The essence of the model is as follows. Two adjacent, parallel polymers are held together by two classical springs, one permanently attached and having constant K_{perm} and the other variably attached, having constant K_{SS} . The values of the constants reflect the concentration of each type of crosslinker in the gel. Let x denote the relative position of the two polymers, and let $x = 0$ be defined as the equilibrium displacement for the permanent crosslinker; that is, when the anchors for the permanent spring are directly on top of one another (see Fig. 7).

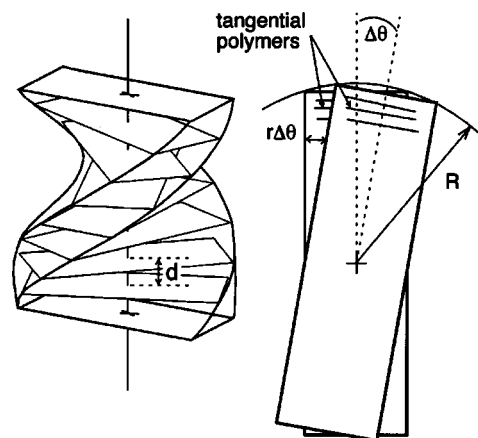


FIG. 6. To model the distortion dependence data, we describe the gel as a stack of plates spaced by a distance d . R is the radius to the edge of the gel. The relative motion of tangential polymers varies linearly with r . By matching the behavior of two adjacent plates to that of the whole gel, we can estimate d and thereby evaluate the model.

Before we start the experiment, the variable crosslinker will be at some x_0 which is not necessarily zero. However, since the gel is by definition in equilibrium after synthesis, when averaged over the whole gel, $\langle x_0 \rangle = 0$.

During the experiment, the $-SS-$ bonds are cut, leaving only the permanent crosslinkers attached, and the top polymer in the figure is translated a distance $x_d = r\Delta\theta_t$. In the reduced state, the potential “new” partners form a Poisson distribution, which is translationally invariant. However, we know there to also be a set of original partners for which $\langle x_0 \rangle = 0$. The original partners break down the translational invariance of the distribution of binding sites. Upon reoxidation, a portion of the $-SH$ groups will bind to the original sites. This portion behaves like a spring centered at $x = 0$. The portion which find new partners will behave like a spring centered about $x = x_d$. To determine what fraction of the $-SH$ groups fall into each of these two portions (and thus the relative strengths of the springs), we take the probability

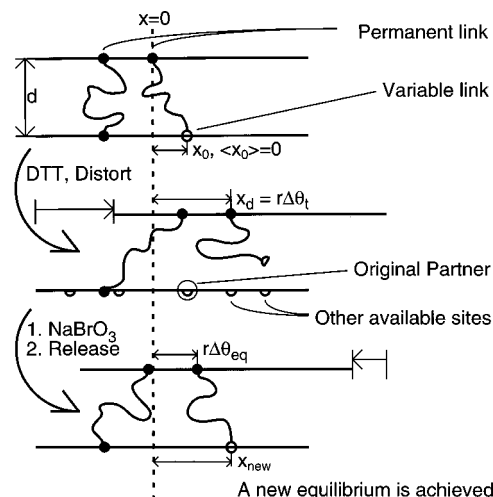


FIG. 7. The linear “submodel” approximates the interaction of tangential polymers in adjacent plates. The polymers are translated relative to one another by $x_d = r\Delta\theta$. The closed circles represent the permanent crosslinkers; the open ones represent the variable disulfide links.

distribution for the loose –SH group to be Gaussian about x_d with root mean square σ . The probability of binding to a site at x_i is

$$p(x_i) = \frac{1}{C} \exp \left[-\frac{(x_d - x_i)^2}{2\sigma^2} \right]. \quad (1)$$

The normalization constant C is given by summing the exponential term for each x_i . The binding sites x_i are randomly distributed except for x_0 , the original partner. Therefore

$$C = \exp \left[\frac{(x_d - x_0)^2}{2\sigma^2} \right] + \sum_{i \neq 0}^s \exp \left[\frac{(x_d - x_i)^2}{2\sigma^2} \right] \quad (2)$$

$$\langle S \rangle = \int_{-\infty}^{\infty} \frac{1}{\delta} \exp \left[\frac{(x_d - x)^2}{2\sigma^2} \right] dx = \sqrt{2\pi} \frac{\sigma}{\delta}. \quad (3)$$

If the –SH group recombines at some $x = x_{\text{new}}$, the force between the polymers in the x direction is

$$F_x = -K_{\text{perm}}x - K_{\text{SS}}(x - x_{\text{new}}), \quad (4)$$

$$\langle x_{\text{new}} \rangle = \underbrace{x_0 p(x_0)}_{\langle x_0 \rangle = 0} + \underbrace{\sum_{i \neq 0}^{\infty} x_i p(x_i)}_{\text{Symmetric about } x_d} \quad (5)$$

$$= x_d(1 - p(x_0)) \quad (6)$$

$$= \frac{x_d}{1 + \frac{1}{\sqrt{2\pi}\sigma} \exp \left[\frac{-x_d^2}{2\sigma^2} \right]}, \quad (7)$$

$$\langle F_x \rangle = -(K_{\text{perm}} + K_{\text{SS}})x + \frac{K_{\text{SS}}x_d}{1 + \frac{1}{\sqrt{2\pi}\sigma} \exp \left[\frac{-x_d^2}{2\sigma^2} \right]}. \quad (8)$$

This is the force by one polymer on the other as a function of displacement. Upon release, the gel as a whole must twist until it finds the equilibrium angle where the total torque is zero. We integrate the force to find the torque. Let $x_d = r\Delta\theta_t$:

$$T(\Delta\theta) = \int_{r=0}^R r F(r, \Delta\theta) dr \quad (9)$$

$$= \int_{r=0}^R r \left[-(K_{\text{perm}} + K_{\text{SS}})r\Delta\theta + \frac{K_{\text{SS}}r\Delta\theta_t}{1 + \frac{1}{\sqrt{2\pi}\sigma} \exp \left[\frac{-(r\Delta\theta_t)^2}{2\sigma^2} \right]} \right] dr \quad (10)$$

$$= 0 \quad \text{for } \Delta\theta = \Delta\theta_{\text{eq}}. \quad (11)$$

This equation is solved numerically. Appropriate values must now be chosen for K_{perm} , K_{SS} , δ , and σ so that a microscopic shape imprinting curve ($\Delta\theta_{\text{eq}}/\Delta\theta_t$ vs $\Delta\theta_t$) may be plotted and compared to the experimental data for the macroscopic twist.

The radius R of the gel strips is 1.25 mm (half of their width). K_{perm} and K_{SS} are simply the concentrations of permanent and disulfide crosslinkers during relaxation. The first of these is designed to be 10 mM, and the second can be calculated from the high-distortion limit of the shape imprinting ratio, where $\langle x_{\text{new}} \rangle \approx x_d$:

$$K_{\text{SS}} = K_{\text{perm}} \lim_{\theta_t \rightarrow \text{large}} \frac{\theta_{\text{eq}}/\theta_t}{1 - \theta_{\text{eq}}/\theta_t} = 10 \text{ mM} \times \frac{0.82}{1 - 0.82} \approx 50 \text{ mM}. \quad (12)$$

It is apparent that complete reoxidation does not occur; some groups are left without partners.

Typically, for a polymer bound at one end, the Gaussian probability distribution describing the other end has $\sigma = a\sqrt{N}$ where a is the size of one “bead,” the smallest unit of a polymer chain that can be said to rotate freely, and N is the number of beads in the chain. In our case, the loops of polymer bearing –SH groups are bound at both ends, so we will let $\sigma = a\sqrt{N}/2$. We will approximate a as two monomer units, or about 6 Å. This makes N equal to half the number of monomer units between crosslinks:

$$N = \frac{1}{2} \frac{\overbrace{[\text{AAm}] + [\text{SH}]}^{\text{monomers}}}{\underbrace{2[\text{SS}] + 2K_{\text{perm}}}_{\text{two sides per crosslinker}}}. \quad (13)$$

To find δ , the average distance between available binding sites, we divide the total concentration of polymer chain components by the concentration of –SH groups, and multiply by the length of a monomer, $a/2$. Thus

$$\sigma = \frac{a}{2\sqrt{2}} \sqrt{\frac{[\text{AAm}] + [\text{SH}]}{2[\text{SS}] + 2K_{\text{perm}}}}, \quad (14)$$

$$\delta = \frac{a}{2} \times \frac{[\text{AAm}] + [\text{SH}] + 2[\text{SS}] + 2K_{\text{perm}}}{[\text{SH}]}. \quad (15)$$

Both σ and δ depend on $[\text{SS}]$ and $[\text{SH}]$. These concentrations change over the course of the reaction, with $[\text{SS}]$ rising from zero at the start of reoxidation to its maximum, K_{SS} . To simplify the problem, we will pick a single characteristic $[\text{SS}]$ to use such that the experimental data is most closely matched. This characteristic $[\text{SS}]$ signifies in a rough way the point in the reaction at which the new equilibrium is selected.

In Fig. 8, curves for several $[\text{SS}]$ values are compared to the experimental data from Fig. 3. The theoretical curve is plotted against $\Delta\theta_t$, the microscopic twist between adjacent “plates” in the model, measured in degrees. The data are plotted against the macroscopic twist θ_t , measured in degrees per millimeter. A characteristic $[\text{SS}]$ of 10 mM is selected as the best fit. The length scales are adjusted to best

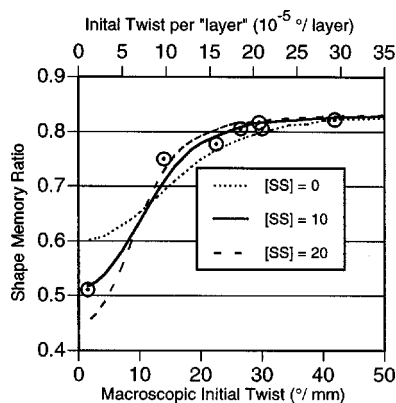


FIG. 8. Over the course of reoxidation, the concentration of disulfide bonds, $[SS]$, varies, and this affects the flexibility of the polymer chains and the density of binding sites. Thus we pick the best-matching intermediate value of $[SS]$ and adjust the axes for the best fit. The top axis measures $\Delta\theta_i$, the bottom measures θ_i . Dividing the uppermost values of the axes gives $d = 70 \text{ \AA}$, which is reasonable.

match the points, and we divide the scales to obtain a length d , the separation between plates, equal to 70 \AA . Of course the gel is not nearly so regular in structure, but the point is that by considering a Gaussian probability density for the motion of a loop of polymer, and a Poisson distribution for binding sites along an adjacent chain (except for the known sites), we can reproduce the observed distortion dependence assuming that these chains are separated by a distance which, to an order of magnitude, is believable.

The concentration dependence curve (Fig. 4) is roughly linear, with a higher fraction of variable crosslinkers giving rise to a higher shape imprinting ratio, as might be expected. Once the concentration gets high enough, there are so many new partners to choose from that the original shape seems to be entirely forgotten and the new one perfectly retained. Of course, this is only a limiting case and one must assume that the 100% measured for the gel with a $[BAC]$ of 150 mM means simply that at that point the resolution limit of the experiment has been reached. Note also that the data do not appear to extrapolate to 0 at zero distortion, but rather to reach a finite limit. We assume this is due to some nonlinear behavior of the curve near zero concentration, or perhaps due to some small malleability of the permanently crosslinked gel.

The relaxation time dependence is one of the most puzzling parts of this experiment. As can be seen clearly in Fig. 5, the gels relaxed some immediately following release (before measurement could begin), but then underwent a very slow oscillation back toward further distortion, sometimes even assuming more than the applied twist, before finally relaxing again to equilibrium within an hour. While we have not been able to come up with a good explanation for this, we can rule out several possibilities.

When a mechanical spring is distorted and released, it exhibits damped harmonic oscillations until it finally settles at equilibrium. However, it is clear that the period of the gels' oscillation is far too long for such a mechanism.

It is worth noting that the gels were transferred out of the sodium bromate solution and into pure water to observe the relaxation. It is natural to suspect that the gel may have absorbed or released liquid after the transfer, thus affecting the data. However, during preliminary experiments, switching between sodium bromate solution and water was observed to have no effect on the size of the gels in the oxidized state. Furthermore, it remains to be seen how absorbing or releasing liquid could be responsible for both the extra twisting and the subsequent relaxation.

It is probable that the three motions: initial relaxation, hypertwisting, and long-term relaxation are due to three different forces, given the different time scales of each. The first lasts just seconds, the second 5–10 min, and the last 30–60 min. Further experiments would be necessary for a more thorough explanation.

VI. CONCLUSIONS

We have synthesized polyacrylamide-based gels which can be given a new shape due to the inclusion of variable disulfide bonds. Gels can be permanently distorted into any desired shape, as demonstrated in Fig. 1. The coils of gel that we formed as a demonstration (Fig. 1) inspired us to nickname this process the "gel perm effect" after the similar process of rearranging (protein) polymers in hair to imprint a permanent wave.

Shape imprinting improves with increasing concentration of disulfide bonds, and with increasing distortion from the gel's original shape. The kinetics of relaxation from the new shape are bizarre, featuring a fluctuation back toward and even beyond the original distortion before equilibrium is finally achieved. In Sec. V, we offer an explanation for the distortion dependence, and discuss possible causes for the behavior seen in the other sets of data. These or similar gels may one day allow the creation of gels in shapes that are difficult to mold, and may also find use in situations where the desired shape is not yet known at the time of polymerization, but may be applied at any later time.

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