A New Opto-Mechanical Effect in Solids

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We propose that large, reversible shape changes in solids, of between 10%–400%, can be induced optically by photoisomerizing monodomain nematic elastomers. Empirical and molecular analysis of shape change and its relation to thermal effects is given along with a simple model of the dynamics of response. Our experiments demonstrate these effects for the first time and theory is compared qualitatively with our results.

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Nematic elastomers have the remarkable property of being able to change their shape by up to 400% in a relatively narrow temperature interval straddling their nematic-isotropic (NI) transition temperature, T_{ni} [1]. This extreme effect is a reversible elongation (contraction) along the director, $\mathbf{n}$, on entering (leaving) the nematic state. Simultaneous measurements of the nematic order parameter with length change [2] confirm old molecular pictures [3,4] that molecular shape is coupled to macroscopic sample shape and that molecular shape depends dramatically on the state of nematic order. Neutron scattering further confirms this dependence [5].

One would accordingly expect that if nematic order could be suppressed (or restored) by other methods, then there would be equally dramatic accompanying mechanical responses. In this Letter we demonstrate experimentally that this can be achieved optically and then show empirical and theoretical relations to the well-established thermomechanical phenomenon.

When azo dyes and other photoisomerizable molecular rods adsorb light, they suffer a *trans* → *cis* isomerization whereupon they are bent (until undergoing the reverse *cis* → *trans* reaction, whereupon the rods are restored). Such rods leave the nematic distribution and indeed dilute the nematic mean field, thereby lowering the nematic order parameter [6]. (It is also possible to rotate the director by the mechanism, but we ignore such effects in this Letter by assuming illumination with light either polarized along the director or unpolarized and propagating along the director.) The pioneering work of Eisenbach [7] explored the rate constants for photoinduced and thermal back reaction *cis* → *trans*. Eisenbach also looked at the contractions (~0.25%) of loaded, isotropic networks under illumination. Our work uses nematic-mechanical coupling to magnify these opto-mechanical effects by factors of 10^2–10^3.

Experimental.—We synthesized a wide range of monodomain nematic elastomeric networks by the technique of two-stage cross-linking, the second stage being under imposed extension and either in the nematic or isotropic state [8]. Here we are simply interested in establishing the phenomenon and report only on one elastomer, AE4. The backbone was Poly[oxy(methylsilylene)] (PHMS) and the (side chain) pendant mesogenic rod was $\mathrm{M4OCH_3}$ (62%). A small amount of M4CN (1%) is taken as a side chain since IR dichronism on its CN bond yields the nematic order parameter. Some nonliquid crystal side chain, $\mathrm{MOCH_3}$ (7%), is added to influence the glass temperature. A first-stage linker V1 (10%) and a photoisomerizable linker AV2 (20%) create the network. The bracketed percentages denote the concentration per HMS unit. The structures are given in Fig. 1.

Extinction measurements at 450 nm (sensitive to the *cis* population) confirmed that the UV light at 365 nm actually induced photoisomerization of AV2 units in the networks just as would have been achieved in solution. The back reaction *cis* → *trans* occurs thermally in the dark, with a relaxation time of some 100 s of min [7] (at 298 K). It can otherwise be optically induced; indeed it appears that our UV light overlaps with the tail of the *cis* absorption and optically induces a back reaction. We shall report at

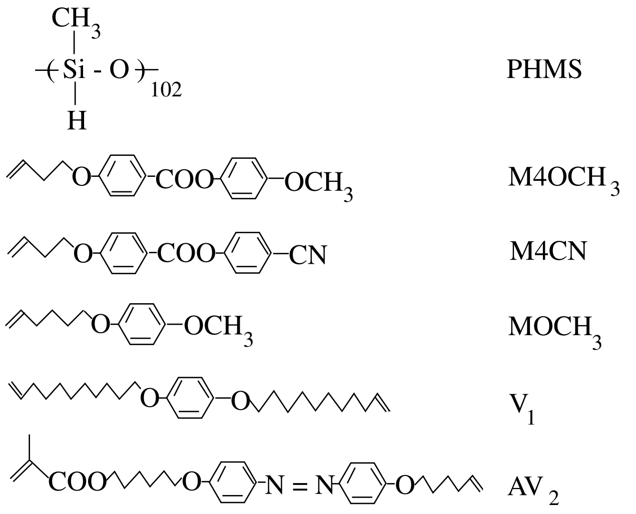

FIG. 1. Chemical structure of elastomer AE4.

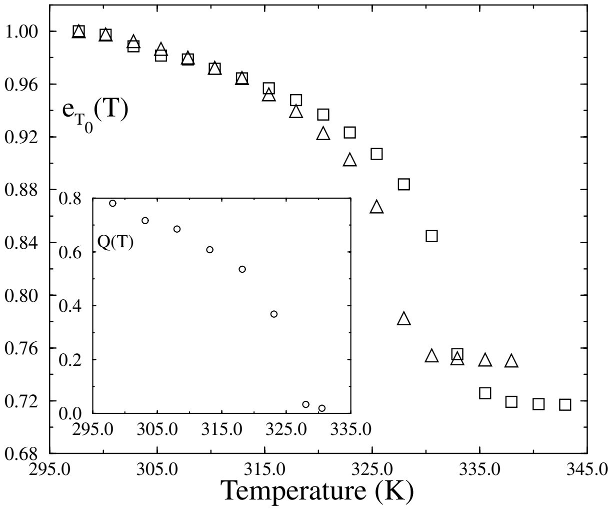

FIG. 2. Relative contraction $e_{T_0}(T) \equiv L(T)/L$ ($T = 298$ K) versus temperature, T, for AE4 cross-linked in an isotropic (△) or nematic (□) second stage. Inset: Change in order parameter, Q, as a function of temperature, for the second-stage isotropic cross-linked elastomer.

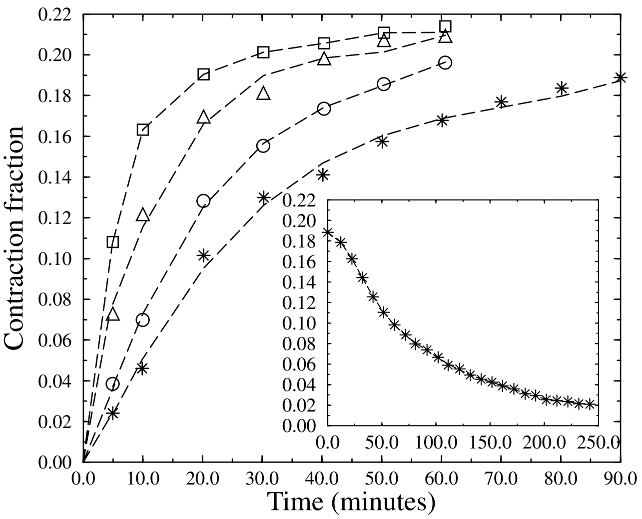

FIG. 3. Contraction fraction, $1 - e_{T_0}(t)$, versus time exposed to UV radiation for $T_0 = 298$ K (⋆), 303 K (∘), 308 K (△), and 313 K (□). Dashed lines are guides for the eye. Close to the origin curves may have an inflexion point. Inset: Recovery of the contraction for the 298 K elastomer after the 90 min of illumination.

length on these characterization checks and the elastomers elsewhere.

Figure 2 shows the relative contraction $e_{T_0}(T) \equiv L(T)/L$ ($T_0 = 298$ K) versus temperature, T, for AE4 cross-linked in an isotropic (△) or nematic (□) second stage, where L is the sample length. The subscript T_0 on e reminds us of the temperature at which the reference length defining the thermal strain is measured. We concentrate on the isotropic second-stage system which is seen to undergo a 24% contraction in going from 298 K to its isotropic state. The inset in Fig. 2 shows the accompanying change in order parameter, Q.

Figure 3 shows the fractional contraction of elastomers, $1 - e_{T_0}(t)$, at various temperatures against the time they are exposed to UV radiation. We now write $e_{T_0}(t)$ to indicate the time dependence (t) of the photostrain induced at an actual fixed temperature, T_0, of illumination. The elastomer at 313 K achieves essentially all (22%) it would experience on heating from 313 K to the isotropic state. The elastomer at 298 K suffers a 17% change (relative to the 24% change found on heating to isotropy). Figure 3 (inset) also shows the recovery of the 298 K elastomer, after illumination is switched off. These optical effects are large. Solids optically and reversibly changing their dimensions by 20% are unknown. Since photostrains are comparable to thermal effects, we can ultimately expect nematic elastomers to generate optical strains up to 400%, since this strain is easily achievable thermally [1].

Empirical analysis.—We can qualitatively explain the optical behavior in terms of thermal response if we assume both induce order parameter change and that mechanical strains follow order, irrespective of how it is induced to change. The nematic mean field potential is $U(\theta) = -JQP_2(\cos\theta)$, where θ is the angle a rod makes with the nematic director and P_2 is the second Legendre polynomial. The nematic mean field coupling constant J depends on the concentration, ρ, of other nematogenic (nonbent) rods present as ρ^{ϵ} [9]. In turn, the NI transition temperature, $T_{\rm ni}$, scales with J. The dependence is $T_{\rm ni} = J/(4.541 k_B)$ in Maier-Saupe theory [10] and hence thermal effects scale with $T_{\rm ni}$. In Landau theory $F \sim \frac{1}{2}A_0 T^*(T/T^* - 1)Q^2 + \ldots$, $T_{\rm ni}$ is close to T^* and where again T^* scales with J, i.e., $T^* = J/(5k_B)$. In either case, one can represent any change of J or T^* as being equivalent to an effective change in T at constant T^*. Therefore, illumination changing ρ and thus J are equivalent to shifting temperature. Accordingly we can map optical response onto independently measured thermal effects; see Fig. 2.

If ρ_0 denotes the concentration of rods at the start of illumination and ρ denotes its current concentration, the coupling constant changes from J_0 to $J = J_0(1 - \Delta\rho/\rho_0)^{\epsilon}$ as the bent rod population varies, where $\Delta\rho \equiv \rho_0 - \rho$. Given $\Delta\rho$ is relatively small we have $[T^*(t) - T^*]/T^* \equiv \delta T^*/T^* \equiv (J - J_0)/J_0 \approx -\epsilon\Delta\rho/\rho_0$. In Landau–de Gennes or Maier-Saupe theory, changing T^* by δT^* is equivalent to changing the real temperature T_0 to an effective temperature $T = T_0 - \delta T^*$, since the temperature appears only in the free energy through T/T^*. Thus $\delta T/T_{\rm ni} = \epsilon(T^*/T_{ni})\Delta\rho/\rho_0$.

To find the current order from the dark state order at this real temperature, T_0, we shift $Q(T_0)$, inset in Fig. 2, by δT (>0). Equivalently, in the same figure, the shift yields the percentage contraction in the sample, initially (and actually) at T_0 and finally effectively at $T_0 + \delta T$. Ignoring for the moment back reactions, the change in rod concentration is proportional (with proportionality constant

α) to the radiation, R, adsorbed by the dye rods in the sample, $\Delta\rho = \alpha R = \beta t$. The constant β adsorbs α and the proportionality between R and t (time). We see that T is shifted by about 30 in 330 K and thus $\Delta\rho/\rho_0 \sim 0.045$. From above we have $\delta T^*/T^* = -\epsilon\Delta\rho/\rho_0 = -\gamma t$, where in γ we have absorbed β and ϵ/ρ_0. Thus the optically induced effective change in temperature is $\delta T = T_{\mathrm{ni}}\gamma t(T^*/T_{\mathrm{ni}})$. Using Fig. 2 we can qualitatively explain the opto-elastic response of Fig. 3.

The initial slope $de_{T_0}(t)/dt$ is greater for the elastomers at the higher temperatures, T_0, since these correspond to steeper points on the $e_{T_0}(T)$ curve in Fig. 2. Thus the strain and the strain rates are

$$\begin{aligned} e_{T_0}(t) &\equiv L(t, T_0)/L(T_0) \equiv L[T_0 + \delta T(t)]/L(T_0), \\ \frac{de_{T_0}}{dt} &= \frac{1}{L(T_0)}\left[\frac{dL(T)}{dT}\right]_{T_0+\delta T}\frac{d(\delta T)}{dt} \\ &\equiv \frac{L'(T_0 + \gamma T_{\mathrm{ni}}t)}{L(T_0)}\gamma T^*, \end{aligned} \tag{1}$$

whereupon $e'_{T_0}(t = 0) = \gamma T_{\mathrm{ni}}L'(T_0)/L(T_0)$ where we have set $T^* = T_{\mathrm{ni}}$. For the cases of Fig. 3, this is greatest at $T_0 = 313$ K and least at 298 K. Equally (1) shows (a) that de_{T_o}/dt is maximal at times which lead to an effective temperature $T_0 + \delta T$ where L' is maximal and (b) that $e_{T_0}(t)$ tends at large times to $L(T > T_{\mathrm{ni}})/L(T_0) = e_{T_0}(T > T_{\mathrm{ni}})$, the maximal thermal strain possible.

Despite the qualitative agreement with (1), Fig. 3 shows deviations from (a) and in the times shown does not quite attain (b), even for the 298 K sample.

Back reactions and dynamics.—We now look at the role of the order parameter, back reaction, and other related dynamical questions. The rate of photoisomerization [11] for a given rod depends on the intensity of illumination, I, and $\cos^2\theta$, where θ is the angle between the given rod and the electric vector of the light wave. If this is along $\mathbf{n}$ then averaging along all rods yields $\langle\cos^2\theta\rangle = \frac{1}{3}(1 + 2Q)$. Thus the rate of reduction in the concentration ρ of *trans* dye molecules is $d\rho_{tc}/dt = -\eta(Q)\rho$, where the rate η adsorbs I, the above function of Q, and other proportionalities. For diffuse illumination by unpolarized light we can ignore the Q dependence in η (setting $Q = 0$).

The back reaction proceeds either thermally or can be stimulated by illumination of color appropriate to the *cis* state. It depends on the *cis* density $\rho_0 - \rho$, where ρ_0 is the equilibrium *trans* concentration before illumination. Thus $d\rho_{ct}/dt = \frac{1}{\tau}(\rho_0 - \rho)$ where the rate $1/\tau$ (with lifetime τ) depends in principle on the nematic order Q and on the intensity of back stimulating light (if any). Thus the rate equation is given by $d\rho/dt = d\rho_{tc}/dt + d\rho_{ct}/dt$:

$$\frac{d\rho}{dt} = -\eta(Q)\rho + \frac{1}{\tau(Q)}(\rho_0 - \rho). \tag{2}$$

Equation (2) can be highly nonlinear, if we retain the Q dependence in η and τ, since Q depends on ρ [see the above Maier-Saupe and Landau pictures of $T^*(\rho)$]. If we use diffuse illumination and assume τ and η are independent of Q, then (2) is linear and gives

$$\rho(t) = \frac{\rho_0}{1 + \tau\eta}\{1 + \tau\eta\exp[-t(1 + \tau\eta)/\tau]\}, \tag{3}$$

with finally $\rho(\infty) = \rho_0/(1 + \tau\eta)$ and initially $\rho(t \sim 0) = \rho_0(1 - \eta t)$.

Recall that in the empirical analysis we ignored the back reaction. Equation (3) shows that initially $\Delta\rho(t) = \rho_0 - \rho(t) = \rho_0\eta t$, thereby identifying the rate β as $\rho_0\eta$ and also $\eta = \gamma/2$. In analyzing the early slopes this way we were assuming that $t \ll \tau/(1 + \eta\tau)$, but for times longer than this the full form (3) must clearly be used. This explains why the initial slope analysis given below (1) is correct, but that the expectation (a) that $e_{T_0}(t)$ curves can have higher slopes at later times [when effective δT takes $L(T_0 + \delta T)$ to its steepest point] can be confounded by the back reaction dynamics included in (3). There are hints of upward curvature in Fig. 3, but reduction of slopes generally points to the back reaction slowing the growth in the population of bent rods. Figure 3 suggests that the time constant of this decay must be in the region of 10–15 min, in agreement with magnitudes of optically stimulated back reactions determined by Eisenbach [7]. Our primary illumination at 365 nm evidently also interacts with the *cis* isomers. As a preliminary test of our theory, we analyze this $e_{T_0}(t)$ data using linear dynamics and present a full analysis of the slopes and the nonlinear forms of (2) elsewhere.

To determine $\rho(t)$ fully we require η and τ. The strain given in Eq. (1) can be related to $\rho(t)$ through the latter's connection with δT, namely, $\delta T = 2T_{\mathrm{ni}}\Delta\rho(t)/\rho_0$ with $\rho(t)$ given by Eq. (3). Thus $e_{T_0}(t) = e_{T_0}[T(t)] = e_{T_0}[T_0 + 2T_{\mathrm{ni}}\Delta\rho(t)/\rho_0]$. Thus $\Delta\rho(t)$ translates to $e_{T_0}(t)$ by its being filtered through the thermal function $e_{T_0}(T)$. The data are most complete for $T_0 = 298$ K. The initial slope gives η, as explained above. Putting $\Delta\rho(t = 90 \text{ min})$ into the theoretical e [filtered through $e_{T_0}(t)$ of Fig. 2] and fitting this e to the experimental value gives an estimate of the whole function $e_{T_0}(t)$; see Fig. 4. Considering that the $\rho(t)$ is filtered through a highly nonlinear function, the match is very good. Deviations arise perhaps from nonlinear dynamical effects and a lack of precision in the thermal data of Fig. 2 in the region that is most critical, that is, where the slope is greatest. We have taken T_{ni} to be the temperature of greatest slope. There is scope for error here too since the number of experimental points in this region of $e_{T_0}(T)$ is not large.

By contrast, the decay of contraction after all illumination is switched off has a conspicuously longer time scale. Applying the analysis above and assuming the contraction is purely due to the recovery of the distribution of rods, then a time constant of $\tau_f \sim 200$ min is required;

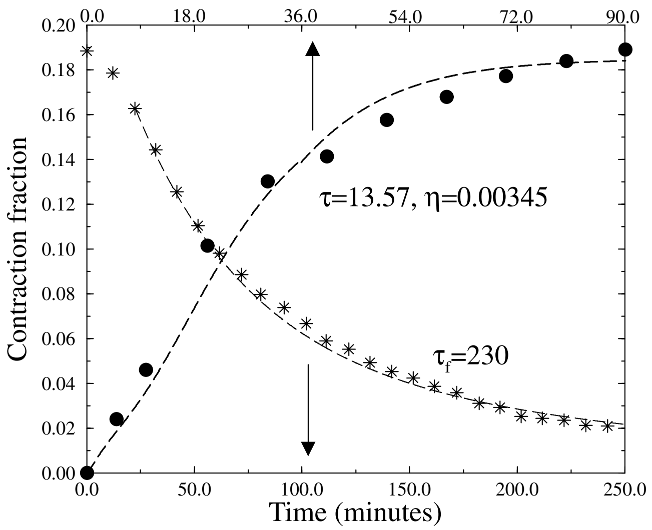

FIG. 4. Theoretical fitting (dashed curves) of fraction $1 - e_{T_0}(t)$ for both contraction (upper scale) and recovery (lower scale) versus time for the elastomer at 298 K. Symbols are experimental data.

see the form achieved in Fig. 4. The initial points, beyond the point of inflection, have not been fitted to since they correspond to an initial point for recovery that is at an effective temperature above the point of inflection in Fig. 2. The thermal data in this region are not precise enough to give this turnover meaningfully. This dark-state, thermal relaxation rate is again entirely expected from the investigations of Eisenbach.

We have shown experimentally and theoretically that large (here 20%, but other thermal models [1] have shown 400%) shape changes in solids can be generated optically. These are reversible and offer interesting possibilities as actuators and other devices which can generate mechanical work. We report elsewhere on a number of issues outstanding in this Letter: materials optimized for larger effects, photo units in other than a linkage position, selectively stimulated back reactions, a full matching of models of both photochemical and network dynamics when their time scales are comparable, forward and back reaction rates dependent on order parameter and other causes of nonlinearity in dynamics, mechanical bias of the *trans-cis* equilibrium, director rotation and its mechanical effects, and the extraction of mechanical work.

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