

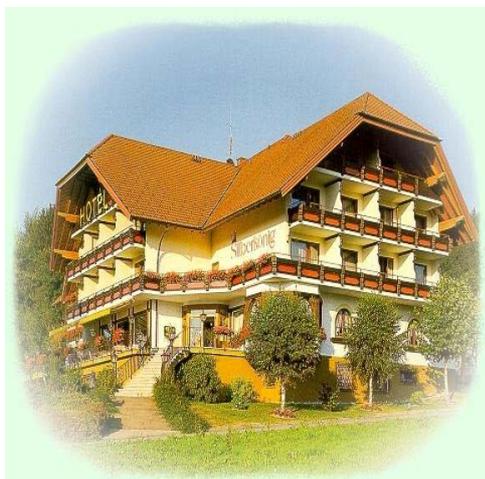
Under the auspices of the  
German Liquid Crystal Society, Arbeitsgemeinschaft in der Bunsengesellschaft,  
SFB 428, Deutsche Forschungsgemeinschaft, and  
European Research Training Network FULCE

# **Second International Workshop on Liquid Crystalline Elastomers**

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**ABSTRACTS**

**LIST OF PARTICIPANTS**



**Bleibach im Elztal**

**Germany**

**September 25 - 27, 2003**

# 2<sup>nd</sup> LC Elastomer Workshop



25<sup>th</sup> – 27<sup>th</sup> September 2003 / Bleibach, Germany

## PROGRAMME

### Wednesday, September 24<sup>th</sup>

Arrival 18:00 *dinner*

### Thursday, September 25<sup>th</sup>

8:00 *breakfast*

**9:00 A. Griffin, Atlanta, GA**

Polyester liquid crystalline elastomers having transverse rods in the main chain

**9:45 K. Hiraoka, Atsugi**

X-ray and electromechanical studies on chiral smectic C liquid-crystalline elastomers

10:30 *coffee break*

**11:00 F. Weiss, Freiburg**

Lyotropic liquid crystalline epoxide amine addition polymers and elastomers

**11.45 D. Lambreva, Amsterdam**

Synchrotron studies of smectic elastomers with small crosslinking densities

12:30 *lunch*

16:00 *coffee*

**16:30 P. Martinoty, Strasbourg**

Mechanical properties of mono-domain liquid crystalline gels and elastomers

**17:15 J.-D. Marty, Toulouse**

Mesomorphic imprinted networks: synthesis and separation properties

18:30 *dinner*

## Friday, September 26<sup>th</sup>

8:00 *breakfast*

**9:00 M. Warner, Cambridge**

Soft elasticity

**9:45 J. Schmidtke, Freiburg**

Cholesteric films as photonic band gap materials and the role of crosslinking

10:30 *coffee*

**11:00 I. Rousseau, Storrs, CT**

New siloxane-based liquid crystalline blends, copolymers, and main-chain elastomers with mixed mesogens for tailored properties

**11:45 B. Zalar, Ljubljana**

The I-N transition in LC elastomers probed by deuteron NMR of guest nCB molecules and by proton NMR relaxometry

12:30 *lunch*

16:00 *coffee*

**16:30 H. Brandt, Freiburg**

Main-chain liquid crystalline elastomers

**17:15 K. Urayama, Kyoto**

Volume phase transition of liquid crystalline gels in nematic solvents

18:30 *dinner*

**19:30 Poster Introduction / Poster**

## Saturday, September 27<sup>th</sup>

8:00 *breakfast*

**9:00 H. Finkelmann, Freiburg**

Mechanical orientation of LC elastomers

**9:45 R. Stannarius, Magdeburg**

Electrically and mechanically induced layer shrinkage in smectic LCE films

10:30 *coffee*

**11:45 General discussion / Conclusion**

12:30 *lunch*

departure

## Polyester Liquid Crystalline Elastomers Having Transverse Rods in the Main-Chain

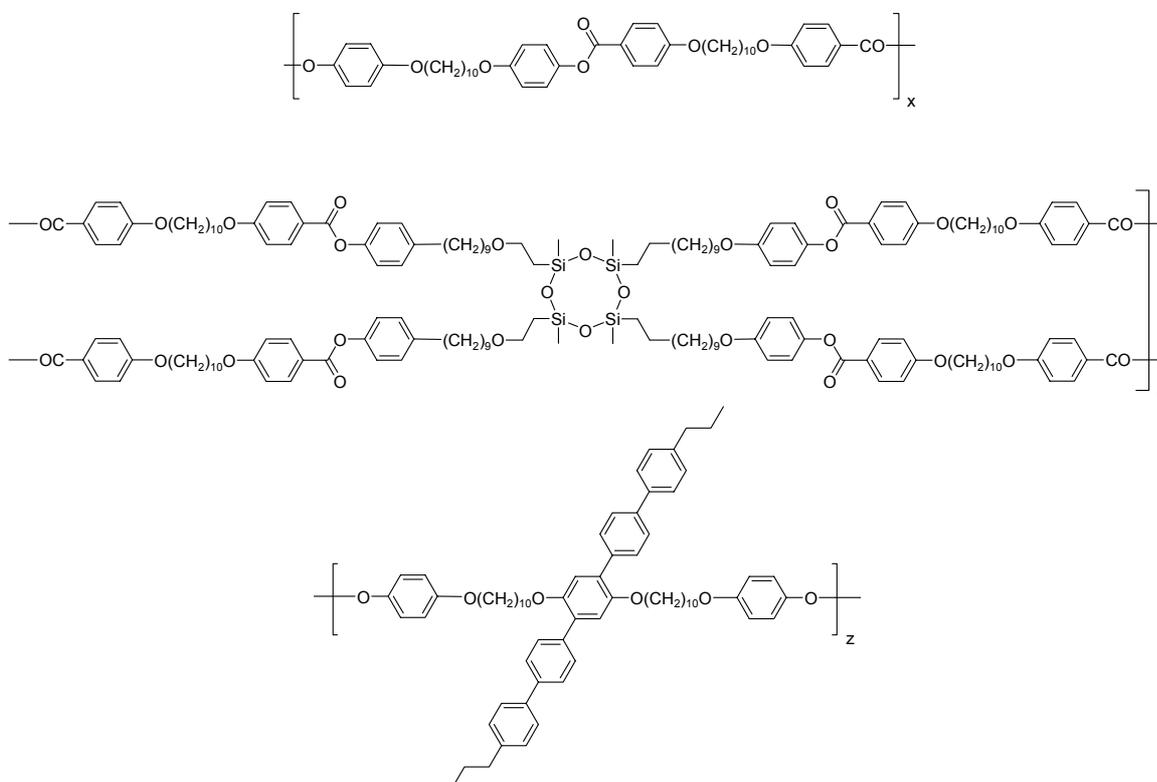
P. Liu<sup>a</sup>, C.J. Booth<sup>a</sup>, and A.C. Griffin<sup>a,b</sup>

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We have prepared liquid crystalline elastomers having transverse rods in the polymeric main chain. The liquid crystallinity arises from phenyl benzoate mesogens in a (rigid-flexible)<sub>n</sub> alternating main-chain LCP. Transverse rigid rods were incorporated as potential auxetic-promoting components. A tetrafunctional siloxane crosslinker was used to effect network formation. The structures below show the various partial structures of these polymers. Variations in crosslinker density and in transverse rod incorporation were examined.

We will report on the thermal and phase behavior of these polymers; on their elastic behavior; and on the WAXD experiments performed on these and structurally-related related liquid crystalline elastomers.



This work was supported by the National Science Foundation and the Air Force Office of Scientific Research.

# X-ray and Electromechanical Studies on Chiral Smectic C Liquid-Crystalline Elastomers

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## 1. Introduction

Smectic C elastomers composed of chiral mesogens have recently attracted both industrial and scientific interests, because of their functional properties such as ferroelectricity, second harmonic generation and piezoelectricity due to the point group  $C_2$ . In this study, an X-ray analysis on the layer structure of chiral smectic C ( $SmC^*$ ) elastomers is shown firstly.<sup>[1]</sup> Here, we demonstrate the biaxial deformation of a  $SmC^*$  elastomer yields a monodomain sample with the macroscopic  $C_2$  symmetry. In addition, piezoelectric properties of a  $SmC^*$  elastomer are investigated by means of dynamic electromechanical measurements.

## 2. Experimental

A liquid-crystalline elastomer used is synthesized by a hydro-silylation reaction of liquid crystalline side groups with a polysiloxane backbone according to the well-known synthesis route.<sup>[2]</sup> The elastomer film (thickness 400  $\mu m$ ) is prepared by spin-casting technique in solution. Before completion of the crosslinking reaction, a uniaxial stress is applied to a swollen elastomer so as to obtain a uniform orientation of the molecular long axis of mesogens to the stress direction. With further drying the elastomer becomes a liquid crystalline phase with the smectic layers ordered at an angle  $\pm\theta$  of the layer normal to the mesogen long axis, where  $\theta$  is identical to the tilt angle of the mesogenic groups in the smectic layers. To obtain a uniform layer orientation, a second uniaxial stress is applied with an angle of  $\phi = 90^\circ - \theta$  to the first deformation direction within the  $SmC^*$  phase at about 50°C. It is confirmed that these mechanically aligned elastomer films have the  $C_2$  symmetry of the unwound  $SmC^*$  phase by means of X-ray measurements.

In the dynamic electromechanical investigation of the  $SmC^*$  elastomers, complex piezoelectric constants ( $d^* = d' - id''$ ) are measured over a frequency range from 0.01 to 100 Hz. The elastomer film is sandwiched between two gold-covered electrodes, one of which is connected to a piezotranslator for applying a sinusoidal compressive strain with an amplitude of 1  $\mu m$ . The other electrode is attached to a piezosensor for measuring a stress. The electrical response to the mechanical excitation is detected by a charge amplifier connected to the electrodes. Through the measurements, the static compressive deformation due to 3 % of the sample thickness is applied as an offset strain, so as to obtain a linear response between the stress and the strain.

## 3. Results and Discussion<sup>[3]</sup>

As for a multidomain sample obtained by a uniaxial deformation, there is no net spontaneous polarization even in the  $SmC^*$  phase. However, an induced polarization by a mechanical excitation, namely a piezoelectric effect is expected, because the point group is macroscopically assigned to  $D_\infty$  corresponding to one of the piezoelectric crystalline symmetries.

In the measurements, we have confirmed that an alternative polarization is induced by applying a sinusoidal compressive stress/strain in the  $SmC^*$  phase. Typical frequency dispersion curves of real parts of piezoelectric constants in the  $SmX^*$  and  $SmC^*$  phases of the multidomain sample are shown in Fig. 1. Here, the relaxation of piezoelectric response is clearly observed in the  $SmC^*$  phase, although any relaxation is not recognized in the temperature range of the  $SmX^*$  phase in our measurements.

The dynamic electromechanical measurements of a monodomain sample are also carried out. Though any relaxation is not recognized below 35°C (namely in the  $SmX^*$  phase) in our measured frequency range, as same as the result of a multidomain sample, a resonance peak is observed in the frequency dispersion curves of  $|d^*|$  in the  $SmC^*$  phase. We would like to tentatively explain the emergence of the resonance on the basis of an electric repulsive force between an induced polarization by a compressive deformation and a net spontaneous polarization due to the macroscopic  $C_2$  symmetry of the monodomain sample. If both of the polarizations align in the same direction, the electric repulsive force occurs and brings about a resonance in the electromechanical spectroscopy of the monodomain  $SmC^*$  elastomer obtained by a biaxial deformation.

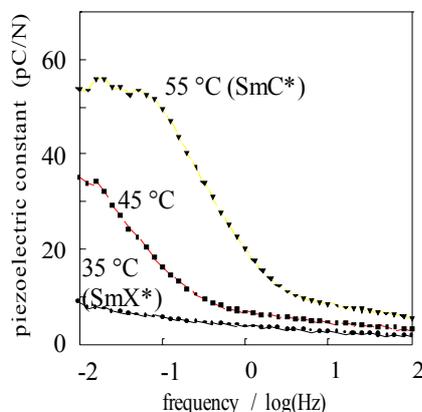


Fig. 1 Frequency dispersion of piezoelectric constant in a uniaxially deformed  $SmC^*$  elastomer.

**References:** [1] K. Hiraoka, H. Finkelmann, *Macromol. Rapid Commun.* **2001**, 22, 456. [2] H. Finkelmann, H.-J. Kock, G. Rehage, *Makromol. Chem., Rapid Commun.* **1981**, 2, 317. [3] K. Hiraoka, P. Stein and H. Finkelmann, submitted.

# **Lytropic Liquid Crystalline Epoxide Amine Addition Polymers and Elastomers**

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**Abstract** New lyotropic liquid crystalline polymers and elastomers with a new molecular constitution, bearing the possibility to affect the concentration regime of the liquid crystalline phase by variation of the pH value are investigated. Monodomain elastomers are accessible by uniaxial deformation and reveal pH-dependent, anisotropic swelling with water. The polymers are prepared by polyaddition of tetra-, hexa- and octaethylene diglycidyl ether and n-dodecyl- and n-hexadecyl amine and results in head type polysoaps having a water-soluble backbone and hydrophobic tails directly attached to the monomer units. The variation of the HLB reveals a uniform polymorphism in water. A broad miscibility gap and a hexagonal phase can be found at polymer concentrations at 70-80 wt% polymer. Due to the amino-group in the repeating unit, a partial protonation of the polymer is feasible which modifies the HLB. The melting point of the hexagonal phase increases. Consequently by variation of pH it is possible to switch between liquid crystalline and isotropic phase behaviour. Crosslinked polymers reveal the same polymorphism when swollen with water. If a uniaxial mechanical field is applied, a macroscopic orientation of the hexagonal director is accessible. Such an oriented sample shows pH-dependent anisotropic swelling properties.

# Synchrotron studies of smectic elastomers with small crosslinking densities

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Long-range translational order is a defining quality of 3D crystals; it leads to the existence of Bragg reflections in x-ray scattering. It can be shown quite generally that for ordering in a dimension less than 3D any translational periodicity is destroyed by diverging thermal fluctuations. Examples include surfactant membranes, smectic liquid crystals and liquid crystalline polymers. In these systems stacks of fluid layers are formed that show weak 1D ordering in 3D space, and instead of true Bragg reflections only power-law singularities are found in the x-ray intensity. The positional order is not long-range but decays algebraically.

Smectic elastomers form a class of polymers in which crosslinks between the polymer chains provide macroscopic elasticity while the molecular mobility is maintained. Using high-resolution x-ray diffraction Wong et al [1] previously reported for such a low-dimensional system evidence of *true long-range order* – in agreement with theoretical predictions – even though the translational ordering is still 1D as in a non-crosslinked smectic polymer. Renewed interest in this problem has come up because of the theoretical insight that the random nature of the crosslinks should have a profound *disordering influence*, contrary to the observations so far.

Recent experiments at NSLS in Brookhaven have led to remarkable result. The first-order smectic peak confirms the original observation of true long-range order *in* direction of layer periodicity. However, the second-order peak still shows clear evidence of algebraically decaying positional correlation. A speculative explanation relates this to the length  $L$  of the cross-link relative to the smectic layer spacing  $d$ . For the present sample  $L > d$ , which means that long-wavelength layer fluctuations are quenched, but short-wavelength ones not so much as they can use the ‘freedom’ provided by the relatively long crosslinks. This would influence the various diffraction orders differently.

[1] Wong G.; de Jeu W. et al Nature **389**, 576 (1997)

MECHANICAL PROPERTIES OF MONO-DOMAIN LIQUID CRYSTALLINE  
**GELS AND ELASTOMERS**

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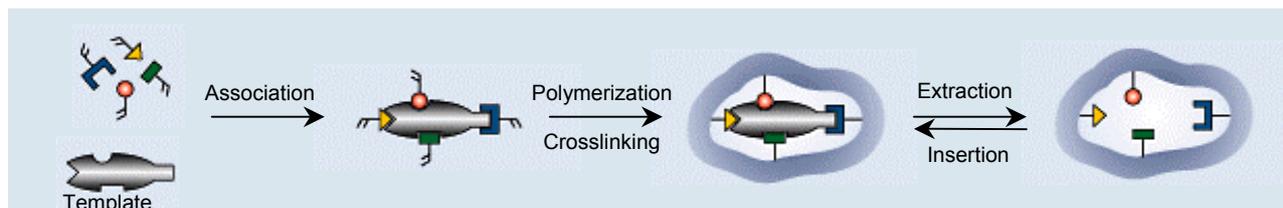
We present a study of the behavior of the shear rigidity modulus in mono-domain side-chain elastomers, main-chain elastomers, and side-chain gels. For each type of compounds, the following points will be discussed: the mechanical anisotropy, the soft elasticity, the separation of time scales, the equivalent of Rouse modes, and the percolation mechanism for the gel.

## Mesomorphic imprinted networks : synthesis and separation properties

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The **molecular imprinting technique** (MIT) is a valuable polymerization method for preparing synthetic materials able to mimic the molecular recognition phenomena present in living systems. Its principle is described in the scheme below. Upon removal of the template species, functionalized cavities, which have remembered the spatial features and bonding preferences of the template, are left inside the polymer network.



Most of the drawbacks of MIT were linked to the fact that a large amount of cross-linking agent (usually around 80-90 %) was needed to restrict the relaxation phenomena of the polymer backbones. The resulting stiffness of the network hindered the mechanisms of extraction and reinsertion of the template in the imprinted cavities and drastically decreased the capacity of the material.

In order to soften the network while preserving the memory of the template, the use of **liquid-crystal networks** in MIT should be a useful tool. In such systems, the interactions that developed between mesogenic substituents conferred a stiffness on the network through reversible cohesive effects. Moreover any manifestations of the interaction between the polymer backbone and the mesogenic side-groups could be transmitted to the macroscopic level providing that chemical cross-links are introduced between the polymer backbones to form liquid crystal elastomers. The effect of cross-linking biases the structure towards the backbone configuration present at the time of network formation; any distortion of this configuration is opposed by the elasticity of the network.

Several side-end liquid-crystal polysiloxanes imprinted materials, were synthesized. The template was linked covalently to the mesomorphous network or via hydrogen bonding.

Analysis of the **mesomorphic order** underlined a memory effect of the liquid-crystal structures set up in the presence of the template that was preserved even after heating to the isotropic state. It occurs even though the amount of cross-linker was low (5%).

The initial **capacity** of the networks is much more important than in the non mesomorphous previously studied systems. The rebinding studies, performed in the mesogenic phase, show a significantly higher **affinity** of the imprinted material towards the template than the unimprinted one. The liquid-crystal polymer networks kept the memory of the template while preserving the flexibility of the network. Moreover, these materials exhibited a good selectivity and capacity towards the printed molecule.

Lastly we can imagine to specifically turn the liquid crystalline character introduced to good account. For instance, the use of chiral templates could induce a chiral structure of the mesophase. This could then be retained even after the extraction of the template, and so could improve the resolution of racemic mixtures.

## Softness and semi-softness in nematic elastomers

Mark Warner, Cavendish Laboratory, Cambridge.

Molecular shape change and macroscopic deformation mirror each other in nematic elastomers. In the simplest, Gaussian model of nematic elastomers observed thermal shape changes fix the anisotropy  $r = \ell_{\parallel} / \ell_{\perp}$  of the molecular distribution. Thereafter, all elastic properties depend on  $r$ . Monodomain nematic elastomers can show huge shape changes.

Imposing deformations along or perpendicular to the director (while director rotation is suppressed) elicits a classical rubber response. But imposing perpendicular extension when the director is permitted to rotate is altogether different: macroscopic shape changes associated with the extension can arise which leave the molecular distribution's shape intact (as it rotates). The changing shape of the body accommodates the molecules in their optimal distribution. Thus the free energy does not rise. This so-called "soft elasticity" is of a highly specific form and has been found by the Finkelmann group. I discuss when semi-soft deviations from softness arise, and the physical basis of the celebrated Golubovic and Lubensky theorem governing such phenomena in general.

I explore soft deformations in practical geometries, including the notion of the "quasi-convexification" of the free energy.

# **Cholesteric Films as Photonic Band Gap Materials and the Role of Crosslinking**

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Recently, much interest has focused on the photonic properties of cholesteric liquid crystals (CLCs). The periodic refractive index modulation due to the helical molecular order gives rise to a photonic stop band for circularly polarized light with the same handedness as the cholesteric helix. Modified photoluminescence as well as band edge laser emission of dye doped CLC films has been repeatedly reported.

After giving a quantitative description of the modified spontaneous emission of fluorescent guest molecules in cholesteric films, we report on photonic defect modes in CLCs, *i.e.* additional resonant modes inside the stop band, which may be generated by defects in the cholesteric order. Well defined defects can be realized in stacks of highly crosslinked CLC films. We report on first experimental proof for a defect mode created by a 'twist defect', *i.e.* a phase jump of the cholesteric helix: using a dye doped sample, the resonant mode shows up as an additional emission peak inside the stop band, and it gives rise to low threshold laser emission. The optical properties of twist defects as well as defects including a defect layer will be briefly discussed.

# **New Siloxane-based Liquid Crystalline Blends, Copolymers, and Main-Chain Elastomers with Mixed Mesogens for Tailored Properties**

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It was long expected and recently shown that main-chain liquid crystalline elastomers (MC-LCEs) may serve as high performance soft actuators due to a coupling of their intrinsic characteristics of high, yet labile, ordering and network strain. Here, we present the synthesis of new siloxane-based main-chain liquid crystalline polymers and copolymers, as well as some of the resulting MC-LCEs. To achieve targeted transition temperatures required for facile actuation, we have designed and prepared polymeric blends and copolymers incorporating two distinct mesogenic groups, termed 5H and 5tB, coupled with varying siloxane spacers. Both mesogens, varying in their pendant group, were synthesized in our laboratory following well-known synthetic routes. Despite their similar structure, the thermal, physical, and optical behaviors of these LC dienes differ considerably as revealed by DSC, POM and WAXD studies. Furthermore, a thorough investigation of the physical, thermal and optical properties of new homopolymer blends and copolymers is given. The influence of mesogen structure and siloxane spacer architecture on the LCPs phase behavior is examined. Finally, a few MC-LCE compositions selected with interest towards the design of improved actuators were synthesized. Uniaxially oriented liquid crystalline elastomers exhibiting subambient  $T_g$  and having relatively low clearing transition ( $\leq 70^\circ\text{C}$ ) were successfully prepared. Their phase behavior and thermomechanical properties are also presented for discussion by means of WAXD, DSC, POM and DMTA studies.

The N-I transition in LC elastomers probed by deuteron NMR of guest nCB molecules and by proton NMR relaxometry

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Deuteron NMR measurements are widely considered to be the key tool for the determination of the degree of orientational order in liquid crystals. Specifically, they can resolve between the first order character and continuous character of the nematic order behavior at the nematic to isotropic phase transition in liquid single crystal elastomers (LSCE). Selective deuteration of mesogenic components is however imperative in order to achieve satisfactory resolution. This requirement radically restricts the usefulness of deuteron NMR. An alternative approach is to dope the LSCE with a small amount of selectively deuterated guest LC material like nCB.

We have measured the temperature and angular dependences of deuteron NMR spectra of EC4OCH3 conventional nematic side-chain LSCE ( $T_{NI}^{LSCE} = 355$  K), doped with  $\alpha d_2$ -deuterated 8CB ( $T_{NI}^{8CB} = 308$  K). At vanishing 8CB concentrations, the nematic order parameter of 8CB is expected to match the nematic order parameter of LSCE. The continuous increase of the spectral doublet frequency splitting upon cooling from  $T > T_{NI}^{LSCE}$  to  $T < T_{NI}^{LSCE}$  clearly reveals a continuous increase of the local orientational order, with no sign of the coexistence of nematic and isotropic phases around  $T_{NI}$ . On increasing the 8CB concentration, however,  $T_{NI}$  gradually shifts to lower values, as expected, since  $T_{NI}^{8CB} < T_{NI}^{LSCE}$ , and, simultaneously, the two-phase coexistence becomes increasingly pronounced. At high 8CB concentrations, the first order transition nature of 8CB prevails over the supercritical character of pure LSCE. The observed behavior can be described in terms of the Landau-de Gennes free energy expansion by including the term that couples the orientational order parameter to the internal mechanical field.

Fast field cycling relaxometry is also a valuable tool for molecular dynamics studies of thermotropic and lyotropic liquid crystals. Here, frequency dependent proton relaxation rate of LSCE system was measured in both isotropic and nematic phases. A significant difference of molecular dynamics in the sub-MHz frequency range was clearly observed.

# Main-chain liquid crystalline elastomers

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Following a new synthetic route for the preparation of main-chain liquid crystalline elastomers<sup>[2]</sup>, we synthesized a variety of new systems. By applying an uniaxial mechanical field during the crosslinking process, the director of the liquid crystalline phase becomes macroscopically, uniformly aligned. Subsequent cross-linking reaction locks-in this order and liquid single-crystal elastomers with almost perfectly oriented director are obtained.

The elastomers were characterized by swelling experiments, differential scanning calorimetry (DSC), X-ray and thermo-elastic measurements. By variation of the spacer length and the symmetry of the mesogens the temperature regime of smectic phases can be reduced and elastomers with broad nematic phases were obtained.

At the isotropic-to-liquid crystalline phase transition the monodomain samples spontaneously change their dimensions parallel to the director by about 150%. This change in length considerably exceeds the thermoelastic effect of side-chain liquid-crystalline elastomers.

## References

[1] Wermter H., Finkelmann H.; Polym.Mater.Sci.Eng. 82, 319 (2000)

[2] Donnio B., Wermter H., Finkelmann H.; Macromolecules 33: 7724-7729 (2000)

## Volume Phase Transition of Liquid Crystalline Gels in Nematic Solvents

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In the present study, we have investigated the equilibrium swelling and phase behavior of liquid crystalline (LC) polymer networks swollen in low molecular mass LCs[1-3]. The system of LC network in LC solvent has the two independent nematic-isotropic transition temperatures: One is that for the swollen gels ( $T_{NI}^G$ ), while the other is that for the solvent outside the gel, i.e., the pure nematic solvent ( $T_{NI}^S$ ). The correlation between the swelling and phase behavior is closely investigated, particularly in the vicinity of  $T_{NI}^G$  and  $T_{NI}^S$ .

The side chain LC networks were prepared by radical copolymerization of the mesogenic acrylate monomers and 1,6-hexanediol diacrylate (cross-linker). The cross-linker concentration ( $C_x$ ) was varied from 1 to 10 mol%. The cylindrical gels with diameter of several hundreds micron were immersed in the nematic solvents, and the swelling was equilibrated at each temperature. The measurement of degree of equilibrium swelling ( $Q$ : the volume ratio of the swollen state to the dry state) and the phase observation were made by polarizing microscopy.

Figure 1a displays the equilibrium swelling-temperature curve of the LC gel with  $C_x = 1$  mol% in the nematic solvent. There exists the three characteristic temperature regions depending on the LC phase of each LC molecule. In the region  $T > T_{NI}^G$ , the system is totally in the isotropic phase. In the regime  $T_{NI}^S < T < T_{NI}^G$ , the phases inside and outside the gel are different, i.e., nematic and isotropic, respectively. The system is totally nematic in the region  $T < T_{NI}^S$ . The equilibrium swelling behavior is strongly correlated with the phase characteristics. At  $T_{NI}^G$ , the swollen isotropic gel (the mixture of the LC network and the LC solvent) is discontinuously transformed into the shrunken nematic gel. The nematic ordering inside the gel drives the discontinuous reduction in gel volume. Upon further cooling, in the region  $T_{NI}^S < T < T_{NI}^G$ ,  $Q$  increases again. The solvent outside the gel changes from the isotropic phase to the nematic phase at  $T_{NI}^S$ , which yields an inflection in the swelling-temperature curve without discontinuity. In the totally isotropic and nematic phases ( $T > T_{NI}^G$  and  $T < T_{NI}^S$ ),  $Q$  weakly depends on  $T$ . Thus the degree of swelling is dominated by nematic order of each LC molecule instead of isotropic mixing interaction between network and solvent, which is characteristic of LC gel. Essentially the same behavior is observed in the LC networks composed of dissimilar mesogens and different nematic solvents, which indicates that the swelling and phase characteristics observed are universal for nematic gel in nematic solvent with  $T_{NI}^G > T_{NI}^S$ . The swelling and phase behavior observed is well described by a mean field theory for nematic gel [4,5]. Figure 1b shows the comparison of the theoretical prediction with the data. Part c of the figure illustrates the orientational order parameters of mesogen on gel and the solvents inside and outside the gel ( $S_m$ ,  $S_o$  and  $S_b$ , respectively) as a function of temperature.

References: [1] K. Urayama, Y. Okuno, T. Kawamura, S. Kohjiya, *Macromolecules*, **35**, 4567 (2002). [2] K. Urayama, Y. Okuno, T. Nakao, S. Kohjiya, *J. Chem. Phys.*, **118**, 2903 (2003). [3] Y. Okuno, K. Urayama, S. Kohjiya, *J. Chem. Phys.*, **118**, 9854 (2003). [4] Wang, X. J., Warner, M., *Macromol. Theory Simul.* **6**, 37 (1997). [5] Matsuyama, A., Kato, T., *Phys. Rev. E*, **64**, 010701 (2001).

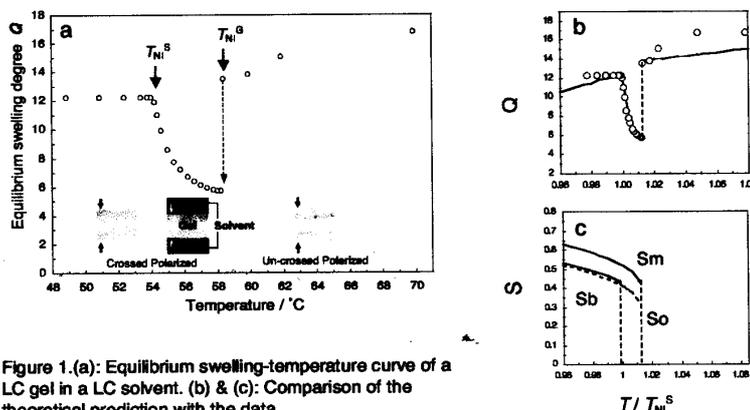


Figure 1. (a): Equilibrium swelling-temperature curve of a LC gel in a LC solvent. (b) & (c): Comparison of the theoretical prediction with the data.

## Polymer Stabilized V-Mode FLCs: Fabrication, Their Molecular Structure and Switching Mechanism

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**Abstract:** We fabricated 4 ferroelectric liquid crystal display (FLCD) cells, which exhibit continuous grayscale V-shaped switching, by adopting a UV photocure of mesogenic monomers doped in a FLC host, where an AC voltage is simultaneously applied. If we apply a DC field during the photocure, we obtain an FLCD showing half V shaped switching, for the first time by using the side chain polymers. We call these LCDs PS-V mode FLCD and PS-H-V mode FLCD.1,2,3) Prior to the photocure, the FLC medium must be well aligned to have defect free molecular structure. In this report we show the electro-optic characteristics of these FLCs and also we discuss their molecular structure and the switching mechanism, particularly by focusing on the discussion of the aligned molecular structure of PS-FLCD at the quiescent condition.

## Volume Phase Transition of Liquid Crystalline Gels in Isotropic Solvents

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In the present study, equilibrium swelling and phase behavior of the liquid crystalline (LC) networks in isotropic (non-mesomorphic) solvents has been investigated especially in the vicinity of the nematic-isotropic (N-I) transition temperature.<sup>1</sup> It is demonstrated that a discontinuous transition in gel volume induced by nematic ordering takes place in conventional isotropic solvents. This finding is of significance to understand the role of nematic ordering in the swelling behavior of LC gels.

The side chain LC networks were prepared by free radical copolymerization of the mesogenic acrylate monomer, styrene monomer, and 1,6-hexanediol diacrylate (cross-linker). The network totally composed of the LC monomers (LCN-100/0) and the copolymeric network comprising the LC monomers (90 mol%) and the styrene monomers (10 mol%) (LCN-90/10) were prepared in capillary. The resulting cylindrical gels were washed with toluene, dried in air, and immersed in some di-*n*-alkyl phthalate homologues. Equilibrium swelling degree ( $Q$ ) and phase behavior were examined as a function of temperature ( $T$ ) by a polarizing microscope equipped with a temperature-controllable sample stage.

The temperature dependence of  $Q$  of LCN-90/10 in diethyl phthalate (DEP), di-*n*-butyl phthalate (DBP), di-*n*-amyl phthalate (DAP) or di-*n*-octyl phthalate (DOP) is displayed in Fig. 1 where  $T_{NI}^G$  represents the N-I transition temperature of the gel. The data were obtained in cooling process. In DBP or DAP, the swollen isotropic gel discontinuously transforms into the shrunken nematic gel at  $T_{NI}^G$ . In DOP, the gel undergoes the N-I transition, but no significant volume change takes place due to the small  $Q$  ( $< 2$ ). It is found that  $T_{NI}^G$  depends on the solvent;  $T_{NI}^G$  decreases as  $Q$  (i.e., the amount of solvent inside the gel) in the isotropic phase increases. The  $T_{NI}^G$  of the gel in DEP with the large  $Q$  ( $\approx 14$ ) is expected to exist below the room temperature. The nematic ordering induced-volume transition observed are satisfactorily described by a mean field theory for nematic gel.<sup>2,3</sup>

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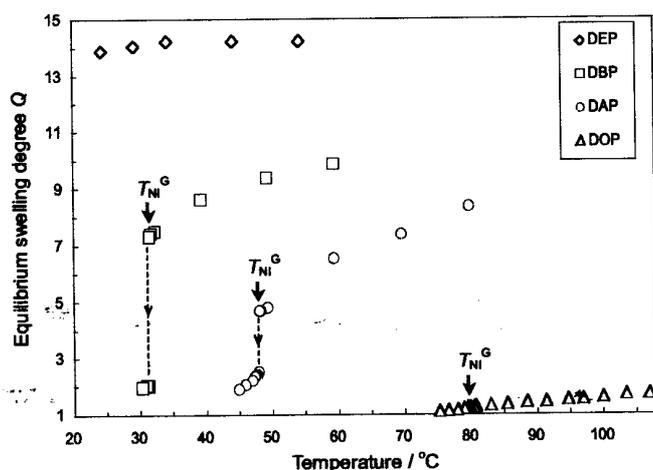


Fig. 1.  $T$  dependence of  $Q$  for LCN-90/10 in DEP, DBP, DAP and DOP.

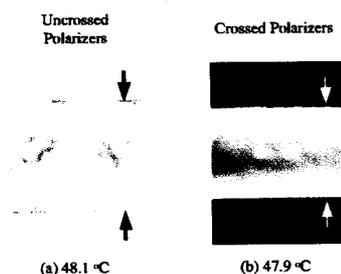


Fig. 2. Optical micrographs for the cylindrical LC gel LCN-90/10 in DAP. The pictures represent (a) swollen isotropic phase at 48.1 °C ( $= T_{NI}^G + 0.2$  °C), (b) nematic shrunken phase at 47.9 °C ( $= T_{NI}^G$ ). The micrographs show that a discontinuous decrease in gel diameter takes place at  $T_{NI}^G$  as a result of nematic ordering. Arrows indicate the boundary of the gel surface.

## Abstract

### Structure and mobility in FLC-polymers and elastomers as studied by time-resolved FTIR spectroscopy

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By use of time-resolved polarized Fourier-transform infrared (FTIR) spectroscopy the structure and mobility of ferroelectric liquid crystal polymers (FLCP) and elastomers (FLCE) in the  $\text{SmC}^*$  phase is investigated. Results from free standing films with the infrared absorbance probed parallel to the layer normal and from bookshelf geometry with the FTIR beam perpendicular to the layer normal are presented. In the later case the FLC is sheared between ITO-coated  $\text{CaF}_2$  windows to orientate the molecules. The ferroelectric mesogens in these materials show field-induced reorientation which is measured in their extension and dynamics by FTIR. In the case of FLCE, the properties of ferroelectric liquid crystals are combined with the advantage of a polymeric network. The crosslinking groups prevent flow in such structures and allow stable free standing films. However, they also change the mobility of the liquid crystal side chains and hinder the reorientation. Time-resolved FTIR spectroscopy is a unique tool to analyse these effects.

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