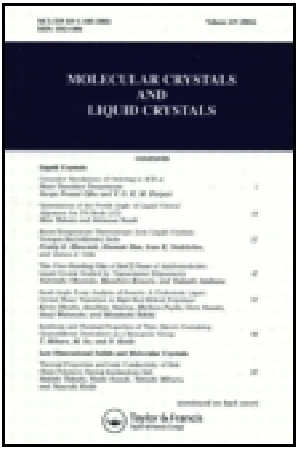


Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

The Development of Materials, Mixtures and Gels for Ferroelectric Displays

Michael Hird [a], John W. Goodby [a] & Kenneth J. Toyne [a]

[a] The Department of Chemistry, The University of Hull, Hull, HU6 7RX, UK

To cite this article: Michael Hird, John W. Goodby & Kenneth J. Toyne (2001): The Development of Materials, Mixtures and Gels for Ferroelectric Displays, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 360:1, 1-15

To link to this article: http://dx.doi.org/10.1080/10587250108025694

Mol. Cryst. and Liq. Cryst., 2001, Vol. 360, pp. 1-15
Reprints available directly from the publisher
Photocopying permitted by license only

Published by license under the
Gordon and Breach Science Publishers imprint.
Printed in Malaysia

The Development of Materials, Mixtures and Gels for Ferroelectric Displays

MICHAEL HIRD, JOHN W. GOODBY and KENNETH J. TOYNE

The Department of Chemistry, The University of Hull, Hull, HU6 7RX, UK

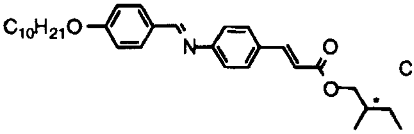
Ferroelectric liquid crystals have developed from the early single component chiral systems, that brought a wealth of fundamental knowledge, to multi-component achiral host systems with optimised physical properties that have a small quantity of chiral dopant added to provide the required ferroelectricity. The research into ferroelectric liquid crystals has been intense, but the technology has not yet proved commercially viable. This paper discusses the developments in ferroelectric materials and focuses on the ferroelectric mixtures generated from *ortho*-difluoroterphenyl host materials and the chiral cyanohydrin dopants which have a high dielectric biaxiality and are suitable for use in τV_{min} devices. Such ferroelectric mixtures have been incorporated into structurally matched diacrylates and polymerised to form a gel network, and the interesting results of these systems are discussed in comparison with the conventional ferroelectric mixtures.

Keywords: liquid crystals; ferroelectrics; displays; materials

INTRODUCTION

In 1974, Meyer[1] used elegant symmetry considerations to show that ferroelectric properties could be exhibited by the tilted, low symmetry, chiral smectic liquid crystal phases (*e.g.*, S_C*). Later in 1980, Clark and Lagerwall[2] invented the surface-stabilised ferroelectric display device. Such display devices offer many advantages over conventional nematic displays, such as much shorter switching times, better viewing angles through in-plane switching, and a much greater level of multiplexability through bistability. The massive commercial potential of this device resulted in intense research into the synthesis and physical properties of new materials, and into device engineering.

In terms of materials, the realisation of ferroelectricity simply requires a non-racemic (scalemic) chiral compound that exhibits the S_C* phase, such as DOBAMBC (1) used by Meyer in his initial experiments.[1] However, for any commercial exploitation, materials would need to be optimised for their mesomorphic and physical properties, and need to be chemically and photochemically stable, inexpensive and easy to synthesise. An ideal ferroelectric material should have a very low melting point with no underlying ordered smectic phases and a wide range S_C* phase to high temperature for a wide operating range, and short range S_A and nematic phases above for good alignment.



1

C 76.0 (S_I* 63.0) S_C* 95.0 S_A* 117.0 I

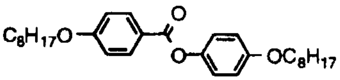
Equation 1 shows that for a short switching time (τ) at minimal applied voltage (E), a low viscosity (γ), a high spontaneous polarisation (P_S), and a low tilt angle (θ) are required. However, for optimum contrast the tilt angle should be 22.5° (equation 2), and the birefringence (Δn) must be matched according to the cell spacing (d). The many requirements can only be achieved by appropriate design and synthesis of compounds with the correct combination of structural units. Many of the requirements are mutually exclusive and so a compromise has to be reached to enable optimum device performance.

$$\tau \propto \frac{\gamma \sin\theta}{P_S\, E} \quad (1) \qquad I = I_0 \sin^2(4\theta) \sin^2\left(\frac{\pi\, d\, \Delta n}{\lambda}\right) \quad (2)$$

Early developments of ferroelectric materials involved the 'all chiral' approach and centred around increasing the P_S to higher levels than DOBAMBC (**1**) which has a very low P_S (4 nC cm^{-2}),[1] this was achieved by using polar groups at the chiral centre and/or longer chains to dampen rotation and/or moving the chiral centre closer to the molecular core; however, this also brought disadvantages, such as increased viscosity and reduced S_C* phase stability. It became well-recognised that it was not possible to achieve the correct combination of mesomorphic behaviour and physical properties from a ferroelectric mixture composed wholly of chiral compounds.

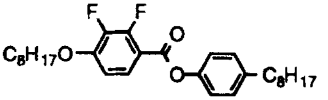
The 'host-dopant' approach to ferroelectric mixtures is far more flexible, and enables the mesomorphic behaviour and physical properties to be tailored through the use of achiral host materials. This approach particularly favours a low viscosity because the branched chiral system with a polar group is only present in small quantity (2 to 10%). There are many achiral materials that exhibit a smectic C phase, but they are far less abundant than nematic liquid crystals.

Molecular tilting requires the presence of a lateral dipole from a polar moiety, and so esters are common smectic C materials (*e.g.*, **2**-**4**),[3,4] but the ester group confers a high viscosity.



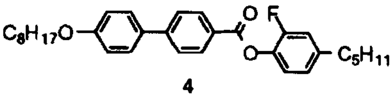
2

C 63.0 S_C 74.0 N 91.0 I



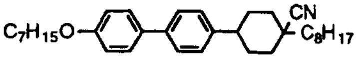
3

C 37.0 S_C 49.0 N 57.0 I



4

C 49.0 S_C 121.0 S_A 128.0 N 164.5 I

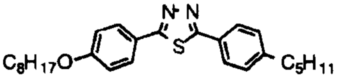


5

C 85.0 (S_F 43.0) S_C 112.0 S_A 148.0 N 151.0 I

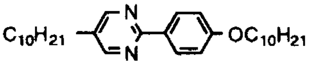
The biphenylcyclohexylcarbonitriles (**5**)[5,6] have an axial nitrile and the alkoxy substituent to drive the smectic C phase, but the nitrile group confers a high viscosity. The use of heteroatoms (*e.g.*, **6**-**8**)[7-10] to generate molecular tilting helps maintain a long, lath-like shape and so minimise viscosity. The phenylpyrimidines in particular make excellent ferroelectric host materials because low melting points and fairly high smectic C phase stability can be generated through just two rings, thus giving a low viscosity, however, the need for a terminal alkoxy chain is somewhat disadvantageous.

Fluoro substituents are highly beneficial to the physical properties of liquid crystals due to their unique combination of small size and high polarity.[11] A lateral fluoro substituent will disrupt molecular packing through a steric effect which ensures low melting points and in some cases eliminates ordered smectic phases, but the disruption is not sufficient to preclude the generation of liquid crystal phases. The high polarity of the fluoro substituent facilitates molecular tilting and hence the smectic C phase is often exhibited over a wide temperature range. The small size of the fluoro substituent also ensures that the viscosity is minimised. Fluoroterphenyls (*e.g.*, **9**) have very low melting points and high smectic C phase stability.[12,13]



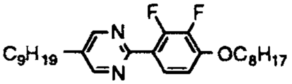
6

C 80.0 S_C 167.0 N 182.0 I



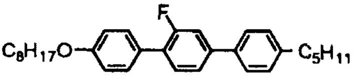
7

C 36.0 S_C 73.0 S_A 77.0 I



8

C 43.0 S_C 54.0 I

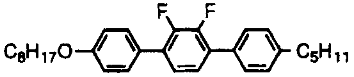


9

C 47.0 (J 40.0) S_I 53.5 S_C 116.5 S_A 130.0 N 155.0 I

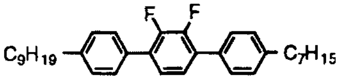
ORTHO-DIFLUOROTERPHENYLS

A wide range of terphenyls has been prepared with two lateral fluoro substituents inherently fixed on the same side of the molecules (*e.g.*, **10**-**13**). Two distinct environments are possible for the fluoro substituents, inner core (*e.g.*, **10** and **11**) and outer edge (*e.g.*, **12** and **13**).[14]



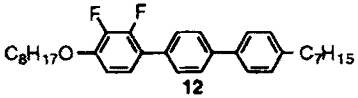
10

C 48.5 S_C 95.0 N 141.5 I



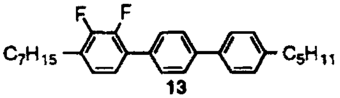
11

C 49.0 S_C 77.0 S_A 93.0 N 108.0 I



12

C 89.5 S_C 148.0 S_A 151.5 N 154.0 I



13

C 56.0 S_C 105.5 S_A 131.0 N 136.0 I

This *ortho*-difluoro arrangement ensures a narrow molecule (no broader than the monofluoroterphenyls) which ensures low melting points and wide smectic C ranges to high temperatures, yet the additional fluoro substituent tends to eliminate the ordered smectic phases. The narrow molecules ensure that viscosity is minimised and in some cases it is lower than the analogous monofluoroterphenyls. The reinforcing effect of the two fluoro substituents also generates a high lateral dipole which confers a high dielectric biaxiality, an important feature in ferroelectric mixtures operating in τV_{min} mode.[15,16] The compounds with the two fluoro substituents in the outer ring and one alkoxy terminal chain have the highest smectic C phase stability, but these also have the highest melting points and the highest viscosity. One of the major advantages of the *ortho*-difluoroterphenyls is that the smectic C phase is exhibited over a wide range to high temperatures through the use of two alkyl chains (*e.g.*, **11** and **13**), which facilitates the formulation of ferroelectric host mixtures with low melting points and low viscosity through the avoidance of any oxygen function.

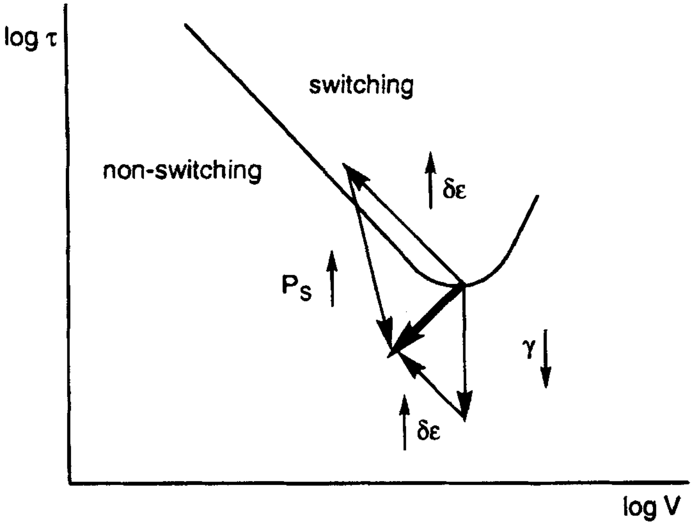


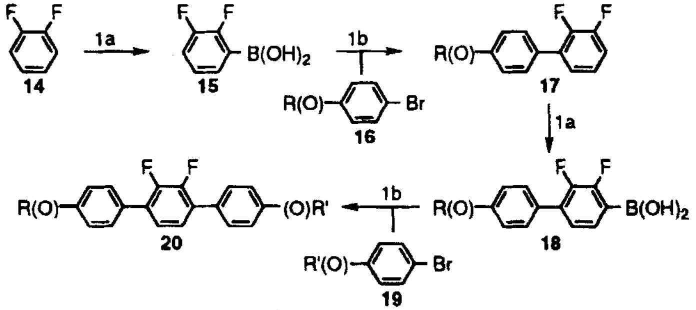
FIGURE 1, the time-voltage characteristic of ferroelectric mixtures based on *ortho*-difluoroterphenyls that have a high dielectric biaxiality.

An important characteristic of ferroelectric mixtures based on the *ortho*-difluoroterphenyls is the minimum produced in the response time-voltage curve (figure 1), the minimum is generated through high dielectric biaxiality and a low spontaneous polarisation (P_S).

$$\tau_{min} \propto \frac{\gamma\,\delta\varepsilon}{P_S^2} \quad (3) \qquad\qquad V_{min} \propto \frac{P_S}{\delta\varepsilon} \quad (4)$$

Ideally, the minimum should be moved so that it occurs as close to the origin as possible, *i.e.*, low voltage and short switching time. The movement to lower voltage (equation 4) can be achieved by reducing the P_S or by increasing the dielectric biaxiality (δε), but such moves will cause the minimum to move towards longer switching time (τ) (equation 3). However, the switching time is affected by P_S^2 and so it is possible to use a higher P_S as long as the dielectric biaxiality is high. Of course, the best way to reduce the switching time is to employ a low viscosity (γ) ferroelectric mixture which would not affect the minimum voltage. In reality a compromise must be reached to bring the minimum in the time-voltage curve towards low voltage and short switching time. The *ortho*-difluoroterphenyls are ideal in respect of ferroelectric mixtures for τV_{min} devices because they have a high negative dielectric anisotropy which confers a high dielectric biaxiality and they are of low viscosity.

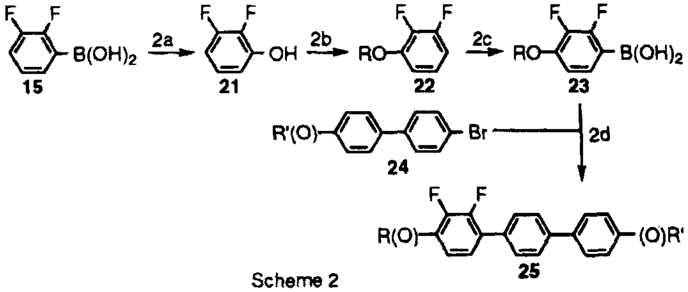
The synthesis of the *ortho*-difluoroterphenyls (schemes 1-3)[14] was accomplished through the sequential exploitation of the two equivalent acidic protons in 1,2-difluorobenzene with butyllithium at low temperature. Palladium-catalysed cross-coupling reactions involving arylboronic acids and aryl bromides were then employed to generate the aryl-aryl bonds.



Scheme 1

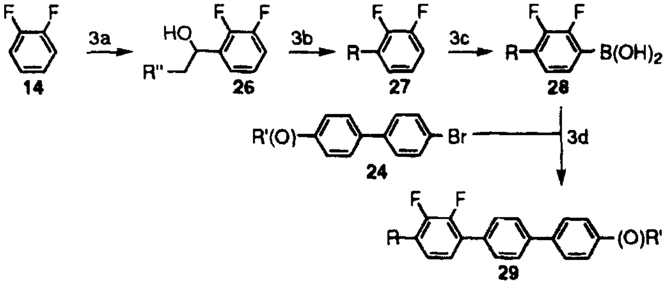
1a ... (i) n-BuLi, THF; (ii) $(MeO)_3B$, THF; (iii) 10% HCl.
1b ... $Pd(PPh_3)_4$, 2M Na_2CO_3, DME.

Scheme 1 shows the generation of boronic acid **15** which was coupled with an aryl bromide. The other acidic proton was then converted into a boronic acid (**18**), and a coupling reaction with a different aryl bromide generated unsymmetrical (or symmetrical) difluoroterphenyls (**20**) with the fluoro substituents in the centre ring. Conversion of boronic acid **15** to the phenol **21** (scheme 2) was followed by *O*-alkylation to provide the desired intermediate with an alkoxy chain (**22**). Exploitation of the acidic proton of **22** generated boronic acid **23** which was then coupled to a bromobiphenyl (**24**), which can itself be prepared through palladium-catalysed cross-coupling methodology, to give difluoroterphenyls (**25**) with the two fluoro substituents in the alkoxy end ring.



Scheme 2

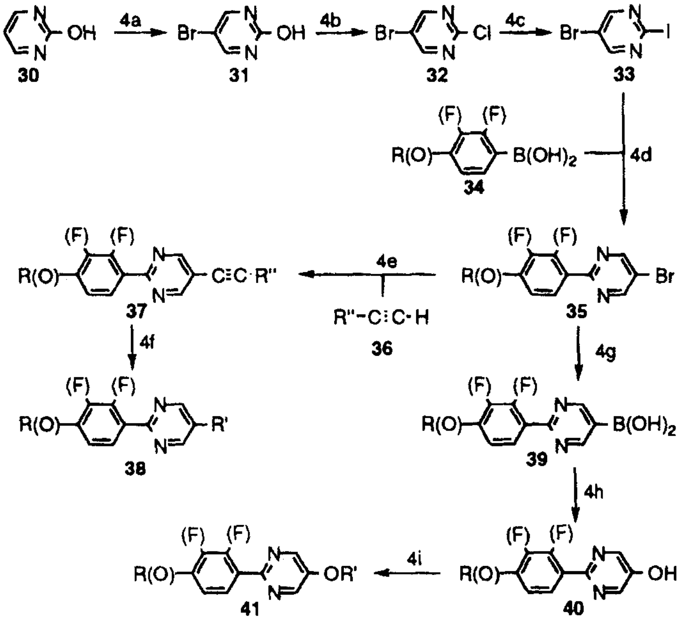
2a ... H_2O_2, THF.
2b ... RBr, K_2CO_3, butanone.
2c ... (i) n-BuLi, THF; (ii) $(MeO)_3B$, THF; (iii) 10% HCl.
2d ... $Pd(PPh_3)_4$, 2M Na_2CO_3, DME.



Scheme 3

3a ... (i) n-BuLi, THF; (ii) $R''CH_2CHO$, THF; (iii) NH_4Cl.
3b ... (i) P_2O_5; (ii) H_2, Pd/C.
3c ... (i) n-BuLi, THF; (ii) $(MeO)_3B$, THF; (iii) 10% HCl.
3d ... $Pd(PPh_3)_4$, 2M Na_2CO_3, DME.

For the difluoroterphenyls with the two fluoro substituents in the alkyl end ring (**29**), the difluorophenyllithium was quenched with an aldehyde to yield the benzylic alcohol (**26**) which was dehydrated and hydrogenated to generate the necessary alkyl chain (compound **27**). The remainder of the synthetic route is analogous to that described for scheme 2.



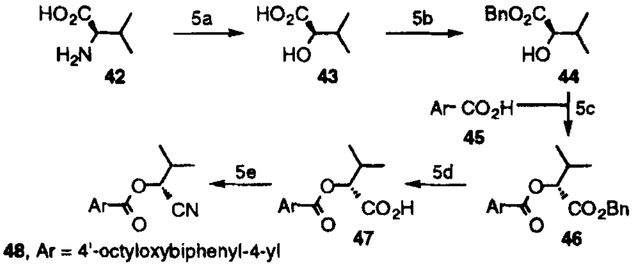
Scheme 4

4a ... Br_2, water.
4b ... $POCl_3$.
4c ... KI.
4d ... $Pd(PPh_3)_4$, 2M Na_2CO_3, DME.
4e ... (i) **36**, n-BuLi, THF; (ii) $ZnCl_2$; (iii) $Pd(PPh_3)_4$.
4f ... H_2, Pd/C.
4g ... (i) n-BuLi, THF; (ii) $(MeO)_3B$, THF; (iii) 10% HCl.
4h ... H_2O_2, THF.
4i ... R'Br, K_2CO_3, butanone.

The importance of the low viscosity, two-ring phenylpyrimidines (*e.g.*, **7** and **8**) in ferroelectric mixtures, in particular the *ortho*-difluoro analogues of high dielectric biaxiality for τV$_{min}$ devices, led to the development of an efficient, systematic synthetic route (scheme 4).[17] The route involves the synthesis of 5-bromo-2-iodopyrimidine (**33**) which is then used in selective palladium-catalysed cross-coupling reactions to generate the liquid crystal phenylpyrimidines with the desired substitution pattern.

CHIRAL CYANOHYDRIN DOPANTS

The dopant required to confer the ferroelectric properties on the mixture must be a chiral non-racemic compound, but need not necessarily be liquid crystalline. The synthesis of the cyanohydrin dopants (scheme 5) involves the modification a naturally occurring chiral amino acid (**42**). The amino function was converted into the alcohol, which was used as the point of attachment to the core. The acid group was functionalised to provide the polar cyano moiety at the chiral centre which ensures a high polarisation for chiral dopant **48**.[18]



48, Ar = 4'-octyloxybiphenyl-4-yl
C 67.0 I
P_S = 200 nC cm^{-2} (extrapolated)

Scheme 5

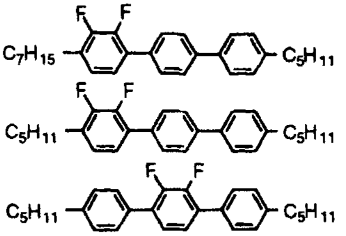
5a ... NaNO$_2$, H$_2$SO$_4$.
5b ... BnBr, DMF.
5c ... DCC, DMAP, DCM.
5d ... H$_2$, Pd/C.
5e ... (i) (COCl)$_2$, DMF; (ii) NH$_3$; (iii) SOCl$_2$, DMF.

The high extrapolated P_S of chiral dopant **48** is beneficial for the τV_{min} ferroelectric mixtures even though the P_S is required to be low because only a very small quantity need then be used (1 to 10%) which helps to minimise viscosity. Additionally, this type of chiral dopant confers a long nematic pitch to the ferroelectric mixture to facilitate the unwinding of the helix.

FERROELECTRIC MIXTURES

Ferroelectric mixtures that are based on the *ortho*-difluoroterphenyls and chiral dopant **48** have a wide temperature range smectic C phase, are of moderate P_S, low viscosity, long nematic pitch and give very short switching times. A great many such mixtures have been formulated through collaboration between the University of Hull and DERA (Malvern), and figure 2 shows a basic example; more recent mixtures include a greater range of host components to give a much lower melting point, and only 1 or 2% of the chiral dopant to give a higher smectic C phase stability and much better overall performance.[15,16,19]

The ferroelectric mixture shown in figure 2 contains a component (**50**) that does not itself exhibit a smectic C phase, nevertheless in mixtures this compound upholds the smectic C phase stability much better than expected. The ability to generate good mesomorphic behaviour from materials that have relatively short terminal chains, and a compound (**50**) that has the fluoro substituents in the centre ring minimises the viscosity of the mixture and hence generates a very short switching time. It is perhaps surprising that the melting point of the host mixture (15.5 °C) is so low given the relatively high melting points of the individual components.



13 C 56.0 S_C 105.5 S_A 131.0 N 136.0 I

49 C 81.0 S_C 115.5 S_A 131.5 N 142.0 I

50 C 60.0 N 120.0 I

host mixture 33.3% **13**, **49**, **50**
C 15.5 S_C 91.5 S_A 97.0 N 127.0 I
ferroelectric mixture (90% host + 10% **48**)
S_C* 60.0 S_A* 105.5 N* 116.0 I; $\theta = 21.5°$; nematic pitch = 12 μm;
$\Delta n = 0.19$; $\Delta\varepsilon = -2.0$; $P_S = 30$ nC cm^{-2}; $\tau = 3$ μs (25 °C, 10 V μm^{-1})

FIGURE 2, the composition, mesomorphic behaviour and some physical properties of a ferroelectric mixture based on *ortho*-difluoroterphenyls and a chiral cyanohydrin dopant.

FERROELECTRIC GELS

One reported difficulty of ferroelectric displays is their susceptibility to shock which destroys the alignment. Ferroelectric polymers have been investigated as shock-stable systems, but their use is disadvantaged by slow switching and high voltage requirements. Gel polymer networks have been developed as a compromise to maintain reasonably short switching times, but also to have a degree of shock stability.[20,21]

The work on the *ortho*-difluoroterphenyls was extended to gel systems, and a significant aspect of this work is that the structures of the polymerisable gel network and the ferroelectric materials have been matched to give compatibility and hopefully improved properties.[22] A ferroelectric host mixture (**HM1**) was formulated (figure 3) to which a structurally matched chiral dopant (**53**) was added to provide a ferroelectric mixture (**FM1**). A structurally matched diacrylate (**54**) was then added to generate a polymerisable ferroelectric mixture

(**FM2**) which was polymerised to give the desired ferroelectric gel network (**FG1**). The gel network enhances the smectic C phase stability and prevents nucleation which makes the smectic C phase stable to a lower temperature.

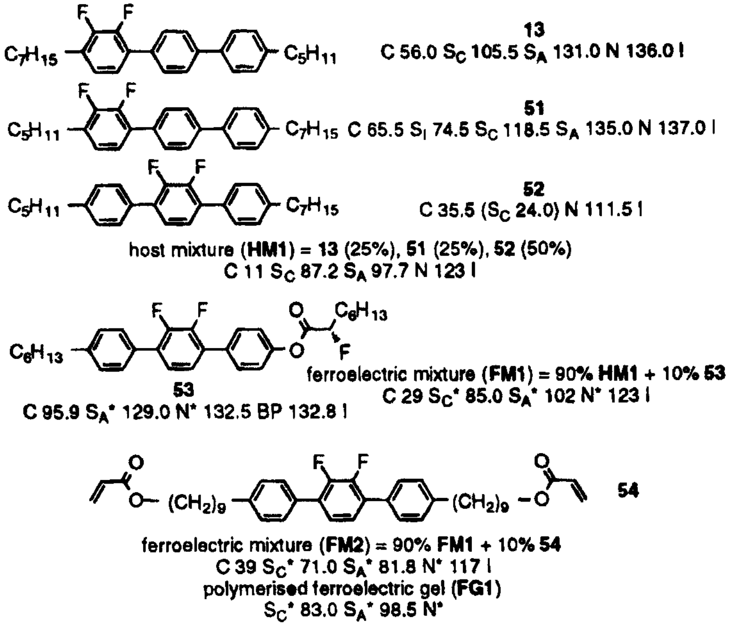


FIGURE 3, the composition and mesomorphic behaviour of a ferroelectric gel network based on *ortho*-difluoroterphenyls (host, dopant and polymerisable diacrylate have matched structures).[22]

As can be seen from figure 4, the gel network actually switches faster than the original ferroelectric mixture (**FM1**) over a range of applied voltages.

This remarkable result is thought to arise from the structurally-matched environment of the ferroelectric mixture within the network. Since the usual constraints of molecular interaction with the alignment layer are not present and the molecules are held within a framework of compatible structure then switching is faster.

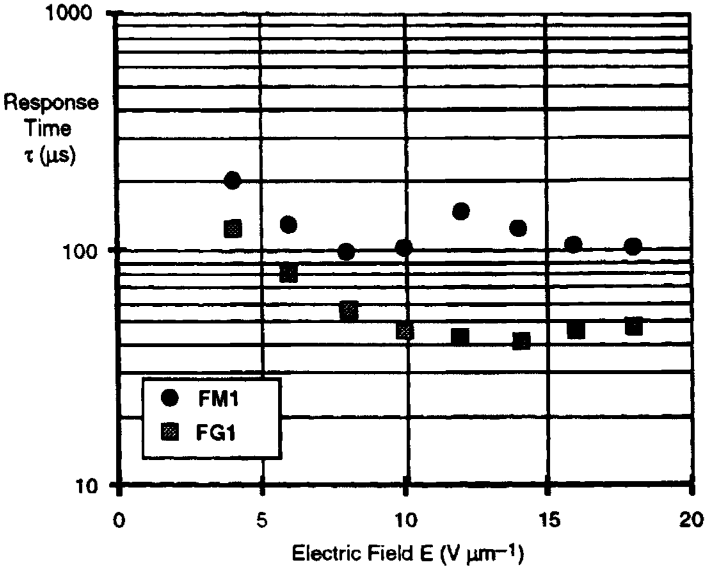


FIGURE 4, a graph to show the switching times of ferroelectric mixture **FM1** and the analogous ferroelectric gel network (**FG1**).

SUMMARY

The long-standing collaboration between the University of Hull and DERA (Malvern) has developed ferroelectric mixtures to a high level of performance. The *ortho*-difluorophenyl moiety in terphenyls and phenylpyrimidines provides some fast-switching ferroelectric mixtures with a high dielectric biaxiality. The latest investigation into the gel systems looks very promising, and illustrates the importance of matching the structures of components in the system.

References

[1] R.B. Meyer, L. Liebert, L. Strzelecki, and P. Keller, *J. Phys. Lett.*, **36**, L69 (1975).
[2] N.A. Clark and S.T. Lagerwall, *Appl. Phys. Lett.*, **36**, 899 (1980).

[3] M. Chambers, R. Clemitson, D. Coates, S. Greenfield, J.A. Jenner, and I.C. Sage, *Liquid Crystals,* **5**, 153 (1989).
[4] V. Reiffenrath, J. Krause, H.J. Plach, and G. Weber, *Liquid Crystals,* **5**, 159 (1989).
[5] R. Eidenschink, G. Haas, M. Romer, and B.S. Scheuble, *Angew. Chem.*, **96**, 151 (1984).
[6] T. Geelhaar, H.-A. Kurmeier, and A.E.F. Wachtler, *Liquid Crystals,* **5**, 1269 (1989).
[7] T. Geelhaar, *Ferroelectrics,* **85**, 329 (1988).
[8] T. Geelhaar, H. Lannert, B. Littwitz, A. Pausch, V. Reiffenrath, and A.E.F. *Wachtler, presented at the 13th International Liquid Crystal Conference, Vancouver, Canada,* (1990). Liquid.
[9] H. Zaschke, *J. Prakt. Chem.*, **317**, 617 (1975).
[10] U. Finkenzeller, A.E. Pausch, E. Poetsch, and J. Suermann, *Kontakte (Darmstadt),* 3 (1993).
[11] M. Hird and K.J. Toyne, *Mol. Cryst. Liq. Cryst.*, **323**, 1 (1998).
[12] G.W. Gray, M. Hird, and K.J. Toyne, *Mol. Cryst. Liq. Cryst.,* **195**, 221 (1991).
[13] L.K.M. Chan, G.W. Gray, and D. Lacey, *Mol. Cryst. Liq. Cryst.,* **123**, 185 (1985).
[14] G.W. Gray, M. Hird, D. Lacey, and K.J. Toyne, *J. Chem. Soc., Perkin Trans. 2*, 2041 (1989).
[15] J.C. Jones, M.J. Towler, and J.R. Hughes, *Displays,* **14**, 86 (1993).
[16] A.J. Slaney, V. Minter, and J.C. Jones, *Ferroelectrics,* **178**, 65 (1996).
[17] J.W. Goodby, M. Hird, R.A. Lewis, and K.J. Toyne, *J. Chem. Soc., Chem. Commun.*, 2719 (1996).
[18] L.K.M. Chan, G.W. Gray, D. Lacey, R.M. Scrowston, I.G. Shenouda, and K.J. Toyne, *Mol. Cryst. Liq. Cryst.,* **172**, 125 (1989).
[19] J. Constant, E.P. Raynes, and A.K. Samra, *presented at the 13th International Liquid Crystal Conference, Vancouver, Canada,*(1990).
[20] R.A.M. Hikmet, H.M.J. Boots, and M. Michielsen, *Liquid Crystals,* **19**, 65 (1995).
[21] R.A.M. Hikmet and M. Michielsen, *Adv. Mater.,* **7**, 300 (1995).
[22] A. Beer, J.W. Goodby, M. Hird, S.M. Kelly, and K.J. Toyne, *patent applied for,* application number 9825124.2 (1998).