

LETTERS

Nonideal Elasticity in Liquid Crystal Elastomers

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Nematic elastomers undergo a phase change from an orientationally ordered nematic phase to a disordered isotropic phase when subjected to a temperature change. It is shown that such a phase change is both entropically and energetically driven. Isostrain data on a liquid crystal elastomer material is analyzed in terms of classical rubber elasticity theory. By separating the contributions to the total elastic restoring force into energetic and entropic components, the role of internal energy is assessed and shown to be significant.

De Gennes, in 1975, predicted that cross-linked nematic networks (elastomers) will exhibit nonlinear stress-strain relations and have the potential to behave as artificial muscles.¹ Recently, these predictions have been experimentally verified in real systems.² For instance, by attaching a mesogen side on to a polymer backbone through a spacer and cross-linking, as shown schematically, an experimental system can be realized. The bulk properties of such a system depend on the nature of the mesogen, the length of the spacer and the type of polymer backbone used. A muscle-mimetic system can be obtained by varying the temperature since thermotropic mesogens are utilized in the elastomer. In the nematic phase, the orientational order of the mesogen, forces the polymer backbone to be elongated along the average direction of orientation of the mesogens. However, upon heating into the isotropic phase, the nematic order is lost, thereby allowing the polymer backbone to relax into its coiled conformation. We have demonstrated the viability of such a muscle-like action by coating a film of the elastomer with a thin layer of carbon and shining a laser beam onto it.³

The response times of actuation in such systems would depend on the cooperative relaxations.⁴

Although De Gennes'² predictions have been borne out through experiments, an important issue that is yet to be addressed is the role of entropy and energy during the phase change of the elastomer from the ordered nematic phase to the disordered isotropic phase. In particular, is the phase change entropically driven or does energy also play a role? In classical rubbers (cross-linked elastomers without any orientational order), for example, it was assumed for a long time that entropy alone determines the behavior of rubber elasticity; i.e., the elastic restoring force that allows an elastomer to return to its original shape is completely dictated by the entropic contribution. However, it was shown in a classic paper published by Ciferri, Hoeve, and Flory,⁵ that the assumptions of classical rubber elasticity theory, that entropy alone determines the behavior of polymer networks is not strictly valid. The contributions from internal energy to the total elastic restoring force of polymer networks was shown to be finite. Following this observation, more experimental evidence of nonideal elasticity was found in other cross-linked polymer networks.⁶⁻⁹ In the case of polymer networks with liquid crystalline properties, derived from the chemical attachment of liquid crystal mesogens side on to

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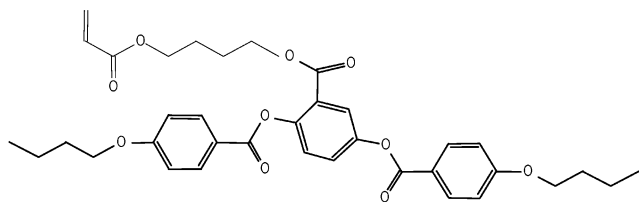


Figure 1. Chemical structure of the mesogen linked via a spacer to the polymer backbone.

the polymer backbone, the deviation from ideal behavior may be expected to become even more pronounced due to the presence of nematic orientational order.

Clearly then, an experiment that would allow us to obtain the entropic and energetic components to the elastic restoring force will resolve this issue. Isostrain experiments, wherein the strain of a film of the elastomer material is held constant while the stress (and therefore the elastic restoring force) is monitored as a function of temperature, can be used to extract the energy and entropic contributions to the elastic restoring force.¹⁰ We report such measurements in this manuscript and show that there are large deviations from ideal classical rubber elasticity and that the energetic contributions to the elastic restoring force can become comparable to the entropic contributions.

The chemical structure of the mesogen, the cross-linker, and the polymer backbone are shown in Figure 1. A number of measurements to determine the bulk properties of the elastomer have been performed earlier (such as thermoelastic response to determine the mechanical properties, polarized FTIR to determine the anisotropy of the system, dynamic shear and dielectric relaxation experiments for understanding the dynamics of the system, and differential scanning calorimetric measurements to confirm the phase behavior).^{2–4} Free-standing films of the elastomer were prepared as follows: a mixture of the monomer, photoinitiator, and cross-linker were filled into a liquid crystal cell. The cell was fabricated as follows: two microscope slides, approximately 1 cm², were first cleaned and coated with a poly-(vinyl alcohol) alignment layer (details for this procedure are given in ref 3). The two plates were then placed one on top of the other such that the alignment layers formed the inside surfaces of the cell. A gap of 50 μ m between the two slides was obtained by placing thin Mylar spacers, approximately 2 mm wide and 1 cm long, at the edges of the cell. The opposite edges of the cell were then glued to provide a seal. The cell was filled with the mixture at 85 $^{\circ}$ C (isotropic phase) under vacuum. To obtain a cross-linked sample (hereafter referred to as CPMOAC4), the cell (containing 0.1 mol % Irgacure 369 photoinitiator) was exposed to 1 mW of radiation from an Oriol Xenon UV lamp equipped with a 365 nm low pass cutoff filter. A free-standing film was then gently separated from the glass cell by dissolving the glue in hot distilled water at around 90 $^{\circ}$ C for 20 min. The film was then set aside to dry before any measurements were performed. For the experimental measurements, a film approximately 3 mm wide and 10 mm long was used.

Isostrain measurements are, as the term implies, measurements performed at constant strain. Isostrain data were collected using a TA Instruments DMA 2980 equipped with a film tension clamp. If the temperature of the sample, that is clamped in place using a tension clamp, is ramped up through the phase transition (we used a ramp rate of 0.5 $^{\circ}$ C/min after an initial isothermal hold at 65 $^{\circ}$ C), the stress and therefore the elastic restoring force in the sample continuously increases with temperature. The strain can be held at various values and for our measurements, we used values of 5%, 6%, and 7.5%.

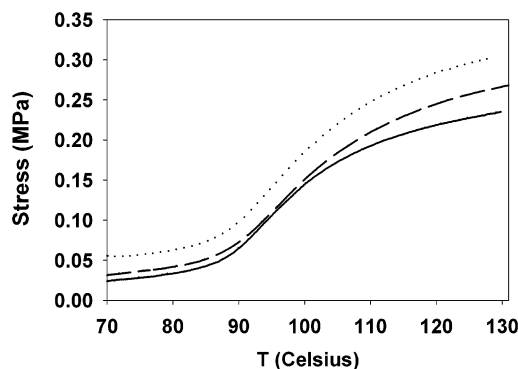


Figure 2. Isostrain plots of stress versus temperature for CPMOAC4 for the three strain values of 5% (solid line), 6% (dashed line), and 7.5% (dotted line). The force is obtained by multiplying the stress with the cross-sectional area of the film. Note that unlike with classical elastomers, where the plot would be linear, regions of changing slope representing the nematic, nematic–isotropic transition, and isotropic regions are observed.

A theoretical expression that enables evaluation of the energetic and entropic contribution to the elastic restoring force in elastomers was developed for understanding the origin of rubber elasticity. To extract the energetic contribution to the elastic restoring force, the following equation is used.¹⁰

$$f = \left(\frac{\partial H}{\partial L} \right)_{T,P} + T \left(\frac{\partial f}{\partial T} \right)_{P,L} \quad (1)$$

where f is the elastic restoring force, H is the enthalpy, L is the length, P is the pressure, and T is the temperature. The energetic contribution, f_e , is represented by the first term on the right and the entropic contribution, f_s , by the second term.¹¹ Thus, the internal energy contribution may be obtained from the intercept of the straight line fits (setting $T = 0$, the first term is obtained) to experimental data of force versus absolute temperature (as shown in ref 11, the enthalpic term is equivalent to the internal energy term). The entropic contribution, f_s , is obtained by multiplying the slope of the straight line with the absolute temperature.

The three data sets corresponding to strains of 5%, 6%, and 7.5% for (CPMOAC4) are shown in Figure 2. Note that the slope of the line, unlike in classical rubbers, changes due to the presence of a phase transition from the ordered nematic phase into the disordered isotropic phase. We obtained f_e and f_s for each of the isostrain curves by dividing the experimental data into approximately three regions, i.e., nematic, nematic–isotropic transition region, and isotropic. The slopes and intercepts for the three curves in the isotropic and nematic phases are then obtained from straight line fits over limited temperature ranges in the two regions (the nematic phase and the isotropic phase). Example linear fits to the two regions are shown in Figure 3a,b (in the nematic and isotropic phases) for a strain corresponding to 6%. The slope in the NI-transition region is also determined for the various strains again using a straight line fit over a limited temperature range in the NI region. The slope in the NI region is about the same (of the order of 9×10^{-3}) for all three strain values used and much larger than in the nematic and isotropic phases.

Table 1 show the ratios of the entropic (f_s/f) and energetic contributions (f_e/f) to the total restoring force calculated from the slopes and intercepts in the nematic and isotropic phases. It is clear that the ratio f_e/f , which represents the energetic contribution to the restoring force is comparable in magnitude to the entropic contribution represented by f_s/f . To understand

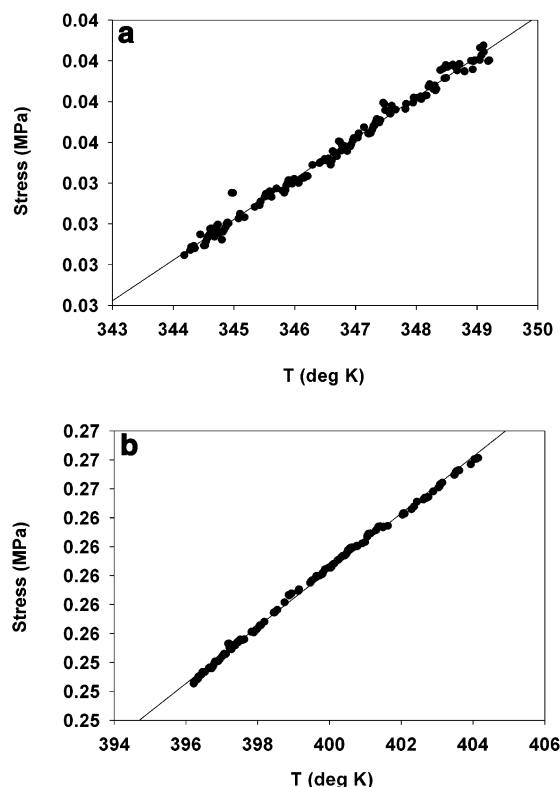


Figure 3. Typical linear fits of stress vs absolute temperature for the nematic and isotropic regions are shown for a sample under 6% strain. The force is obtained by multiplying the stress with the cross-sectional area of the film.

TABLE 1: Showing Relative Energetic (f_e/f) and Entropic (f_s/f) Contributions for the Three Data Sets Corresponding to Strains of 5%, 6%, and 7.5% in Both the Nematic and Isotropic Phases

| strain % | $f_e/f, f_s/f$ (nematic phase) | $f_e/f, f_s/f$ (isotropic phase) |
|----------|-------------------------------------|-----------------------------------|
| 5 | $f_e/f = -12.27$ $f_s/f = 13.27$ | $f_e/f = -1.8$ $f_s/f = 2.81$ |
| 6 | $f_e/f = -8.86$ $f_s/f = 9.86$ | $f_e/f = -1.97$ $f_s/f = 2.97$ |
| 7.5 | $f_e/f = -2.32$ $f_s/f = 3.32$ | $f_e/f = -1.79$ $f_s/f = 2.79$ |

the physical meaning of the sign and magnitude of the ratio of the entropic contribution to the total elastic restoring force (f_s/f), we use the following equation, which relates the ratio f_e/f to the temperature derivative of the mean square end to end distance of the unperturbed chain.¹¹

$$\frac{d \ln \overline{r_f^2}}{d \ln T} = \frac{f_e}{f}$$

where $\overline{r_f^2}$ is the mean square end to end distance of the polymer chain between cross-links and the other symbols have the same meaning as before.

The negative sign of the ratio f_e/f shows that the slope of $\ln \overline{r_f^2}$ vs $\ln T$ is negative. This arises when the mean square end to end distance decreases with increase in temperature. In the

elastomeric system, the chain dimensions are dictated by the cross-linking density. The negative sign implies that when the temperature of the elastomer film is raised, the chain dimensions shrink, which on a macroscopic scale corresponds to a contraction of the film with increasing temperature.

We should point out, however, that the assumptions made in the theory of rubber elasticity are not strictly valid in nematic systems. For example, the chains are not Gaussian with energy independent of the conformations.¹⁰ In the nematic phase, for example, the chains tend to be ellipsoidal.^{12,13} Due to interactions between nematic molecules that stabilize the nematic phase and give rise to orientational order, a change in the ellipticity of the ellipsoid can change the interaction energies. Hence, given the uncertainty in the model, it is difficult to draw conclusive quantitative inferences from the numerical values shown in the tables. Nevertheless, the general conclusion, that entropy alone cannot account for the elastic restoring force remains valid. It is interesting to note, however, that f_e/f is independent of strain in the isotropic phase although the magnitude is still a large fraction of the ratio f_s/f , and therefore, the Gaussian model may be valid in this phase although even in this phase the energetic contributions are large.

In summary, isostrain data are presented and analyzed for a cross-linked liquid crystal polymer network CPMOAC4. The equation representing the elastic restoring force for classical polymer networks is used to separate out contributions arising from entropy and energy. The energetic contribution to the elastic restoring force is shown to be almost equal to that of the entropic contributions. The inherent orientational ordering present in these nematic elastomers, unlike in classical rubbers, is believed to be responsible for the large energetic contribution and hence the nonideal elasticity exhibited in this system.

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- (11) The first term in eq 1 is a sum of two terms, the first arising from internal energy (U) changes and the second due to volume (V) changes. The latter is ignored because this is negligible.

$$\left(\frac{\partial H}{\partial L}\right) = \left(\frac{\partial U}{\partial L}\right)_{T,P} + P \left(\frac{\partial V}{\partial L}\right)_{T,P} \quad (2)$$

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