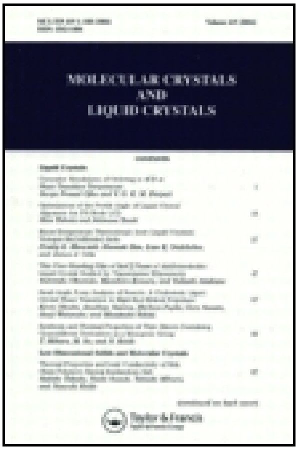

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Ferroelectric Liquid Crystalline Materials: Hosts, Dopants and Gels for Display Applications

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Ferroelectric Liquid Crystalline Materials: Hosts, Dopants and Gels for Display Applications

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Over the last ten years, the study and exploitation of chirality in liquid crystal systems has been one of the fastest, and largest, growth areas in the research of self-organising fluids, leading to technological applications in the area of display devices. In particular ferroelectric liquid crystals have been shown to be capable of being used as fast-switching light-valves. Such devices could form the basis of the next generation of flat panel liquid crystal displays, projection devices, and 3D imaging systems.

Keywords: ferroelectrics; gels; hosts; dopants; terphenyls

INTRODUCTION

Liquid crystal phases are a unique collection of states of matter; apart from their obvious scientific curiosity, they possess many attributes that can be utilised in device technology making them quintessential *organo-molecular-electronic* systems. Moreover, the time from discovery to the development of a device prototype and its introduction into the market place gets shorter with each new advance, thereby making liquid crystals one of the most rapidly exploited areas of research in the electronics industry. In this context the study of chirality, and its subsequent exploitation, in liquid crystal systems has been one of the fastest, and largest, growth areas in the research of self-organising fluids. Indeed over the last decade, the majority of the research in the field of liquid crystals has been concerned with materials that possess some degree of molecular chirality, leading to technological applications in the area of display devices such as the super-twist LCD's used in lap-top computers, surface stabilised ferroelectric LCD's [1] used in spatial light modulators, antiferroelectricliquid crystal displays (AFLCDs) used in full-colour video-frame ratedevices, and optical networking, where polymeric versions are being evaluated for use in wave guides. Ferroelectricity in smectic liquid crystals, in particular, has proven to be one of the most exciting topics of research in the development of large area and projection displays suitable for high definition applications.

FERROELECTRIC HOST MATERIALS

1. Requirements of Ferroelectric Liquid Crystals for Displays

Great interest has been shown in the properties of ferroelectric liquid crystals because the molecules in such mesophases can be reoriented (switched) rapidly by small electric fields. In thin cells where the helix is unwound response times can be as low as a few microseconds (two to three orders of magnitude faster than a conventional nematic phase). Moreover, the poled optical states generated in such devices can have inherent bistability [1]. These properties made ferroelectric liquid crystals candidates for exploitation in large area display devices, spatial light modulators, and linear arrays [2]. The response time is approximated to be proportional to the viscosity of the material, but inversely proportional to the polarization multiplied by the electric field, as shown below [3].

$$\tau_n \propto \gamma \sin^2\theta / P_s E$$

Thus, the switching speed can be increased by reducing the viscosity or by raising the polarization, with shorter switching times being desirable so that large area displays can be addressed at video frame rates.

Initially, researchers attempted to create fast switching chiral materials for displays via simply increasing the polarization by in turn increasing the polarity associated with the asymmetric centre(s) in the liquid crystal molecules themselves [4]. However, this approach leads to the problem of a build up of large internal fields in such devices, thereby making polarization reversal difficult. Thus, the contemporary way to alleviate this effect is to produce a low viscosity non-ferroelectric smectic C host mixture and to add a high polarization dopant to it in order to produce a low viscosity, low polarization mixture. Consequently, the additive need not be (and usually is not) a liquid crystal. This change in emphasis on material development has led to somewhat of a reduction in the variety and number of novel high polarization ferroelectric liquid crystals being synthesised.

The use of doped smectic C mixtures for devices also allows us to control phase type and transition temperatures. Thus, mixtures possessing a chiral nematic-smectic A*-smectic C* phase sequence can be produced with suitable temperature profiles where the helical phases could be engineered to have long helical pitches. Long helical pitches and a N*-SmA*-SmC* phase sequence are required in order to generate, during cell fabrication, an aligned ferroelectric liquid crystal phase over a large area.

It was also found that the switched bistable states produced in the switching process in ferroelectric surface stabilised displays were subject to relaxation once the electric field was removed. Thus, AC fields were used to augment the DC bias and to maintain fully switched states. In addition AC fields were found to aid multiplexing addressing schemes for such devices, leading to the creation of well-known addressing schemes such as the Joers-Alvey τV_{min} approach [5]. This addressing technique can be better implemented for materials that have a large dielectric biaxiality and a low spontaneous polarization. As the achiral and chiral smectic C and C* phases are biaxial the dielectric permittivities perpendicular to the director are different for directions parallel and perpendicular to the plane of the tilt. The three permittivities are given as follows:

ε_3 - corresponds to the permittivity parallel to the long axis of the molecule,

ε_2 - corresponds to the permittivity in the direction parallel to the polarization (Ps), and

ε_1 - corresponds to the permittivity perpendicular to both ε_2 and ε_3.

Thus the dielectric anisotropy is given by

$$\Delta\varepsilon = \varepsilon_{\parallel} - \varepsilon_{\perp} \approx \varepsilon_3 - \varepsilon_1$$

and the biaxiality by

$$\delta\varepsilon = \varepsilon_2 - \varepsilon_1.$$

Increasing the dielectric biaxiality was found to improve performance in devices having C2 chevron geometry [6] as follows,

$$\delta\varepsilon = 3/2(\varepsilon_{\perp} - n_o^2).c$$

where c is the biaxial order parameter describing the degree of hindrance of rotation of the transverse molecular dipole about the molecular long axis. Thus, increasing the lateral molecular dipole has the effect of increasing the dielectric biaxiality.

2. The Design of Host Materials for Ferroelectric Liquid Crystal Mixtures

The chemical features required in the design of molecular structures of ferroelectric hosts and dopants have been qualitatively recognised and to a lesser extent quantitatively understood. It is difficult to fully quantify the effects of molecular design on viscosity, tilt angle, mesophase temperature range, and dielectric biaxiality because of the complex interplay between dipolar interactions, steric hindrance and molecular dynamics. Nevertheless, we have had considerable success in modelling these interactions and relating them to experimental results obtained through the synthesis and evaluation of designer molecules. This work allows us some predictive capacity in the design of novel ferroelectric materials [6,7].

For example, we found that the transverse polarity and hence the dielectric biaxiality of smectic compounds can be increased by the incorporation of lateral fluorosubstituents in the aromatic region of the core of a material. In addition, the incorporation of fluorosubstituents has the effect of suppressing ordered smectic phases and lowering the melting point. Figure 1 shows how lateral fluoro-substitution affects the liquid crystal properties of alkyl-alkoxy substituted terphenyls.

It can be seen from figure 1 that the use of two fluorosubstituents in terphenyls instead of one has the effect of suppressing ordered smectic and soft crystal phases, eg, SmI and G, and enhancing the temperature range of the smectic C phase. Using this molecular design technique, a wide range of substituted difluoroterphenyls have been prepared [8] and used as components in achiral host mixtures for applications in display devices. It is interesting to correlate the physical properties of dialkyl- and alkoxy-alkyl-substituted difluoroterphenyls with the positions of the fluorosubstituents. Figure 2 shows a number of examples of difluoroterphenyls where the two fluorosubstituents are positioned on the same phenyl ring. In all of these cases either nematic-smectic-A-smectic-C, or nematic-smectic-C phase sequences are observed. Where the fluorosubstituents are located in adjacent rings nematic phases are found. The largest negative values of the dielectric anisotropy were found when the two fluorosubstituents are positioned in a terminal ring adjacent to a terminal alkoxy chain. When the two fluorosubstituents are positioned on the same side of the middle ring the materials have lower viscosities. The birefringences, however, were found to relatively high and constant across the series of compounds. The relatively high birefringences make these materials suitable for applications in cells where the cell gap spacing is approximately 1-2 μm. However, for reflective mode devices the values are a little on the high side.

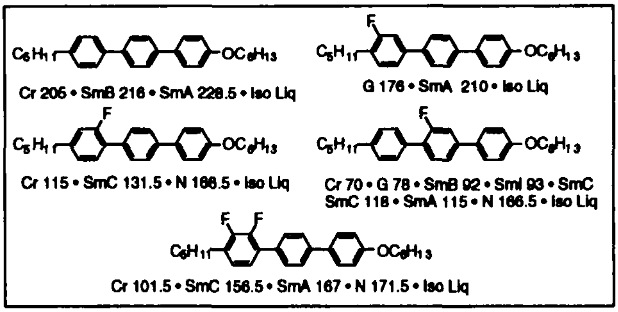


FIGURE 1 Effect of fluoro-substitution on mesomorphic properties of terphenyls.

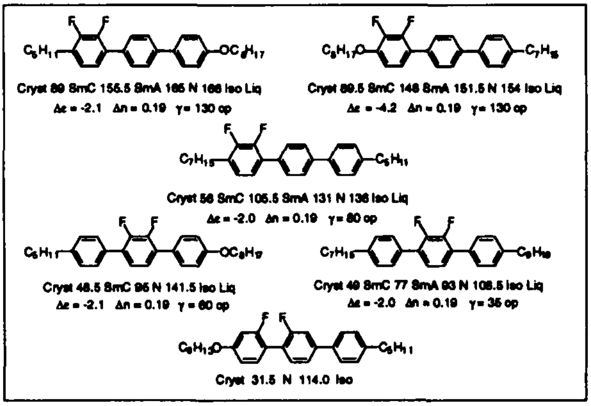


FIGURE 2 The effect of the position of fluoro-substitution on the properties of alkoxy-alkyl- and dialkyl-terphenyls.

Mixtures of difluoroterphenyls thus can be used as the base components in achiral host mixtures to which chiral dopants can be added to give ferroelectric blends [8]. Figure 3 shows a set of typical difluoroterphenyls which when mixed together in equal proportions give smectic C phases that exist over a temperature range of 70 to 80 °C, and figure 4 shows examples of chiral dopants that are used to impart ferroelectric properties to the host mixture.

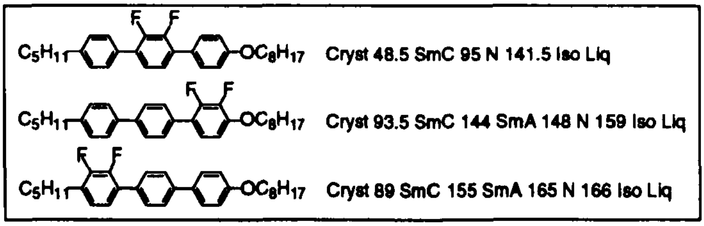


FIGURE 3: Terphenyls used in host mixtures.

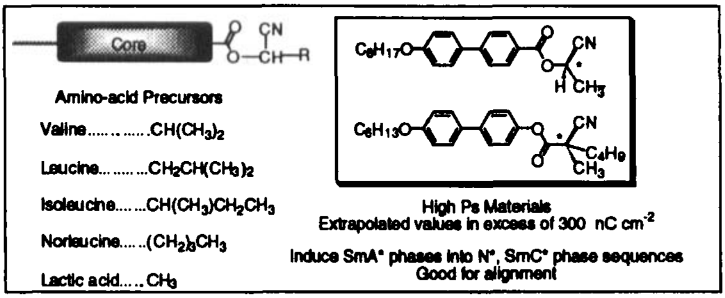
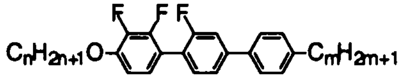


FIGURE 4 Dopants derived from amino acids that can be used with terphenyl hosts to give fast switching ferroelectric mixtures.

As noted, chiral dopants are added to the achiral host in order to generate a ferroelectric phase. Interestingly, the chiral dopant does not have to be liquid crystalline, but instead it can be designed to give a large spontaneous polarization, and even in some cases to induce phase transitions and phase types into hosts, eg, a smectic A* phase, that may not have a suitable phase sequence. The chiral dopants shown in figure 4 are designed to do this; they induce high spontaneous polarizations at low concentrations in achiral hosts, and they are capable of inducing smectic A* phases in hosts that exhibit only smectic C and nematic phases.

The technique of adding chiral dopants to host achiral mixtures to induce ferroelectric properties can be extended to enhancing the dielectric biaxiality through the addition of materials that have large transverse dipole moments. Trifluoro-substituted terphenyls have thus been developed in order to be used as additives for increasing the dielectric biaxiality. Moreover, these materials can also be designed to exhibit liquid crystal phases, and their addition to ferroelectric mixtures can be made with little depression in respect to the Curie point. Table 1 lists a variety of examples of substituted trifluoroterphenyls [9]. The fact that these materials improve on the negative dielectric biaxialities of mixtures of difluoroterphenyls suggests that the fluoro-substituents in adjacent phenyl rings spend an appreciable amount of time aligned with one another.

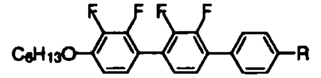


n	m	Cryst		SmC		SmA		N		Iso
4	9	•	57.7	•	87.0	•	89.1	•	112.9	•
6	5	•	43.8	•	(38.1)	-		•	112.3	•
6	7	•	40.1	•	75.7	-		•	111.8	•
6	9	•	47.9	•	91.5	-		•	109.6	•
6	11	•	51.2	•	95.2	•	98.6	•	106.2	•
8	5	•	47.3	•	50.2	-		•	110.3	•
8	7	•	48.0	•	81.0	-		•	108.8	•
8	9	•	55.4	•	95.0	-		•	107.3	•
10	5	•	56.1	•	(52.1)	-		•	102.1	•
10	7	•	56.0	•	83.2	-		•	104.5	•
10	9	•	59.6	•	95.9	-		•	104.4	•

TABLE 1 Transition temperatures for 4-alkoxy-4"-alkyl-2,2',3-trifluoroterphenyls.

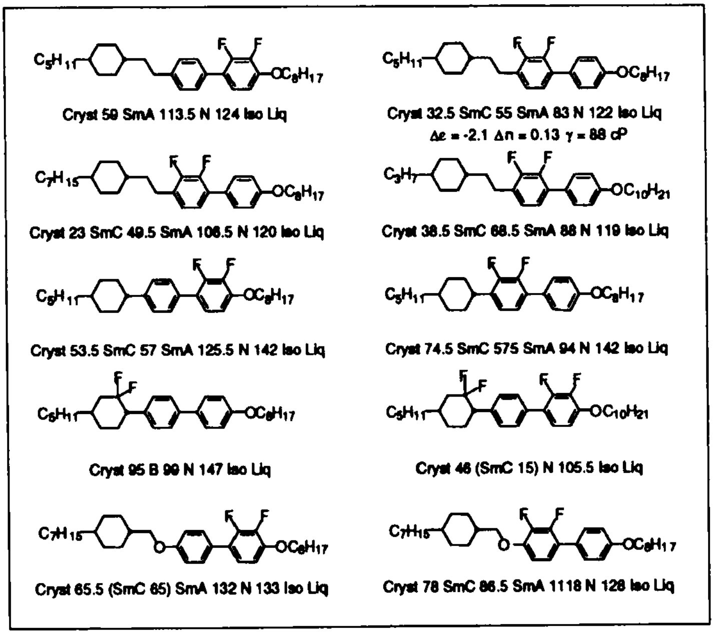
The negative dielectric biaxiality can be improved further by increasing the number of fluorosubstituents to four. Figure 5 lists a number of tetrafluoroterphenyls. It can be seen from the results obtained on the mesomorphic properties of these materials that the transition temperatures to the smectic C phase are lower with respect to the di- and tri-fluoroterphenyls, and that no smectic A phases are observed. Thus these materials are of limited value in ferroelectric mixtures as they can detrimentally affect the Curie point.

Low birefringence host materials are more difficult to design and synthesise because in order to achieve a lower birefringence it is usual to introduce aliphatic moieties, in particular carbocyclic rings, into the central "rigid" cores of the mesogens. The introduction of carbocyclic rings, although beneficial to lowbirefringence, can be fatal for the smectic C phase, and it is common to find that its upper transition temperature is lowered dramatically. Figure 6 shows some examples of potential host materials that possess carbocyclic (cyclohexane) rings in their central rigid cores. The cyclohexyl rings can be either directly connected to the rest of the aromatic core or by a bridging group such as a methyleneoxy or a dimethylene linkage. It can be seen for these examples that the upper transition temperatures for the smectic C phase are much lower than for the terphenyls described previously. Moreover, these materials do not readily mix with conventional terphenyls and thus tend to be used in mixtures with like-materials, ie, other materials that contain carbocyclic rings.



C_5H_{11}	Cryst 61.1 N 107.5 Iso Liq
C_7H_{15}	Cryst 55.1 (SmC 50.7) N 103.1 Iso Liq
C_9H_{19}	Cryst 60.7 SmC 64.5 N 100.7 Iso Liq

FIGURE 5 Transition temperatures for some 4-hexyloxy-4"-alkyl-2,2',3,3'-tetrafluoroterphenyls.



Cryst 59 SmA 113.5 N 124 Iso Liq

Cryst 32.5 SmC 55 SmA 83 N 122 Iso Liq
$\Delta\varepsilon = -2.1$ $\Delta n = 0.13$ $\gamma = 88$ cP

Cryst 23 SmC 49.5 SmA 106.5 N 120 Iso Liq

Cryst 38.5 SmC 68.5 SmA 88 N 119 Iso Liq

Cryst 53.5 SmC 57 SmA 125.5 N 142 Iso Liq

Cryst 74.5 SmC 575 SmA 94 N 142 Iso Liq

Cryst 95 B 99 N 147 Iso Liq

Cryst 46 (SmC 15) N 105.5 Iso Liq

Cryst 65.5 (SmC 65) SmA 132 N 133 Iso Liq

Cryst 78 SmC 86.5 SmA 1118 N 128 Iso Liq

FIGURE 6 Host materials containing carbocyclic rings.

Figure 6 also shows some examples of materials that have two fluorosubstituents attached directly to a cyclohexane ring. However, although this technique is useful in the design and engineering of aromatic systems, it is less useful where alicyclic rings are concerned.

Both materials either have low transition temperatures or else do not exhibit a smectic C phase.

Low birefringence is however a useful property for a material to have particularly for use in reflective mode displays. Thus the compound shown in the top right of figure 6 is interesting is useful because it has a low meting point, a reasonable smectic C to smectic A phase transition temperature, a low viscosity and a relatively low birefringence in comparison to the terphenyl host materials.

The temperature range of the smectic C phase can be improved, however by introducing heteroatoms into the alicyclic ring. One of the simplest ways to achieve this is through the incorporation of a dioxanyl; ring system. Figure 7 shows examples of dioxanyl host materials that have structures based on the difluoroterphenyl systems. Here one of the rings of the terphenyl core is replaced by a dioxanyl ring. This results in materials possessing reasonable smectic C temperature ranges and upper transition temperatures for the smectic C phase, suitable mesophase sequences for processing purposes, ie, nematic, smectic A, smectic C phase sequences, and low birefringences. Figure 7 gives two examples of dioxanyl derivatives plus an example of a ferroelectric mixture composed of dioxanyl compounds blended with suitable dopants. Of the two dopants that were added, one was employed as a high polarization additive and the other as a pitch compensation material. The temperature of the ferroelectric phase ranged from below room temperature to over 60 °C. The lower part of figure 7 shows the optical properties and the results of switching studies performed on this mixture [10]. The birefringence was found to be similar to that of cyclohexyl materials, and the switching time was in the range of 200 μs for a monostrobe pulse response (at 16 $V\mu m^{-1}$), and a multiplexing response time of 150 ms for a 2-slot JOERS-Alvey multiplexing scheme. Thus the materials, although having low birefringence, are relatively slow in their response to applied electric fields in comparison to the terphenyls. This indicates that their reorientational viscosities are slightly higher than some of the terphenyl mixtures that have been tested and optimised. Nevertheless, these materials show promise as suitable low birefringence hosts in reflective displays and actively addressed devices.

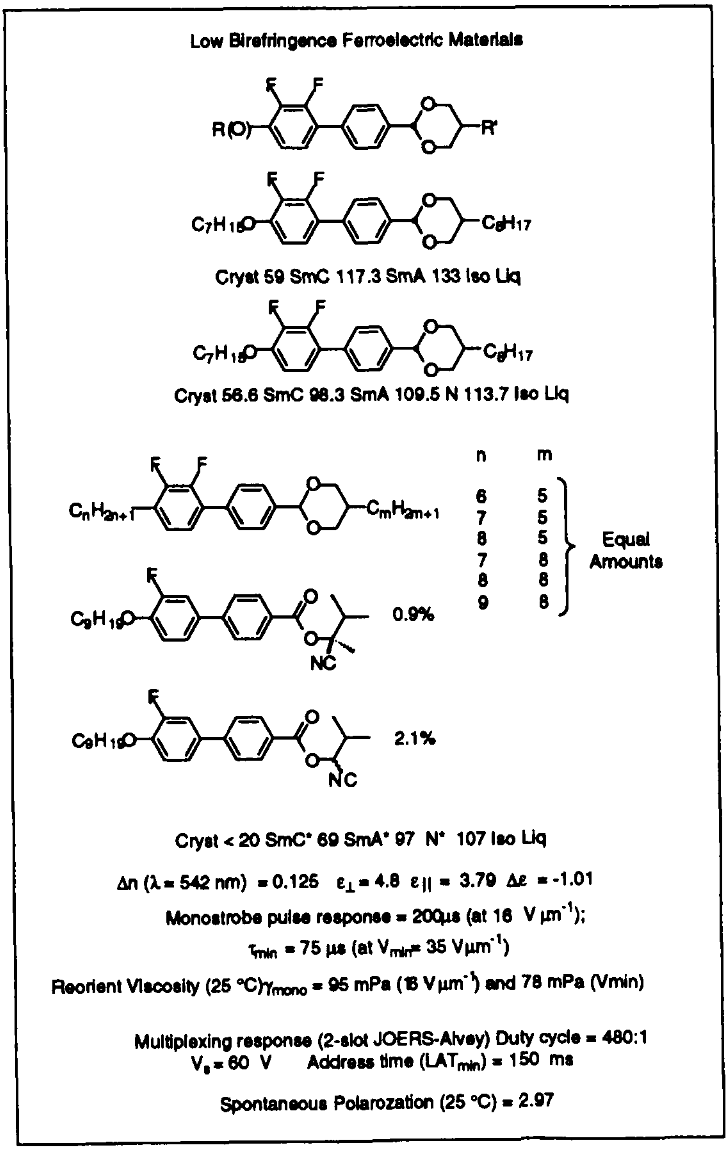
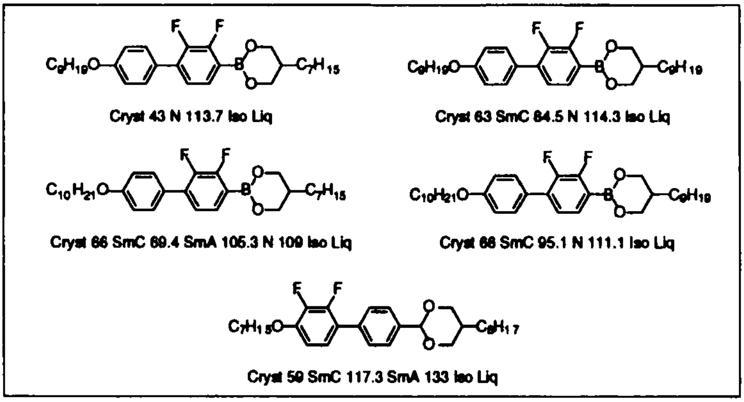


FIGURE 7 Physical properties of ferroelectric liquid crystal mixtures based on dioxanyl derivatives.

Analogous materials with low birefringence are those based on dioxanyl rings systems with a boron atom introduced at the linkage point to the aromatic core. The examples shown in Figure 8 have structures based on terphenyl systems, and exhibit smectic C phases over suitable temperature ranges, and they can be designed to exhibit smectic C, smectic A and nematic phase sequences. Thus these compounds are valuable adjuncts to the diaxanyl and the cyclohexyl host materials.



Cryst 43 N 113.7 Iso Liq

Cryst 63 SmC 84.5 N 114.3 Iso Liq

Cryst 66 SmC 69.4 SmA 105.3 N 109 Iso Liq

Cryst 66 SmC 95.1 N 111.1 Iso Liq

Cryst 59 SmC 117.3 SmA 133 Iso Liq

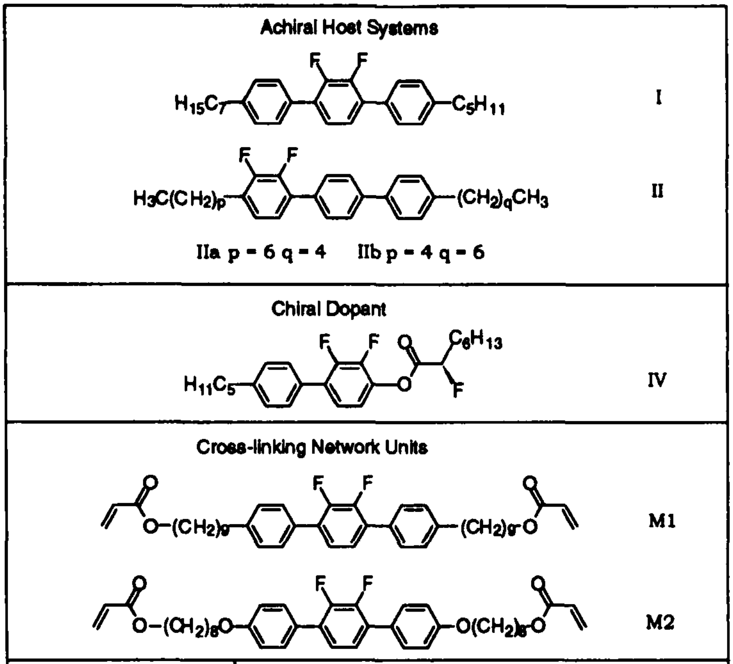
FIGURE 8: Dioxaboranyl host liquid crystals for ferroelectric applications.

FERROELECTRIC GELS BASED ON TERPHENYLS

One of the problems encountered in the development of ferroelectric devices is the shock instability of the smectic C phase. One way to circumvent this problem is through the development of more robust materials, for example polymers and gels. The development of ferroelectric gels is an attractive proposition because the physical nature of the low molar mass mixture is retained while the material is contained within a polymer matrix. Thus it might be expected that gels will reorient relatively quickly but at the same time possess some resistance to shock instability.

We chose to incorporate terphenyl based low molar mass materials into gels because they reorient particularly quickly in applied electric fields. However, rather than encase the low molar mass material in a conventional polymer we decided to incorporate it within a matched polymer framework consisting of a cross-linked polymer network based on a monomer system of comprising terphenyls. Figure

9 shows how the prepolymerisation blend was created. The achiral host system was based on equal proportions the difluoroterphenyls shown, to this was added five percent by weight of the chiral dopant shown. Two different monomer species were added in either 10% or 20% proportions.



Materials	Phase Sequences
SmC-host (I and II)	part. Cryst ~11 SmC 87.2 SmA 97.7 N 122.9-123.5 Iso
Ferro mix (10% IV Host)	part. Cryst ~4.5 SmC* 72 SmA* 81 N* 110-112 Iso
Ferro mix + 10% M1	part. Cryst ~37 SmC* 49.4-50.2 N* 104.7-106.5 Iso
Network + 10% P1	SmC* 69.6 SmA* 77.2 N*
Ferro mix + 10% M2	part. Cryst ~50 SmC* ~52.0 N* 108-110 Iso
Network + 10% P2	SmC* 69.6 SmA* 77.2 N*

FIGURE 9 Materials and phase transitions (°C) for ferroelectric gels.

The mixture was then polymerised at various temperatures, in the various mesophases, and in aligned and unaligned cells. The transition temperatures of the achiral host mixture, the doped low molar mass ferroelectric mixture, the prepolymerisation ferroelectric mixture, and the polymerised system are give in figure 9. Remarkably the gel is more stable than the low molar mass systems with respect to the recrystallisation temperature. Formation of the network prevents nucleation from occurring and so they have much more stable smectic C phases to lower temperatures. Processing of the materials is also much simpler than for a true side-chain polymer system.

The reorientational switching times for the gels were found in some cases to be comparable to their low molar mass hosts. In the example shown in figure 10 the gel switches about half as fast as the low molar mass mixture at room temperature for low electric fields. As the field strength is increased the switching times become comparable, reaching a response time of less than 100 μs, which corresponds to very a fast response for a polymer system.

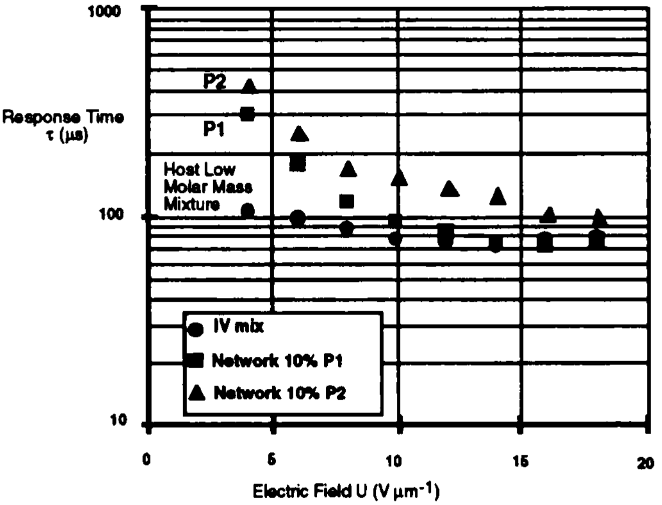


FIGURE 10 Response time as a function of applied field for terphenyl low molar mass and gel systems.

CONCLUSION

Liquid crystal materials based on the fluoro-substituted terphenyl core

can yield ferroelectric systems with wide temperature ranges, low viscosities, short response times, good alignment with suitable processing characteristics, good UV and thermal stabilities, and the possibility of developing fast switching gels with good shock stabilities.

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