

UNIVERSITY OF LJUBLJANA
FACULTY OF MATHEMATICS AND PHYSIC

LIQUID CRYSTAL ELASTOMERS

Adviser: prof. dr. Rudi Podgornik
Coadviser: prof. dr. Zdravko Kutnjak

Author: Marta Lavrič

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1 Introduction

Liquid crystal elastomers (LCE) are made from liquid crystals and elastomers. Liquid crystals main microscopic properties are orientation, positional order and the smectic order to the layer normal. We see these properties as different phases of material. We can find them not only in crystal and liquid phase but in phases between those: in liquid crystal phases. Liquid crystals may flow, drip and they take a shape of holder like a liquid, but they are similar to crystals because their molecules may be oriented in a crystal-like way.

Elastomers are made from polymeric chains, which form an elastomeric net. That gives them macroscopic properties like shape and deformation. If we act on them with force they stretch in the direction in which they are being pulled. When a deforming force is removed, they resume their original shape, if the force is not too strong.

LCE have properties of both. Their very interesting property is thermomechanical response. The liquid crystals in them go with heating from the nematic phase into the isotropic one. LCEs are in the direction of director in the nematic phase longer than in the isotropic phase.

There have been investigations how the crosslinking density, external field and temperature of crosslinking affect the isotropic to nematic phase transition of liquid single crystal elastomers (LSCEs). It was shown recently that the critical point exists in LSCEs and can be controlled by this three parameters mentioned above. Thus allowing tailoring of the LSCE thermomechanical response to be either on-off or continuous type. Recently observations of the crosslinking density affecting to the isotropic to smectic A phase transition have been made. In those investigations two samples with different crosslinking density have been used. Both samples exhibit the first order I-SmA phase transition. By changing the crosslinking density the anomaly of the I-SmA heat capacity and by that thermomechanical response is widened.

Liquid crystal elastomers are proper materials for artificial muscles because they resemble many similar properties. Here, we can use their thermomechanical response for actuators.

2 Liquid crystals

Liquid crystals (LC) are organic matter, which during melting does not have just one phase transition like conventional materials, but has a liquid crystal mesophases between crystal and liquid phases. For example, there are three phases: liquid, liquid crystal and crystal phase of liquid crystal MBBA, synthesized in laboratory of Faculty of Education in Ljubljana, below.

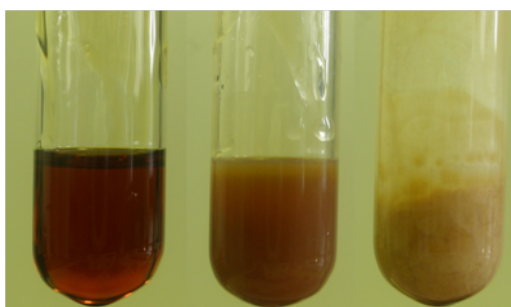


Figure 1: From left to the right: liquid, liquid crystal and crystal phase of liquid crystal MBBA, synthesized in laboratory of Faculty of Education in Ljubljana [1].

Reason for extra phase is in shape and chemical structure of LC. Molecules are relatively stiff rods, with flexible part on the side. For instance, the size of 5CB is 1,8 nm in longitudinal direction and 0,5 nm in transversal one [2].

Main property of LC is long range orientational order and consecutive the LC are anisotropic medium which makes them different from conventional liquids. Anisotropy originates from molecular asymmetry [3] and is indicated by the optical anisotropy, and anisotropic response on external electric or magnetic field [2].

There are two influences connected with anisotropy.

Steric influence is a consequence of shape anisotropy. It stimulates LC molecules to be parallel, since they can translate more freely without overlapping. They thereby maximize the disorder of translation, increase the entropy and thus lower the free energy. Shape exclusion is clearly much more effective at higher rod concentration in solution. Such nematic where concentration and its entropic consequences dominate are known as lyotropic [3]. We can find them in natural environment as in a cell membrane, nervous tissue and membranes inside the cells [2].

Thermotropic influence on the other hand is consequence of anisotropy of polarisability. Molecular polarisability along the rod axis creates a greater van der Waals attraction between two rods when they are parallel than per-

pendicular. When long-range van der Waals forces of anisotropic attraction are the dominant ordering influence, a reduction of temperature will lead to the nematic ordering. Such system is known as thermotropic and we focus on them [3]. This kind of LCs can be found in nature very rarely, but they can be made artificially in laboratory. We use them in liquid crystal displays (LCD) [2].

At low temperatures the LC is positional and orientational ordered - crystal phase. With heating the positional order is destroyed, but not orientational one - liquid crystal phase (see Figure 2). Under this condition LC may flow, drip and they take a shape of holder like a liquid.

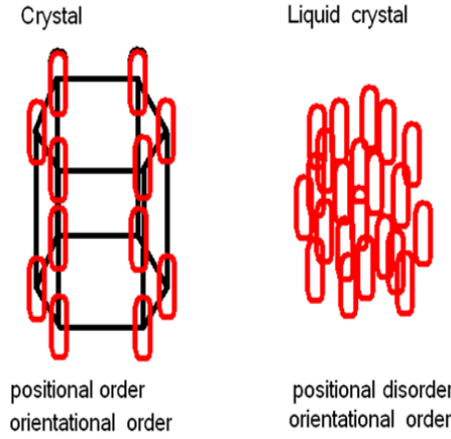


Figure 2: Transition of crystal to liquid crystal is directly related to changes in on positional and orientational order.

If we continue with heating the orientational order is destroyed too and material become isotropic - liquid phase.

2.1 Phases of liquid crystals and Landau - de Gennes theory

There are nematic, different smectic, cholesteric and other liquid crystal phases.

To describe them we have to define a director \vec{n} and an order parameter Q . The director is a unit vector presenting direction of orientational order while the order parameter Q is defined via average of second Legendre polynomial as

$$Q = \langle P_2 \cos \Theta \rangle = \frac{1}{2} \langle 3 \cos^2 \Theta(t) - 1 \rangle,$$

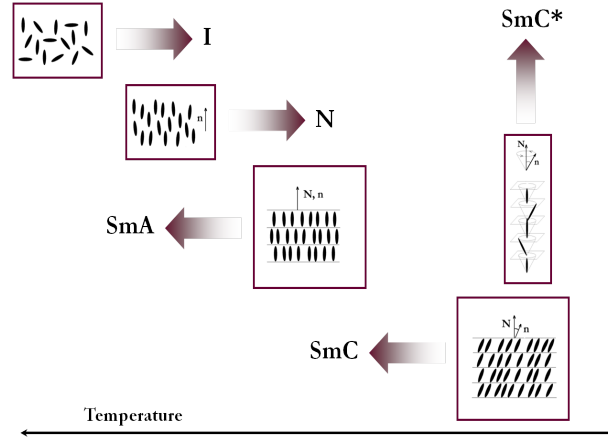


Figure 3: Schematic representation of phase transitions in liquid crystals

where Θ is the angle between the direction of a molecule and the vector \vec{n} . Generally $Q = 1$ when Θ for all molecules is 0° . In this case all molecules are parallel to each other like in crystal. In contrast, in isotropic fluid molecules are in every moment with the same probability directed in whichever direction in space, that's way $Q = 0$. For nematic LC Q is between 0,3 and 0,6 and never approaches to the above limits. The order parameter Q depends on temperature throughout the whole liquid crystal phase and reaches the smallest value right before the phase transition to the isotropic phase when typically discontinuously falls to zero. In nematic phase we can not distinguish two molecules which are in opposite direction. When $Q = -1/2$ all rods are confined to the plane perpendicular to \vec{n} .

Besides, vector \vec{n} can vary in bulk LC due to formation of domains. Each part of LC with the same \vec{n} we call domain. LC with many domains is called polydomain while monodomain samples has everywhere the same \vec{n} .

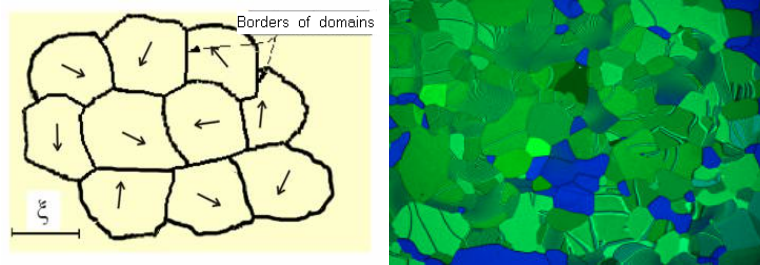


Figure 4: Shematic representation of a polydomain liquid crystal [4] and the real example [5]

Polydomain LC has the same direction only in range of several micrometers. The order or domain wall between two different domains can be continuous or discontinuous. If it is continuous we can not define the direction of order on the boundary. Such defect called the disclination can be found in nematic LC, which give them the name. Namely, “nema“ means “thread“ and depends on threads, which are observed in nematic LC under polarising microscope [2].

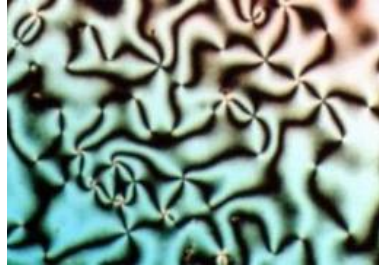


Figure 5: Disclinations of nematic liquid crystal that are observed under polarising microscope seen as black threads [6].

In contrast to the nematic LC the smectic LC have positional order in one direction. In this case, the molecules are ordered in layers, which are for one molecule length apart. Smectic liquid crystal phases are divided on Smectic A, smectic C, chiral smectic C* and others. Smectic A and smectic C phases are distinguished by an angle between the layer plane and the tilt of molecules in a layer. Molecules in the smectic A phase are perpendicular to layers. Their order parameter is approximately from 0,6 in 0,9. If would observe them under polarising microscope we would see oblong structures related to domains called focal conics. In the smectic C phase molecules are tilted for angles typically from 0° to 30°, depending on their temperature.

Cholesteric LCs have a helical director distribution. Locally they are very nearly conventional nematics since their director twist occurs typically over microns, a much longer length scale than that associated with nematic molecular ordering.

To take into account both Q and director components we use tensor order parameter with director components

$$Q_{i,j} = Q \left(n_i n_j - \frac{1}{3} \delta_{ij} \right),$$

where Q_{ij} is the symmetric second rank traceless tensor with eigen frame

$$Q_{ij} = \begin{pmatrix} -Q/2 & 0 & 0 \\ 0 & -Q/2 & 0 \\ 0 & 0 & Q \end{pmatrix}$$

and allows the general Landau de-Gennes free energy expansion in powers of the modulus of the order parameter Q_{ij} , as

$$F_{NEM} = F_0 + \frac{1}{2}A_0(T - T^*)Q^2 - \frac{1}{3}BQ^3 + \frac{1}{4}CQ^4 + HQ + \dots$$

where A_0 , B and C are dimensionless coefficients slightly different for different materials [3], T is the temperature, F_0 is the free energy in the isotropic phase, the linear HQ term represents the application of an hypothetical external field and T^* marks the limit of metastability of the isotropic phase upon cooling in the case of the first order transition [3]. In the isotropic phase where $Q = 0$, the free energy is minimal.

3 Elastomers

Elastomers, of which the most known representative is natural rubber besides neoprene, hypalon and silicones, are microscopically polymeric chain, entangled to a net. Here the net is made by crosslinkers. Essential segments known as monomers are made of hydrogens bind to carbon or silicon. If we switch one of them with reactive element or group, we get a polymer chain out of monomers. Some of chains can be bind together with crosslinkers and some of them without them.

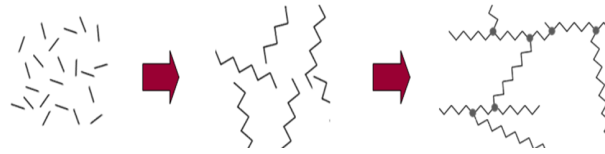


Figure 6: Formation of elastomers - we bind monomers into polymer chains, which we entangle with crosslinkers.

Crosslinkers are very important because they make elasticity possible. Main property of elastomers is reversible or semireversible response on external force. We can stretch elastomer with external force, but not with too strong one. Rubber recovers its original state when external forces are removed. Polymeric chains are entangled, but when we stretch them they become ordered. If crosslinkers would not be present the elastomers would get unentangled and would never return in the initial state.

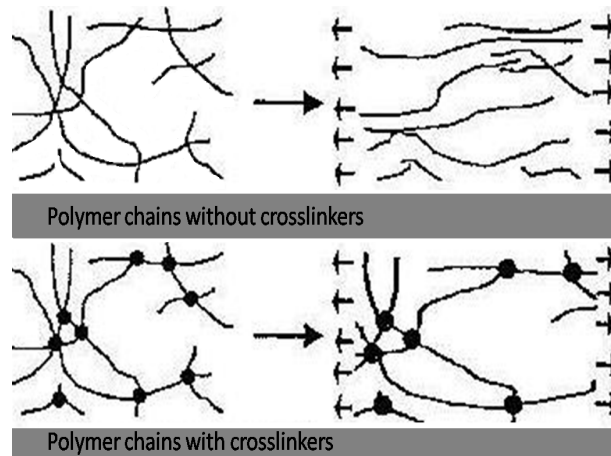


Figure 7: Deformation of polymer chains caused by external force with or without crosslinkers [7].

3.1 Flory-Rehner theory of polymers

Rubber resists mechanical deformation because the network chains have maximal entropy in their natural, undeformed state. Crosslinking creates a topological relation between chains. They collectively make up the solid matrix and theaters chains to it. Naturally average shape of each network strand is spherical, but macroscopic deformation inflict a change. The entropy (\mathcal{S})

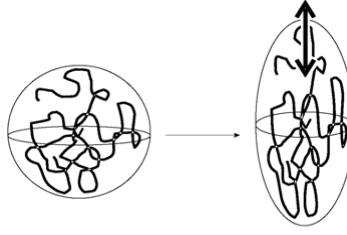


Figure 8: Deformation of elastomers caused by the external force (macroscopic deformation) [3]

then falls. The free energy, which depend only on an entropy change itself driven by molecular shape change ($\Delta\mathcal{F} = -T\Delta\mathcal{S} > 0$), rises. That is why polymers are sometimes thought of as entropic spring. Macroscopic changes are coupled with molecular ones [3].

So, to understand the behavior of LCE we must tell something about configuration of polymers on microscopic level. In the melt, chain conformations are non-excluding random walks as a trajectory of a Brownian particle diffusing in space under the influence of a fixed-magnitude stochastic force and thus are Gaussian. Let us take a chain composed of N monomers of length a freely jointed together as in Figure 9. In terms of the joint vectors

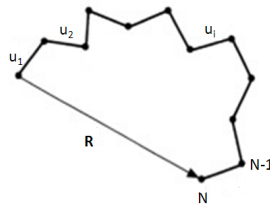


Figure 9: Polymer composed of N monomers and end to end vector \mathbf{R} .

u_i of length a , R is given by

$$\mathbf{R} = \sum_i \mathbf{u}_i.$$

Since vectors \mathbf{u}_i are uncorrelated with each other in their direction, the average $\langle \mathbf{u}_i \mathbf{u}_j \rangle = \frac{1}{3} \delta_{ij} a^2$.

The mean square end-to-end vector for such a random walk of N steps is then, in each direction,

$$\langle \mathbf{R}_x^2 \rangle = \langle \mathbf{R}_y^2 \rangle = \langle \mathbf{R}_z^2 \rangle = \frac{1}{3} \langle \mathbf{R}^2 \rangle = \frac{1}{3} a^2 N = \frac{1}{3} aL$$

where $L = Na$ is the actual arc length of the chain and corresponds to the total time of analogous Brownian diffusion.

If Z_N present all of configurations where no restrictions are made on starting and ending of the idealized point. If we chose an end place as point R , the number of configuration is

$$Z_N(\mathbf{R}) = P_N(\mathbf{R}) Z_N.$$

P_N is the probability that a given chain configuration will have an end-to-end vector \mathbf{R} . In limit, where N goes to infinity it has Gaussian distribution

$$P_N(\mathbf{R}) = \left(\frac{3}{2\pi R_0^2} \right)^{3/2} \exp \left(-\frac{3\mathbf{R}^2}{2R_0^2} \right),$$

characterized by its variance R_0 in connection with a and L as $R_0^2 = aL$.

The free energy of the single polymer chain is

$$\mathcal{F} = -k_B T \ln Z_N(\mathbf{R}).$$

If we use equation above, we finally get

$$\mathcal{F}(\mathbf{R}) = \mathcal{F}_0 + k_B T \left(\frac{3\mathbf{R}^2}{2R_0^2} \right) + C.$$

\mathcal{F}_0 and C are both additive constants. $\mathcal{F}_0 = -k_B T \ln Z_N$ is the free energy of an unconstrained chain while C is connected with normalization of probability distribution. They both do not depend on the chain distance \mathbf{R} , so we neglect them.

From this equation we see that free energy is quadratic in \mathbf{R} and can represents Hooke's law for the extension of a single chain. Polymer can be seen as entropic springs with Hooke's constant $3k_B T/R_0^2$.

If the the internal energy per molecule, for which above we assumed that it is equal for all configurations of chain, associated with bond distortion were $\mathcal{U}(\mathbf{R})$, than we would instead have:

$$\mathcal{F}(\mathbf{R}) = \mathcal{U}(\mathbf{R}) - TS(\mathbf{R}).$$

\mathcal{S} is the entropy per molecule.

As we know the classical freely jointed model evidently has $\mathcal{R} = 0$ so entropy is minus free energy divided with T , that is

$$\mathcal{S}(\mathbf{R}) = -k_B \left(\frac{3\mathbf{R}^2}{2R_0^2} \right).$$

The stored energy is entropic, because it measures a change (reduction) in the number of possible conformations (and thus entropy) when the end of such a chain is pulled apart (U increases). However chains are always driven by the need to maximize their disorder - the number of their possible conformation [3].

Since elastomers are crosslinked, end to end vector for chain is vector from one to another crosslink \mathbf{R}_f which act on chain as deformation λ_{ii} in the three direction. New end to end vector is then

$$\mathbf{R} = \underline{\lambda} \times \mathbf{R}_f.$$

Where $R_x = \lambda_{xx}R_x^f$, $R_y = \lambda_{yy}R_y^f$ and $R_z = \lambda_{zz}R_z^f$. The free energy of an particular strand and probability distribution can be calculated. Then in the end the free energy density of a deformed rubber (in our case deformed because of crosslinkers) becomes

$$F = \frac{1}{2}n_s k_B T (\lambda_{xx}^2 + \lambda_{yy}^2 + \lambda_{zz}^2),$$

where $n_s k_B T = \mu$, n_s is the number of chain strands per unit volume (equal to the inverse volume occupied by an average chain between two connected network crosslinks) and μ ($\sim 10^4 - 10^6$ Pa) is characteristic rubber modulus. The lowest free energy density would apparently be at $\lambda_{xx} = \lambda_{yy} = \lambda_{zz} = 0$.

The model discussed above is the simplest model where we neglect overlapping of molecules, the effect of volume change and the fact that N of chain between crosslinks does not go to infinity but the chain between crosslinks is made out of 5 – 10 monomers. The first leads to the limit of chain entanglements at large extensions/compressions, when the later leads to the limit of finite extensibility [3].

4 Liquid crystal elastomers

As we already said the LCEs are composed of LCs and elastomers.

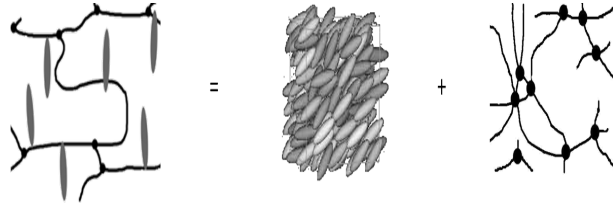


Figure 10: LCE is composed of liquid crystal and elastomer.

The most important new properties of such newly engineered material are related to the elasticity of elastomer and anisotropy of LCs. LCE are made from silicon or carbon elastomeric net, which dictate macroscopic properties like deformation and shape. On the net are, in different ways, attached mesogenic groups with microscopic properties of LCs thus introducing the liquid crystal order. Mesogenic groups can be bind as a part of the chain or can be just pendant on the chain. We call this two kind of LCEs main chain and side chain LCEs, respectively. We can see representation of both kind of LCEs in Figure 11 below. As we already told the chains are connected with crosslinkers [8].

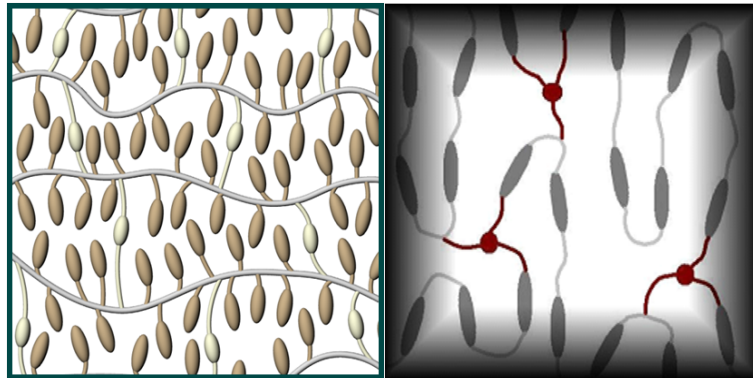


Figure 11: LCE with mesogenic groups on the side (left) and as a part of the chain (right).

As we know the liquid crystals have different phases and consequently one can find LCE having different phases such as the nematic, smectic and cholesteric phase. Correspondingly we talk about nematic and smectic LCEs.

One important property of nematic LCEs is that they possess only a nematic order and not smectic one, i.e., they are not ordered in layers.

Smectic LCE possesses either only smectic or both nematic and smectic order. Because of that, their properties are more close to properties of solids with much smaller thermomechanical response and are rarely used for technological use [7].

We differentiate monodomain and polydomain LCEs. We can make monodomain LCE from polydomain by stretching them during the final crosslinking procedure or by cooling them from the isotropic to the nematic phase under the strong external stress field [8].

In former chapter we wrote that polymer tends to order in an isotropic or spherical shape and we can describe them with only one dimension (R_0). On the contrary, nematic polymers, whether side or main chain, have backbones with average shape distorted by the nematic ordering of the associated rods. Because of that more than one dimension is needed to describe their anisotropic shape. The aligned rod-like segments of a main chain polymer will clearly elongate the average shape of gyration, essentially stretching the backbone along their principal axis, the director \vec{n} . When the nematic order is high, the whole chain is forced into direct shape: short chains unfold and become rods themselves, albeit slightly flexible. In chains, long enough, entropy is partially recovered by the creation of the celebrated hairpin defects. On the side chain pendant rods can be linked on backbone with two types, so called, spacers. This caused different conformations for the same degree of nematic ordering. Side-on linking enhances extension along director when the end-on type sometimes do the same but often flatten the liquid crystal in plane perpendicular to director as seen in Figure below [3].

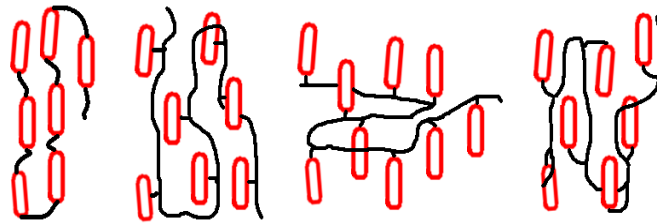


Figure 12: The shapes of nematic polymer backbones. From left main chain polymer show very high anisotropy, the intermediate case of side-on polymer LC show weaker, but still substantial backbone alignment, while in the right two end-on side chain polymer LC the mesogenic groups may be only weakly coupled to the backbone, here the choice between the oblate and the prolate backbone arrangement is made by spacer selection

Instead of R_0 now are the radius of gyration along the director \vec{n} , $R_{\parallel} \sim \sqrt{l_{\parallel}}L$, and perpendicular to the director \vec{n} , $R_{\perp} \sim \sqrt{l_{\perp}}L$, where l_{\parallel} and l_{\perp} are the effective length of steps in the direction perpendicular and parallel to \vec{n} , respectively, and depend on Q . The three mean square quantities are $\langle R_i R_j \rangle = \frac{1}{3} l_{ij} L$, where l_{ij} is a tensor of effective step lengths.

In the case of uniaxial LCE the $R_x = R_y = R_{\perp}$. And if the \vec{n} is in the direction of z axis the tensor step length become:

$$\underline{l}_0 = \begin{pmatrix} l_{\perp} & 0 & 0 \\ 0 & l_{\perp} & 0 \\ 0 & 0 & l_{\parallel} \end{pmatrix}.$$

In anisotropic case the Gaussian distribution is

$$p(\mathbf{R}) = \left[\left(\frac{3}{2\pi L} \right)^3 \frac{1}{\text{Det} [\underline{l}]} \right]^{1/2} \exp \left(-\frac{3}{2L} R_i l_{ij}^{-1} R_j \right)$$

or

$$p(\mathbf{R}) = \left[\left(\frac{3}{2\pi L} \right)^3 \frac{1}{\text{Det} [\underline{l}]} \right]^{1/2} \exp \left(-\frac{3R_x^2}{2l_{\perp}L} - \frac{3R_y^2}{2l_{\perp}L} - \frac{3R_z^2}{2l_{\parallel}L} \right) [3].$$

We can describe anisotropy as $r = \frac{l_{\parallel}}{l_{\perp}}$.

Now, when we know how to describe an anisotropic state, we can describe the effect of the mesogens on the polymeric chain conformation.

If the α^{th} link in the polymeric chain is a rod forming an angle Θ_{α} with the direction of \vec{n} (chosen to lie along the z axis) and angle Φ_{α} , then the unit vector along the α^{th} link to be \mathbf{u}^{α} . The end-to-end vector is then $\mathbf{R} = a \sum_{\alpha=1}^N \mathbf{u}^{\alpha}$ and step lengths is then

$$\underline{l} = \frac{3}{Na} \langle \mathbf{R} \mathbf{R} \rangle = \frac{3a}{N} \sum_{\alpha, \beta} \langle \mathbf{u}^{\alpha} \mathbf{u}^{\beta} \rangle.$$

Being freely jointed there is no correlation between the directions \mathbf{u}^{α} and \mathbf{u}^{β} of the links α and β . The average is nonzero then only for $\alpha = \beta$ and gives $\langle \mathbf{u} \mathbf{u} \rangle$ for all N links of the chain. If director is along z, then the coordinate projection are $u_z = \cos \Theta$, $u_x = \sin \Theta \cos \Phi$ and $u_y = \sin \Theta \sin \Phi$. Since $\langle \cos \Theta \sin \Theta \rangle = 0$ and $\sin \Phi \cos \Phi = 0$ because Θ and $\Pi - \Theta$ are equivalent states only diagonal terms survive in $\langle \mathbf{u}_i \mathbf{u}_j \rangle$. In a uniaxial nematic

all Φ values are equally likely in the plane perpendicular to the \vec{n} , therefore $\langle \cos^2 \Phi \rangle = \langle \sin^2 \Phi \rangle = \frac{1}{2}$. Thus in a uniaxial phase

$$\underline{l} = 3a \begin{pmatrix} \frac{1}{2}\langle \sin^2 \Theta \rangle & 0 & 0 \\ 0 & \frac{1}{2}\langle \sin^2 \Theta \rangle & 0 \\ 0 & 0 & \langle \cos^2 \Theta \rangle \end{pmatrix}.$$

In the first chapter we learned that $Q = \frac{3}{2}\langle \cos^2 \Theta \rangle - \frac{1}{2}$ and hence there is a direct relationship between Q and the components of \underline{l}

$$\underline{l} = a \begin{pmatrix} 1 - Q & 0 & 0 \\ 0 & 1 - Q & 0 \\ 0 & 0 & 1 + 2Q \end{pmatrix}.$$

Order parameter is so related to the shape anisotropy of the polymer chain, where

$$\begin{aligned} l_{\parallel} &= a(1 + 2Q), \\ l_{\perp} &= a(1 - Q). \end{aligned}$$

The anisotropy for a nematic main chain freely jointed polymer is

$$r = \frac{l_{\parallel}}{l_{\perp}} = \frac{1 + 2Q}{1 - Q}$$

and is approximately $1 + 3Q$ for small Q [3].

There are many phenomena that can be observed in LCEs. Among them the soft elasticity - the macroscopic shape changes at relatively low energy. Changes are possible because of the high liquid-like molecular mobility on elastomer which allow the director to easily achieve gross changes in orientation. Since the molecular elongation of polymer chains relates to this direction, nematic rotation will be mirrored by soft elasticity. It depend critically on how nematic monodomains have been formed. It is evidenced much more by networks with a more isotropic genesis. The loss of total softness, arising from the formation process, gives rise to what we call semi softness. There are thermomechanical response, electromechanical Fredericks effect, photo-elastomers that drastically change shape on illumination, rheology and viscoelasticity that crosses between soft and conventional depending upon frequency and geometry. [3].

In next chapter we will focus on only thermomechanical response.

5 Calorimetric investigation of phase transition of liquid crystal elastomers and thermomechanical response

Long polymer chains, with incorporated mesogenic groups can also order nematically. The liquid crystals in LCE go with heating from the nematic phase into the isotropic one. LCEs are along the direction of director in the nematic phase longer than in the isotropic phase. A change of average shape has thus been introduced from spherical to spheroidal. In the prolate spheroidal case, the long axis of the spheroid points along the nematic director \vec{n} . Thermomechanical response is spontaneous and reversible [9].

Thermomechanical effect can only be observed in monodomain, well aligned samples. Without very special procedure while making LCE, liquid crystals are always found in polydomain form, with very fine texture of director orientations. The great breakthrough in this field, developing a method of obtaining large, perfect monodomain nematic elastomer was made by Küpfer and Finkelmann [8].

Conventional polymers change shape only in response to external forces. Opposite to that LCE change shape spontaneously when they orientationally order [3].

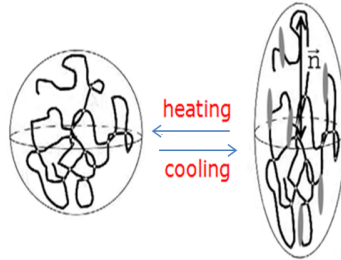


Figure 13: Thermomechanical response of LCEs: During cooling LCEs go from the isotropic to the nematic phase and spontaneously stretch. During heating opposite happened.

Depending on the type of the I-N phase transition we differentiate fast (on-off) response or slow (continuous) response. Fast response in the case of discontinuous or first order I-N phase transition, while slow or continuous response is obtained in the case of continuous or supercritical phase evolution. At discontinuous I-N phase transition the LCE is stretching slowly during cooling, but in the vicinity of the I-N phase evolution LCEs length very drastically increase. At continuous phase transition the length is increasing continuously with changing temperature.

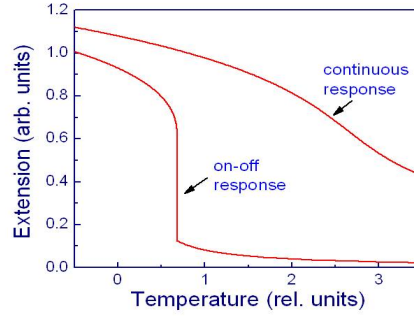


Figure 14: Thermomechanical response.

Now we will focus on the nematic LCEs and will discuss on, which quantities their thermomechanical response depends on. Large thermomechanical response can be obtained only in monodomain LCEs, which we can get by ordering polydomain LCEs by applying either external or intrinsic mechanical fields. Because of that the nature of the I-N phase transition depends on intrinsic and extrinsic mechanical fields. Intrinsic and extrinsic fields can be imprinted in the LCEs during the final crosslinking procedure. Specifically, LCE's preparation starts in the isotropic phase where mesogenic groups are attached on polymer chains which are then also partially crosslinked. Then we cool down LCE to the nematic phase and stretch it with the external force. Stretching results in ordered monodomain state and that's how polydomain LCE become monodomain. Monodomain LCEs are also called liquid single crystal elastomers (LSCEs). At the end, LSCE is crosslinked up to the desired density of crosslinkers. LSCE "remember" what happened during preparation and that they have to be stretched in nematic phase. By changing the temperature LSCEs cross over the isotropic to the nematic phase transition which results in considerable change of the length in the direction of director of mesogenic groups. Different magnitude of the LSCEs stretching was reported by different groups with the maximum value reported of 600%.

At the beginning of LSCE research only samples with continuous or supercritical I-N phase transitions were known. Recently, it was discovered that type of phase transition and thus the type of the thermomechanical response can be controlled by changing density of crosslinkers. Higher density drives phase transition to critical point, which separate supercritical and discontinuous phase transitions. If density of crosslinkers is low enough, the phase transition becomes discontinuous with ON-OFF thermomechanical response. In Figure 15 below excess heat capacity as a function of temperature is shown. For instance, if there is a difference between the ac run (solid

circles) and relaxation run (open circles) the latent heat is present and phase transition is discontinuous. Larger difference means more latent heat, i.e., stronger first order phase transition [10, 11, 12].

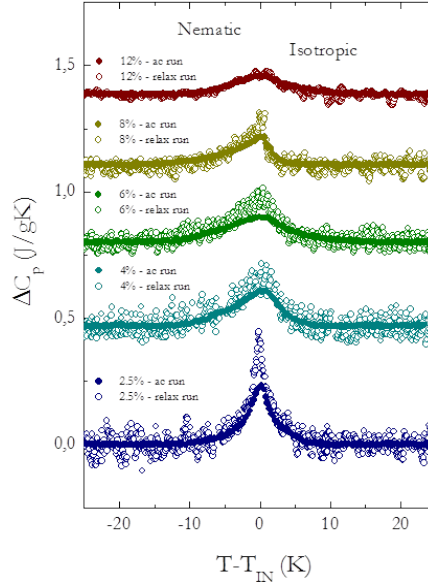


Figure 15: The nature of the I-N phase transition in LSCEs depend on the density of crosslinkers [12].

It was also found that the type of the I-N phase transition depends on the magnitude of the imprinted external mechanical field and the crosslinking temperature. [9].

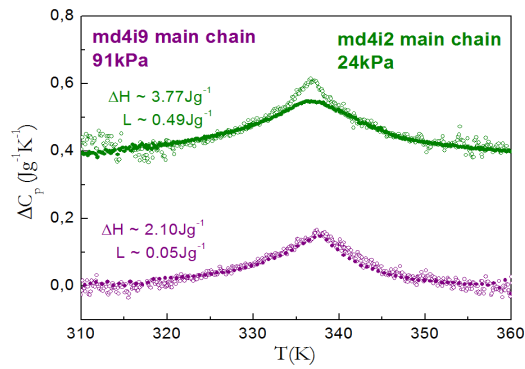


Figure 16: The nature of the I-N phase transition can also be controlled by the imprinted external mechanical field [12].

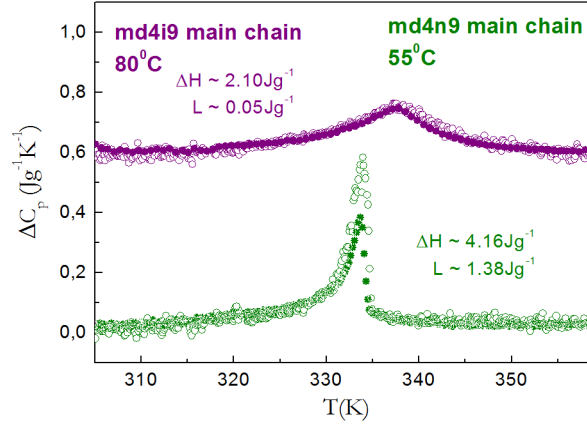


Figure 17: The nature of the I-N phase transition can also depend on different temperature of crosslinking [13].

So, the liquid-vapour type of critical point exists in LSCEs and its position in the composition-temperature phase diagram can be controlled by the internal random mechanical fields (via density of crosslinkers), the external mechanical field and the crosslinking temperature. Thus allowing tailoring of the LSCE mechanical response to be either on-off or continuous type.

Recently studies on side chain smectic LCE have been done. Two samples with different crosslinking density ($x = 5$ mol% and $x = 10$ mol%) have been used in studies. Both samples exhibit first order I-SmA phase transition. The presence of crosslinkers can suppress the long-wavelength fluctuations, which tends to enhance a long-range smectic order. At the same time, the crosslinking points act as defects and tend to destroy ordering and thus have the opposite influence on the phase transition behavior. By increasing the crosslinking density the anomaly of heat capacity and by that the temperature range of the thermomechanical response is widened. The heat capacity anomaly is more suppressed and moved to lower temperatures. The increasingly pronounced broadening of the transition may be attributed to the increased random-fields originating from the increased crosslinking density. The latent heat is decreasing with increasing crosslinker density. That is shown in Figure 18.

In the case of smectic LCEs the orientational and the translational orders are coupled and it is possible that this coupling shifts the I-SmA phase transition towards a critical point. In contrast to nematic LSCEs some recent results and measurements suggest that smectic LCEs exhibit first order transitions even for rather high crosslinking concentrations [14].

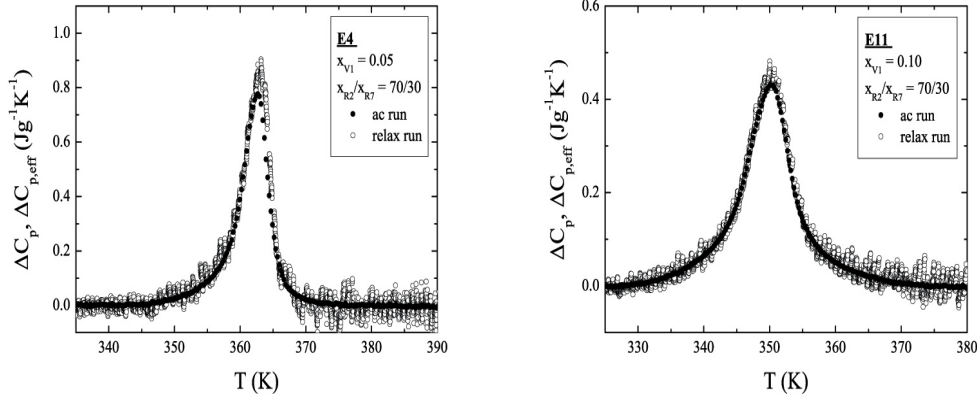


Figure 18: Excess heat capacity obtained in Smectic A LCE with smaller and higher density of crosslinkers [14]

5.1 Applications

While no one has discovered material which would be perfect for artificial muscles yet, the world shows great interest in LCE, when they were discovered. Muscles are anisotropic, while they are stretching in only one direction along muscle fiber. That is the same as for LCE, which are stretching only in direction of director \vec{n} . Other properties describing muscles are maximal contraction, maximal mechanical strength and maximal frequency of contraction. Researchers find LCE with exactly same value of this properties as natural muscles [7].

Thermomechanical response can be used for sensors and temperature-controlled actuators. In our case we can convert computer signal through changing of temperature into physical stretching of LCE [8].

The nematic photo-elastomers make the light-driven actuators possible. Due to optical clarity of LCE in the monodomain state, bifocal contact and intra-ocular lenses can be made. A bi-rubber strip of the monodomain nematic and ordinary isotropic rubbers can be welded together. Photo-actuation possibilities can also be explored in micro-pumps, micro-manipulators and valves [3].

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