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Thermal and Photo-actuation in Nematic Elastomers

Mark Warner, Eugene Terentjev*

Cavendish Laboratory, Madingley Road, Cambridge, CB3 0HE, UK
Email: mw141@cam.ac.uk

Summary: Mono domain nematic elastomers change shape by as much as 400% on being heated from the nematic to isotropic state. The reason is that nematic order, *Q*, elongates the distribution of chains and thus the network that they form. Experimental evidence for this, and simple theory is presented. A novel method to change Q, and hence obtain an analogous elastic strain, is to bend the nematic's rods by photoisomerization. On absorbing a photon, photochromes such as azo rods leave the (straight) *trans* state and adopt the *cis* (bent) form. We show data and give simple theory to explain this remarkable, reversible elastic phenomenon.

Keywords: actuation; nematic elastomers; photochromes; photo-isomerization; photo-thermal strains

Introduction

Nematic polymers have incorporated into their structure rod-like elements that orientationally order. These can be pendant as in side chain polymers, or in the backbone as in main chain polymers. These polymers retain sufficient flexibility that they can easily be long enough to remain Gaussianly (random walk-like) distributed. They have a different effective step length along the director (the direction of ordering) from that in the two perpendicular directions.

Elastomers composed of nematic polymers cross-linked together can be made as large monodomains.[1] They then are found to have remarkable elastic and optical properties. For instance some shape changes can be made without energy cost (so called "soft elasticity") when they involve changes in the director.[2] The property of most interest here is that of spontaneous mechanical shape change when the degree of ordering is changed. Most typically this has been done by heating through the temperature T_{ni} from the nematic to the isotropic state. Another more novel route is to lower the order optically, that is by photoisomerizing the nematic rods to a bent state where they dilute the nematic ordering. In either case, as we shall show, the effects are very large – up to 400% strains have been observed. This thermo-optic elastic response offers possibilities for actuation that will become clear from our results. We shall also discuss

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the dynamics of optical actuation – how the disordered state is achieved and how recovery takes place. This can be thermally activated or optically stimulated, offering a wide range of time scales and measures of control.

There is a literature of actuation in classical elastomers, both thermally and optically, which we review. The mechanism is rather different and there are constraints upon routes to mechanical response that do not apply to nematic elastomers. The contrast reveals an insight into these new materials.

Polymer Conformations and Classical Rubber Elasticity

An isotropic polymer melt has a Gaussian distribution of chain shapes characterized by its second moment, the mean square size of chains, $\langle \underline{R}^2 \rangle = \ell\, L$. Here ℓ is the effective step length, expressing the local stiffness of the polymer, and L the arc length of the chain. The mean square sizes in the three perpendicular directions are the same and have been added together. By contrast, nematic polymers have a mean square size differing along and perpendicular to the ordering, with corresponding effective step lengths. In fact the effective step length is replaced by a matrix (tensor) of effective step lengths, defined by the averages below:

$$\langle \underline{R}\underline{R} \rangle = \tfrac{1}{3}\underline{\underline{\ell}}\, L \qquad \langle R_{\parallel}{}^2 \rangle = \tfrac{1}{3}\ell_{\parallel}\, L \qquad \langle R_{\perp}{}^2 \rangle = \tfrac{1}{3}\ell_{\perp}\, L \qquad \underline{\underline{\ell}} = \begin{pmatrix} \ell_{\parallel} & 0 & 0 \\ 0 & \ell_{\perp} & 0 \\ 0 & 0 & \ell_{\perp} \end{pmatrix}$$

The vital point is that the nematic order, Q, creates a step length tensor $\underline{\underline{\ell}}$ that is no longer isotropic (a sphere $\underline{\underline{\ell}} = a\underline{\underline{\delta}}$) but has become a prolate spheroidal average shape, that is, an elongated object. The nematic order is defined as $Q = \langle P_2(\cos\theta) \rangle$ where $P_2(\cos\theta)$ is the second Legendre Polynomial and the average $\langle \cdot\ \cdot\ \cdot \rangle$ is over angles θ that the rods make with the ordering direction, the director $\underline{n}$. Q is a measure of the order, where $Q = 1$ for perfect alignment of rods and $Q = 0$ for the isotropic state.

Changes in the natural shape of chains between network formation and current conditions are well known in classical elastomers.[3] Let the current and formation state chain distributions of the end-to-end vectors $\mathbf{R} = \underline{\underline{\boldsymbol{\lambda}}}\cdot\mathbf{R}^0$ and $\mathbf{R}^0$ be respectively:

$$P(\mathbf{R}) \sim \exp[-3\mathbf{R}\cdot\mathbf{R}/2\ell L] \quad \rightarrow \quad \exp[-3(\underline{\underline{\boldsymbol{\lambda}}}\cdot\mathbf{R}^0)\cdot(\underline{\underline{\boldsymbol{\lambda}}}\cdot\mathbf{R}^0)/2\ell L] \qquad \text{(current)}$$

$$P_f(\mathbf{R}^0) \sim \exp[-3\mathbf{R}^0\cdot\mathbf{R}^0/2\ell_0 L] \qquad \text{(formation)}$$

The deformation since formation is $\underline{\underline{\boldsymbol{\lambda}}}$ which took the formation span to the current value, $\mathbf{R}$. The free energy of a strand is the logarithm of the statistical weight, quenched averaged with $P_f(\mathbf{R}^0)$, the probability of finding the span $\mathbf{R}^0$ that the current span derived from during deformation:

$$F_{class} = -\mathrm{k_B}T < \ln[P(\mathbf{R})] >_{P_f(\mathbf{R}^0)} = \mathrm{k_B}T\, 3 < \frac{(\underline{\underline{\boldsymbol{\lambda}}}\mathbf{R}^0)\cdot(\underline{\underline{\boldsymbol{\lambda}}}\mathbf{R}^0)}{2\ell L} >_{P_f(\mathbf{R}^0)} \qquad \text{giving}$$

$$F_{class} = \tfrac{1}{2}\mathrm{k_B}T\,\frac{\ell_0}{\ell}\mathrm{Tr}\{\underline{\underline{\lambda}}^{\mathrm{T}}\cdot\underline{\underline{\lambda}}\} \;\rightarrow\; \tfrac{1}{2}\mu\left\langle\alpha_i^2\right\rangle\left(\lambda^2+\frac{2}{\lambda}\right) \text{ (the free energy density)}$$

where the shear modulus $\mu = n_s k_B T$ converts the energy per strand into an energy density (n_s is the number density of strands) and where we have taken an extension of λ in one direction and compressions of $1/\sqrt{\lambda}$ in the other two. The distortion tensor $\underline{\underline{\lambda}}$ is uniaxial and will also be used below:

$$\underline{\underline{\lambda}} = \begin{pmatrix} \lambda & 0 & 0 \\ 0 & 1/\sqrt{\lambda} & 0 \\ 0 & 0 & 1/\sqrt{\lambda} \end{pmatrix}$$

The factor $\frac{\ell_0}{\ell} \equiv \frac{R_0^2}{R^2} = \left\langle\alpha_i^2\right\rangle$ takes account of the mean square size R^2, perhaps changing with, e.g., temperature. The stress derives from this: $\sigma = \mu\left\langle\alpha_i^2\right\rangle\left(\lambda - \frac{1}{\lambda^2}\right)$. It will then change at fixed extension if $\left\langle\alpha_i^2\right\rangle$ does (the experiment of Matejka *et al*[4]) and if the load σ is fixed, then the deformation will change (the experiment of Eisenbach[5]). To get a response, there has to be a pre-stress of some sort. In pioneering experiments Eisenbach and Matejka *et al* changed R^2 and thus $\left\langle\alpha_i^2\right\rangle$ by photoisomerizing rod monomers from the straight *trans* to the bent *cis* form. Matejka *et al* achieved a change of a factor of 2 in $\left\langle\alpha_i^2\right\rangle$ and hence in stress, that would convert into a 1% strain if the experiment had instead been done at constant load.

Nematic Rubber Elasticity

The chain distributions corresponding to the anisotropic mean squares given above are:

$$P(\mathbf{R}) \sim \exp[-3(\underline{\underline{\lambda}}\cdot\mathbf{R}^0)\cdot\underline{\underline{\ell}}^{-1}\cdot(\underline{\underline{\lambda}}\cdot\mathbf{R}^0)/2L] \qquad \text{currently (at deformation } \underline{\underline{\lambda}}\text{) and}$$

$$P_f(\mathbf{R}^0) \sim \exp[-3\mathbf{R}^0\cdot\underline{\underline{\ell}}_0^{-1}\cdot\mathbf{R}^0/2L] \qquad \text{at formation.}$$

The quenched average giving the free energy per strand is:

$$-k_{\mathrm{B}}T < \ln[P(R)] >_{P_f(\mathbf{R}^0)} = k_{\mathrm{B}}T\, 3 < \frac{(\underline{\underline{\lambda}}\cdot\mathbf{R}^0)\cdot\underline{\underline{\ell}}^{-1}\cdot(\underline{\underline{\lambda}}\cdot\mathbf{R}^0)}{2L} >_{P_f(\mathbf{R}^0)}$$

which yields the free energy density:

$$F_{nem} = \tfrac{1}{2}\mu\,\mathrm{Tr}[\underline{\underline{\ell}}_0\cdot\underline{\underline{\lambda}}^{\mathrm{T}}\cdot\underline{\underline{\ell}}^{-1}\cdot\underline{\underline{\lambda}}]$$

This is rather more tensorial looking than the classical result. When the director determining the direction of nematic order and hence the direction of chain extension, the long axis of $\underline{\underline{\ell}}$, rotates with distortion, subtle elastic effects arise such as "soft elasticity" (shape change without energy cost).[2,6] We shall consider only situations where the extent, Q, of nematic order changes, that is changing the magnitudes of $\ell_{\parallel}$ and $\ell_{\perp}$, and not the direction of order.

Take the case of when the formation conditions are isotropic, that is $\underline{\underline{\ell}}_0 = a\underline{\underline{\delta}}$ with a being the single effective step length. Since the distortions and shape tensors are coaxial, everything is diagonal and trivial to evaluate by simple multiplication:

$$F_{nem} = \tfrac{1}{2}\mu\mathrm{Tr}\left\{\begin{pmatrix} a & 0 & 0 \\ 0 & a & 0 \\ 0 & 0 & a \end{pmatrix}\begin{pmatrix} \lambda & 0 & 0 \\ 0 & 1/\sqrt{\lambda} & 0 \\ 0 & 0 & 1/\sqrt{\lambda} \end{pmatrix}\begin{pmatrix} \ell_{\parallel}^{-1} & 0 & 0 \\ 0 & \ell_{\perp}^{-1} & 0 \\ 0 & 0 & \ell_{\perp}^{-1} \end{pmatrix}\begin{pmatrix} \lambda & 0 & 0 \\ 0 & 1/\sqrt{\lambda} & 0 \\ 0 & 0 & 1/\sqrt{\lambda} \end{pmatrix}\right\}$$

$$\equiv \tfrac{1}{2}\mu\left(\frac{a}{\ell_{\parallel}}\lambda^2 + \frac{a}{\ell_{\perp}}\frac{2}{\lambda}\right)$$

The result is most non-classical since the additional factors that account for changing chain shape don't appear together as a prefactor, but separately as coefficients of the distortions in the two unique directions. Minimize over λ to obtain the optimal deformation, λ_s, due to changing conditions:

$$\lambda_s = \left(\ell_{||}/\ell_{\perp}\right)^{1/3}$$

This extension/contraction is an old theoretical result[7] that became readily experimentally accessible when nematic monodomain elastomers were produced.[1] It depends on the ratio of the effective step lengths, that is on the intrinsic anisotropy of the network strands due to nematic order, Q. This ratio, sometimes denoted by $r = \ell_{||}/\ell_{\perp}$, is separately measurable by

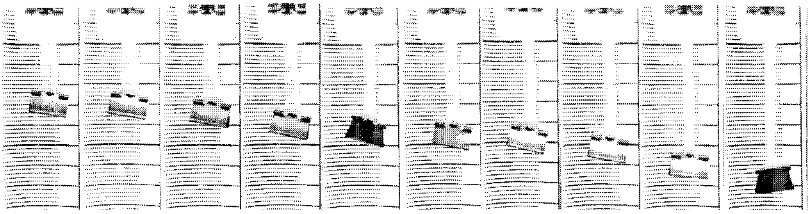

Fig. 1. A nematic elastomer contracting as it is heated (right to left) through the nematic-isotropic phase transition. The contraction-elongation is about 300%. The corresponding extension-temperature relation is measured for a variety of loads (Figure 2).

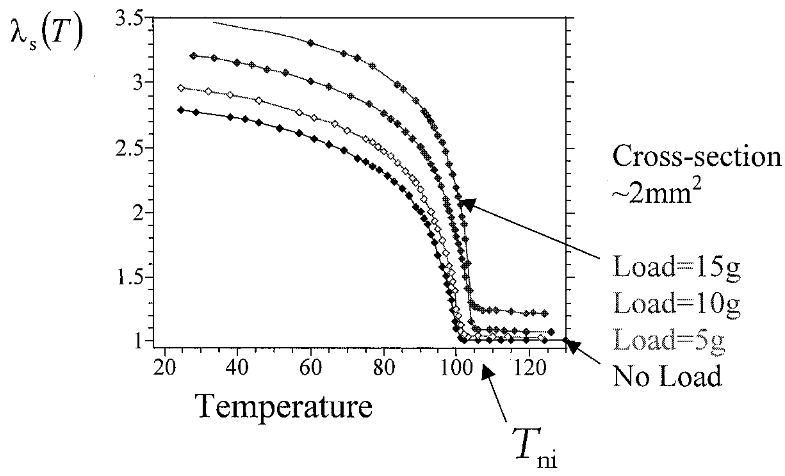

Fig. 2. Spontaneous distortion versus temperature for nematic elastomers under various loads.

neutron scattering[8] and is known to take values in the range 1 – 60. Correspondingly spontaneous distortions are commonly up to 400%. A recent example of this response in main chain – side chain systems of the Finkelmann type is shown in Figure 1.

Photo-elasticity of Nematic Elastomers

If the rods that underpin the nematic ordering of the polymers are comprised of azo units, then they can bend on absorbing a photon, see Figure 3.

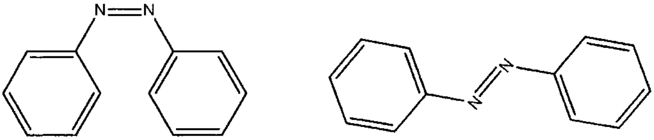

Fig. 3. The *trans* (straight) and *cis* (bent) isomers of azo benzene.

The azo unit photoisomerizes on absorption of a UV photon. It can return to the ground state either stimulated by the absorption of a longer wave length photon, or by thermal activation over a barrier. The dynamics and statics of this process is well understood in the context of these kinds of polymers.[4,5,9] The effect of *cis* isomer formation is to inject "impurities" into the nematic state and thereby weaken the ordering, exactly as temperature elevation does. We expect a correspondence between temperature and *cis* concentration that gives a photo-response exactly analogous to the thermal response seen above.

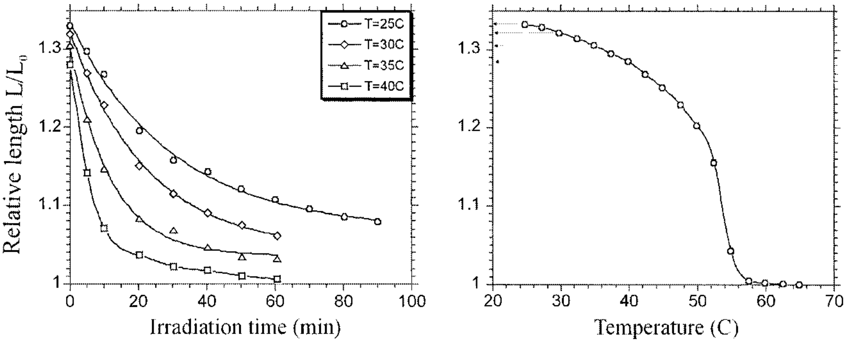

Fig. 4. Photo and thermal contractions of the same nematic elastomer. The photo-contractions are measured at a variety of fixed temperatures as a function of irradiation time. The corresponding positions of the starting points on the strain-temperature curve are denoted by arrows. After Finkelmann *et al.*[10]

The close parallel between thermal and optical response can be seen from the distortions of the *same* elastomer by the two routes,[10] Figure 4.

What is important is the variation of strain with order parameter, which is either changed by temperature or illumination. For comparison the order parameter (*Q*) versus temperature (*T*) curve for the same elastomer is shown, Figure 5. In this work *Q* was measured by circular dichroism. This is a standard technique that relies on the extent of IR adsorption depending upon the angle between a particular molecular transition dipole moment and the direction of polarization of the incident beam. The molecular dipole moment is anchored to the nematic rods and thus reflects their directional character.

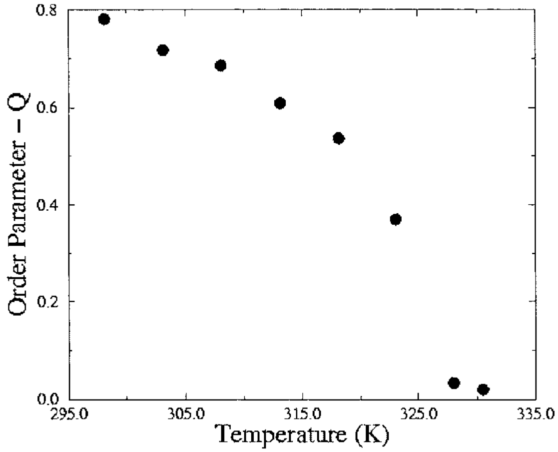

Fig. 5. Order parameter versus temperature for the nematic elastomer undergoing photo and thermal strains in Figure 4, Finkelmann *et al.*[10]

The underlying relation is summarized as $\lambda_s(Q) \to \lambda_s(T)$ or $\lambda_s(I)$. Whether we have thermo- or photo-elasticity depends on what is driving *Q*.

The photo-contraction is reversible, either in the dark or under illumination that stimulates the back reaction. This is seen in the continuation of the 25C contraction curve beyond the point where the UV is switched off and the sample is in the dark. The characteristic time for activated recovery is much longer than the forward reaction rate, Figure 6.

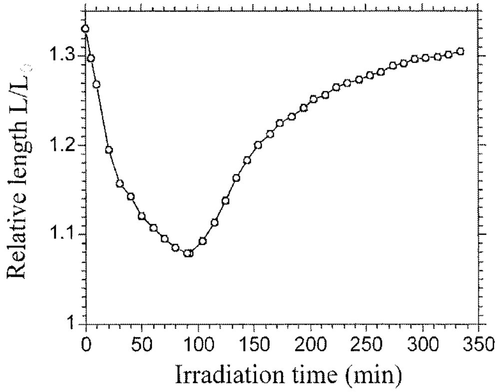

Fig. 6. Photo-contraction and recovery of the nematic elastomer at 25C of Figure 5, after Finkelmann *et al.*[10]

If the sample length is fixed, then photo-contraction cannot take place. However the natural length is changing and the result is a contractile photo-stress,[11] see for instance Figure 7.[12] The order parameter was measured simultaneously with illumination and is seen to proceed with exactly the same dynamics. This is further confirmation that it is order parameter changes that drive the elasticity. Furthermore it suggests that the dynamics of photo-isomerization is what limits the rate of network response, rather than the dynamics of strain response of the network itself (to which we return in discussing dynamics).

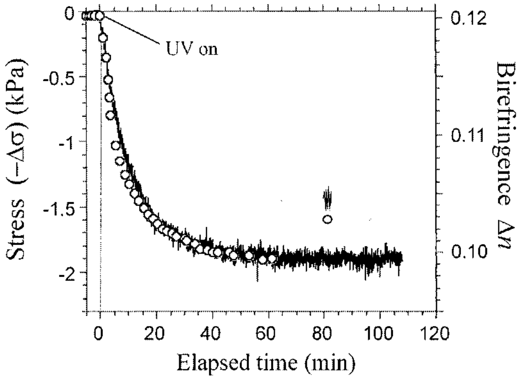

Fig. 7. The dynamics[12] of contractile stress generation and reduction in order parameter (as measured by the birefringence) after UV has been switched on. The dynamics of the two aspects of response appear to be identical.

Photo-stationary Elastic Response

We want to correlate the thermo and photo responses in a quantitative way,[10,11] first addressing the photo-stationary state, that is where the strain no longer increases with illumination time because the forward and backward reaction rates match.

Let the volume fraction of photo rods in total be ϕ_0 and that of the *trans* and *cis* states be ϕ and ϕ_c respectively. Thus one has $\phi_c = \phi_0 - \phi$ which accounts for all photo-rods. Illumination of intensity I depletes the *trans* (straight) population at a rate $-\eta I \phi$ where the absorption coefficient is η. The *cis* concentration then grows and then there is a back reaction to the *trans* state that depends upon the *cis* population and the inverse lifetime $\frac{1}{\tau_{ct}}$. The back reaction rate is: $\frac{1}{\tau_{ct}}(\phi_0 - \phi)$. In the stationary state these two contributors to the overall rate balance, giving $\dot{\phi} = 0$. One thus has $\eta I \phi = \frac{1}{\tau_{ct}}(\phi_0 - \phi)$ or a *cis* "impurity" concentration of $\phi_c(I) = \phi_0 \frac{\eta I \tau_{ct}}{1 + \eta I \tau_{ct}}$.

It is well-known in liquid crystals that a small concentration of impurities that disrupt the nematic order reduces the nematic-isotropic transition temperature by an amount linear in this concentration. Since in these photo-experiments the real temperature is fixed (at T_0, say), then this shift actually brings us closer to the transition and the system is actually at an effective temperature that is appropriately elevated from the actual temperature:

$$T_{eff} = T_0 + T_{ni}\phi_c(I) = T_0 + T_{ni}\phi_0 \frac{\eta I \tau_{ct}}{1 + \eta I \tau_{ct}}$$

Thus illumination shifts us along the $\lambda_s(T)$ curve, the appropriate temperature given as a function of I as above. Precise predictions that connect the photo and thermo strains as in Figure 4 are then possible. We however go on to discuss this connection in the rather more demanding context of dynamic photo-strains.

The Dynamics of Photo-strains

We can combine the rates of decay and recovery from and to the *trans* state to give an overall dynamical equation for the *trans* volume fraction:

$$\dot{\phi} = -\eta I \phi + \frac{1}{\tau_{ct}}(\phi_0 - \phi)$$

This can easily be translated into a time-dependent *cis* volume fraction $\phi_c(t) = \phi_0 - \phi(t)$:

$$\phi_c(t) = \phi_0 \frac{\eta I \tau_{ct}}{1 + \eta I \tau_{ct}} \left(1 - \exp(-t/\tau_{eff})\right)$$

where the effective dynamical rate $\frac{1}{\tau_{eff}} = \eta I + \frac{1}{\tau_{ct}}$ combines the forward and backward rates. Since the *cis* “impurities” determine the spontaneous strain through the equivalent effective temperature, we have thus obtained the strain-dynamics. The effective temperature changes as $T_{eff}(t) = T_0 + T_{ni}\phi_c(t)$, which then translates into a time-dependent strain analogously to the static case through the strain-temperature master curve:

$$\lambda_s(t) = \lambda_s\left(T_{eff}(t) = T_0 + T_{ni}\phi_c(t)\right) = \lambda_s\left(T_{eff}(t) = T_0 + T_{ni}\phi_0 \frac{\eta I \tau_{ct}}{1 + \eta I \tau_{ct}} \left(1 - \exp(-t/\tau_{eff})\right)\right)$$

Before modelling the full dynamical data, one can see trends, for instance the initial rates of photo-strain when illumination is switched on. The rates are higher for the samples at a temperature where the thermal strain varies more quickly with temperature, that is they are on a steeper part of the spontaneous deformation curve. One can see this from the strain rate relation

$$\dot{\lambda}_s(t) = \frac{d\lambda_s(T_{eff})}{dT_{eff}} \cdot \frac{dT_{eff}}{dt} = \frac{d\lambda_s(T_{eff})}{dT_{eff}} T_{ni}\, \dot{\phi}_c(t)$$

that has two contributors, the gradient of the thermal deformation curve and the dynamical factor $\dot{\phi}_c(t)$. At initial times one has $\dot{\lambda}_s(t) = \frac{d\lambda_s(T_0)}{dT_0} T_{ni}\, \eta I \phi_0$ and, given that the dynamical factor is dominated by temperature-independent terms $\eta I \phi_0$, the initial strain rates are determined by $\frac{d\lambda_s(T_0)}{dT_0}$. Figure 4 shows how this correlation is borne out where the photo-strain curves at lower temperatures have lower initial slopes.

Figure 8 shows the modelling of the dynamical data after it has been passed through the full temperature dependence of $\lambda_s(T)$.

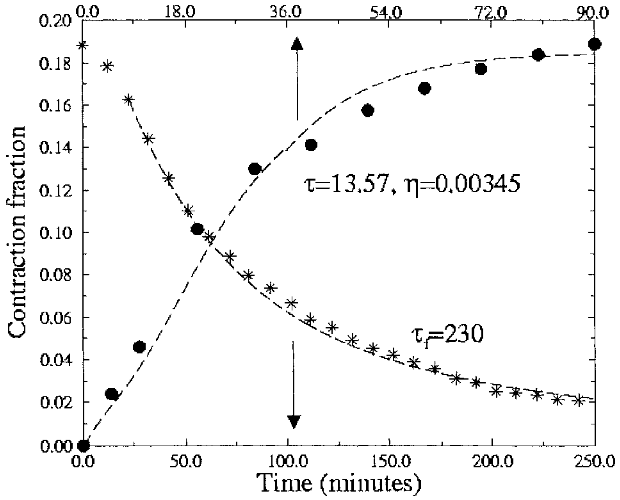

Fig. 8. The contraction fraction against illumination time (top axis) and the recovery of the contraction fraction against time in the dark (bottom axis) for the nematic photo-elastomer of Figures 4 and 6 at 25C. The contraction fraction is $1-\lambda_s(I,t)$, after Finkelmann *et al.*[10]

The two characteristic times are very different, reflecting the very different processes involved. The folding function is very non-linear, but agreement is satisfactory, considering the limited number of data points and that the photo-contraction did not attain its fully photo-stationary state.

Conclusions

We have shown that nematic order induces molecular shape changes that in nematic elastomers is reflected in mechanical changes of sample shape. The order change can be achieved thermally or through photoisomerization. The equivalence between the two is borne out by the ability to predict details of and the full form of the photo-strain dynamics from a knowledge of the strain-temperature master curve. The response involved can be very large, up to 100s% in strain which offers possibilities for thermal and photo actuation, artificial muscles and the like.

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