

# Liquid crystalline elastomers: Thermally and optically effected ordering

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## Abstract

The nature of the phase transition in nematic liquid crystalline elastomer is investigated using NMR and calorimetry. The balance between ordering and disordering effects of the polymer network is identified as crucial for the behavior of the order parameter near the phase transition. The change from supercritical to critical regime with adding low molecular weight liquid crystal to the elastomer is proven.

## 1. Introduction

Applications of liquid crystals are widespread and encompass a range of electro-optical technologies. The essential progress in all of these technologies is based on gradual improving materials. Over the years, high molar mass systems have been essential only as supporting materials for liquid crystalline technologies. New possibilities challenges appear with the development of multifunctional materials like liquid crystal elastomers (LCEs) that are composed of cross linked polymer networks with either main-chain or side-chain mesogenic units [1]. Here we will limit our discussion to side-chain structures (See schematic presentation in Figure 1a). Such materials possess interesting mechanical,

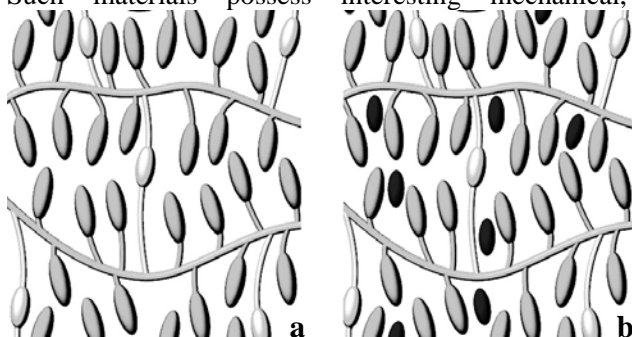


Figure 1. Schematic presentation of: (a) LCE as a cross linked network with side-chain mesogenic

units; (b) LCE with diluted mesogenic molecules (black).

optical, electrical and thermal properties that lead to new possibilities for technological applications. The combination of the entropic elasticity of polymer networks with the orientational ordering of anisotropic, nematogenic molecules yield complex materials with interesting physics and chemistry. Among the many interesting phenomena, the most unusual include spontaneous shape change at phase transitions, strain-induced orientational transitions leading to new organized morphologies, and soft elasticity [1]. They are flexible like a spring but the elastic modulus and the stiffness can be easily controlled. Such systems can be easily disturbed by external stimuli. Their large susceptibility to electrical, thermal, optical, and mechanical stimuli leads toward many new optical, electrooptical, biological, biomedical and other applications [2].

The development of possible applications requires detailed understanding of the structure and ordering of LCEs. One of the major open questions of the physics of LCEs is the nature of the isotropic-nematic phase transition and its relation to the elasticity (soft, semisoft, or normal). The shape of the stress-strain [3] curve is strongly related to the coherence of the nematic director field. The degree of this ordering crucially depends on the cross linking of the polymeric network and history of the material preparation [4]. The debate about the applicability of the concept of soft elasticity to LCEs has been recently reopened by the measurements of dynamical shear modulus [5]. Low molecular weight nematogenic liquid crystals exhibit a first-order nematic-isotropic (NI) phase transition characterized by a discontinuous jump of the nematic order parameter  $S(T)$  at the transition temperature  $T_{NI}$ , observed in optical measurements [6], deuterium nuclear magnetic resonance (DNMR) [7,8], or by a

discontinuous jump of the enthalpy observed in calorimetric experiments [9]. In LCEs the onset of the nematic order is continuous within a relatively narrow temperature interval (typically a few K)[7]. The change goes from a weakly ordered paranematic (PN) phase characterized by a network induced ordering to a nematic (N) phase with relatively highly ordered mesogenic units. The order is only slightly perturbed by the cross links. In a single domain samples (mostly uniform director field) prepared with the application of stress during the cross linking procedure strain is proportional to the change in the average order parameter. Here we report on the recent NMR in heat capacity experiments that support the picture of a combined ordering-disordering effect of the network on the smearing out of the  $S(T)$  profile. Our description goes beyond the originally proposed one that considers LCEs as inherently heterogeneous materials [10], composed of domains, each with a well-defined transition temperature. The average OP temperature profile of the system,  $\langle S(T) \rangle$ , is then calculated as a superposition of profiles arising from the individual microdomains. In our picture the behavior of  $S(T)$  in LCEs is attributed to the supercritical character of the N-PN transition caused by a "mechanical" field produced by the polymeric network[11]. It is a well-known fact that a linear coupling of the nematic  $S$  with a conjugate field  $G$  yields a linear term  $-GS$ , in Landau free energy that can drive the transition to a supercritical regime, characterized by zero latent heat and continuous  $S(T)$  profile. This occurs whenever  $g$  exceeds the critical value  $G_c$ . In LCEs,  $G$  is the mechanical stress field that consists of the internal, field  $G_{\text{int}}$ , imprinted into the system during the two-step cross linking procedure [12] and the external field  $G_{\text{ext}}$ , applied by straining the sample. The "heterogeneous" and "supercritical" scenario both provide for qualitatively satisfactory description of the  $S$  temperature profile in LCEs. Therefore we decided for a detailed study of DNMR spectra that enables to distinguish between the two scenarios.

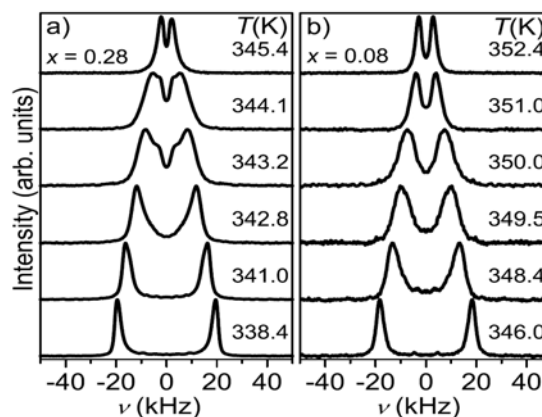
## 2. Deuterium Nuclear Magnetic Resonance

The method is based on the detection of first ( $M_1$ ) and second ( $M_2$ ) moment of the deuterium quadrupole spectrum combined with the corresponding angular dependences. The splitting of the two deuterium lines reflects local order  $S$  and orientation of the director

with respect to magnetic field characterized by an angle  $\theta$ :

$$\Delta\nu = \frac{1}{3} S \nu_Q P_2(\cos\theta),$$

where effective quadrupole coupling constant  $\nu_Q$  is 270 kHz. Details are described in the reference [8]. The DNMR was performed on deuterated probe molecules dispersed in side-chain LCE materials based on poly-[oxy(methylsilylene)] were synthesized as described in Ref. [12]. Using (8CB- $\alpha d_2$ ) as probe molecules we were able to change the relative amount of the mesogenic units in the system. By changing concentration from 0 to 25% we simply go from super critical to critical regime. To introduce 8CB in LSE the liquid crystal was diluted in cyclohexane, to which toluene was subsequently added in small steps to progressively and nondestructively swell the sample. After the evaporation of the solvents the LC-LCE dispersions were ready. DNMR spectra were taken at the deuteron Larmor frequency  $\nu_L = 58.4$  MHz (Figure 2).



**Figure 2. Temperature dependences of the DNMR spectra for magnetic field parallel to the director: (a) 28% 8CB, (b) 8% 8CB.**

To account for the gradual change in the spectrum we assume that beside the mechanical field  $G$  we have also disordering effects caused by cross linking. We separate disordering effects into two independent contributions due to the degree of order and director orientation. The first one is described by a Gaussian distribution in the transition temperatures of local domains characterized by the width  $\sigma_T$ . The second one is described by a Gaussian distribution of the directors in different domains characterized by the width  $\sigma_\theta$ . Nematic director of the sample was

oriented with an angle  $\theta$  in external magnetic field. The angular dependence shows that director is not

LCE the best fit is obtained with  $a_0 =$

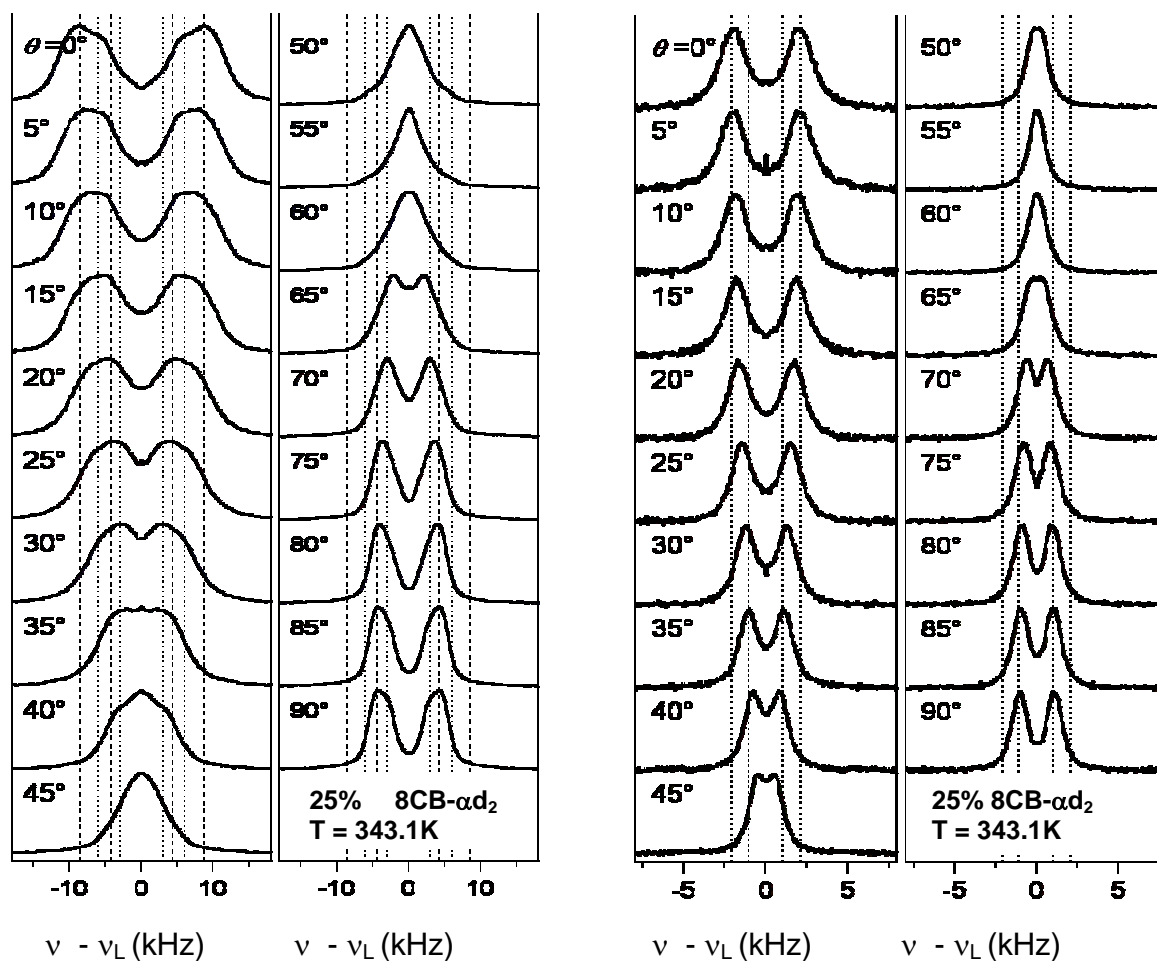


Figure 3: Angular dependences of the DNMR spectra for magnetic field parallel to the director: (a) 28% 8CB, (b) 8% 8CB.

uniformly oriented. Two representative angular sets are shown in Figure 3.

### 3. Modeling of the NMR Data

To model the order parameter temperature dependence Landau free energy expansion is used

$$F(S) = F_0 + \frac{1}{2} a_0 (T - T') S^2 + \frac{1}{3} B S^3 + \frac{1}{4} C S^4 - G S,$$

where  $a_0$ ,  $B$ ,  $C$ ,  $T'$ , are standard Landau coefficients whereas  $G$  is an effective mechanical field. With pure

$0.11 \cdot 10^6 \text{ Jm}^{-3}/\text{K}$ ,  $B = 2.1 \cdot 10^6 \text{ Jm}^{-3}$ ,  $C = 6.2 \cdot 10^6 \text{ Jm}^{-3}$  and  $G=0.032$ .  $G$  exceeds the critical value  $G_C = -B^3/27C^2$  more than 3 times. To also account for the disordering effects that yields a shift in the transition temperature and its distribution, we used a Gaussian distribution of transition temperatures. In the fitting procedure of the first and second moments ( $M_1$  and  $M_2$ ) the following parameters were optimized:  $G/G_C$ ,  $\sigma_T$  (K),  $T_{NI}$  (K), and  $\sigma_\theta$ . Fits are shown in the Figure 4 while the parameters are listed in the table:

x	$G/G_C$	$\sigma_T$ (K)	$T_{NI}$ (K)	$\sigma_\theta$ (deg)
0.28	$0.95 \pm 0.1$	$1.0 \pm 0.2$	$343.4 \pm 0.2$	$14 \pm 1$
0.08	$1.5 \pm 0.1$	$1.0 \pm 0.2$	$349.6 \pm 0.2$	$10 \pm 1$
0.03	$2.4 \pm 0.25$	$3.0 \pm 0.3$	$353.9 \pm 0.2$	$17 \pm 2$

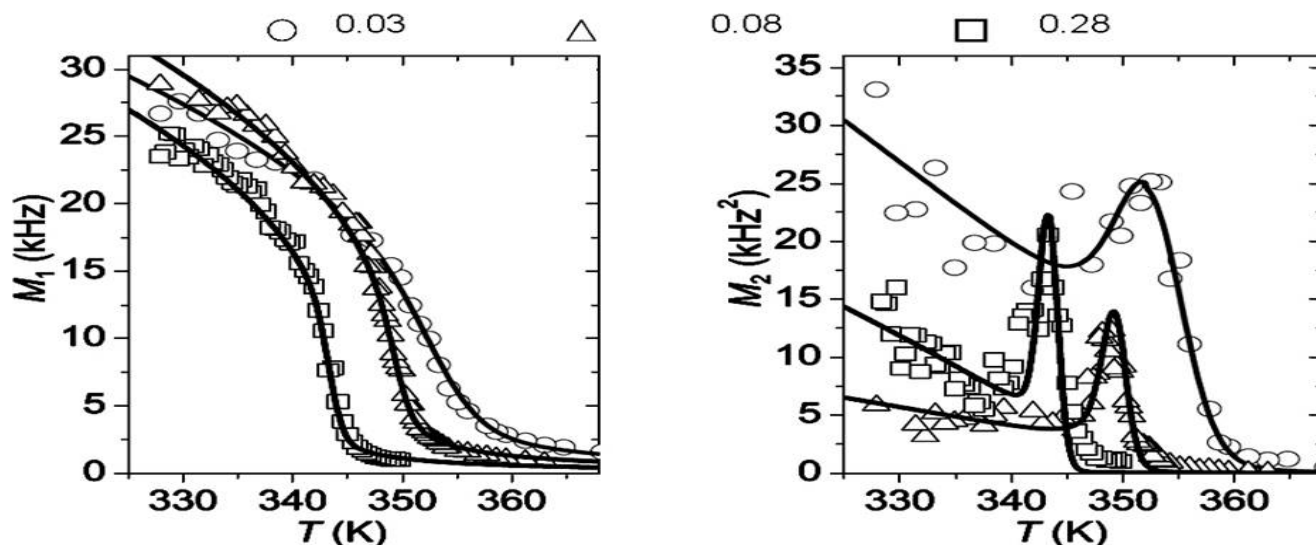


FIG. 4: Temperature dependences of (a) the first and (b) the second moments of DNMR line shapes for 28% mixture of 8CB in LCE.

The supercritical nature of the investigated samples is clearly seen from obtained parameters. Specifically, the increase from  $G=G_C$  in 25% mixtures to 1.5 in 8%, 2.5 in 3% mixtures, and 3.5 in 0% case. It confirms the assumption on a strong internal field in the most of samples. Even in the 28% sample swollen with a relatively high concentration of 8CB that promotes below-critical behavior,  $G$  is only slightly below  $G_C$ . In addition, in all samples a certain degree of heterogeneity coexists with internal fields.

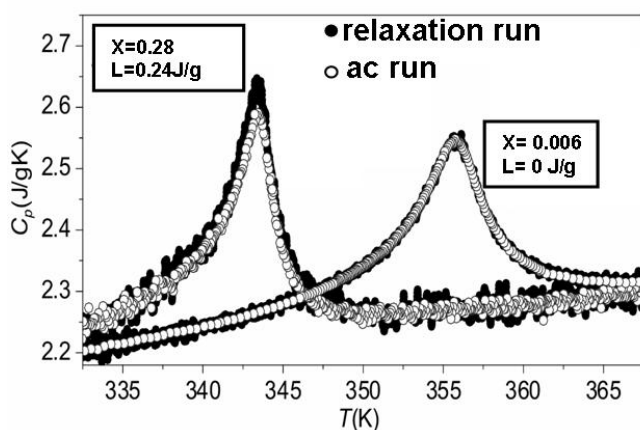
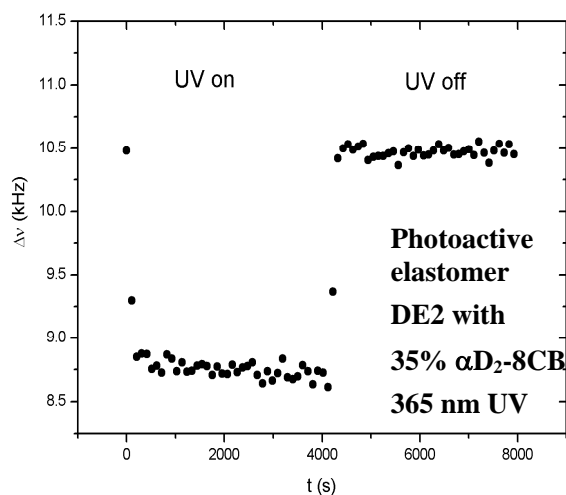


Figure 5: Heat capacity variations in 28% and 6% mixtures of 8CB in LCE indicates the discontinuous transition in the case of high concentrations.

The above DNMR results are consistently supported by the heat capacity data (Figure 5) obtained in the ac and relaxation modes on the same samples. The relaxation mode has much better sensitivity to latent heat  $L$  than the ac mode [13]. The comparison between the ac and relaxation heat capacity data (Fig. 5) allows for a quantitative estimation of the latent heat share in the total enthalpy change due to the first-order phase conversion. The matching ac and relaxation data in 0.6% indicate zero latent heat, whereas the mismatch in 28% reveals nonzero latent heat  $L_- = 0.24$  J/g, evidently related to slightly below-critical behavior as indeed observed in DNMR.

#### 4. Photoactive LCE

To check if we can induce a mechanical change also with an optical stimulus we decided to investigate a nematic with the diazo link where a trans-cis isomerism can be affected by the light; the change is wavelength-specific and reversible. Diazo functions are readily incorporated into mesogens. The cis/trans isomerisation is well investigated for low molar mass azo-group containing liquid crystals and linear polymers. We therefore used this functional group for the synthesis of the networks. Preliminary experiments with photoactive LCE DE2 doped with



**Picture 6: Photo active DE2 polymer with -8CB indicate that even in case of monochromatic UV light (365nm) the dominant effect is of the thermal nature.**

## 5. Conclusions

In conclusion, we show for the first time that temperature dependencies of the first and the second moment of the DNMR line shapes in LSCE elastomers clearly reflect the supercritical nature of the N-PN transition. Moreover, the heat capacity anomaly becomes significantly broader in low concentration mixtures 0.006, in accordance with the proposed supercritical character of the N-PN phase change in the  $x \rightarrow 0$  limit (virgin LCEs). We also demonstrate that the relative strength (with respect to  $G_c$ ) of the frozen-in internal fields can be set by the amplitude of the external stress during the network formation. Further we show that nixing LCE with LC can also make the transition more critical.

## 6. Acknowledgements

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