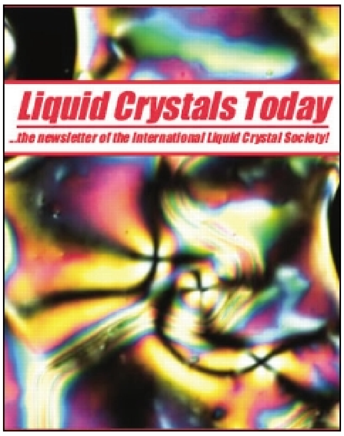

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# Anisotropic Networks, Elastomers and Gels

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# Anisotropic Networks, Elastomers and Gels

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## Introduction

Anisotropic networks [1–3], elastomers [4] and gels [5,6] with liquid crystalline (LC) properties represent an area of research in the general domain of self-assembling materials of rapidly growing fundamental scientific interest and technological potential. Possible applications include passive optical devices, such as solid colour filters, retarders, polarizers, etc., active electrical or electronic devices, such as liquid crystal displays (LCDs), piezoelectric or pyroelectric sensors, nonlinear optic (NLO) films, or structural materials, e.g. in cladding for fibre-optic cables, orientation layers for LCDs, etc. In this article networks are defined as completely crosslinked solids where all the polymerizable monomers possess at least two reactive groups; elastomers are deformable solids derived from monomers with one reactive group and a small amount of reactive bifunctional crosslinker; gels are fluids consisting of a solid network and liquid non-polymerizable, low-molar-mass LCs.

## Anisotropic networks

It is the combination of the ability to flow and the low viscosity of low molar mass LCs and the anisotropy of their properties, which renders LCs of unique interest as the starting materials for anisotropic networks [1–3], elastomers [4] and gels [5,6]. Macroscopic, uniaxially oriented films can be formed by aligning the sample by mechanical force, orientation layers, electric or magnetic fields, polarized light, etc., followed by crosslinking, if some or all of the mixture components contain polymerizable or dimerizable groups. Alternatively amorphous or liquid crystalline side-chain and/or main-chain polymers (LCPs) can be crosslinked.

## Anisotropic elastomers

The translational motion of the backbone of a polymer is suppressed if a limited number (<10 wt%) of crosslinks are introduced to produce an infinitely viscous, anisotropic liquid, i.e. a form retaining but mechanically deformable elastomer. However, the high micro-Brownian motion of the chain segments remains, apart from at the points of crosslinking, which act as a plasticizer at low concentrations and often leads to a lower value for $T_g$.

## Anisotropic gels

Anisotropic gels are a mixture of a crosslinked LC network and nonreactive low-molar-mass LCs produced by the *in situ* polymerization of LC monomers with polymerizable groups in the presence of normal-low-molar mass LCs [5,6]. The solid polymer network possesses the three-dimensional structure of the original LC mixture. Although the low-molar-mass LCs are not chemically bound to the network, strong intermolecular forces between them and the network result in a residual orientation even at temperatures significantly above the clearing point ($T_c$) of the original mixture.

*(continued on page 3)*

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* EPSRC Advanced Fellow

# Victor Titov Murdered in Moscow

**The liquid crystal world was shocked to hear of the assassination of Professor Victor Titov at his home on the evening of 25 October 1996. He was returning from the banquet of the Russian Liquid Crystal Society Conference, which had been attended by Russian liquid crystal scientists and foreign guests from Europe. The murder was reported by Moscow TV and the press, but the identity of the killer and the motive is unknown. As Director of the Institute of Graphic Art, Victor Titov was not known to have any enemies, and the heart-felt sympathy of the liquid crystal community is extended to his family and friends and colleagues. Over 500 mourners attended the funeral of Professor Titov in Moscow, and a tribute to his life and achievements is printed on page 8.**

## In this issue:

# 1st Polish–German Seminar

## Self-organization in Chiral Liquid Crystals

**30 September–5 October 1996, Kobylniki/Poznan, Poland**

*Report by Professor Horst Stegemeyer, Universität Gesamthochschule, Paderborn*

The 1st Polish–German Seminar took place in the beautiful palace Kobylniki near Poznan built in 1886 in the style of neo-renaissance and was organized by W. Kuczynski *et al.*, Polish Academy of Science. Self-organization in chiral liquid crystals provided a topic for discussion amongst German research groups from Clausthal, Halle, Leipzig and Paderborn and the liquid crystals group of the Institute of Molecular Physics at Poznan which are linked together by joint research projects. The meeting was sponsored by the Foundation for Polish–German Co-operation, Warszawa, with the aim to stimulate friendship among Poland and Germany. Consequently, the number of 35 participants comprised young German students who came into contact with Polish culture for the first time during the closing excursion to Poznan.

There were six plenary lectures dealing with problems of chirality especially in ferroelectric smectics and lyotropic liquid crystals and TGB phases. Sixteen brief reports were given combined with posters at which extensive discussions took place after the lecture sessions. This was found to be a good idea for deepening the exchange of views on the different topics. As an example of the significant content of the meeting, the wavelength dispersion of the optical tilt angle in $S_C$ phases presented by F. Giesselmann, Clausthal, should be emphasized. The consequence of this result concerning the Landau theory and for the definition of the local director in $S_C$ phases was a matter of violent discussion.

The warm hospitality of the Polish hosts was gratefully acknowledged by all German participants hoping that the second seminar will take place two years later.

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2. Articles must contain suitable headings and sub-headings.
3. References should be numbered serially in the text by means of superscript Arabic numerals.
4. Bibliographic references (not footnotes) should follow the main text and should have the format:
   REDMOND, M., COLES, H., WISCHERHOFF, E., and ZENTEL, R., 1993, Ferroelectrics, **148**, 323.
   BAUR, G., DELAVIER, P., ETZBACH, K.H. MEYER, F., KIEFER, R. SIEMENSMEYER, K., and WAGENBLAST, G., 1994, Abstracts of *15th International Liquid Crystals Conference*, Budapest, Hungary, p.780.
5. Journal titles should be abbreviated according to the Chemical Abstracts Service Source Index (CASSI).
6. Tables should be typed on separate sheets at the end of the manuscript.
7. Diagrams should be accompanied by a separate list with captions. Original artwork to be supplied wherever possible. Colour photographs will be accepted subject to approval.

(continued from page 1)

# Anisotropic networks

## Nematic networks

Nematic networks with a high crosslink density can be produced by the polymerization in the nematic state of various LC monomers with more than one polymerizable group attached to each molecule. If the monomers are aligned in the LC state before and/or during polymerization, then macroscopically oriented, thin solid films of high mechanical strength, anisotropic thermal and electrical resistivity can be produced. Such networks possess a minimal temperature dependency of their physical properties.

### *Nematic thermosets*

As the tensile modulus and expansion coefficient in the direction of molecular orientation is often several times greater than that observed perpendicular to the orientation direction, nematic networks are of direct interest as structural materials, e.g. as protective cladding material for fibre optical cables in order to limit microbending. The anisotropic high thermal and low electrical conductivity of such networks is of use in microelectronics as electrically isolating, but thermally conducting casings. They can also be used as insulating layers with low dielectric constants and exceptionally high thermal stability. The good rheological properties of liquid crystalline monomers render them particularly advantageous for thermoplastic injection molding applications.

### *Nematic hybrid linearly photopolymerized polymers (HLPP)*

As most LCDs based on field effects are surface stabilized, stable alignment layers with reproducible anchoring for the LC are required. Non-contact alignment layers, such as Linearly Polarized Polymer (LPP) and Hybrid Linearly Polarized Polymer (HLPP) layers [7, 8], are potentially of great importance in this respect. This is especially so for active matrix LCDs, where the presence of even very small amounts of dust particles or static surface charges can give rise to pixel damage. Almost any value of the pretilt angle ($\theta$) can now be obtained by illumination of an LPP containing a coumarin moiety with linearly polarized light at a given angle of incidence to the substrate [8]. However, the generally low value for the birefringence ($\Delta n$) of LPP layers means that relatively thick layers are required. Hybrid systems (HLPPs) combine the orienting properties of LPP layers with the high birefringence of LCs. The thermal and UV light stability of HLPP networks are also much higher. They have great potential as photo-patterned optical retarders and interference colour filters.

### *Nematic networks as polarizers*

Solid state polarizers can be produced by the crosslinking of macroscopically oriented nematic monomers incorporating an amount of a suitable pleochroic dye. Such polarizers can be patterned by the application of an electric field before the orientation is fixed by crosslinking.

### *Chiral nematic networks as optical filters*

Planar-oriented, short-pitch, chiral nematic (N*) LC layers reflect circularly polarized light within the wavelength range ($\Delta\lambda$) of their selective reflection band, when the handedness of the incident polarization corresponds to the direction of rotation of the N* helix. As the circularly polarized light of opposite handedness is transmitted, they can be used either as non-absorbing optical filters or circular polarizers. N* networks exhibit a minimal temperature dependence of the pitch. Such networks can be prepared by crosslinking side-chain LCPs (e.g. silicones) incorporating additional polymerizable side chains (e.g. methacrylate) in the Grandjean configuration or polymerization of N* mixtures incorporating reactive bifunctional crosslinkers. The high UV and thermal stability of such filters combined with their ability to selectively reflect instead

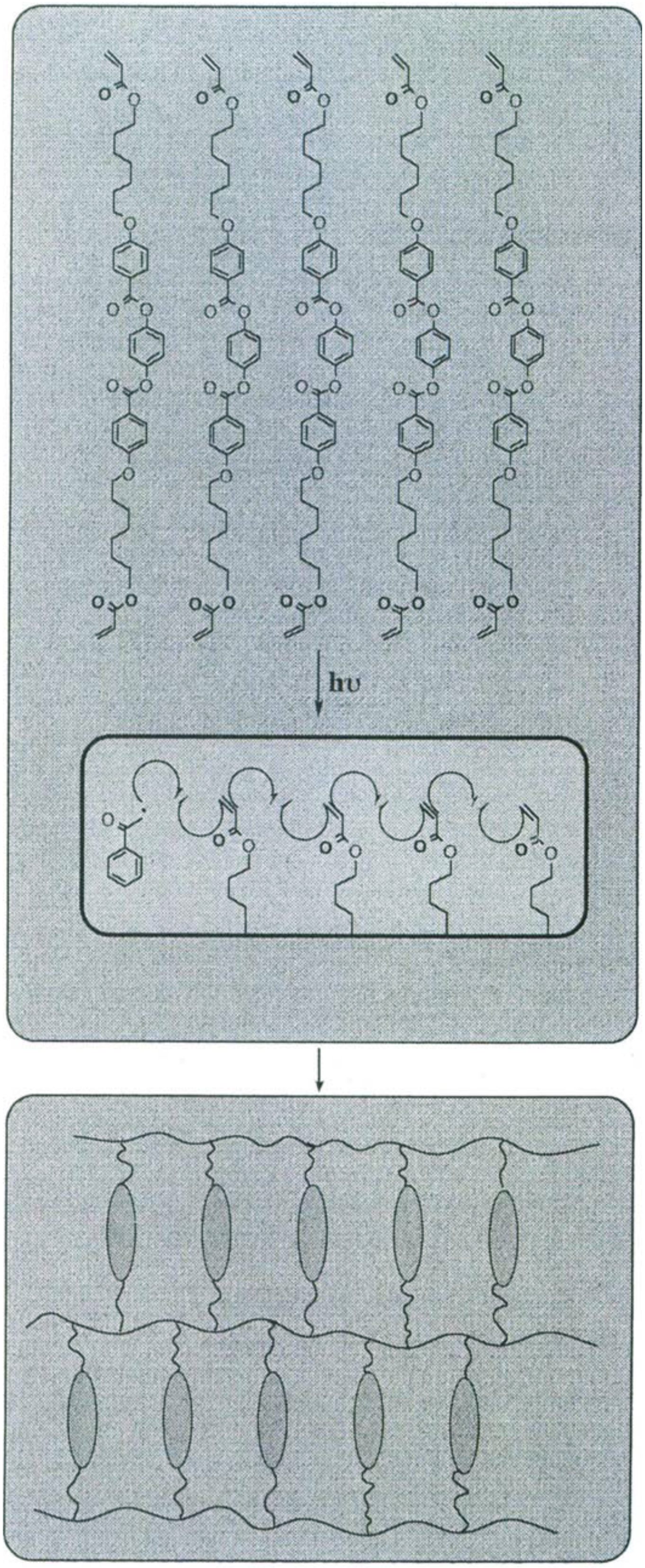

*Figure 1.* Chemical structure of reactive bifunctional liquid crystalline monomers and a simple schematic representation of the polymerization/crosslinking reaction and the resultant anisotropic network.

of absorbing, light renders them especially suitable for high-light-flux/heat exposure applications such as projection displays, band-pass filters, notch filters, circular polarizers, band reflectors, *in situ* colour filters for STN LCDs and in large aperture light sources. They can also be used to replace one absorbing polarizer in LCDs, leading to either greater brightness or lower power consumption.

## Smectic networks

Polymerization of bifunctional, non-optically-active, mesogenic monomers in the smectic state, gives rise to smectic networks, which exhibit similar properties to those of the analogous nematic networks. The latter are generally preferred for practical applications due to the higher degree of processability associated with the lower viscosity of the nematic state.

### *Chiral smectic networks as piezoelectric and pyroelectric sensors*

Macroscopically uniaxially oriented, chiral smectic C ($S_C^*$) networks with a uniform directional ordering of the dipoles at the optically active centre are transparent and exhibit a higher $\Delta n$ than the networks polymerized in the N* phase.

$S_C^*$ networks can exhibit piezoelectric, pyroelectric and ferroelectric properties due to the macroscopic dipolar ordering of the dipoles. The piezoelectric coefficient is strongly dependent on the relative orientation of the applied stress and molecular orientation. As the high crosslinking density of $S_C^*$ networks produced in this fashion leads to solid materials, they are less sensitive to mechanical deformation than comparable elastomers. Pyroelectric and piezoelectric devices based on organic materials have great potential to replace ceramics in many applications and especially in sensors.

### *Chiral smectic networks for second harmonic generation (SHG)*

Such networks possess NLO properties and can be used as frequency doublers (Second Harmonic Generation) to produce blue/green laser light [1]. Their temporal stability is much higher than that of analogous low molar mass ferroelectric $S_C^*$ compounds, even stabilized in a glassy state [9], as the dipolar order is fixed permanently in the anisotropic network. Ferroelectric monomers with a transverse chromophore axis with respect to the optic axis are used for this application due to the noncentrosymmetrical polar ordering and ease of alignment in a desired configuration.

## Other anisotropic networks

### *Discotic networks as photoconductors*

Discotic LC networks are becoming of increasing interest as self-organizing molecular wires and especially as photoconductors for Xerography and laser printer applications [10]. This is due to the high charge mobility found for certain columnar LCs (discotics), especially with triphenylene cores on illumination with light, and is sometimes up to two orders of magnitude higher than that observed for the amorphous organic polymers currently used.

### *Non LC anisotropic networks for nonlinear optics (NLO)*

Organic NLO materials, which exhibit nonlinear polarization of electron density and a nonlinear response under the influence of magnetic, electric or electromagnetic fields, are of interest for applications in integrated electro-optic systems, where they can be used to influence the spatial, temporal and frequency properties of propagating light beams [11, 12]. Potential applications include waveguides, electro-optical modulators (EOMs), switches for digital fibre-optic-based telecommunication systems, frequency doublers for digital data storage systems and tunable filters for wavelength division multiplexing. Organic EOMs and waveguides incorporating side-chain liquid crystal polymers are commercially available. However, anisotropic networks derived from side chain polymers incorporating NLO chromophores and other side chains, both of which bear photocrosslinkable units, exhibit higher temporal stability. It has also been claimed recently that sufficient thermal stability can still be achieved using poled chromophores dissolved in amorphous polyimides or side-chain LCPs with a polyimide backbone, if $T_g$ is exceptionally high. Fundamental properties still to be optimized include the long term stability of the NLO material with respect to signal decay due to relaxation, and optical damage over the operational lifetime of the device.

# Anisotropic elastomers

The first reported LC elastomers were produced by radical polymerization of binary LC mixtures of a monoreactive acrylate and various amounts (0–30%) of a diacrylate crosslinker or tertiary LC mixtures incorporating an additional cholesteryl component. They can also be prepared by statistical addition reactions using mixtures of monoalkenes and dialkenes and reactive preformed polymer backbones like siloxanes, or by copolymerization of, e.g. acrylates or methacrylates, to form a side-chain polymer incorporating reactive groups, such as an hydroxy group, which are then crosslinked by addition of a bifunctional compound such as a diisocyanate. As most LC elastomers should generally be deformable at room temperature, siloxane backbones are most often preferred as these often produce low $T_g$ values. Liquid Single Crystal Elastomers (LSCEs) exhibiting a uniaxially oriented monodomain, required for practical applications, can be obtained either by application of an electric or magnetic field or mechanically in a stress field before the orientation is fixed by crosslinking. Piezoelectricity has been observed for chiral nematic elastomers and, although initially unexpected due to the absence of a layer structure, has been explained.

### *Chiral smectic elastomers for piezoelectric/pyroelectric sensors*

Smectic elastomers incorporating optically active moieties are of especial interest due to their noncentrosymmetrical layered structure. Elastomers exhibiting piezoelectric, pyroelectric and ferroelectric properties can be created by the crosslinking of side-chain polymers possessing a ferroelectric $S_C^*$ phase. LC elastomers possessing an $S_C^*$ structure are potentially interesting as piezoelectric and pyroelectric sensors, as the state of order at crosslinking is stabilized. Therefore, the resultant elastomer is capable of stress-optical memory effects. The mechanical deformation of the orientation of the elastomer side chains is similar to that exerted by electric or magnetic fields on low molar mass LCs.

### *Discotic elastomers as photoconductors*

Discotic LC elastomers are of increasing interest as organic conductors because their columnar phase structure is similar to the columnar structure of polycyclic aromatics in the crystalline state. The major problem still to be overcome is the production of uniformly oriented discotic phases without defects. Discotic LSCEs offer the prospect of achieving this goal by utilizing mechanical forces to overcome the high viscosity of the non crosslinked side-chain polymer precursors, to induce uniform director alignment. This structure is then fixed by crosslinking.

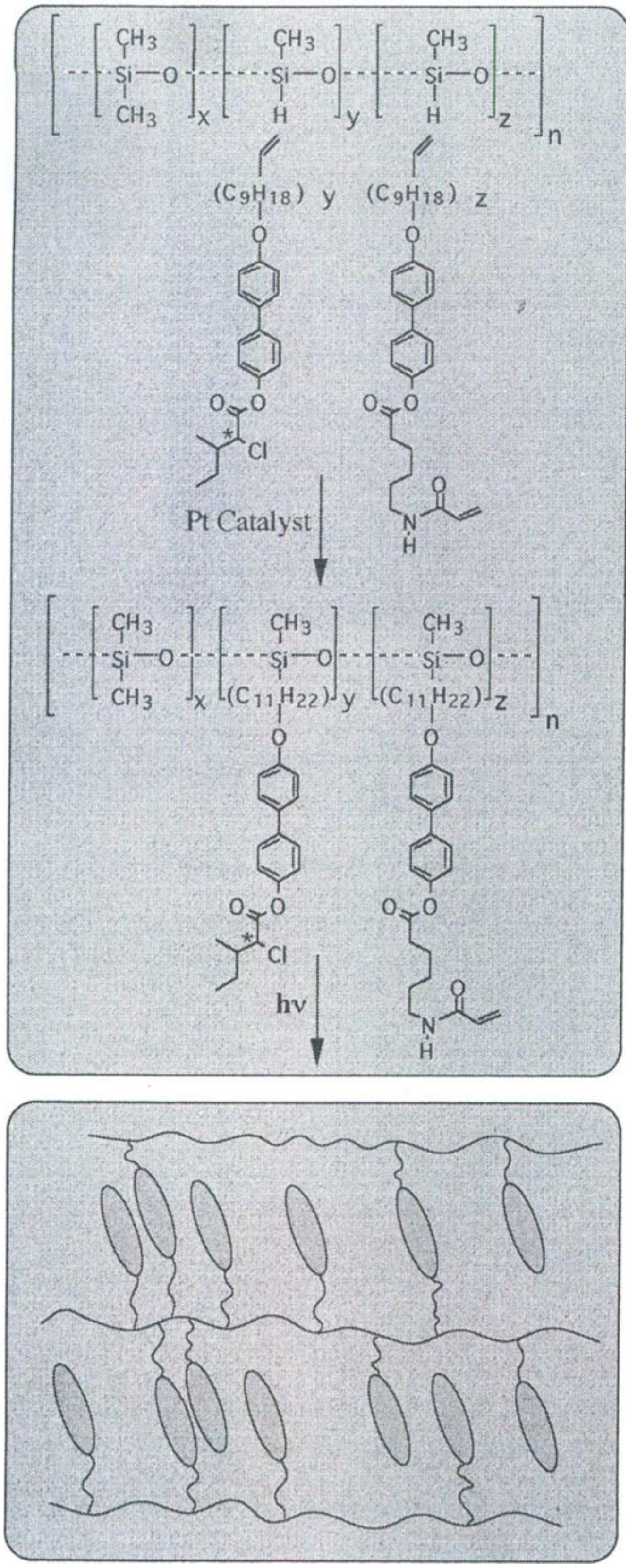

*Figure 2.* Chemical structure of reactive polymer backbone, monofunctional and bifunctional liquid crystalline monomers, the intermediate side-chain polymer and a simple schematic representation of the resultant anisotropic elastomer after crosslinking.

# Anisotropic gels

### Nematic gels for LCDs

Nematic gels are normally prepared from the polymerization of mixtures of achiral low-molar-mass nematic LCs and limited amounts of reactive bifunctional crosslinkers. An alternative method is to swell a preformed anisotropic elastomer with achiral low-molar-mass nematic LCs. The long-range orientation of a nematic gel can be uniaxially planar or homeotropic, and LCDs with the director twisted through a well-defined angle can be produced. However, polarizers are required in order to obtain a sufficiently high contrast. Threshold voltages and response times are up to a factor of 10 higher than for normal LCDs. Possible applications include uses as electrically controllable polarizers, orientation layers for LCDs and, with dye molecules, Guest–Host LCDs with grey scale.

### Chiral nematic gels for filters

The addition of optically active dopants to low-molar-mass nematic mixtures with reactive bifunctional crosslinkers converts them to chiral nematic mixtures of monomers and nonreactive nematic LCs as precursors to N* gels. N* gels derived from such polymerizable chiral nematic mixtures incorporating optically active dopants can be used to produce devices that reflect circularly polarized monochromatic light in the visible region of the spectrum. The wavelength of light ($\lambda_o$) reflected by the N* gel in the planar Grandjean configuration with the helix perpendicular to the substrate surfaces can also be modulated by electric fields. However, a relatively high network concentration (>30 wt%) is required in order to avoid the creation of two separately weakly or strongly bound populations of chiral domains resulting in two distinct reflection peaks.

### Chiral nematic gels for LCDs

The bistable switching of a lightly crosslinked N* gel (≈ 1–3 wt%) from the reflecting coloured Grandjean configuration to the strongly scattering white focal conic configuration can be used as the basis of LCD type. As such LCDs are reflective, they can be brighter than analogous TN-LCDs. One disadvantage is that the degree of scattering is generally not very high (90%). It is also not only strongly dependent on the wavelength of light used, but also on the polymerization conditions of the N* mixture. The threshold voltages are high (≈ 40–70V) and the switch off times are long.

### Chiral smectic gels for ferroelectric liquid crystal displays (FLCDs)

The first achiral smectic gels were formed by crosslinking a smectic mixture of a non-reactive, low-molar-mass liquid crystal and a non-liquid crystalline crosslinker. Chiral smectic ferroelectric gels can also be prepared, but unlike low molecular weight analogues, the orientation of the non-attached molecules is determined by the network and not by surface forces. Switching times and operating voltages are considerably greater than those observed for the same mixtures in SSFLCDs. The spontaneous polarization, effective birefringence and extinction angles are also considerably lower. Domains are formed due to the proximity of the molecules to the network. This has the advantage of allowing actively addressed or passively addressed ANSFLCDs to exhibit continuous switching over a range of voltages in thick cells (*d* = 8 μm) without interference colours.

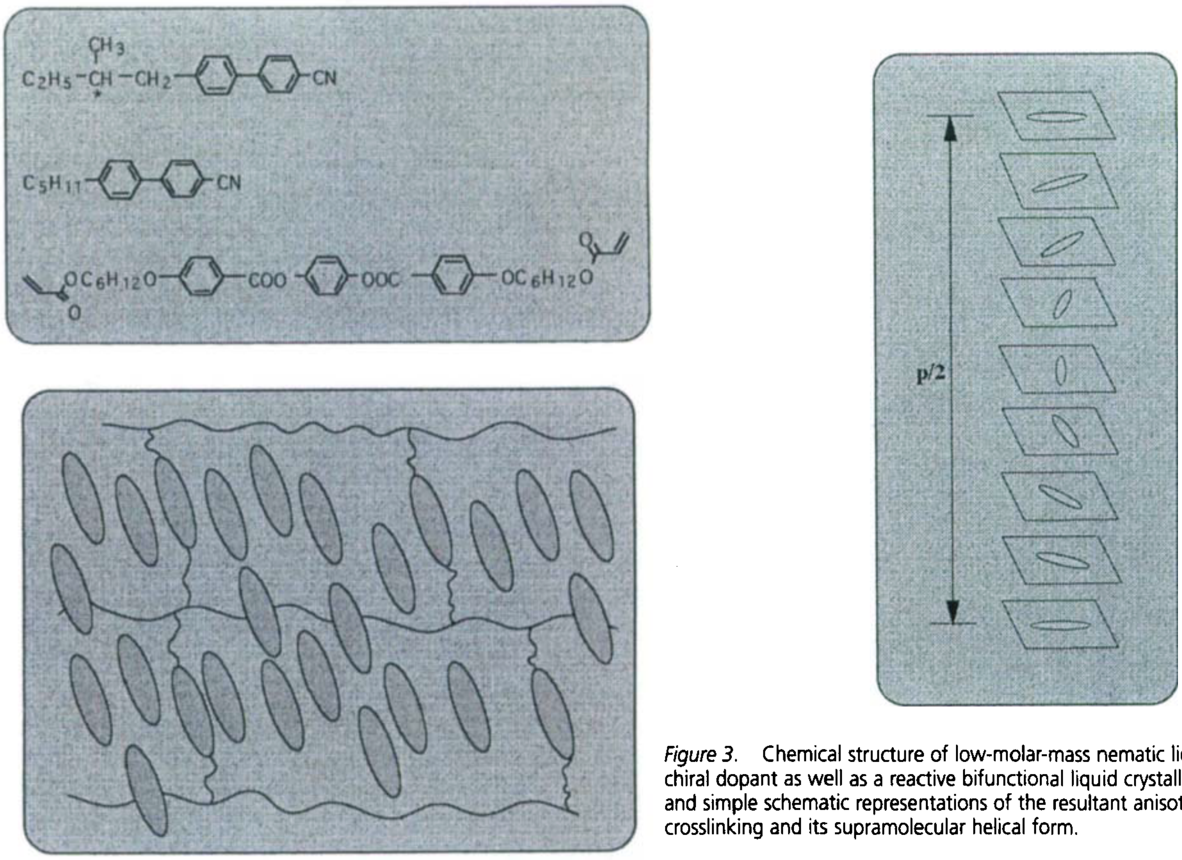

*Figure 3.* Chemical structure of low-molar-mass nematic liquid crystal and chiral dopant as well as a reactive bifunctional liquid crystalline monomer and simple schematic representations of the resultant anisotropic gel after crosslinking and its supramolecular helical form.

## References

1. Kelly, S.M., 1995, *J. Mater. Chem.*, **5**, 2047.
2. Kelly, S.M., 1996, *Proc Euro Display '96*, Birmingham, UK, Paper **7.1**.
3. Barclay, G. G., and Ober, C.K., 1993, *Prog. Polym. Sci.*, **18**, 899.
4. Finkelmann, H., 1987, *Angew. Chem.*, **99**, 840.
5. Hikmet, R.A.M., 1992, *Adv. Mater.*, **4**, 679.
6. Hikmet, R.A.M., Boots, H.M.J., and Michielson, M., 1996, *Liq. Cryst.*, **19**, 65; 1996, *J. Appl. Phys.*, **79**, 8098.
7. Schadt, M., Seiberle, H., Schuster, A., and Kelly S. M., 1995, *J. Appl. Phys.*, **34**, 3240; **34**, L764.
8. Schadt, M., Seiberle, H. and Schuster, A., 1996, *Nature*, **381**, 212.
9. Schmitt, K., Benecke, C., Schadt, M., Fünfschilling, J., Herr, R.-P., and Buchecker, R., 1994, *J. Phys. III France*, 387.
10. Adam, D., Schumacher, P., Simmerer, J., Häussling, K., Siemensmeir, K., Etzbach, K. H., Ringsdorf, H., and Haarer, D., 1994, *Nature*, **371**, 141.
11. Buckley, A., 1992, *Adv. Mater.*, **4**, 153.
12. Nie, W., 1993, *Adv. Mater.*, **5**, 520.

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