Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

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To cite this Article Kelly, S. M.(1998) 'Anisotropic networks, elastomers and gels', Liquid Crystals, 24: 1, 71 — 82
To link to this Article: DOI: 10.1080/026782998207596
URL: http://dx.doi.org/10.1080/026782998207596

LIQUID CRYSTALS, 1998, VOL. 24, NO. 1, 71–82

Anisotropic networks, elastomers and gels

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Presented at the Capri Symposium in Honour of George W. Gray, FRS held at the Hotel Palatium, Capri, 11–14 *September* 1996

Anisotropic networks, elastomers and gels exhibit piezoelectric, pyroelectric, ferroelectric and NLO properties of potential interest for use in many electro-optic devices for optical communication and processing technologies. The formation, properties and applications of such anisotropic, mainly liquid crystalline, networks are described. If some of the molecules in a liquid mixture contain at least two reactive groups which can be either photochemically or thermally polymerized, then crosslinked, anisotropic networks, elastomers and gels can be produced. Solid macroscopically aligned elastomers or networks can be formed as required beforehand or simultaneously by orientation of the sample. Anisotropic gels consist of a solid anisotropic network and non-covalently bonded, but strongly oriented domains of low molar mass liquid crystals. Anisotropic networks, elastomers and gels can be prepared from preformed amorphous or liquid crystalline polymers incorporating additional reactive groups, which can be macroscopically oriented in the liquid crystalline state and then fixed by additional crosslinking reactions. Reversible networks, elastomers and gels can be prepared either non-covalently or covalently by thermally reversible linkages between, for example, side group polymers and low molar mass molecules, neither of which necessarily exhibit liquid crystalline properties in the pure state.

1. Introduction

Anisotropic networks [1–5], elastomers [6, 7] and gels [8] with liquid crystal (LC) properties represent an area of research in the general domain of self-assembling materials of rapidly growing fundamental scientific interest and technological potential [1, 2]. They have many potential uses, for example passive solid-state optical devices such as colour filters, retarders, polarizers, etc. active electrical or electronic devices, such as liquid crystal displays (LCDs), piezoelectric or pyroelectric sensors, NLO films, or as structural materials, e.g. in cladding for fibre-optic cables, orientation layers for LCDs, etc. In this article networks are arbitrarily defined as almost completely crosslinked solids whose monomers before polymerization each possess two reactive groups; elastomers are designated as deformable solids derived in one or two steps from monomers with one reactive group and a small amount of bireactive crosslinker; gels/are defined as fluids consisting of a solid, three-dimensional crosslinked network and non-polymerizable, low molar mass LCs. Although somewhat artificial in terms of polymer chemistry, this nomenclature serves a useful purpose in providing general terms for three distinct classes of anisotropic systems with liquid crystalline or otherwise anisotropic properties. Reversible, self-assembling anisotropic networks, elastomers and gels can be prepared either non-covalently, e.g. via hydrogen bonding or ionic forces or covalently, e.g. by thermally reversible linkages—for example, between side group polymers and low molar mass molecules, neither of which necessarily exhibit LC properties in the pure state.

1.1. *Anisotropic networks*

It is the combination of the ability to flow and the low viscosity of low molar mass nematic (N) and smectic (Sm) LCs and the anisotropy of their mechanical, optical, electrical and electronic properties, which renders liquid crystals of unique interest as the starting materials for anisotropic networks, as well as for anisotropic elastomers and gels. Macroscopic, uniaxially oriented films can be formed by orientation of the sample by mechanical force, orientation layers [9], electric or magnetic fields [10], polarized light [11], etc. and then crosslinked to form an anisotropic network (figure 1), if the mixture components contain polymerizable or crosslinkable, e.g. dimerizable groups; see the table for typical chemical structures of such bireactive monomers. Alternatively, amorphous or liquid crystalline side group and/or main chain polymers incorporating additional reactive groups can be transferred onto a suitable substrate, macroscopically oriented and then crosslinked. Interpenetrating liquid crystalline polymer networks, which are physically interlocked, have also been reported. It should be noted, however, that although crosslinking reactions normally freeze in and fix the

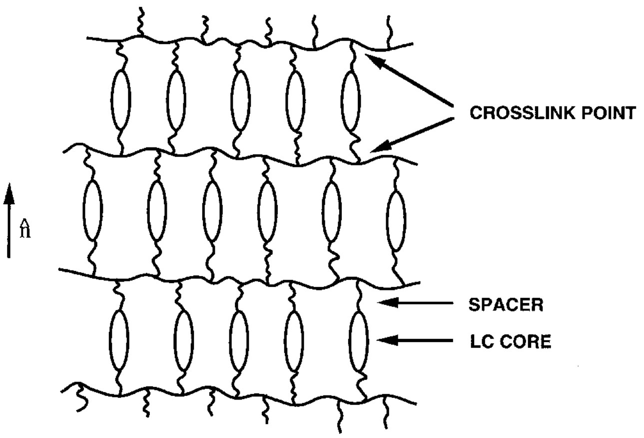


Figure 1. A simple schematic representation of the supramolecular structure of an anisotropic network.

liquid crystal state of the reactive mixture, crosslinking to form a network can lead to the formation of a different mesophase, e.g. a nematic phase can be converted to a smectic phase [12].

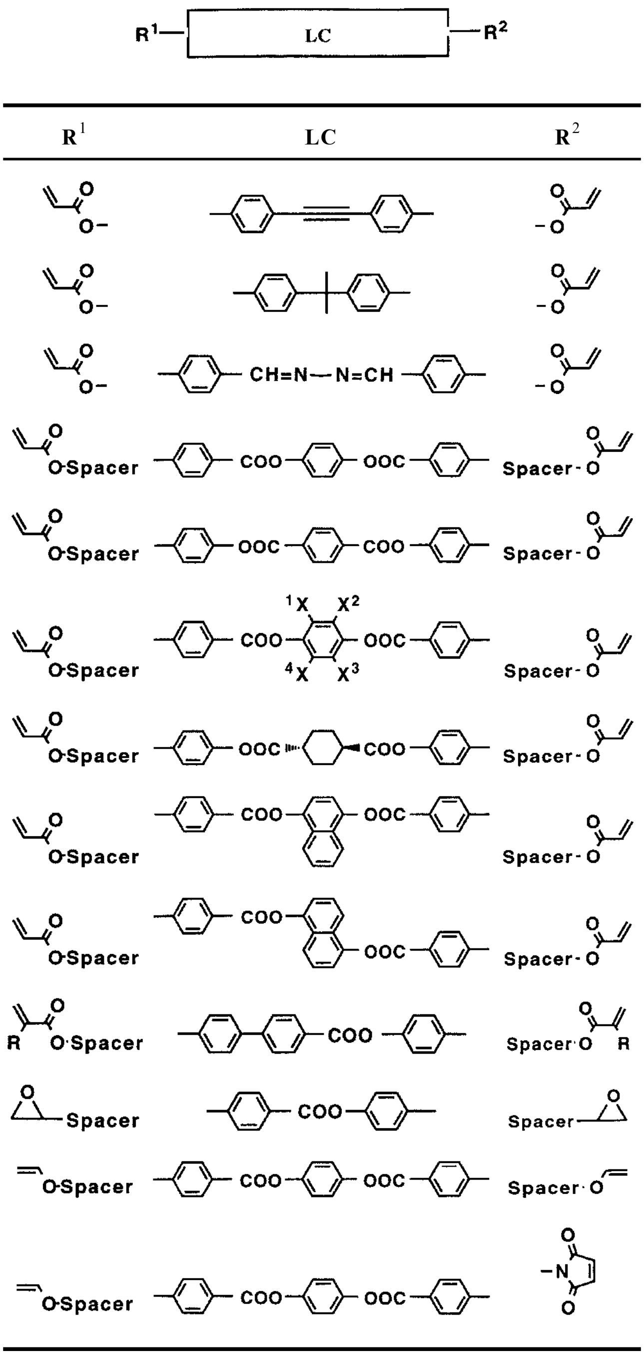
1.2. *Anisotropic elastomers*

The translational motion of the backbone of an LC polymer is eliminated if a limited number (<10 wt %) of crosslinks are present (figure 2). However, the high micro-Brownian motion of the chain segments remains between the points of crosslinking. The product is then an infinitely viscous, anisotropic elastomer, which regains its initial shape upon removal of a distorting force. Therefore, a problem associated with all LC elastomers is the inability to shape or otherwise process them after formation. The crosslinks act as a plasticizer at low concentrations and often lead to a lower T_g with only small depressions in the other transition temperatures of a polymer before crosslinking occurred. The phase in which the crosslinking is carried out is substantially stabilized by the crosslinks [6, 7]. The side groups sometimes lie parallel and sometimes perpendicular to the main chain director depending on the spacer length [6, 7]. Hence, these anisotropic elastomers simultaneously exhibit properties associated with low molar mass LCs and standard elastomers. Therefore, the mechanical and optical properties of such networks are anisotropic below the clearing point (T_c) and are also dependent upon stress/strain fields caused by mechanical deformation.

1.3. *Anisotropic gels*

Anisotropic gels are a mixture of a solid crosslinked LC network and fluid non-reactive low molar mass LCs [8] produced by the *in situ* polymerization of LC monomers with at least two polymerizable groups, such as diacrylates, in the presence of normal low molar mass LCs without reactive units—for example cyanobiphenyl mixtures (figure 3) [8]. The resultant solid polymer network incorporates the three-dimensional structure of the original LC mixture. The low molar mass LCs are not chemically bound to the network, remain fluid and therefore are, in principle, free to move. However, strong

Table. General structure and examples of typical polymerizable and crosslinkable monomers for anisotropic networks, elastomers and gels



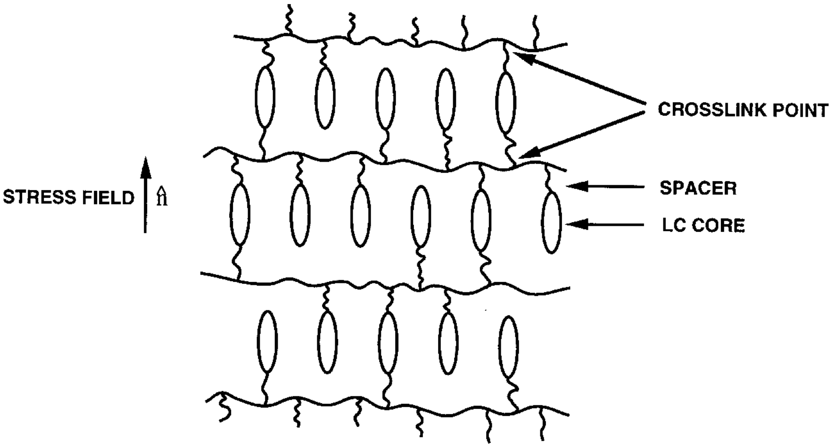


Figure 2. A simple schematic representation of the supramolecular structure of an anisotropic elastomer.

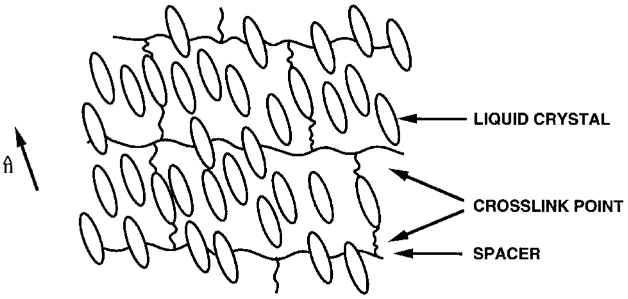


Figure 3. A simple schematic representation of the supramolecular structure of an anisotropic gel.

intermolecular forces between the network and the LC molecules result in a residual orientation even at temperatures significantly above T_c of the original mixture. Even at relatively low network concentrations (<30 wt %) most of the LC molecules (≈ 80 wt %) are estimated to be bound in domains dominated by the network with no measurable T_c.

2. Polymerization reactions

2.1. *Spontaneous polymerization of low molar mass monomers*

2.1.1. *Radical polymerization*

The first reported anisotropic networks were produced by spontaneous polymerization under the action of light and heat at high temperatures (<250°C) of diacrylate monomers in the liquid crystalline state [13–16]. This uncontrolled reaction of single components or mixtures of monomers produces solid nematic, smectic and chiral nematic networks with a high degree of crosslinking and a low degree of micro-Brownian motion, since all the monomers possess two identical polymerizable end groups and, therefore, most of the mesogenic units are fixed at both ends in the polymer network. The crosslinking reactions are the result of the spontaneous generation of radicals in the bulk. Most compounds with polymerizable end groups can undergo this type of spontaneous light or heat catalysed reaction and, therefore, small amounts of radical inhibitors are generally added to such monomers and reaction intermediates in the pure state and to reaction mixtures throughout their synthesis.

2.1.2. *Condensation polymerization*

Thermosets are networks produced by the formation of discrete chemical bonds between generally two types of monomers each of which incorporates different reactive end groups, which can react with each other. The crosslinking reactions are generally initiated by the action of heat. An example of this approach is the copolymerization of an LC compound with two reactive groups such as a diepoxide cured with a non-LC crosslinking agent, also with two reactive groups, such as an aromatic diamine [17]. This approach allows greater control over bulk properties for coating applications. Thermally induced condensation polymerization of either non-liquid crystalline diepoxides, which form the liquid crystal phase during the polymerization reaction due to the formation of linear prepolymers, or polymerization of four-ring bis-binaphthyl diepoxides requires very high temperatures [17]. Advantages of networks based upon diepoxides are a high order parameter (S) and birefringence (Δn) of the network compared with the monomer, less polymer shrinkage and good adhesion to substrates. Problems associated with many of these compounds for thin solid film applications are the high T_m, their thermal instability, the high polymerization temperatures, the unsuitability for lithographic patterning and the production of volatile compounds as a result of the chemical crosslinking reaction.

2.2. *Photopolymerization*

Photochemically crosslinking anisotropic monomers allows the polymerization to be carried out isothermally.

This allows a greater degree of control of the properties of the resultant network, e.g. over S, Δn, etc. An added advantage of utilizing photopolymerizable or dimerizable monomers, oligomers or polymers is the ability to structure relatively large surface areas using standard lithography procedures well known from photoresist technology [18].

2.2.1. *Radical photopolymerization*

Photoinduced radical polymerization of monomers such as acrylates, methacrylates, etc. involves the generation of radicals by the photolysis of an initiator such as Igacure (Ciba-Geigy), often by the action of UV light, and subsequent radical polymerization of the monomers present (figure 4). Crosslinking reactions involve the joining together of two or more propagating chains in a termination step. The maximum rate of polymerization is found in the LC state due to the enforced proximity of the reactive groups and increases at higher temperatures until just below the clearing point; it then slows down in the isotropic state. The rate of polymerization decreases considerably over time as high degrees of monomer conversion to crosslinked polymer increase the viscosity significantly. This may become zero due to vitrification of the reaction mixture with considerable amounts of unreacted monomer still remaining (≈20%). Radical photopolymerization to form an anisotropic network, elastomer or gel in the absence of an initiator can be achieved with mesogenic molecules incorporating an electron donor at one end of the molecule and an electron acceptor at the other [19].

2.2.2. *Cationic photopolymerization*

Photoinduced cationic polymerization, e.g. of divinyl ethers, requires relatively complicated procedures for isothermal polymerization such as utilizing a UV sensitive cationic initiator, which is slow compared with radical polymerization [19, 20]. A disadvantage of this procedure is the presence of significant amounts of ionic residues in the resultant polymer.

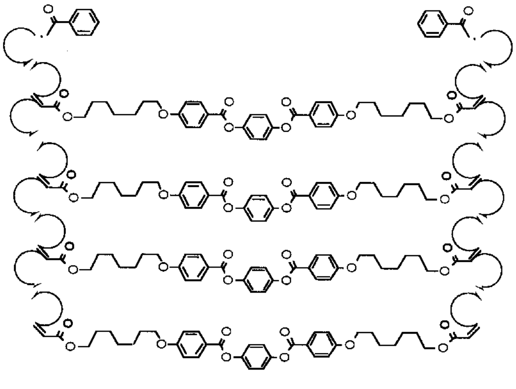


Figure 4. Typical chemical structures and method of radical polymerization of photopolymerizable monomers for anisotropic networks, elastomers and gels.

2.2.3. *Cycloaddition photopolymerization*

Cycloaddition polymerization of monomers, such as cinnamates, involves concerted Diels–Alder reactions between neighbouring carbon–carbon double bonds to form alicyclic systems, such as cyclobutane derivatives. This is the basis of many photoresists for the electronics and LCD manufacturing industries [11, 21].

2.2.4. *Crosslinking reactions of side group polymers*

Side group and/or main chain LCPs incorporating additional reactive groups can be crosslinked to form anisotropic networks [1–3]. Main chain polymers without lateral side groups, but containing photopolymerizable groups incorporated in the main chain, can also be crosslinked in the liquid crystalline state to produce an anisotropic network or elastomer [22].

3. Anisotropic networks

3.1. *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; see figure 1 and the table for typical LC crosslinkable materials. If the monomers are oriented by electric or magnetic fields, orientation layers, etc. in the LC state into unidirectional monodomains before and/or during polymerization, then homogeneous, macroscopically oriented, thin solid films of high mechanical strength, and anisotropic thermal and electrical resistivity can be produced. Anisotropic networks possess a minimal temperature dependence of their physical properties, apart from minor changes due to density changes before decomposition of the network occurs at elevated temperatures. Nematic monomers are generally easier to align and process than smectic monomers due to the lower viscosity of the former. Various nematic monomers with two reactive end groups have been prepared in order to produce components for nematic mixtures at room temperature with a moderate clearing point (table), so that heating the substrate in order to be able to align and photopolymerize the polymer film in the nematic state, before the frequently super-cooled mixtures crystallize, is no longer required. Heating to even higher temperatures is normally necessary for most practical applications, as the viscosity of the nematic state is lowest just below T_c despite the fact that the photoinitiator reduces both parameters, sometimes substantially, depending on the concentration.

3.1.1. *Nematic thermosets*

As the tensile modulus and expansion coefficient in the direction of molecular orientation, i.e. parallel to the director, are often several times greater than those 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 [1–3]. The anisotropic high thermal and low electrical conductivity of such networks is of use in microelectronics as electrically isolating, but thermally conducting casings to conduct away heat generated by the electrical components. This is becoming increasingly important as more components are produced per unit area. They can also be used as insulating layers with low dielectric constants and exceptionally high thermal stability. The greatest potential lies perhaps in their use, in conjunction with light-polymerized, photopatternable (LPP) orientation layers, in hybrid applications (HLPP) as *in situ* optical retarders, interference filters, etc. (see below) [1, 11]. The good rheological properties of liquid crystalline monomers render them particularly advantageous for thermoplastic applications, where high mechanical strength, chemical stability and low expansion coefficients are required. The relatively high cost of anisotropic thermosets, as opposed to standard amorphous thermosets, is often the determining factor in limiting their wider general use.

3.1.2. *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 [1–3, 11, 23, 24], are potentially of great importance in this respect and especially for active matrix, e.g. TFT, TFD, MIM, etc. LCDs, where dust particles or static surface charges produced by the standard alignment procedure of buffing conventional polyimide alignment layers can give rise to mechanical damage and dielectric breakdown. This results in low production yields and high unit costs.

Anisotropic LPP alignment layers produced by illumination with linearly polarized light of the standard photoresist poly(vinyl 4-methoxycinnamate) (PVMC) orient LCs with predetermined azimuthal orientations on a substrate [23]. This induces a preferred unidirectional reorientation of the polymer side groups perpendicular to the electric field vector and produces cyclobutane photoproducts as crosslinks as a result of a non-reversible, photoinduced 2+2 cycloaddition between the cinnamate double bonds. This alignment procedure does not involve a mechanical treatment of the substrate surface and is also compatible with electronic component and LCD production techniques. High resolution photopatterned LC alignment with different azimuthal director orientations can be generated by using appropriate masks and sequential illumination of the LPP layer at different angles in the plane of the substrate with linearly polarized light. As LPP films are optically anisotropic, and therefore birefringent, they could be used to generate photopatterned, high-resolution optical retarders, polarization converters, multidomain pixels for high contrast STNs and interference filters [24]. However, as Δn is low, relatively thick layers would be required. HLPPs solve this problem by combining the orienting properties of LPP layers with the high Δn of nematic liquid crystals. The LPP orienting layer induces a uniform orientation in a nematic mixture of photopolymerizable monomers with two reactive end groups such as those shown in the table. This layer is then polymerized in a reaction initiated by unpolarized UV light and a photoinitiator to create a macroscopically aligned HLPP. The HLPP network layer not only has a much higher Δn, but also the thermal and UV light stability are much higher than observed for LPP layers consisting of crosslinked acrylates [11]. The required optical retardation (δ) can be induced easily, since δ depends directly on the product of Δn and the thickness (d) of the layer, both of which can be varied as required. Many new effects and hybrid LCDs such as combined orientation layers and *in situ* colour filters for STN LCDs are possible using this new technique. The thermal and optical alignment stability of the original PVMC polymer [23] has also been improved by making the precursor cinnamate monomer more like an LC and also increasing T_g of the prepolymerized LCP before crosslinking [11].

These standard LPP orientation layers based on cinnamates only induce a planar alignment, due to the equal probability of inducing opposite inclined tilt angles ($+\theta$ and $-\theta$), or small non-homogeneous pre-tilt angles ($\approx 0{\cdot}3°$) in separate domains. It has recently been reported that almost any value of θ could be obtained by illumination of a new type of LPP containing a coumarin moiety with linearly polarized light at a given angle of incidence to the substrate and not orthogonally [24], as the resultant liquid crystal alignment is parallel to the electric field vector (figure 5). This process can also be used to improve the viewing-angle dependency of super twisted nematic liquid crystal displays (STN-LCDs) by producing multidomain pixels. If these new LPP layers are sufficiently heat and light stable [24], then HLPP layers would not be required as non-contact orientation layers for LCDs.

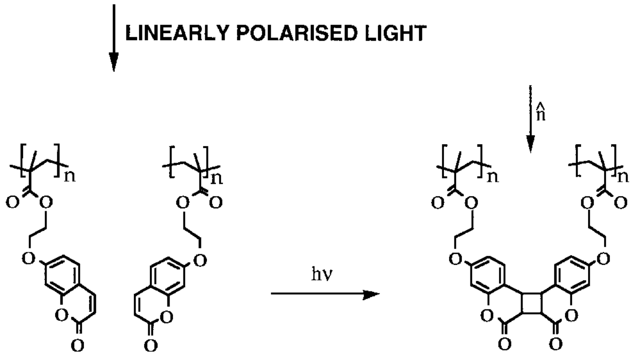


Figure 5. Chemical structures of photopolymerizable coumarin derivatives for LPP alignment layers with non-zero tilt angle.

3.1.3. *Nematic networks as polarizers*

The potential commercial applications of such nematic networks derived from improved monomer mixtures are very diverse. Solid state polarizers can be produced by the crosslinking of macroscopically oriented nematic monomers incorporating an amount of pleochroic dye. Such polarizers can be patterned by the application of an electric field before the orientation is fixed by crosslinking (either thermally or photochemically) [25].

3.2. *Achiral smectic networks*

Polymerization of bifunctional, non-optically active mesogenic monomers in the smectic state [26, 27] gives rise to smectic networks. These anisotropic networks exhibit similar properties to those of the analogous nematic networks, but with an additional layer structure. Nematic networks are generally preferred for practical applications due to the higher degree of processability associated with the lower viscosity of the nematic state.

3.3. *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 [28, 29]. As the circularly polarized light of opposite handedness is transmitted, they can be used either as non-absorbing optical filters or circular polarizers. For symmetrical light incidence and reflection under the angle (α), the central wavelength $\lambda(\alpha)$ of the selective reflection band decreases with increasing angle of incidence according to the Bragg law of reflection [28, 29]. The pitch (p) of the N* layer, as well as its ordinary and extraordinary indices of refraction, (n_o, n_e) are temperature dependent. However, N* networks prepared from a mixture consisting of polymerizable N monomers and an optically active (chiral) dopant, in order to induce the desired value of λ_o, by polymerization of the mixture isothermally to form a solid film, also exhibit a minimal temperature dependence [28]. Such networks can also be prepared by crosslinking side group LCPs, e.g. silicones, incorporating additional polymerizable side groups, e.g. methacrylates, in the Grandjean configuration, obtained for example after shearing between glass substrates covered with an orientation layer [29]. The advantage of using N* networks is the simplicity of preparation of films whose thickness (d) and λ_o can be chosen as required; λ_o exhibits a small residual temperature dependence due to density changes before thermal decomposition of the network (≈140°C). Solid polymer filters can be combined without protective barrier layers to produce compact optical filters of low weight, with high UV and thermal stability. These properties, combined with their ability selectively to reflect instead of absorb infra-red light, render them especially suitable for high light flux/heat exposure applications such as projection displays [29]. Other applications include use as band-pass filters, notch filters, circular polarizers, band reflectors, *in situ* colour filters for STN LCDs and in large aperture light sources [29]. They can also be used to replace one absorbing analyser in LCDs [30]. This leads to either greater brightness or lower battery consumption.

3.4. *Chiral smectic networks*

Macroscopically uniaxially oriented chiral smectic C (SmC*) networks with a uniform directional ordering of the dipoles at the optically active centre have been prepared by two methods. In the first, a monomer mixture consisting of a host mixture exhibiting a smectic C (SmC) phase and an optically active dopant with no reactive groups, i.e. a guest–host system, [31] was simultaneously poled under a very high field strength and polymerized. In the second approach, mixtures of monomers all of which possess two reactive end groups were aligned in an electric field and then fixed in position by photopolymerization [32]. Although both approaches produce solid films in which the dipolar order is fixed, the latter approach produces networks with a higher degree of stability (figure 6). The networks polymerized in the SmC* phase are transparent and exhibit a higher Δn than the networks polymerized in the N* phase due to the higher value of S. The temperature dependence of these properties is as usual much lower than that of the precursor low molar mass monomer mixture.

3.4.1. *Chiral smectic networks as piezoelectric and pyroelectric sensors*

Networks formed from tilted chiral smectic phases can exhibit piezoelectric, pyroelectric and ferroelectric

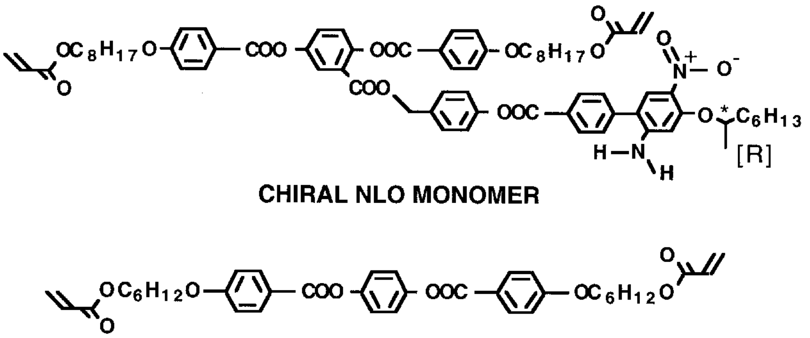


Figure 6. Chemical structures of the photopolymerizable monomers of a binary mixture used to prepare a ferroelectric SmC* network for SHG and waveguiding.

properties [31, 32]. This is due to the macroscopic dipolar ordering of the dipoles responsible for the spontaneous polarization (P_S) in the layer structure, which exhibits C_2 symmetry. The piezoelectric coefficient is strongly dependent on the direction, parallel and perpendicular to the molecular orientation of the applied strain, and a difference up to a factor of 2 was found. However, the high degree of mobility of the dissolved chiral dopant primarily responsible for the piezoelectric effects in guest–host networks led to rather fast relaxation times [31]. Additionally the high crosslinking density of SmC* networks produced in this fashion leads to solid materials. They are less sensitive than comparable elastomers (§ 4) and require a greater mechanical force to generate a comparable piezoelectric signal. Pyroelectric and piezoelectric devices based on organic materials have great potential to replace ceramics in many applications, especially sensors.

3.4.2. *Chiral smectic networks for second harmonic generation*

Macroscopically oriented chiral smectic C networks made from compounds with a transverse chromophore axis with respect to the optic axis, such as those shown in figure 6, exhibit NLO properties due to the noncentrosymmetrical polar ordering. They can be used as waveguides or as frequency doublers, e.g. in second harmonic generation (SHG) to produce blue/green laser light. Their temporal stability is much higher than that of analogous low molar mass ferroelectric SmC* compounds as the dipolar order is fixed in the anisotropic network (figure 7). A related approach involves the use of ferroelectric low molar mass materials also stabilized in a glassy state [33].

3.5. *Columnar networks: as photoconductors*

Columnar liquid crystals (discotics) are becoming of increasing interest as organic molecular wires and especially as photoconductors for Xerography and laser printer applications [34, 35]. This is due to the high charge mobility found for certain columnar liquid crystals, especially with triphenylene cores, on illumination with a defined wavelength of light and is sometimes up to two orders of magnitude higher than that observed for the amorphous organic polymers currently used commercially in the majority of photocopiers and laser printers, e.g. polyvinylcarbazole, PVK [34, 35]. Although stabilization of the otherwise fluid columnar photoconducting layer can be achieved by polymerizing monomers in the columnar liquid crystalline state to produce a stabilized, three-dimensional lattice as a thin solid film, the charge mobility decreases by more than an order of magnitude as the result of molecular reorganization within the bulk in order to allow polymerization of neighbouring molecules to take place.

3.6. *Non-LC anisotropic networks*

3.6.1. *Non-LC anisotropic networks for non-linear optics*

Organic non-linear optical (NLO) materials are of interest for applications in integrated electro-optic systems, which can be used to influence the spatial, temporal and frequency properties of propagating light beams [36–38]. Potential applications include waveguides, electro-optical modulators (EOMs) or switches for digital fibre-optic based telecommunication systems, frequency doublers for digital data storage systems and tunable filters for wavelength division multiplexing. These materials exhibit non-linear polarization of electron density and a non-linear response under the influence of magnetic, electric or electromagnetic fields.

The first attempts to produce second order organic NLO polymers, e.g. for frequency doubling, involved guest–host polymers with a chromophore simply dissolved in an amorphous polymer stabilized below the glass transition temperature (T_g). However, such systems suffer from low solubility of the chromophore in the polymer matrix leading to phase separation and/or low NLO efficiency. Side group chain copolymers incorporating liquid crystal and dye molecules chemically bound to the polymer backbone enable higher chromophore

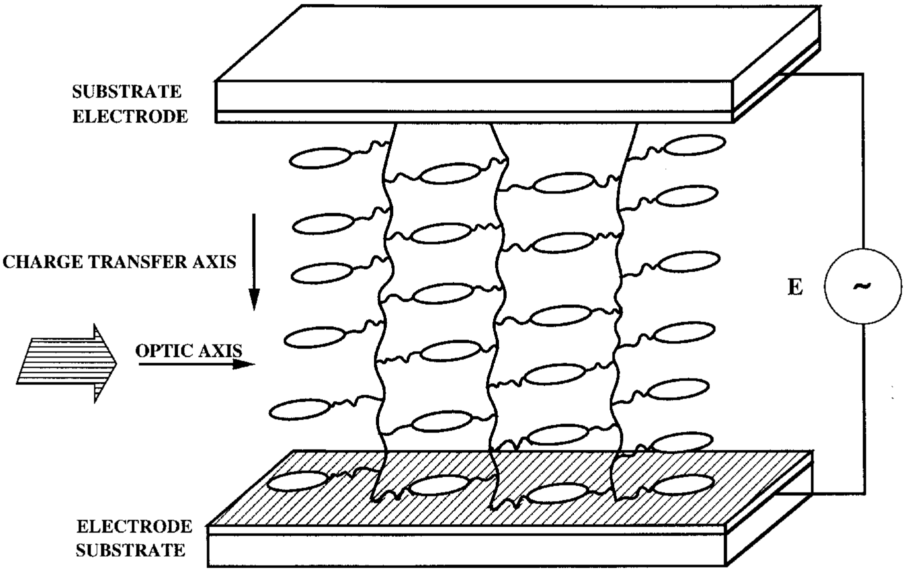


Figure 7. A simple schematic representation of a non-linear optical waveguide incorporating an aligned three-dimensional ferroelectric SmC* network between two electrodes.

concentrations and improved dipolar alignment, but the signal decay times even at room temperature are often still too short for device application due to relaxation of the polymer backbone into holes below T_g. However, despite this, organic EOMs and waveguides incorporating side group chain liquid crystal polymers are available commercially. Improved temporal stability of the dipolar alignment was achieved using poled networks of host amorphous crosslinked polymer and guest NLO chromophores. However, the chromophore concentration, and therefore the signal intensity, was too low for efficient operation. Further improvements were achieved with anisotropic networks derived from side chain polymers incorporating photocrosslinkable, chemically bound NLO chromophores and side chains [39, 40]. These can be ordered using high field strength Corona poling and the resultant dipolar ordering achieved fixed by polymerization. However, the signal intensity still decreased substantially on removal of the orienting electric field, although the remaining signal appeared to be temporally stable. It has been claimed that sufficient thermal stability can also be achieved using poled guest–host systems incorporating chromophores dissolved in amorphous polyimides [41] or side group LCPs with a polyimide backbone [42] with a very high T_g.

Intrinsic properties to be optimized still include the long term stability of the NLO material with respect to signal decay due to relaxation or photobleaching over the operational lifetime of a practical device. The wavelength of chromophore absorption is of critical importance, as most chromophores absorb in the visible region close to the blue or green light produced by SHG. The energy transmitted by an NLO material in a waveguide, for example, is considerable ($\approx 10\,\mathrm{kW\,cm^{-2}}$) and can result in irreversible optical damage. Switching voltages should also be low in order to be compatible with semiconductor power supplies, and high purity is required to minimize optical loss.

3.6.2. *Vesicles*

Polymerized micelles and vesicles are a special case in that a self-assembled, three-dimensional ordered structure is formed in solution and then fixed by polymerization [43, 44]. However, the mono- and bi-layers of such fluid structures are often liquid crystalline in nature, although the bulk mixture may be non-liquid crystalline, transparent, or milky due to light scattering. The solvent is enclosed within the spherical or cylindrical structure [43, 44]. Polymer-stabilized vesicles and micelles are of interest as stable drug delivery systems.

4. Anisotropic elastomers

4.1. *Nematic/smectic elastomers*

The first reported LC elastomers were produced by radical polymerization, initiated with UV light, of binary LC mixtures of an LC monoreactive acrylate and various amounts (0–30%) of a bireactive acrylate crosslinking agent or of tertiary LC mixtures incorporating an additional cholesteryl component. As the composition of an LC elastomer is essentially that of the constituent monomers, many different LC elastomers have been prepared in essentially the same way using statistical copolymerization from LC monomers [6, 7]. They can also be prepared by statistical addition reactions using mixtures of monoalkenes and dialkenes and reactive preformed polymer backbones like siloxanes [6], and copolymerization of acrylates or methacrylates to form a side group polymer incorporating reactive groups such as a hydroxy group, which are then crosslinked by addition of a bifunctional compound such as a di-isocyanate [7]. As most LC elastomers must generally be deformable at room temperature, siloxane backbones are most often preferred, as these are associated with low T_g, often at or below room temperature. An added attraction of siloxane elastomer synthesis is the commercial availability of well characterized reactive polymer chains with reproducible polydispersity. However, care must be taken to ensure complete reaction at all the reaction sites on the siloxane backbone. Slightly crosslinked main chain LCP elastomers and combined main and side group LCP elastomers are also known. A large variety of LC elastomers including acrylates, methacrylates, vinyl ethers, cinnamates and mixed systems has been prepared by free radical, group-transfer, anionic and cationic polymerization reactions. 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 [6]. Another approach is to crosslink a monomer mixture slowly in the N phase under a strong external field before the gel point is reached.

4.2. *Chiral nematic elastomers*

Piezoelectricity has been observed for chiral nematic elastomers and, although apparently rationalized erroneously at first [45], explained theoretically [46]. Although less common than the analogous SmC* elastomers, they can be utilized as described below for SmC* elastomers.

4.3. *Chiral smectic elastomers*

Smectic elastomers incorporating optically active moieties are of special interest due to their noncentrosymmetrical layered structure. Elastomers exhibiting piezoelectric, pyroelectric and ferroelectric properties can be created by crosslinking of side group polymers possessing a ferroelectric SmC* phase [6, 7].

4.3.1. *Chiral smectic elastomers for piezoelectric/pyroelectric sensors*

LC elastomers possessing a SmC* structure are interesting as potential piezoelectric and pyroelectric sensors. As the network state of order at crosslinking is stabilized, the resultant elastomer is capable of stress-optical memory effects. The mechanical deformation of the orientation of the elastomer side groups is similar to that exerted by electric or magnetic fields on low molar mass LCs. Such elastomers also exhibit NLO properties [6, 7]. Analogously to LC networks, the director orientation in the LC state of the LSCEs exhibits almost no dependence on temperature, electric or magnetic fields.

4.3.2. *Chiral smectic elastomers for surface stabilized ferroelectric liquid crystal displays SSFLCDs*

Long response times are observed for SSFLCDs and very high voltages are required for normal ferroelectric switching between the two bistable configurations of SmC* elastomers due to the extremely high viscosity caused by crosslinking. Hence, they are of limited interest for commercial SSFLCDs [6, 7].

4.4. *Columnar elastomers: as photoconductors*

Columnar LC elastomers are of increasing interest as organic conductors. Their columnar phase structure is similar to the column structure of polycyclic aromatics in the crystalline state [47, 48]. The major problem still to be overcome for practical applications is the production of uniformly oriented columnar phases without defects. Columnar LSCEs offer the prospect of achieving this goal by utilizing mechanical forces to overcome the high viscosity of the non-crosslinked side group polymer precursors, to induce uniform director alignment. This structure can then be fixed by crosslinking.

4.5. *Amphiphilic elastomers*

Amphiphilic LC elastomers are generally prepared by crosslinking a lyotropic mixture of an amphiphilic polymer swollen with a solvent, e.g. water [49]. Amphiphilic liquid single crystal elastomers are prepared by crosslinking the lyotropic prepolymer mixture in a mechanically deformed state. Such elastomers may be of interest as hydrogel, water-retaining eye lenses or as permeable membranes with properties similar to that of natural tissue.

5. Anisotropic gels

5.1. *Nematic gels: use in LCDs*

Nematic gels are normally prepared by the polymerization of nematic mixtures of achiral low molar mass nematic liquid crystals and limited amounts of reactive bifunctional crosslinkers [9, 50]. An alternative method is to swell a preformed anisotropic elastomer with achiral low molar mass nematic liquid crystals [51].

As in low molar mass LC configurations, the long-range orientation of a nematic gel can be uniaxially planar, homeotropic or twisted through a well-defined angle [9, 50]. This allows LCDs to be produced using nematic gels incorporating nematic LCs of negative or positive dielectric anisotropy ($\Delta\varepsilon$). However, since polarizers are normally required for these LCDs, linearly polarized light is generally required in order to obtain a sufficiently high contrast. The presence of the solid, three-dimensional network also results in very high threshold voltages up to a factor of 10 higher than for normal LCDs and response times are also long. Possible applications include uses as electrically controllable polarizers, orientation layers for LCDs and with dye molecules guest–host LCDs with grey scale, where fast response times are not required.

5.2. *Smectic gels*

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 (tetraethylene glycol dimethylacrylate) [52]. The applications of smectic gels differ from those of nematic gels due to the smectic layer structure.

5.3. *Chiral nematic gels*

The addition of optically active dopants to low molar mass nematic mixtures with bireactive crosslinkers converts them to chiral nematic mixtures of monomers and non-reactive nematic LCs as precursors to chiral nematic gels [9].

5.3.1. *Chiral nematic gels for filters*

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 (§ 3). The wavelength of light (λ_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 [9]. However, a relatively high network concentration (>30 wt %) is required in order to avoid the creation of two separate weakly or strongly bound populations of chiral domains resulting in two distinct reflection peaks. This has the disadvantage of increasing the operating voltages, which are already relatively high, as the gel resembles a solid. As λ_o is determined initially by the pitch, p and Δn of the gel, it can be chosen as required by altering the composition of the N* mixture to be polymerized.

5.3.2. *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 a type of LCD [53–55]. Such LCDs are particularly interesting at the moment, because they are reflective. Therefore, they can be brighter than analogous TN-LCDs due to the absence of absorbing polarizers. Additionally high-energy-consuming backlighting is no longer necessary. However, such LCDs also possess a range of disadvantageous properties for commercial applications, which will have to be addressed and resolved in order to permit broader market acceptance and penetration. 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 (≈40–70 V), as p is small in order that visible light be reflected, and they are also dependent to some extent on the polymerization conditions of the gel.

5.4. *Chiral smectic gels: use in ferroelectric liquid crystal displays (FLCDs)*

The mechanical shock instability of SSFLCDs, in which the molecular orientation is determined by alignment layers on the cell walls, is a major factor hindering their successful commercialization. These problems can be alleviated by using ferroelectric gels, in which the orientation of the non-attached molecules is determined by the network and not by surface forces (figure 8) [56, 57]. Switching times and operating voltages are considerably greater than those observed for the same mixtures in SSFLCDs and increase with increasing network concentration. The P_s, effective Δn and extinction angles are also considerably lower at high network concentrations due to strong interactions between the free molecules and the network. This leads to the formation of domains depending on the proximity of the molecules to the network. This has the advantage of allowing actively addressed [57] or passively addressed [56] anisotropic network stabilized ferroelectric liquid crystal displays (ANSFLCDs) to exhibit continuous switching over a range of voltages in thick cells ($d \approx 8$ μm) without interference colours. In contrast to SSFLCDs, the switching behaviour of ANSFLCDs allows full-colour LCDs to be produced by the use of grey scale.

5.5. *Amphiphilic gels*

Liquid crystalline lyotropic gels were first prepared by the polymerization of a mixture of 11-sodium sterylundecanoate and water with divinyl benzoate as the crosslinker [58]. The properties of amphiphilic gels depend, of course, on the concentration and retention of the solvent.

6. Reversible anisotropic networks

The ability to crosslink and then reverse the crosslinking mechanism controllably should lead to a different spectrum of physical properties for reversible networks than that of the analogous covalently bonded networks. Although one of the first examples of such a network

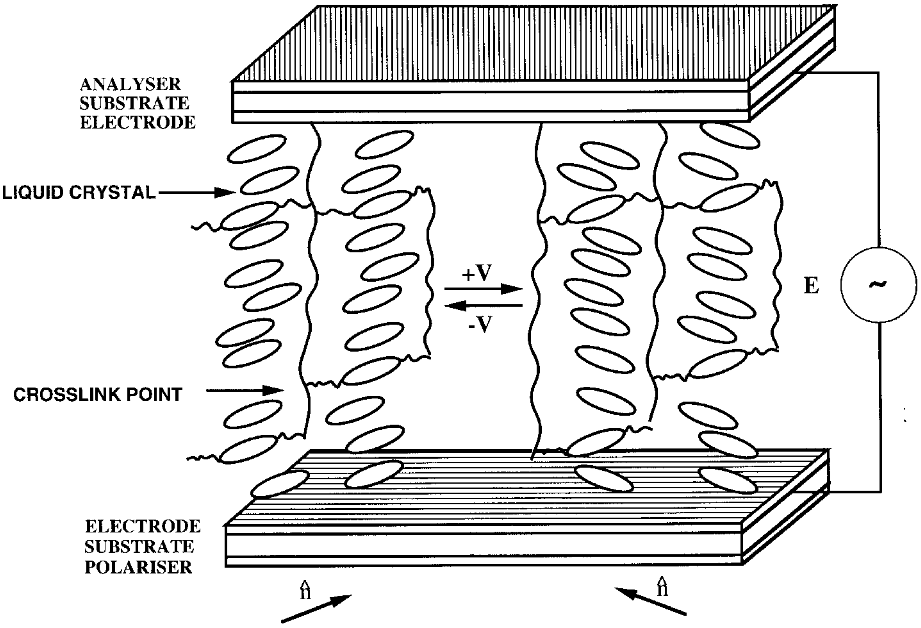


Figure 8. A simple schematic representation of an ANSFLCD.

was produced by polymerization of hydrogen bonded LC benzoic acids incorporating polymerizable groups, such anisotropic networks are normally cast from mixtures of low molar mass LCs with one or two ionic or ionizable terminal groups or their salts as crosslinkers and preformed polymers like poly(acrylic acid), poly(vinyl pyridine), etc. The network is formed as the result of attraction between the appropriate functional groups *via* hydrogen bonding or ion–ion interactions. The liquid crystalline properties are then observed on removal of the solvent during curing. These non-covalently bonded reversible networks are an interesting new area with many potential applications such as in information storage, as orientation layers and as polymer blends.

6.1. *Hydrogen bonded reversible networks*

Most reversible networks make use of the non-covalent hydrogen bond [59, 60] as the reversible crosslinking unit and the first thermotropic systems of this type were based on hydrogen bond crosslinks between side group polymers of benzoic acids with long spacers. Related reversible networks are formed from either side group or main chain LCPs with carboxylic acid groups and nitrogen-containing crosslinking molecules such as stilbazole or bipyridyl derivatives. Anisotropic networks consisting of various amounts of a poly(methacrylate) backbone, a stilbazole side group and a bipyridyl crosslinking unit can be mesomorphic (SmA and SmB) across the complete phase diagram, although T_g increases with the concentration of the bipyridyl crosslinking unit, as expected.

6.2. *Metal co-ordinated reversible networks*

The co-ordination of mesogenic ligands with metals as crosslinking units has also been used to prepare non-covalently bonded anisotropic networks [61]. The 4-cyano-4′-biphenyl side groups of poly(acrylic esters) have been found to co-ordinate with platinum in ligand exchange reactions with dichlorobis(benzonitrile) platinum(II) to produce a non-covalently bonded anisotropic network. Although a smectic phase is observed at low platinum concentrations, a nematic phase is then observed as the concentration is further increased. At a critical value, the crosslinking density is so high that LC properties can no longer be observed. These anisotropic networks are formed in solution and then cast as thin solid films, e.g. by spin coating and subsequent solvent evaporation during curing. This can result in impurities formed in the ligand exchange reactions being retained in the resultant network.

6.3. *Chemically bonded reversible networks*

The temperature dependent Diels–Alder reaction and the thermal dissociation of the resultant product at higher temperatures to reform the original diene and dienophile can give rise to chemically bonded reversible networks [62]. Solutions of an LC methacrylate copolymer incorporating a diene in one of the side groups and a small amount of a low molar mass component incorporating two dienophile groups in an appropriate solvent can be applied to a suitable substrate and then thermally crosslinked in a Diels–Alder reaction during curing. A homogeneous LC film is obtained by action of an orientation layer on the substrate or by drawing below T_c. This crosslinking reaction can be reversed by increasing the temperature. Possible applications of such polymer films include, for example, optical retarders, antireflection screens and, with suitable dichroic dyes, polarizers.

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