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Anisotropic networks and gels formed by photopolymerisation in the ferroelectric state

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Anisotropic networks are obtained by *in situ* photopolymerisation of liquid crystal (LC) molecules with reactive end groups in the macroscopically oriented state. Such cross-linked networks show high thermal stability and have passive electrical and optical applications. *In situ* polymerisation of LC reactive molecules in the presence of non-reactive LC molecules on the other hand leads to the formation of anisotropic gels. As opposed to the anisotropic networks, gels can be switched under the influence of electric fields and can therefore be used in display applications. In this review, a short introduction will be given to the technique of *in situ* photopolymerisation and ferroelectricity in LC. Subsequently various properties and various applications of anisotropic gels and networks obtained in the ferroelectric state will be described.

Introduction

Liquid crystals flow like a liquid while showing crystal-like properties such as birefringence. In the case of thermotropics, the liquid crystal (LC) phase is usually observed as an intermediate phase between the isotropic transition point and the melting or the glass transition temperature. There are a number of LC phases with various optical and electrical properties. The diversity of the properties of liquid crystals makes them suitable for applications ranging from displays to ultra-strong heat resistant fibres.[1,2] In applications where the orientation obtained in the LC phase needs to be preserved in the solid-state, polymer LCs are used.[3,4] In polymer LCs the orientation of the molecules is induced by mechanical shearing forces. The system is subsequently cooled rapidly below the glass transition temperature, freezing in the structure obtained in the LC state. However, due to the high viscosity of the polymer the orientation is usually not uniform or complete and there are also often problems arising from the presence of sub-phases between the LC phase used and the glass transition temperature of the system. In display applications where high switching speeds are required, low molar mass LC molecules are used.[5,6] Such molecules with a low viscosity can be oriented in a display at high speeds by using specially treated interfaces and electric fields. In most display applications, the orientation of the LC from the rest state is altered by the application of an electric field. However, in some displays the influence of the cell surfaces is not always sufficient to obtain some desired optical effects.[7,8] In this review, the technique of *in situ* photo-polymerisation of reactive mesogenic molecules[9–25] in producing anisotropic structures is described. They can be used in displays where the function of the surfaces is replaced by the network and in the production of solid structures with optical and electrical properties. In the technique of *in situ* polymerisation, the LC system is brought into the desired phase where the desired orientation is induced. Subsequently polymerisation is induced photochemically and the order present becomes permanently fixed by the creation of a three dimensional network. In this article, the main emphasis will be on networks formed in the ferroelectric phase. Therefore a short introduction on ferroelectricity in LCs is given.

Liquid crystals and their ferroelectricity

Thermotropic rod-like liquid crystals can broadly be classified as nematic and smectic liquid crystals. Fig. 1 shows schematically the temperature sequence for the observation of various phases in thermotropic LC systems. In systems showing nematic and smectic phase the smectic phase is observed at temperatures below the nematic phase. However, there are examples where re-entrant nematic phase[26] is observed below the smectic temperature range. In the nematic phase the molecules on average tend to align with their long axis parallel to a common axis called the director <n>. There is no long-range correlation between the centres of gravity of the molecules and there is no macroscopic polarisation. Addition of chiral molecules to a nematic phase induces the cholesteric (chiral nematic) phase where the director rotates about a helix with an axis perpendicular to the director. In the smectic phase, in addition to the orientational order, there is also a degree of lateral order and the centre of the molecules is confined to planes. Smectic phase can in turn be divided into two categories: orthogonal and tilted smectics. The most common orthogonal smectic phase is the smectic-A phase (S_a) where the director on average is oriented at right angles to the smectic layers. In the tilted smectic-C phase, however, the director is tilted at an angle to the layers. As in the case of the nematic phase, these smectics do not possess macroscopic polarisation.

It was R. B. Meyer in 1974[27] who predicted the presence of spontaneous polarisation; hence, the ferroelectricity in LC systems based on symmetry arguments as follows. In the nematic and S_a phase, the following symmetry elements are operational.

$$C_{2x},\ C_{2y},\ C_{\infty z}$$

$$\sigma_{xy},\ \sigma_{xz},\ \sigma_{yz}$$

Where C_{nm} indicates the n-fold rotational symmetry about the

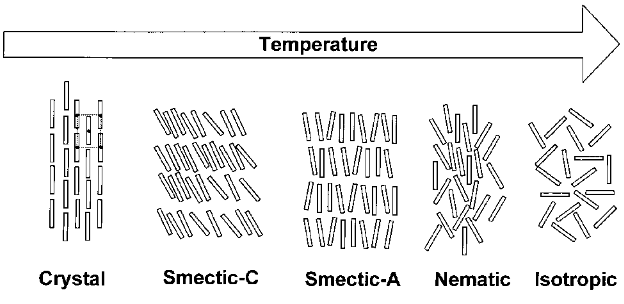

Fig. 1 Temperature sequences for liquid crystal phase formation.

m axis where $\sigma_{m'}$ is the mirror abut the *mm′* plane. If the above symmetry elements are applied to molecules with a dipole *P* with components P_x,P_y,P_z along the *xyz* coordinates then the systems are centrosymmetric and in such systems dipole moments of the molecules cancel each other out and the net dipole moment is zero. In the case of an S_c, however, only the symmetry operations C_{2y}, σ_{xz} can be applied.

$$C_{2y}: \quad P_x \Leftrightarrow -P_x \qquad P_y \Leftrightarrow P_y \qquad P_z \Leftrightarrow -P_z$$

As a result of this operation the P_x and P_z components of the molecular dipoles are invariant and cancel each other out. Furthermore applying the mirror symmetry operation

$$\sigma_{xz}: \quad P_y \Leftrightarrow -P_y$$

cancelling out the *y* component of the dipole. Therefore, the symmetry of an S_c phase can be broken if a molecule which is not the same as its mirror image and which has a lateral dipole is used. Fig. 2 schematically compares various structures. The structure a is the same as its mirror image as a simple horizontal translation superimposes the two structures. Rotation of b by 180 °C and its horizontal translation also superimpose the two mirror images. However, structure c is not the same as its mirror image as the two images cannot be superimposed by a simple operation. If such a molecule or a chemical bond incorporated in a molecule is included in an S_c phase, the symmetry can be broken and ferroelectricity is induced. Chiral smectic-C (S_c*) phase is induced using molecules which have non-superimposable mirror images containing asymmetric substituted carbon atoms called enantiomers. The inclusion of the chiral group is not enough for the ferroelectricity, but the alignment of the dipole with respect to the molecular conformation is also very important for the ferroelectricity of the phase. This point will be discussed in the section on the ferroelectric mixtures. The other effect of the chiral molecules is that they induce helical twist. As mentioned before chiral molecules in the nematic phase cause the rotation of the nematic director about a helix inducing optical activity. However, chirality is not a sufficient condition on its own since the nematic phase is not ferroelectric. This can easily be seen since only the $C_{\infty z}$ symmetry element of the nematic phase is replaced by C_{2z} in the chiral nematic phase. In the S_c* phase, the director is oriented at an angle to the smectic layers and this tilted orientation rotates about a helix with the axis perpendicular to the smectic layers. Applying an electric field unwinds the helix and the polarisation becomes aligned along the field. The direction of the tilt angle that the director makes upon application of the electric field is determined by the sign of the polarisation. Therefore changing the direction of the electric field causes the molecule to change the direction of the tilt. This kind of switching of the ferroelectric molecules forms the basis of their application in displays, which will be described later in the article.

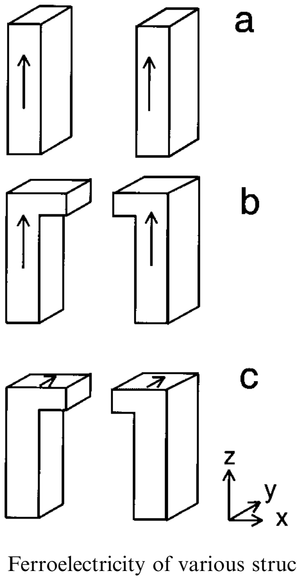

Fig. 2 Ferroelectricity of various structures.

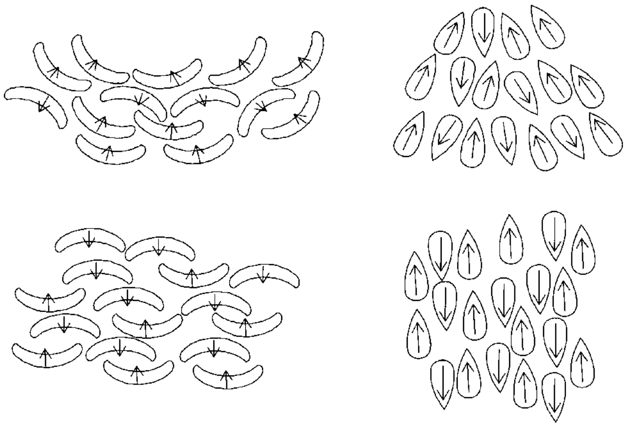

Fig. 3 Flexoelectricity.

Here it is also interesting to consider other LC systems, which have been described in the literature as having net polarisation linked with curvature of orientation. This so-called curvature electricity (flexoelectricity)[28,29] is discussed assuming wedge or banana shaped molecules with a net dipole as shown in Fig. 3. In the undeformed state, both systems show no net polarisation. If deformed under bend or splay and divergence results, then the molecules orient themselves in a polar alignment. The flexoelectric effect has already been measured in hybrid aligned nematic cells where the molecules are subjected to bend deformation. The ease of preservation of such deformed structures will be described in the section on photopolymerisation. However, in this chapter flexoelectricity will not be described any further.

Ferroelectric molecules

In the previous section, it was shown that the chiral molecules in the S_c phase can show ferroelectricity. However in the LC phase the molecules are highly mobile, unlike in a crystal where the position of the molecules is fixed within the crystal lattice. Furthermore in the LC systems, the conformation of the molecules is also not fixed and they also change in time. For this reason initially designed molecules had very low values for spontaneous polarisation $3\,\mathrm{nC\,cm^{-2}}$ (9×10^{-3} D per molecule), which is a few orders of magnitude lower than what is observed for inorganic crystals. However, later work in this area established that the positioning and the nature of the chiral group can increase the spontaneous polarisation considerably and molecules with a spontaneous polarisation as high as $900\,\mathrm{nC\,cm^{-2}}$ have been reported.[30] For example, the chiral group should be close to a polar group or it should be polar itself. In order to hinder the free rotation of the chiral part it should also be close to the central rigid part of the molecule. Care is also taken that the dipole moments of the chiral structure are additive and do not cancel each other out. In Fig. 4, molecules with various spontaneous polarisations are shown. In this figure, examples of slight variations in the molecular structure on the spontaneous polarisation are shown. However, the conformation of the molecule and the configuration of the segments are also very important factors. Changes in temperature can cause changes in the conformation, reducing the polarisation and even leading to the reversal of the sign of the spontaneous polarisation.[30] Such chiral molecules can also be provided with other functional groups, which can become macroscopically aligned in the ferroelectric phase. For example in Fig. 5, the molecule shown contains donor and acceptor groups. Ferroelectric systems

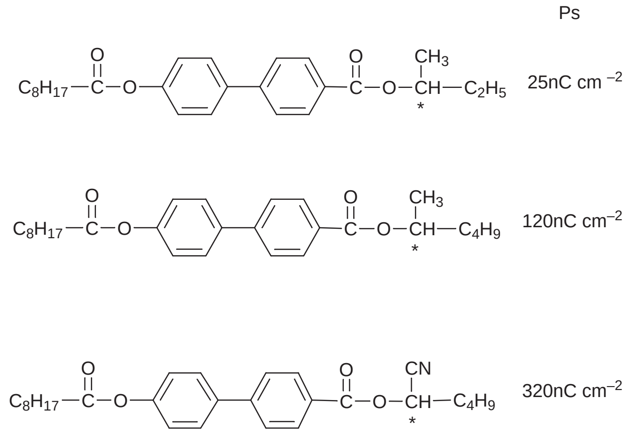

Fig. 4 Molecules with various spontaneous polarisations.

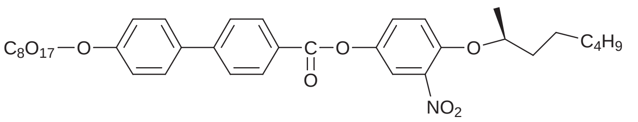

Fig. 5 Example of a ferroelectric molecule with donor and acceptor groups.

containing such molecules can therefore be used in second harmonic generation.[31]

Photopolymerisation of liquid crystal molecules

Reactive LC molecules and photopolymerisation

Liquid crystals are very rich in the phases that they show. For example, only a few kelvin can transform a system from a chiral nematic phase to a ferroelectric phase with a spontaneous polarisation. In some cases, it is desirable to 'freeze in' the phase shown by the liquid crystal molecules isothermally. For this purpose a photo-induced free radical polymerisation processes can be used in combination with reactive LC molecules. The molecule is basically made of three parts as shown in Fig. 6: i) the rigid mesogenic unit; ii) the flexible spacer; iii) the reactive unit. Each of these units in turn determines the liquid crystal phase shown by the molecules before polymerisation, and the properties and the type of network obtained after polymerisation.

A schematic representation of the photopolymerisation process involving reactive acrylate molecules is shown in Fig. 7. In this example under UV radiation ($\lambda < 380$ nm) the cleavage of α,α-dimethoxy-α-phenylacetophenone which is a frequently used photoinitiator is shown. The free radicals are very reactive and attack the double bonds of the acrylate groups inducing a chain reaction until the reaction is terminated by the recombination of two radicals. However, the reaction within the system continues as long as the system is irradiated with UV light, whilst the mobility within the system is retained. The decrease in the polymerisation rate is caused by the reduced mobility or the exhaustion of the reactive molecules within the system.[32]

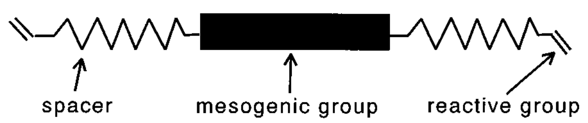

Fig. 6 Schematic representation of reactive LC.

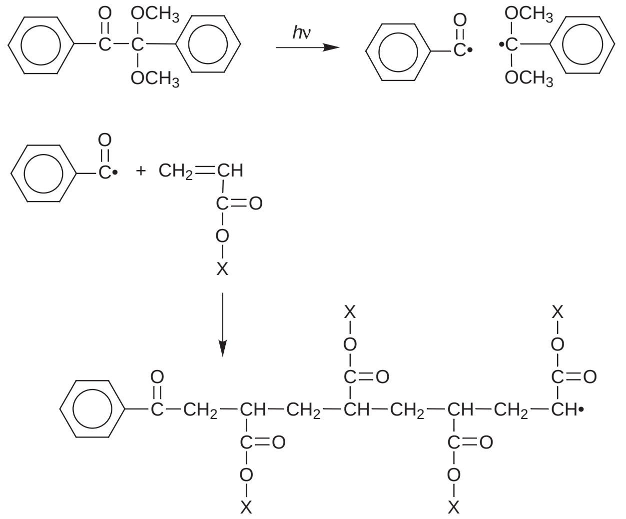

Fig. 7 Schematic representation of photopolymerisation of acrylates.

Anisotropic networks

A photopolymerisation of mesogenic reactive systems leading to the formation of an anisotropic network is schematically shown in Fig. 8. In this process, the long-range orientation of the molecules is induced at specially treated surfaces, electric or magnetic fields. For example, a surface coated with a thin polymer layer subjected to uniaxial rubbing induces uniaxial planar orientation, whereas surfaces treated with surfactant induce homeotropic alignment. However, the photopolymerisation process is not so simple and the order is not always preserved during polymerisation. For example, one of the factors influencing the preservation of the order is the mobility within the system.[19,20] If the photopolymerisation of monoacrylate CB6 shown in Fig. 9 is considered, the order present in the monomeric state of the molecule is lost during polymerisation. The causes of this behaviour are i) the high mobility allowing an isothermal phase transition to take place during the photopolymerisation process; ii) the flow induced as a result of polymerisation shrinkage. When molecules with a single reactive group are mixed together with molecules with double reactive groups (cross-linker), an anisotropic network is formed upon polymerisation of the system. The birefringence of such a mixture before and after polymerisation is shown in Fig. 10. It can be seen that as opposed to the behaviour shown by the side chain polymer within the network, the order is preserved and even when the system is heated to elevated temperatures, the order remains. However, it is important to point out here that within these systems a sufficient amount

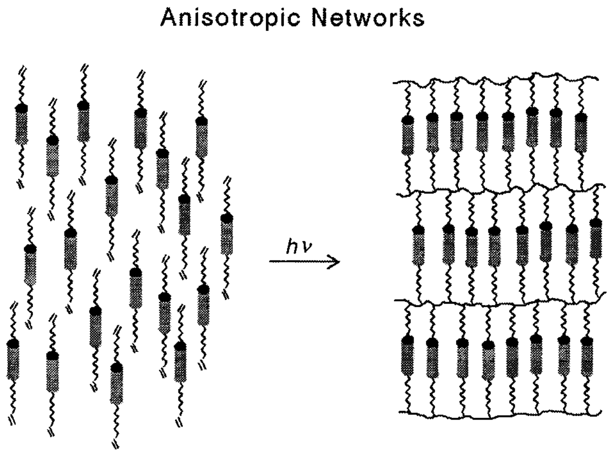

Fig. 8 Schematic representation of network formation using LC acrylates.

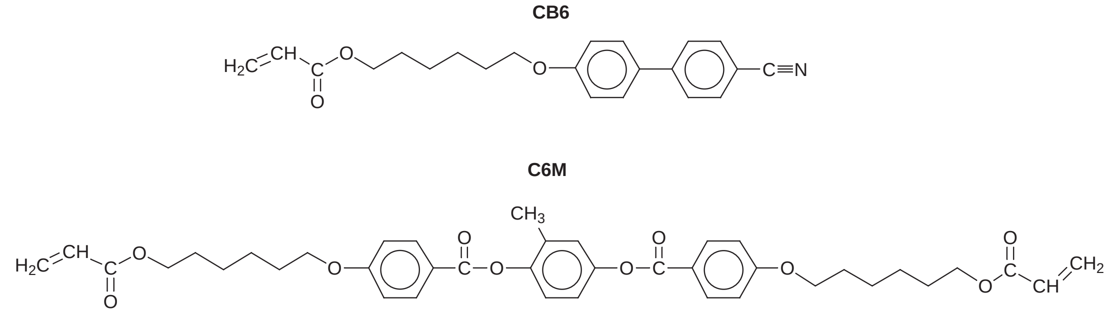

Fig. 9 Structure of CB6 and C6M.

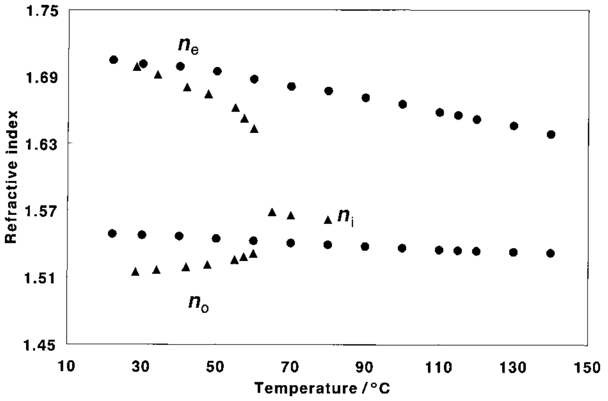

Fig. 10 Birefringence of a LC mixture of monoacrylate CB6 and diacrylate C6M before (▲) and after (●) polymerisation.

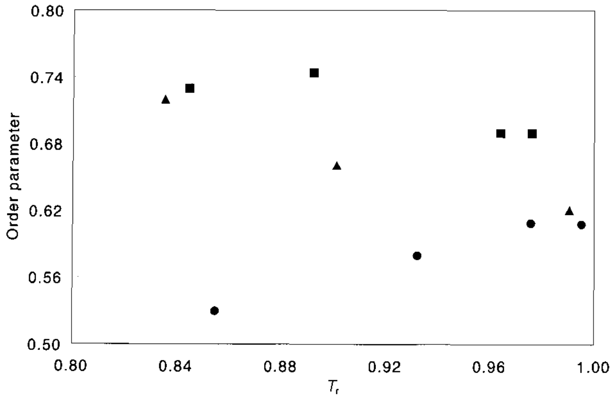

Fig. 11 Order parameter of isomeric diacrylates as a function of reduced temperature (▲) **1**, (●) **3**, (■) **2**.

of cross-linker should be used so that the resultant network does not show any phase transitions. In the case of lightly cross-linked networks, the order totally disappears above the clearing temperature, which in the case of these lightly cross-linked systems might spread over a wide temperature range.

Reducing the mobility is obviously an important factor in the preservation of the order. However, in other cases molecular parameters such as association between the molecules and packing also play an important role.[25] This is best demonstrated when we consider the polymerisation behaviour of three isomeric diacrylates shown in Table 1 where the phase behaviour of the molecules is also shown. It shows that the orientation of the ester groups has a large influence on the phase behaviour. Molecule **1**, in addition to the nematic phase, also shows a smectic-C phase while the molecules **2** and **3** show nematic and smectic-A phases. The order parameter of the molecules as a function of reduced polymerisation temperature ($T_r = T_p/T_c$ where T_p and T_c are polymerisation and clearing temperatures measured in K) is shown in Fig. 11. It can be seen that while for the networks of **1** and **2** the order parameter increases with decreasing reduced temperature, in the case of the networks of monomer **3** the order parameter decreases with decreasing reduced temperature. Especially in the smectic-A phase monomer **3** showed a much reduced order parameter as opposed to the behaviour of monomer **2**. This drastic decrease in the order parameter was associated with the breaking of the smectic layers, which was substantiated by the X-ray diffraction measurements. Using X-ray the diffraction data, the nearest neighbour distance for random arrangement of the rods was estimated to be about 5 Å. Since the width of the phenyl ring is about 6.4 Å, free rotation of the molecules is hindered. At the same time, since the distance between the molecules along the main chain is about 2.5 Å, for the network to maintain a high order parameter after polymerisation it is necessary that to a large extent the adjacent molecules along the same main chain orient in opposite directions as shown in Fig. 12a. The nearest neighbour distance of about 5 Å also indicate that the lateral packing of the molecules albeit on a

Table 1 Transition temperatures of isomeric diacrylates

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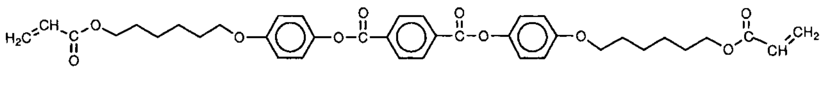
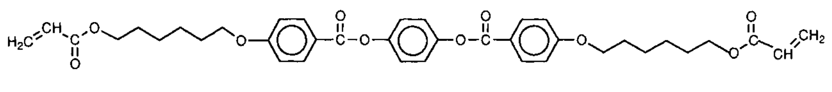


1



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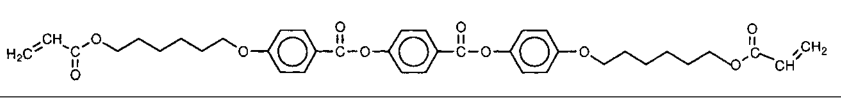

1	S_c	(81 °C)	K	108 °C	N	152 °C	I
2	K	73 °C	S_a	132 °C	N	145 °C	I
3	K	116 °C	S_a	135 °C	N	140 °C	I

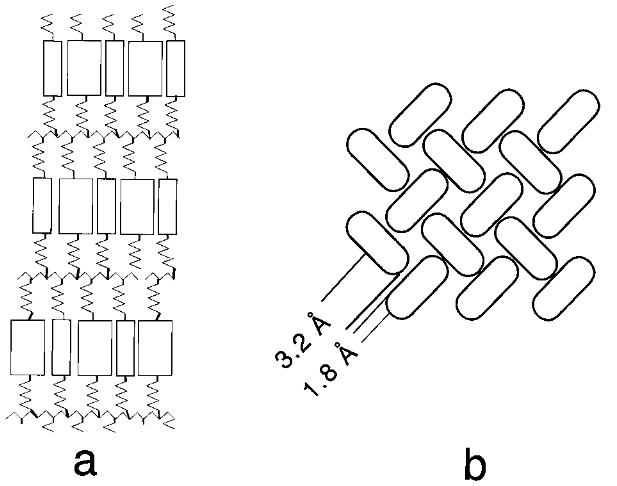

Fig. 12 Arrangement of the molecules. Cross-section a) along b) perpendicular to the length of the molecules.

small scale is probably as shown in Fig. 12b. Molecular modelling and dielectric studies carried out on these molecules also showed that the association between the monomers **1** and **2** was larger than between monomer **3**. Therefore, it is concluded that the specific packing of the molecules with respect to each other and the association between them is an important factor determining the preservation of the order.

Within the anisotropic networks, the high order is sustained even when the system is heated to elevated temperatures. The presence of this high degree of orientational order is very important, as will be discussed below for optical applications. However, the possibility of transforming this orientational order into dipolar order and sustaining it is an interesting prospect. For this study, use was made of CB6 molecules with a single reactive group and dipoles oriented along their long axis as shown in Fig. 8. In order to cross-link the system mixtures of the monoacrylate and diacrylate C6M were used. The molecules were aligned in the nematic phase followed by the polymerisation of the system. In this way, networks with various cross-link densities were produced.[19,20] Upon initiation by UV light, polymerisation within the system proceeded very fast and within less than a minute it was almost complete. Fig. 13 shows the mechanical loss measured at 1 Hz as a function of temperature. This figure shows that with increasing network concentration the glass transition temperature of the system also increases and the loss peaks become broader. This is a well-known effect showing that with increasing network concentration the number of degrees of freedom to be frozen in, in order to reach the glassy state, decreases with increasing cross-link density and spreads over a broader temperature range. In Fig. 14 the order parameters of various networks are compared. It can be seen that the networks containing higher cross-link densities show a smaller temperature-dependent order parameter behaviour. In order to study the mobility within the networks, dielectric spectroscopy was used. In these networks above the glass transition temperature, a strong loss peak could be observed. This peak is associated with the relaxation of the CB6 molecules about the acrylate main chain (δ relaxation). In Fig. 15, relative permittivity loss measured for networks containing various amounts of network is plotted as a function of frequency. It can be seen that with increasing network concentration the relative permittivity loss peak shifts to lower frequencies and becomes broader. Furthermore, the intensity of the peaks gets smaller. The fact that the δ relaxation is observed even in highly cross-linked systems containing 80% C6M indicates that within these networks the CB6 molecules are still highly mobile and their relaxation about the acrylate main chain can still take place. In a network with a random structure, this motion would be expected to be suppressed. Using X-ray diffraction, it was found that the network is probably made out of a blocky structure consisting of cross-linked portions and blocks of monoacrylates. Analysis of the dielectric loss peaks revealed that the networks do not show a single mean relaxation time but a distribution of relaxation times. With increasing network concentration, the distribution of the relaxation times becomes broader. This

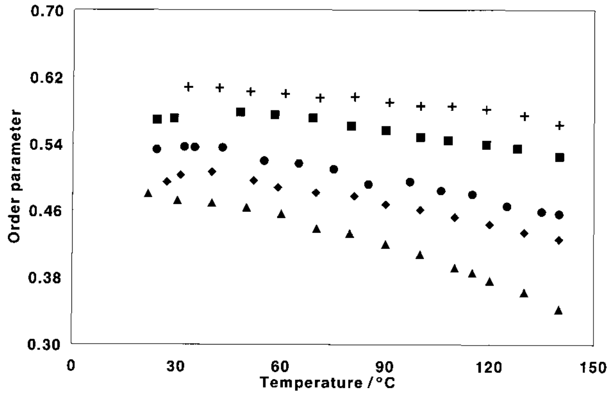

Fig. 14 Order parameter of networks containing various concentrations of C6M (+) 100, (■) 80, (●) 60, (◆) 40, (▲) 20% C6M.

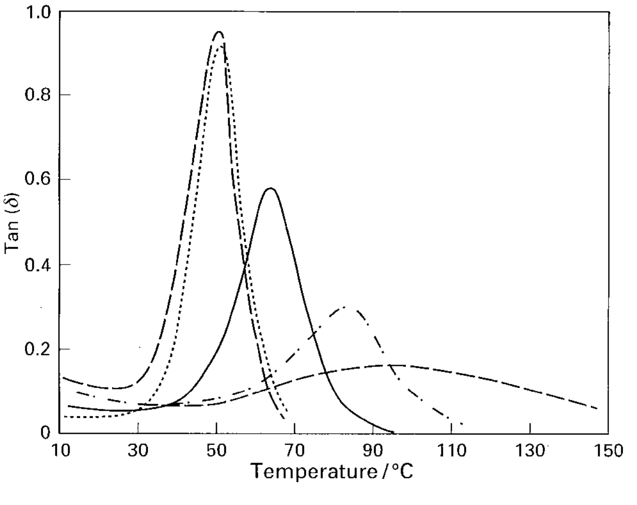

Fig. 13 Mechanical loss tangent for various compositions (- - -) 100%, (-·-·-) 80%, (—) 50%, (.....) 20% C6M, (—–) 100% CB6.

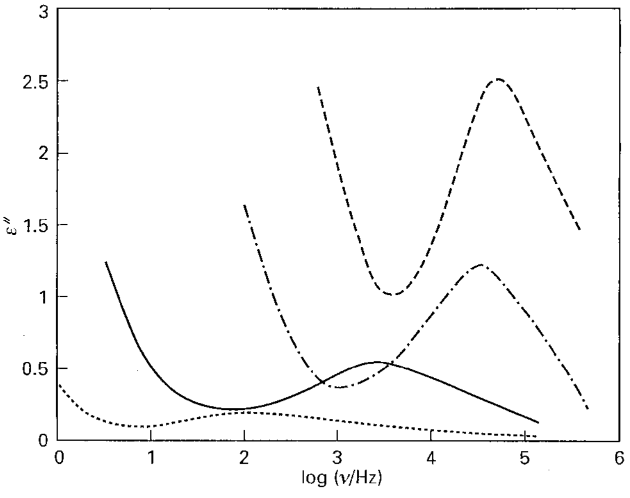

Fig. 15 Dielectric loss as a function of frequency for networks containing various amounts of CB6 (- - - -) 100%, (-·-·-·-) 90%, (—) 50%, (.....) 20% CB6.

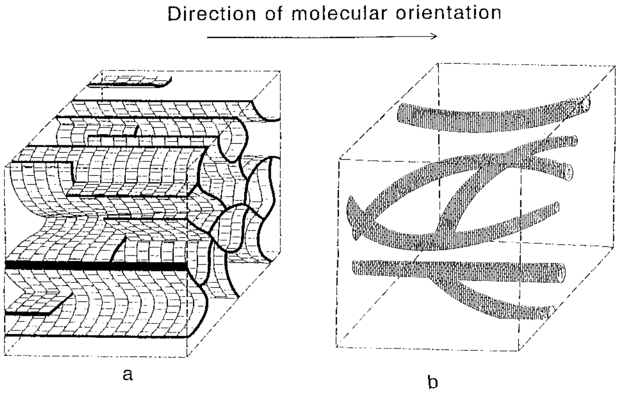

Fig. 16 Various types of gels.

indicates that within the networks, even though the size of the blocks gets smaller and their distribution broader, this blocky nature does not diminish. CB6 molecules within the cross-linked networks, just as in the uncross-linked monoacrylate state, are highly mobile and rotate about their short axis.

Anisotropic gels

As opposed to the anisotropic networks, gels are obtained by photopolymerisation of reactive LC in a mixture of non-reactive LC molecules. In this way, anisotropic networks containing liquid crystal molecules are produced. Extensive studies of gels revealed that in general two types of gels exist.[33] The first type is considered to be made of channels of polymer network elongated in the direction of the long axis of the network molecules. The conventional LC molecules are confined within the walls of the network as shown in Fig. 16a. On the other hand, the second type consists of fibrillar polymer networks dispersed within the non-reactive liquid crystal (Fig. 16b). In gels of type 1 the behaviour of the LC molecules is determined largely by the network. In this type of gel, it was found that a population of the LC molecules, which are not chemically bonded to the network, remain ordered even above their isotropic transition temperature in the bulk. The other population, however, behaved as in the bulk. The electrical switching behaviour of the non-reactive molecules in gels of type 1 was influenced to a larger extent than in gels of type 2. This influence of the network on the LC molecules is used in producing various effects such as electrically induced light scattering[7] and colour changes.[8,21] In the case of electrically induced light scattering the presence of the network causes the LC molecules to orient in various ways in different domains upon application of an electric field, leading to large scale fluctuation in the refractive index, and hence scattering of light. In the case of cholesteric gels it is again the presence of the network that controls the helical rotation leading to electrically induced colour changes.[8,21]

Some uses of networks obtained in the nematic and cholesteric states

Due to the low viscosity and the nature of the nematic phase, it is quite easy to induce macroscopic orientation without any defects. The orientation of the molecules can be uniaxial, tilted, or they can also be twisted from one surface to the other. These orientations and configurations can be induced by the boundary conditions and/or providing the system with a suitable chiral dopant. The birefringence of the system can also be controlled in various ways. Choice of the polymerisation temperature, for example, determines the order parameter within the system, hence the degree of optical anisotropy. On the other hand, by chemical synthesis the intrinsic birefringence of the LC molecules can also be varied to obtain any desired birefringence. Such uniaxially oriented birefringent films can be used in various applications such as wave plates and beam splitters. Polarisers and polarising colour filters can also be obtained when such a uniaxially oriented film is provided with dichroic dye molecules. In Fig. 17 characteristics of such a polariser obtained by using a mixture of dichroic dyes are shown covering the visible range. It can clearly be seen that the absorbance of light plane polarised in the direction of molecular orientation is much higher than in the lateral directions, so that the film works as a polariser. Uniaxially oriented molecules can also be used in producing various other polarising optical components such as beam splitters (Wollaston prism) and gratings.[34] These components can be used in the optical path of various systems such as magneto-optic recorders and projection television.[34]

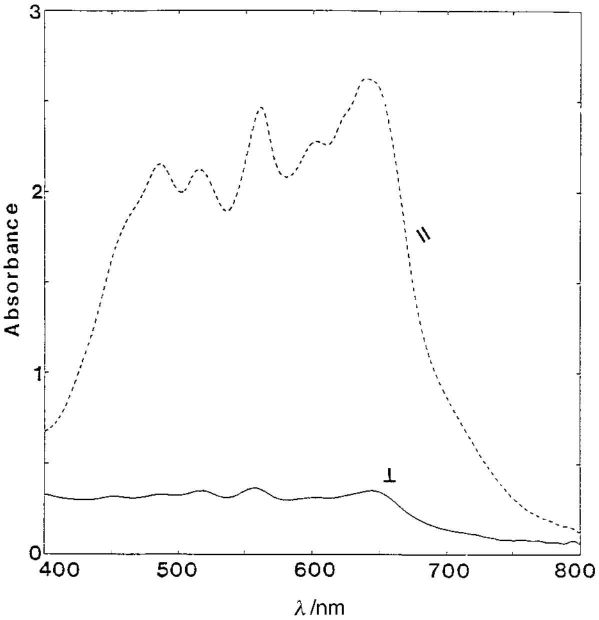

Fig. 17 Liquid crystal polariser.

In the cholesteric phase, the director rotates about a helix and when the helical pitch is in the same order of the wavelength of light, the system selectively reflects a band of circularly polarised light.[35] The position of the reflection band λ is related to the helical pitch and the mean refractive index $n=(n_e+n_o)/2$, as

$$\lambda = p^* n \tag{1}$$

where n_e and n_o are the extraordinary and ordinary refractive indices of the uniaxially oriented layers. Such an arrangement is induced upon doping a nematic system with chiral molecules. The position of the reflection band can be chosen by the concentration of the chiral component present within the system. In Fig. 18 transmission spectra, using circularly polarised light obtained for various mixtures of chiral and non-chiral diacrylates, are shown. It can be seen that the position of the reflection band can be chosen freely. The width of the reflection band is determined by the anisotropy of the material. Therefore, by changing the optical anisotropy of the mixtures the width of the reflection band can also be adjusted. Cholesteric mixtures before polymerisation are also very temperature sensitive. With increasing temperature, the bandwidth decreases while the position of the band can shift to lower or to higher wavelengths. By polymerisation, a cholesteric network with a high temperature stability is obtained. Such cholesteric networks can be used in the production of various optical components such as band-pass filters, notch filters and circular polarisers. They can also be used in LC projection television where polarised colour separation can be made.

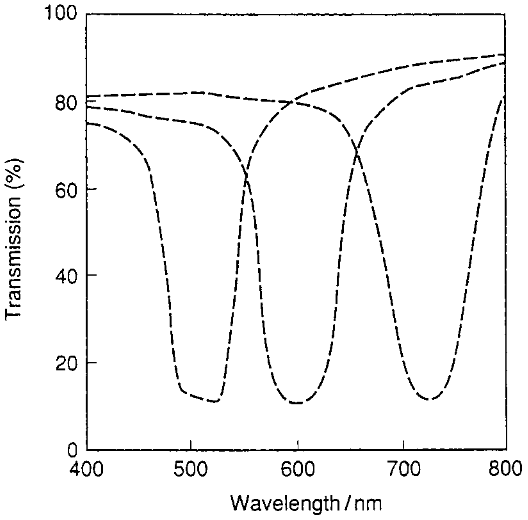

Fig. 18 Reflection band for cholesteric networks containing various amounts of chiral diacrylate.

Such cholesteric layers can also be used in the production of polarised light sources with increased efficiency.

Photopolymerisation in the ferroelectric phase

Networks with stable dipolar orientation

Polymeric systems with stable dipole orientation are of great interest as they show piezo- and pyroelectricity[36] and can also be used in the production of various non-linear optic effects.[37] Polymeric systems with a macroscopic dipole orientation can be divided into two classes:[36] electrets and ferroelectric polymers. Polymer electrets are obtained by poling amorphous polymers under high electric fields around their glass transition temperature (T_g). Upon cooling the system below the T_g of the polymer, the dipole orientation becomes frozen in. However, the dipole orientation in such systems is not stable and the orientation tends to decay even at temperatures below the glass transition of the polymer. Ferroelectric polymers on the other hand have spontaneous polarisation up to their Curie point. Spontaneous polarisation within these systems can be aligned macroscopically and remain stable. Ferroelectric polymers can be semi crystalline[38] or liquid crystalline.[40,41] Semi crystalline polymers such as poly(vinylidene fluoride) PVDF show ferroelectricity only in one particular crystal form. Therefore, they need to be subjected to various heat and mechanical treatments in order to increase the crystallinity and promote the desired crystal form within them. Copolymerisation is also used in order to promote the desired crystal form within ferroelectric polymers.[42] The Langmuir–Blodgett (LB) monolayer transfer method[43] is also used in the architecture of multilayer films. In a controlled way, monolayers of molecules are stacked on top of each other, producing layers with a macroscopic polarisation perpendicular to the surface of the substrate.

Here the use of ferroelectric LC systems in the production of networks with stable dipolar orientation is described. In order to produce such networks two different approaches can be taken. A) Molecules showing ferroelectricity as a single component can be used[34] or B) a system with a smectic-C phase can be doped with chiral molecules having lateral dipoles to obtain a ferroelectric system.[22] Table 2 shows the structure of some such molecules, which have been used in the production of networks. Here we describe two different systems used in the production of networks. In system A monoacrylate **4** (Table 2) which shows ferroelectricity in its pure form was used. However as discussed in a previous section, polymerisation of a monoacrylate does not always lead to the preservation of the structure and the orientation. It is therefore necessary to provide the system with a cross-linker. In Fig. 19 spontaneous polarisation (P_s) of monomer **4** is compared with P_s of a mixture containing 10% cross-linker molecule **6**. The figure shows that the addition of a non-chiral cross-linker diacrylate **6** into the system reduces the spontaneous polarisation of the system by a fraction proportional to its fraction. This is a normal behaviour since only the dipoles of the chiral molecules contribute to the P_s of the system. In system **B**, ferroelectricity is induced by providing molecule **6** showing a smectic-C phase with the chiral dopant **5**. P_s of 10 nC cm^{-2} was obtained when 15% of molecule **5** was mixed in together with molecule **6**. Higher concentrations of molecule **5** could not be used, as molecule **5** in its pure form is not LC.

Molecular alignment was induced by uniaxially rubbed layers. Under the application of a direct electric field, the ferroelectric polarisation was aligned. After polymerisation, highly birefringent networks were obtained. Heating the net-

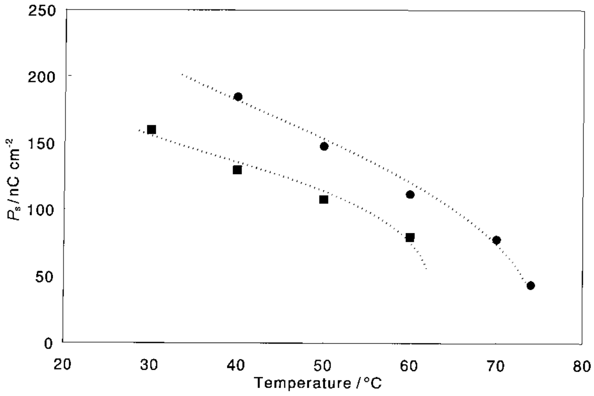

Fig. 19 Spontaneous polarisation as a function of temperature (●) 100% **4**, (■) 90% **4**.

Table 2 Structure and the transition temperatures of molecules used in the networks with dipolar orientation

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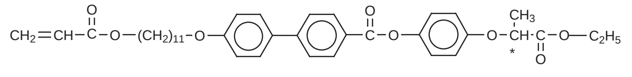

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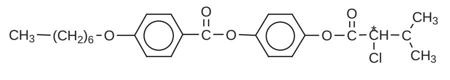

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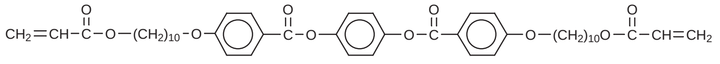

4	K	62 °C	S*$_c$	78 °C	S$_a$	106 °C	I
10% **6** in **4**	K	65 °C	S*$_c$	70 °C	S$_a$	102 °C	I
5	K	69 °C	I				
15% **5** in **6**	K	80 °C	S*$_c$	126 °C	I		
6	K	82 °C	S$_c$	108 °C	N*	149 °C	I

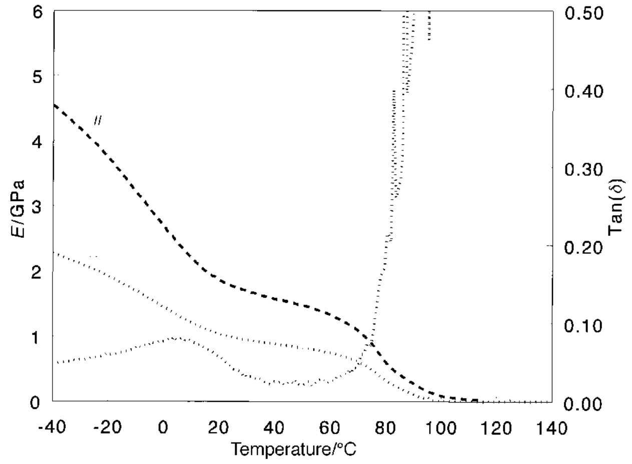

Fig. 20 Tensile modulus and loss tangent as a function of temperature measured in various directions for an anisotropic network.

works to elevated temperatures caused, if anything, only a slight change in the birefringence of the material. An example of the thermo-mechanical properties of the network is shown in Fig. 20 where the dynamic tensile elastic modulus and loss tangent measured at 1 Hz are plotted as a function of temperature. It can be seen that the network has a glass transition temperature of 80 °C, above which it becomes rubbery. The sample also shows a strong secondary relaxation peaking at around 10 °C. This secondary relaxation has a strong effect on the elastic modulus, which shows a rapid increase below this transition. Furthermore, in this figure the large difference in the modulus measured in different directions again clearly demonstrates the anisotropy of the sample.

In order to characterise the dipole orientation within the networks, piezoactivity of the samples was examined. Samples were coated with gold electrodes and a sinusoidally-varying strain was applied across the sample, causing an open field voltage (V_p) which also periodically varied. The voltage across the sample shows a linear increase as a function of applied strain. At a given strain the magnitude and the sign of V_p is highly dependent on the direction of the applied strain. The observed piezoelectricty is therefore associated with the presence of dipole orientation within the system. The fact that at a given strain the sign and the magnitude of the open field voltage depend on the direction of the applied strain indicates that the stress is transferred to the spontaneous polarisation in different ways. From the slopes of the curves the piezoelectric coefficient constant d in the direction parallel (d_z) and perpendicular (d_y) to the molecular orientation was estimated using eqn. (2).[36]

$$d = V_p \varepsilon_o \varepsilon\, A_e / tE\gamma A_c \qquad (2)$$

where V_p is the open circuit voltage, ε_o permittivity of free space, ε is the permittivity, A_e active area of the electrode, t is the sample thickness, E is the tensile modulus in the direction of applied strain γ and A_c is the cross sectional area of the sample. The piezoelectric coefficients in various directions calculated for system A and system B are shown in Table 3. The behaviour observed for system A is different from the behaviour observed for system B. In system B the piezoelectric coefficients were found to be higher when the strain was applied in the direction of the molecular orientation than in the direction perpendicular to the molecular orientation showing the opposite behaviour from what is observed for system A. Furthermore if the values observed here can be compared with the frequently quoted value of $d = 28$ pC N^{-1} for β phase of PVDF with a $P_s = 13$ μC cm^{-2}, assuming that the spontaneous polarisation of 130 nC cm^{-2} observed in the monomeric state is frozen in during the photopolymerisation process, it can be deduced that in the present system the transfer of the force to the dipole orientation within the system is more effective than in PVDF with a much higher P_s as the piezoelectric constants observed for both systems are very similar. These effects are probably the direct result of the presence of the cross-links within the system, which effectively transfer the applied stress to the molecular orientation as well as the layered structure, which is present in the chiral smectic-C phase. X-Ray diffraction was used in order to characterise the smectic layer orientation in various types of networks. In Fig. 21, various orientations satisfying the S_c conditions and having the dipole orientation in the same direction are shown. In this figure, two extreme cases satisfying the chiral smectic-C conditions where the molecules are confined in planes parallel to the substrates are shown. In the bookshelf geometry, the smectic layers are oriented perpendicular with respect to the rubbing direction, whereas the molecules are oriented at an angle. In the second case, in-plane chevrons geometry, the smectic layers are oriented at an angle with respect to the rubbing direction whereas the molecules are oriented in two different directions. Here the effect of the layer orientation on the piezoelectric behaviour is clearly demonstrated. Ferroelectric molecular molecules with donor–acceptor groups have also been used in the production of anisotropic networks for second harmonic generation.[44,45]

Table 3 Piezoelectric coefficients of various networks measured during the application of strain in various directions

Material	Direction of strain	Piezoelectric coefficient (pC/N)
10% **6** in **4**	∥	8
10% **6** in **4**	⊥	29
15% **5** in **6**	∥	3.1
15% **5** in **6**	⊥	−1.4

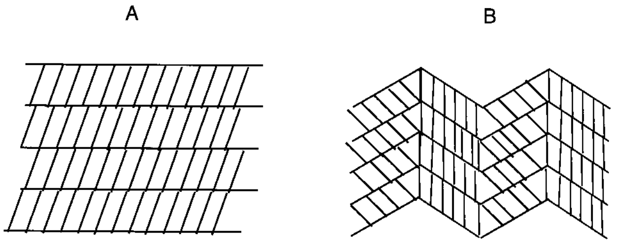

Fig. 21 Chevron orientation in ferroelectric layers.

Ferroelectric gels-network stabilised FLC

After the ferroelectricity of liquid crystals had been predicted by R. B. Meyer in 1974[28,46] it was N. Clark and S. T. Largerwall[47] who demonstrated the prospects of FLC in displays in 1980. In their surface-stabilised concept, they used very thin cells in order to suppress the molecular rotation and cool the FLC into the ferroelectric phase from a uniaxially oriented state. They also demonstrated that bi-stable switching between two states could be achieved in surface stabilised cells. Currently, surface-stabilised FLC have the advantage of high speed and bistability over conventional nematics but they suffer from various other problems; such as the difficulty of obtaining good uniform orientation and sustaining it, the high birefringence, the production of grey levels and the low shock resistance of the cells. In FLC displays, the birefringence mode is used as the molecules switch between two stable states schematically shown in Fig. 22. The cell is placed between crossed polarisers so that at one of the stable states the molecular orientation is in the direction of one of the polarisers. Reversing the electric field brings the orientation to the other stable state where the optimal molecular orientation is at an angle of 45° to the polarisers. Furthermore in order to be able to switch between black and white states while keeping the

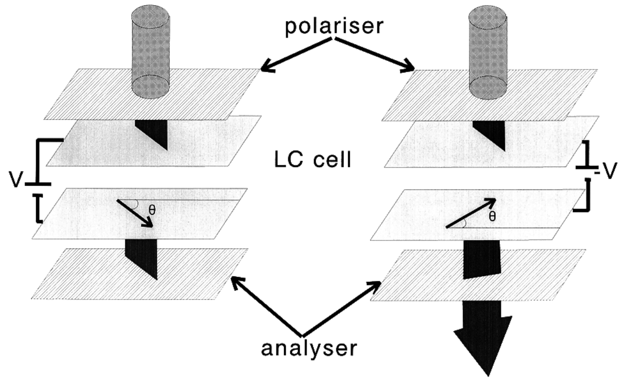

Fig. 22 FLC cell construction.

transmission at maximum, the retardation should be $\lambda/2$. Keeping the retardation in the first order is also necessary in order to avoid a coloured appearance of the cell. Due to the high birefringence of most available FLC materials, the cell thickness must therefore be of the order of 2 µm. For more than a decade, chemists and physicists have been trying to find solutions to these problems. In addition to the surface-stabilised concept, polymer dispersed ferroelectric systems have been described.[48] In this concept, a mixture of FLC and isotropic reactive molecules is made. Droplets of FLC in an isotropic matrix are formed upon polymerisation. However, the system has to be sheared to induce orientation of the FLC. Here ferroelectric gels as a new concept of network stabilised ferroelectric displays are described.[49–51] Recently in the literature, network stabilised anti-ferroelectric systems have also been described.[52]

Ferroelectric gels, which give network stabilisation, are of type 1 shown in Fig. 16. In these gels, the network influences the behaviour of the non-reactive molecules to a large extent and they offer network stabilisation as opposed to the stabilisation by the cell surfaces. Reactive molecules, which are used in the production of FLC gels, can also show LC phases. Therefore, any desired LC phase can be induced in a non-reactive ferroelectric material in the monomeric state before polymerisation. For example in the nematic phase, molecules can be well oriented. When a non-reactive FLC system containing reactive molecules is polymerised in the nematic phase, a very well aligned gel can be obtained. After polymerisation of the reactive molecules, the non-reactive LC molecules revert to showing their phase behaviour as in the bulk. However their orientation behaviour remains influenced to a large extent by the polymer network molecules and a high degree of orientation is sustained even after cooling the system into the FLC phase of the non reactive molecules. This is not only valid for uniaxial orientations which can also be induced in the FLC phase but it can also be used to obtain other configurations such as tilted, hybrid, and twisted, which are difficult to induce in the FLC phase. Therefore, as before, these configurations can be induced in the nematic phase of the reactive mixture before polymerisation and they are sustained after polymerising and cooling the system to the FLC phase of the non-reactive molecules. The other possibility is to induce the polymerisation within the smectic-A phase, hoping to freeze in the smectic layer orientation to avoid the formation of chevrons which reduce the angle between the bistable states. Here it is interesting to consider the gels of non-reactive FLC CS-2004, which do not have a smectic-A phase. A smectic-A phase is usually necessary to prevent the formation of in-plane chevrons, avoiding the formation of domains with different director orientations. Furthermore, due to the small pitch of the system, inducing uniform orientation in thick cells is not possible. In this example chiral and non-chiral reactive LCs were used. The transition temperatures of the materials used are given in Table 4. It can be seen that the ferroelectric LC CS-2004 in a mixture with 20% **8** only shows a nematic phase and the ferroelectric phase disappears.

Here it is interesting to consider the possibility of compensating for the pitch observed in the nematic phase by adding chiral diacrylate (**7**) to the mixtures containing 20% **8** in CS-2004. The compensation of the chiral pitch is very important, for example, to obtain uniaxially oriented ferroelectric samples in thick cells. Fig. 23 shows the effect of the addition of 1% chiral diacrylate on the helical pitch within the mixture measured as a function of temperature. It can be seen that with increasing temperature, the pitch first increases rapidly and then the helix changes its sense and the pitch starts to decrease. This figure clearly shows that the pitch can be fully compensated by adding a small amount of chiral diacrylate. The maximum value of 80 µm obtained for the pitch in this case is much higher than the value of 23 µm (being the highest value measured close to the S_c* transition temperature) obtained for pure CS-2004. Such a mixture was used to produce a ferroelectric gel in a 7.7 µm cell. Using the

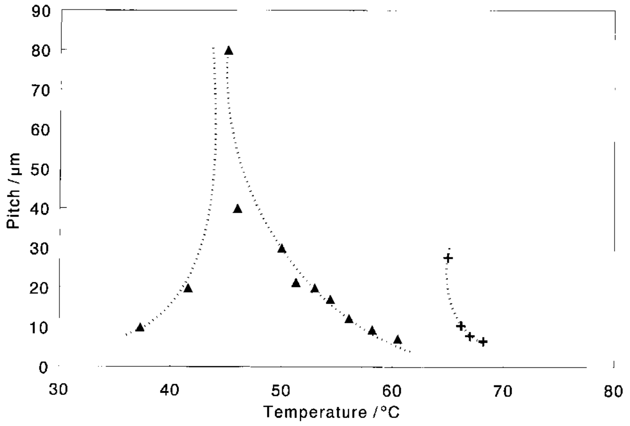

Fig. 23 Chiral nematic pitch as a function of temperature (+) 100% ferroelectric mixture CS2004, (▲) 80% CS2004.

Table 4 Examples of materials used in the in the production of ferroelectric gels

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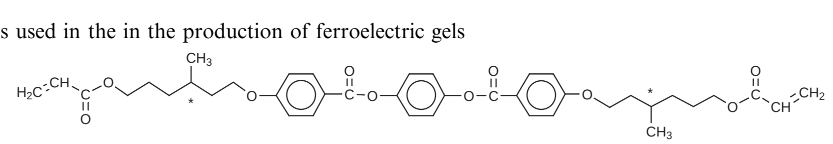

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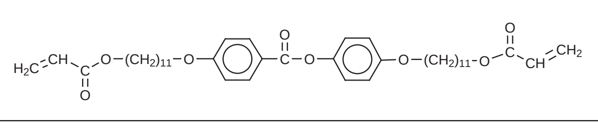

$H_2C{=}CH{-}C(=O){-}O{-}(CH_2)_{11}{-}O{-}C_6H_4{-}C(=O){-}O{-}C_6H_4{-}O{-}(CH_2)_{11}{-}O{-}C(=O){-}CH{=}CH_2$

CS-2004	K	−9 °C	S^*_c	62 °C	N*	71 °C	I
7	K	66 °C	N*	98 °C	I		
8	K	50 °C	S_a	65 °C	I		
8/**7**(1/4)	K	37 °C	N*	60 °C	I		

mixture a cell was filled with the mixture and polymerised in the nematic phase. After polymerisation a uniaxially oriented network containing CS-2004 molecules in the ferroelectric phase was formed. When the system was heated up close to the isotropic transition point or cooled down to the ambient temperature the system remained uniaxial. When pure CS-2004 was placed in such a 7.7 µm cell, the orientation was not uniaxial but twisted at most temperatures in the N* phase. The number of rotations of the helix within the cell increased as the helical pitch decreased with increasing temperature. Only very close to the S_c* transition temperature could uniaxial orientation be obtained in a very small temperature range. Cooling such an orientation into the ferroelectric phase led to a texture with defects. A much better orientation of pure CS-2004 could be obtained in much thinner (2 µm) cells in which surface stabilisation could be induced. The fact that the CS-2004 molecules in the gel remained well uniaxially oriented throughout the entire nematic and ferroelectric ranges of CS-2004 in the bulk indicates the great influence of the network molecules on the ferroelectric CS-2004 molecules which are not chemically attached to the network. For this reason, these gels will be referred to as *anisotropic-network stabilised ferroelectric liquid crystal.*

The influence of the anisotropic network on the behaviour of the non-reactive molecules is manifested in various ways. In Fig. 24, the birefringence of the gel, CS2004 and that of a pure network is shown as a function of temperature. The birefringence of the network remains constant with increasing temperature, showing the common behaviour observed for the anisotropic networks. The birefringence of the ferroelectric LC shows the expected behaviour, becoming isotropic at 71 °C. In the case of the gel it can be seen that with increasing temperature up to 62 °C (in the S_c* phase of CS-2004) the birefringence remains almost constant before rapidly decreasing to reach a constant value above the isotropic transition temperature of FLC (CS-2004). The residual birefringence is to a large extent due to the presence of the three-dimensional anisotropic network, which remains oriented. However, the value of 0.024 measured for the residual birefringence at 90 °C is only slightly higher than the value of 0.0214 expected from 20% network on the basis of the value measured in the bulk. This is also behaviour frequently observed for gels.[7] The excess birefringence is associated with the fraction of the molecules, which are not chemically attached to the network but nevertheless remain oriented even when the system is heated above the clearing temperature of the molecules. The fact that the gels show the same transition temperatures of CS-2004 in the bulk indicates that the network has only a slight influence, if any at all, on the thermal behaviour of the other fraction of CS-2004 molecules within the gels.

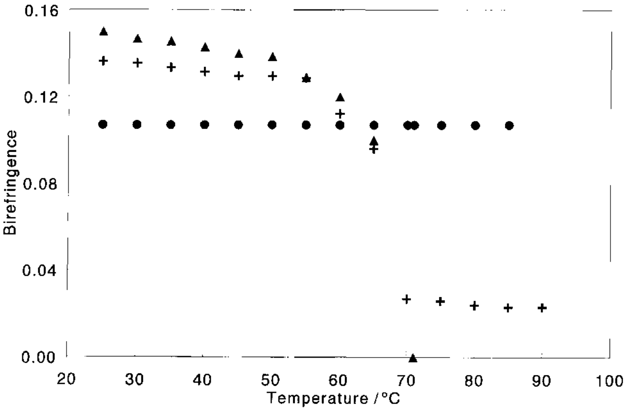

Fig. 24 Birefringence as a function of temperature (▲) 100% ferroelectric CS2004, (+) 80% CS20004, (●) 100% **8**.

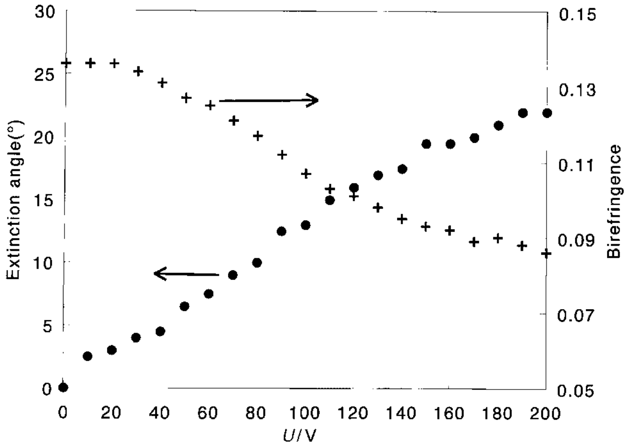

Fig. 25 Birefringence and extinction angle within the gel as a function of voltage.

The switching behaviour in the 7.7 µm cell was investigated by measuring the extinction angle (half of the angle over which the sample has to be rotated to obtain the darkest states between crossed polarisers when the polarity of the field is reversed) and at the same time measuring the birefringence. The results of the measurements are shown in Fig. 25. It can be seen that the birefringence decreases when the voltage increases, whereas the extinction angle shows a steady increase. Here it is important to note that the maximum measured extinction angle of 22° is half of the value of 44° measured for pure CS-2004. The observed behaviour is explained in the following way. The molecules are confined to domains and in some domains molecules rotate to the angle of 44°, whereas the others remain oriented in the same direction as the network. If the process takes place in domains smaller than the wavelength of the light, an average angle is macroscopically measured.

The electrical switching within the gel was measured by applying a triangular voltage wave and measuring the current through the cell. The transmission of white light through the crossed polarisers containing the cell was measured simultaneously to enable comparison of the electrical and optical switching. Fig. 26 shows the transmission and the current as a function of voltage and time in a 2 µm cell. It can be seen that the change in transmission is accompanied by broad current peaks associated with the polarisation reversal. From the surface area of the current peak the spontaneous polarisation (P_s) was calculated to be 26 nC cm^{-2}. For the pure CS-2004 P_s is 68.7 nC cm^{-2}. As the polymer did not contribute to the

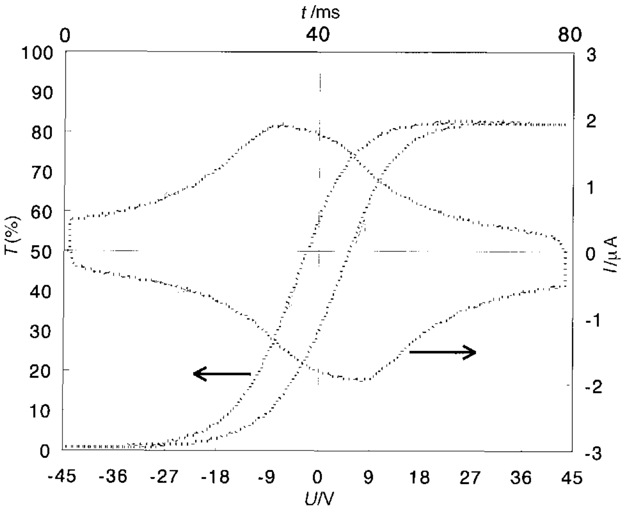

Fig. 26 Transmission and current through the cell measured during the application of triangular voltage.

spontaneous polarisation, P_s was determined by the CS-2004 fraction and in the case of the gel containing 20% **8** the expected value was 54.96 nC cm^{-2}. The fact that the measured value was about half of the value expected indicated that the switching of the molecules within the system was not complete. This is in good agreement with the tilt angle measurements. According to the domain switching theory outlined above, the observed tilt angle can also be explained in terms of about half of the molecules being oriented at an angle of 44° with respect to the rest oriented in the direction of the polymer network.

In Fig. 26, it can also be seen that there is a large contrast between the dark and bright states. Furthermore, due to the reduced birefringence switching between neutral black and white states became possible (pure material had a birefringence of 0.15, which meant that the cells with this cell gap would appear to be coloured in the bright state). In Fig. 26, the presence of hysteresis, as also observed for surface-stabilised ferroelectrics, is quite clear. It is also interesting to point out that the molecules not only react to the changes in the polarity of the electric field but also to its amplitude. This indicated the existence of two stable states within the system. When the field was increased to change the orientation of the molecules from one of the stable states, the molecules were drawn back to the stable state when the voltage was decreased. In order to reach the other stable state it was therefore necessary to change the direction of the field. The bistable states were experimentally determined to be at an angle of ±10° with respect to the rubbing direction. Higher fields induced higher angles, but when the field was subsequently reduced to zero, the angle reverted to 10°. To reduce the angle further towards zero reversing the sign of the field and increasing it slightly was sufficient. The possibility of adjusting the tilt angle by the magnitude of the electric field and its reversal to the original state in the absence of the electric field are interesting with respect to the possibility of active addressing without reset.

The ferroelectric gels described here can be used in display applications where passive matrix addressing is used.[51] A bipolar pulse is applied to switch the molecules. The magnitude of the pulse determines which domain switches from one state to the other. In this way, the number of switched domains in a particular orientation state can be controlled, thus producing grey levels as shown in Fig. 27. In the case of active matrix addressing, the same principle of domain switching is used. However, in the case of active matrix addressing bistability is not required as the field is sustained across the material. Fig. 28 shows the transmission voltage behaviour of a hybrid aligned ferroelectric gel during passive matrix addressing. It can be seen that a smooth curve is obtained which can further be used in active matrix addressing.[50]

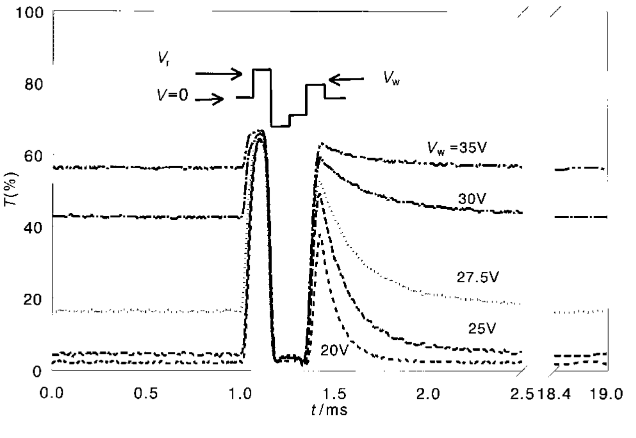

Fig. 27 Transmission as a function of time during and after the application of bipolar pulses across a gel.

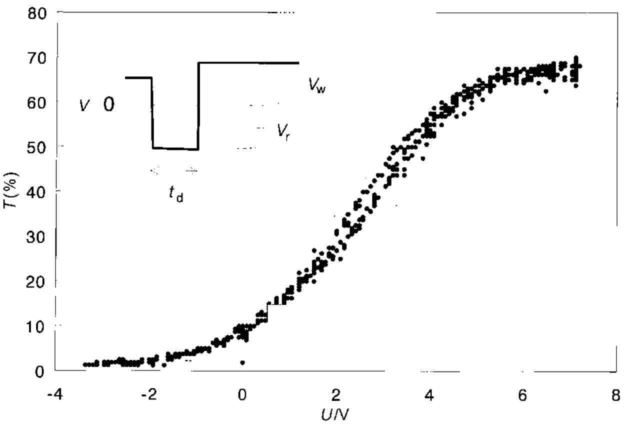

Fig. 28 Transmission through a gel as a function of voltage applied using a transistor.

Outlook

Photopolymerisation of reactive LC molecules has been shown to be a useful tool in producing anisotropic structures with tailor-made properties. Fully cross-linked networks can be used in the production of passive electro-optical components, whereas networks containing non-reactive molecules (anisotropic gels) are used in new devices or in improving the performance of existing devices. The networks and gels are also of academic interest. The polymerisation behaviour of such anisotropic bodies, relaxation processes in anisotropic highly cross-linked media and their properties are currently being studied. In the case of anisotropic gels, understanding the behaviour of non-reactive molecules in anisotropic environments is a great challenge. More research in this relatively new area is needed in order to fully explore the possibilities offered by these materials in the production of active as well as passive electro-optical devices.

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