

Liquid Crystalline Elastomers as Artificial Muscles

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Abstract

We find that low molecular weight liquid crystalline cooperative effects acting over length scales larger than the typical mesh size of a liquid single crystalline elastomer (LSCE), controls the elastomer shape. This result provides a “proof of concept” for the novel suggestion of de Gennes et al. that LSCEs may be used as temperature activated artificial muscles.

INTRODUCTION

For many relatively low molecular weight ($MW \approx 300-500$) organic materials, an isotropic liquid transforms to a nematic phase at a nematic-isotropic transition temperature, T_{NI} . The nematic phase is characterized by long range orientational order in a preferred direction, \mathbf{n} . \mathbf{n} is a unit vector, called the director, for which \mathbf{n} and $-\mathbf{n}$ are indistinguishable. At a lower temperature, T_{NA} , a nematic-smectic A phase transition may take place. The smectic A order parameter is a 1D density wave parallel to \mathbf{n} (layers). However, materials do exist with a direct transition from the isotropic liquid to the smectic A phase at a transition temperature, T_{AI} .

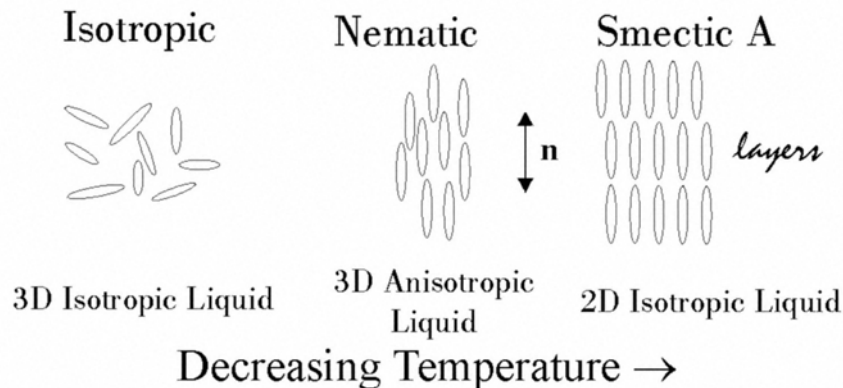


Fig. 1. Sketch of the isotropic liquid and nematic and smectic A liquid crystal phases.

Nematic liquid crystals, in particular, are well-known for their outstanding electro-optic properties now featured in numerous applications such as flat panel displays where light-weight, low power consumption and outstanding color properties are required. Smectic liquid crystals have long

been used in living systems in the structure of e.g. membrane walls.

Liquid Crystalline polymers and elastomers come in two groups, those where the liquid crystalline elements are linked to the polymer backbone on a linear chain (e.g. DNA gels) and those where they hang as side groups from polymer chains. The first are known as main-chain liquid crystalline polymers and elastomers and the second as side-chain liquid crystalline polymers and elastomers. Liquid crystalline elastomers (LCEs) have unusual mechanical properties. Indeed, it has been suggested that LCEs could be used as temperature activated artificial muscles [1,2]. Here we give the first “proof of concept” to this idea using materials available today and suggest ways to extend this idea to electrically driven LCEs as artificial muscles.

NEMATIC LIQUID CRYSTALLINE ELASTOMERS

Side-chain liquid crystalline polymers i.e. polymer chains to which low molecular weight liquid crystalline molecules are attached via a flexible chain known as a spacer (Fig. 2a), can be chemically cross-linked to form permanent networks (Fig. 2b). If the crosslinking density is low enough [3], the system is also orientationally ordered resulting in side-chain liquid crystalline elastomers (LCEs).

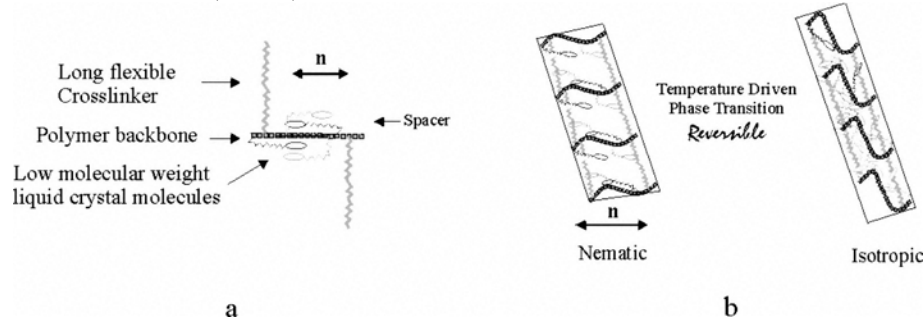


Fig. 2. (a) A liquid crystalline elastomer as a spatially homogeneous multi-component system. (b) The mesh size is delineated by the polymer backbone and crosslinkers.

As side-chain LCEs are approximately 80% low molecular weight material and 20% polymeric backbone and cross-linker, their material properties are different from those of conventional rubbers [4]. In particular, only a small mechanical strain ($\epsilon \sim 10\%$) acting directly on the polymeric backbone is sufficient to induce well-oriented side-chains that can then be crosslinked to create highly ordered macroscopic monodomains [5] of e.g. nematic side-chain liquid crystalline elastomers (idealized sketch in Fig.1) called *Liquid Single Crystalline Elastomers* [LSCEs] by their inventors [4].

LSCEs, the analogue of single crystals in solid state physics, make it possible to investigate well-characterized macroscopic samples by conventional physical techniques [4, 7-10].

LSCEs are obtained using two cross-linking steps on a liquid crystalline side-chain polymer. The first cross-linking process takes about a minute and results in a weakly cross-linked network and a polydomain LCE. The weakly cross-linked polydomain LCE is then mechanically stretched to make a monodomain. It is then left in the stretched state for about 10 hours to give the slow cross-linking process time to complete. After this, the stress is removed and a monodomain LCE, i.e. an LSCE, results. Information about the phase (e.g. nematic, smectic A, isotropic etc.) during the second cross-linking step is frozen-in in the vicinity of the cross-linking points [6]. This information cannot be removed without destroying the network.

We think of LCEs, in particular monodomain LCEs, as spatially inhomogeneous multicomponent systems. The spatial heterogeneity is on the length scale of the mesh size. Even when weakly cross-linked, the orientational order of LCEs can be more easily influenced by mechanical forces rather than by electric or magnetic fields. A mechanical field acts directly on the polymeric network. The network's response is to locally reorient the low molecular weight liquid crystal side-chains through the flexible spacers with which they are attached to the network. For mechanical deformations, then, the applied stress acts directly on the network and rather indirectly on the orientational order, \mathbf{n} . This is the dog (network) wagging its tails (side-chains).

In contrast, an applied electric/magnetic field, acts on the liquid crystalline side chains. They in turn act through the flexible spacers on the polymeric backbone. While each side chain has only one flexible link to its backbone, the cooperative nature of the long range liquid crystalline order amplifies their individual influence by a factor related to the number of side chains inside a mesh. While individually the torque one molecule can exert on the backbone is small, the net effect from cooperative amplification can be many times larger resulting in macroscopic changes in the overall net shape. Very roughly speaking, in the case of electromagnetic fields (and phase transitions), many tails acting as one can wag several dogs.

Summary: Mechanical fields act directly on the polymer network while electric/magnetic field effects act on the liquid crystalline side-chains. As the liquid crystalline cooperativity is limited by the mesh size, large electric/magnetic fields are now needed to reorient \mathbf{n} in liquid crystalline elastomers.

NEMATIC LCE SHAPE CHANGES

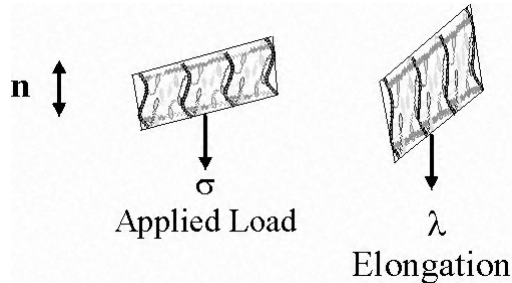


Fig. 3. LSCE shape changes under an applied load.

A much studied feature of LCEs is their dramatic elongation, λ , under an applied load, σ applied parallel to \mathbf{n} [e.g.7-10]. In nematic LCEs, more than a 60% increase has been observed under a load applied parallel to \mathbf{n} . The elongation is even more dramatic in the vicinity of the nematic-isotropic phase transition.

The mechanism invoked by de Gennes et al. [1,2] for artificial muscles is a *spontaneous* shape change triggered by the low molecular weight liquid crystal side-chains transforming from the nematic to the isotropic liquid state (the NI transition), as shown in Fig. 2b. The main question raised by this mechanism is: can the low molecular weight have any influence on the network shape?

We find that when the low molecular weight liquid crystalline elements act cooperatively beyond the network size, as they do at phase transitions, indeed they can influence the network shape. We next quantify this spontaneous phase transition induced shape change in LSCEs.

LSCE SPONTANEOUS SHAPE CHANGE

To evaluate the feasibility of LCEs for artificial muscle applications, we prepared slices of the nematic LSCE from a sample sent to us by Nicole Assfalg, a PhD student in the laboratory of Professor H. Finkelmann. Slices were made parallel and perpendicular to \mathbf{n} .

A sample is made by placing one of these slices across a small hole in a microscope slide. We look at the sample between crossed polarizers using a video-camera and image analysis. A feature of this image analysis system is that one line of a video frame can be collected at fixed time intervals. After collection, the lines for each time interval are plotted in sequence to make another picture called an st plot - for space-time. While the st plot is running, the temperature is scanned at a fixed rate. The start and final temperatures are noted. In this way we convert time to temperature.

Preliminary results are that the nematic elastomer shrinks by nearly 40% in the direction parallel to \mathbf{n} when it becomes isotropic (which it is not optically) and expands about 20% in the other two directions. The shape

change takes place at nearly constant volume and is reversible with only a small hysteresis. This small hysteresis may be due to local features of the sample attachment on the solid substrate and not the first order nature of this phase transition.

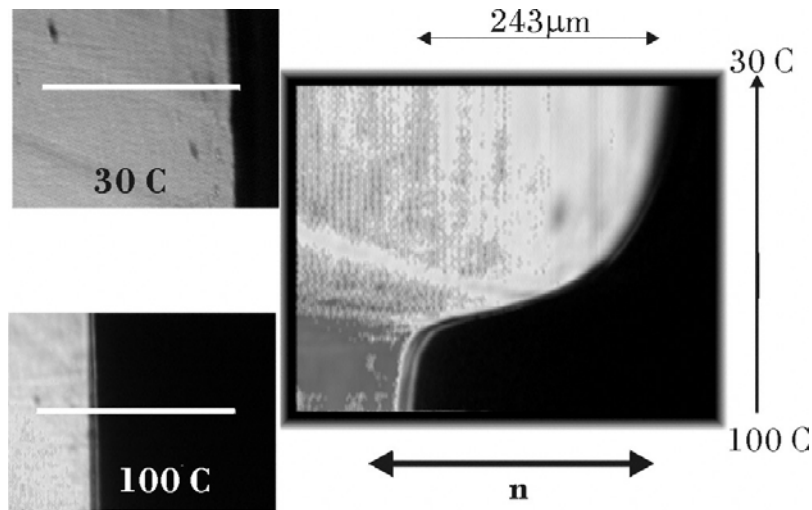


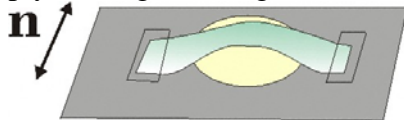
Fig. 4. On the left are snapshots of the field of view in a polarizing microscope at the start of the run (100°C) where the elastomer is isotropic and at the end (30°C) where it is nematic. The direction of orientational order in these scans is shown below the ST scans in the right hand picture and marked n. The ST plot is made at one of the LSCE-air edge while the temperature is scanned from 100°C to 30°C at 0.034K/s. Polarizers are crossed 45° to the picture borders. Between crossed polarizers, the air is black, in the nematic phase (bulged part on right at the top of this frame), the LSCE is brighter than it is in the isotropic liquid state (bottom of this frame) where it is nevertheless still birefringent. A very large change in position of cut edge is evidenced at 76.2°C, the NI transition temperature. The transition is sharp but there is no real evidence of front propagation. At this transition, the LCE-air edge moves ~ 243μm in ~1K (or about 3s i.e. its response time here is that of the scanning rate).

In Fig. 4, the total sample width is $l = 1350\mu\text{m}$. Assuming both sides expand the same (checked later on thinner samples where both edges could be observed), the total extension is $\Delta l \sim 500\mu\text{m}$ or $\Delta l/l \sim 0.35$. This is a very large extension but consistent with thermoelastic measurements. We point out that here, this shape change is independent of gravity and driven only by the director reorientation at the nematic-isotropic phase transition.

The realization that large displacements of the elastomer boundary can take place spontaneously at the nematic-isotropic transition prompted de

Genes et al.[1,2] to suggest liquid crystalline elastomers as potential candidates for artificial muscles.

For example, in Fig. 4, the ends of the sample on the substrate are nearly free. In Fig. 5, we show what happens when the elastomer ends are clamped to the sample substrate at room temperature (where it is nematic) then heated to the isotropic state. Scotch tape (the clamping device) is shown as empty rectangles in Fig. 5.



Flexed LCE muscle

Fig. 5. Bowed sample made by fixing the LSCE ends to the substrate then heating to the isotropic state.

When the sample thins along \mathbf{n} , it expands perpendicular to \mathbf{n} . The sample is clearly seen arching over the substrate hole. The muscle has flexed. This dramatic effect immediately opens the door onto a host of artificial muscle, MEM, MOEM etc. applications for nematic LSCEs as e.g. temperature sensitive switches particularly suited to a low gravity environment. For example, one can imagine a conducting strip attached to the center of the LSCE. When the material is heated to the isotropic liquid state, the conducting strip will be “hoisted” by the large change in elastomer shape e.g. to open/close an electrical connection. This flexing effect also suggests novel ways to estimate LSCE tensile strength and its dependence on materials used to swell the LSCEs for earth bound applications.

Fig. 5 illustrates a temperature driven LSCE artificial muscle. More detailed materials and engineering research and more theoretical modeling to predict relevant materials parameters are needed, to convert this simple observation (Figs. 4 and 5) from a laboratory curiosity to a technology. In addition, as stressed above, the de Gennes et al. artificial muscle concept is particularly valid in a low gravity environment. The overall goal of this project is to learn more about the materials and physical properties of liquid crystalline elastomers thereby extending their range of applications to generic large scale actuators/sensors driven by relatively low frequency and small amplitude electromagnetic fields at constant temperature.

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WHY DO LSCEs EXPAND SO DRAMATICALLY $\parallel \mathbf{n}$?

As the polymer backbones are free in the case of LCPs (Fig. 2), when the low molecular weight attachments become isotropic, the backbones just reptate, i.e. locally move between their constraints, to find an optimal configuration. Reptation in elastomers is a more complex process than it is in liquid crystalline polymers as it alters the position of the cross-linked sites. In the

case of elastomers where the backbones are attached to each other, only that part of the backbone between attachments is free to adjust. Rotation of the low molecular weight side-chains at the transition to the isotropic phase leaves holes in the network so that it contracts parallel to \mathbf{n} while expanding perpendicular to \mathbf{n} . We attribute the birefringence in the isotropic state to the frozen-in order at the cross-linking sites [6].

At the low molecular weight LC's transition to the nematic phase, the selection of a preferred direction, \mathbf{n} , forces the network to expand preferentially along \mathbf{n} because the molecules are longer than they are wide. At nearly constant volume, it shrinks perpendicular to \mathbf{n} as it expands parallel to it.

However, at the isotropic transition, the material shrinks parallel to \mathbf{n} and expands perpendicular to \mathbf{n} , giving rise to a "flexing" effect when the ends of the samples are pinned on the substrate (Fig. 5).

The model used in [1,2] is based on a traveling nematic-isotropic interface, a feature of first order transitions [11]. Fig. 4, shows no evidence for such a traveling interface. Coupled to the fact that the isotropic state is still birefringent, the LSCE transition in these samples is not first order. In LSCEs, the NI transition has been characterized as "beyond the critical point" [12]. A natural inference is that nematic LSCE muscles may be faster than theoretically expected by a first order phase transition model with fundamentally new concepts in the relatively mature topic of fluctuation dominated phase transitions.

Conclusion: At the bulk nematic-isotropic transition, the *degree* of orientational order of the low molecular weight side-chains controls the network shape. The NI transition is a low molecular weight liquid crystalline cooperative effect acting over length scales much larger than a mesh size.

CONCLUSIONS

A large spontaneous shape change is observed at the nematic-isotropic phase transition of liquid single crystalline elastomers (LSCEs). This shape change is at nearly constant volume and is characterized as "beyond the critical point". These results demonstrate the feasibility of using LSCEs as a temperature triggered artificial muscle. It also suggests that temperature driven LSCEs may be faster than theoretically expected.

Future research is directed towards electrically controlling shape changes in LSCEs. The main strategy is to swell LSCEs with low molecular weight liquid crystal materials thereby increasing liquid crystalline cooperativity beyond the typical LSCE mesh size.

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