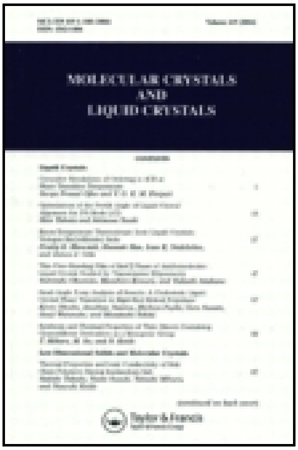

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FLC Mixtures with Broad Temperature Ranges

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A number of ferroelectric liquid crystal mixtures have been formulated which exhibit enhanced S_c^* phase thermal stability. In some cases the S_c^* ranges exceed 100°C (e.g. $-30°C \rightarrow 100°C$). The mixture components were chosen from a series of chiral LC molecules containing 2-methylbutyl head groups and tails which contain oxyethylene moieties some of which are substituted with fluorine atoms. The mesogenic cores comprise three phenyl rings interconnected via a single ester linkage (i.e. —Ph—Ph—CO_2—Ph—). In some cases, the cores contain a single fluorine substituent on one of the aromatic rings.

INTRODUCTION

The potential application of ferroelectric liquid crystals (FLC's) in fast switching, high resolution electrooptical devices is well documented.[1-3] Prompted by the development of a surface-stabilized FLC cell (SSFLC),[4] great strides have been made toward the realization of practical devices. Coupled with these advances in the physics and technology of the SSFLC cell has been the development of a large number of FLC compounds with a variety of physical and electrooptical properties.[5-8] However, none of these molecules alone exhibit all of the properties necessary for device applications. Therefore it has become necessary to develop mixtures of these compounds, in analogy to nematic liquid crystals, in order to achieve these goals.

To date a number of FLC mixtures have been reported. Many of these are cited in the patent literature[8-12] and relatively few in the open literature.[13-15] In addition to the literature, a few FLC mixtures are commercially available from companies such as Merck, BDH, and Chisso. These mixtures have been optimized to some extent with respect to material parameters such as phase range, spontaneous polarization, rotational viscosity, tilt angle, and pitch and usually consist of 5–15 components. Typically the S_c^* phase range is between −20°C and 60°C.

In this paper we report a number of FLC mixtures which exhibit well-defined eutectic points and S_c^* phases over wide temperature ranges. These two and three component mixtures are derived from a series of compounds all of which exhibit a S_c^* phase at room temperature. The fact that such a small number of components are capable of this unusually high S_c^* thermal stability represents a significant advantage over previously reported mixtures.

EXPERIMENTAL

The synthesis of the individual FLC molecules has been reported elsewhere.[16,17] The mixtures were prepared by dissolving the components (total weight 50–100 mg) in 2 mL of CH_2Cl_2, thoroughly mixing the solution, and then removing the CH_2Cl_2 under a gentle stream of nitrogen. Finally, the mixture was dried under vacuum at 60°C for one hour.

Phase diagrams were constructed by varying the molar percentages of the individual molecules and monitoring their phase sequence behavior with DSC and hot-stage polarized microscopy. The thermograms were collected on a Perkin-Elmer DSC-7 at heating/cooling rates of 10°C/min. The peak temperatures were

FIGURE 1

FLC STRUCTURES

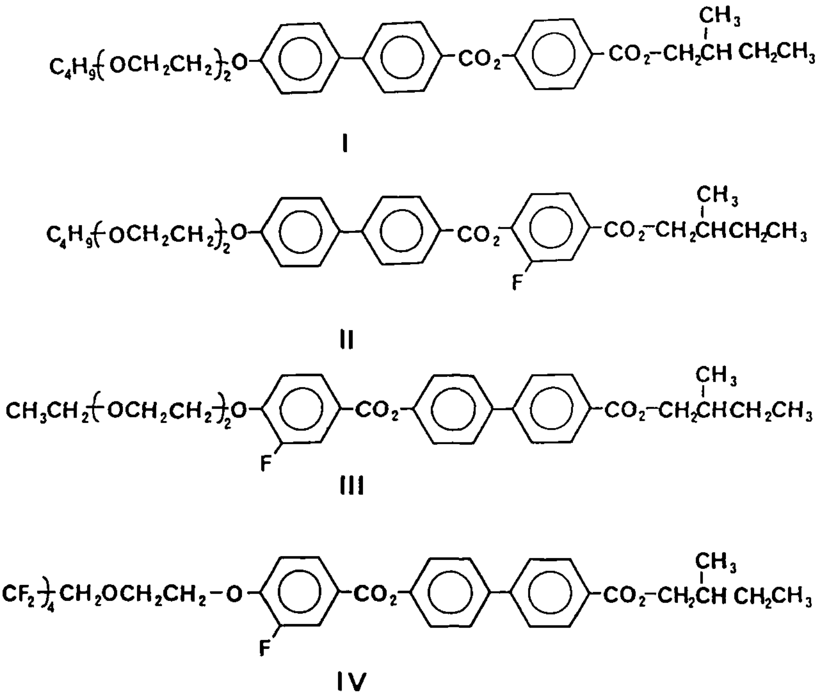


TABLE I

PHASE TRANSITION TEMPERATURES[a]

Compound	Phase Sequence (°C)
I	$\mathrm{Iso} \underset{131^\circ}{\overset{128^\circ}{\rightleftarrows}} S_A \underset{91.1^\circ}{\overset{89.7^\circ}{\rightleftarrows}} S_C^* \underset{28.6}{\overset{3.90^\circ}{\rightleftarrows}} K$
II	$\mathrm{Iso} \underset{84.4^\circ}{\overset{83.8^\circ}{\rightleftarrows}} \mathrm{Ch} \underset{81.2^\circ}{\overset{80.3^\circ}{\rightleftarrows}} S_A \underset{45.3^\circ}{\overset{44.7^\circ}{\rightleftarrows}} S_C^* \underset{27.0^\circ}{\overset{2.5^\circ}{\rightleftarrows}} K$
III	$\mathrm{Iso} \underset{95.2^\circ}{\overset{93.9^\circ}{\rightleftarrows}} \mathrm{Ch} \underset{86.7^\circ}{\overset{85.6^\circ}{\rightleftarrows}} S_A \underset{\xleftarrow[75.2^\circ]{\qquad\qquad\qquad}}{\xrightarrow{71.8^\circ} S_C^* \xrightarrow{24.0^\circ}} K$
IV	$\mathrm{Iso} \underset{142^\circ}{\overset{141^\circ}{\rightleftarrows}} S_A \underset{110^\circ}{\overset{109^\circ}{\rightleftarrows}} S_C^* \underset{75.3^\circ}{\overset{14.6^\circ}{\rightleftarrows}} K$

[a] Temperatures correspond to the peak values obtained from DSC heating and cooling cycles (10°C/min).

taken to be the phase transition point and the samples were run under N_2. Phase texture observations were made with a Zeiss 9902 Pol microscope equipped with a Leitz hot stage.

RESULTS AND DISCUSSION

The structures of the mesogenic compounds and their sequence of phase transitions are listed in Figure 1 and Table I respectively. All of these chiral FLC molecules are composed of three ring cores connected to (S)-(-) 2-methylbutyl head groups via an ester linkage. Compounds I–III belong to a class of FLC's that we have previously reported which contain multiple ether linkages in the tail portion of the molecule.[16,17] We have shown that the presence of these moieties significantly depresses the phase transition temperatures while still maintaining a S_c^* phase when compared by hydrocarbon tailed analogs of the same number of atoms. A similar effect on the clearing points and crystalline to nematic transitions of nematic LC's has also been reported by others.[18] The depression has been attributed to the increased flexibility of these tails due to the number of C—O bonds. Compound

III exhibits monotropic (S_c^*) behavior while I and II are enantiotropic. Under the aforementioned DSC conditions these 3 compounds display supercooling of the $S_c^* \rightarrow K$ transition by as much as 25°C. (See Table I).

The fourth member of the series (IV) also contains ether linkages, and in addition a number of fluorine atoms in the tail. We have also reported on this class of FLC's elsewhere.[17] The effect of the fluorine atoms in the tail significantly increases the phase transition temperatures of these compounds relative to an alkyl tail of comparable length. However, this molecule undergoes an even larger degree of supercooling (60.7°C) than does the alkoxymethylene-tailed compounds. This property has been utilized effectively in mixtures.

The primary difficulties that must be overcome in the development of a FLC mixture are the maintenance of an enantiotropic S_c^* phase and the establishment of a temperature range which would render the mixture useful for device application. To date there have been few systematic mixing schemes found in the literature which address these goals. The Schroeder-Van Laar relationship has been utilized for the prediction of nematic LC eutectic comositions[19] but not so for FLC systems. However, there have been several studies involving the effect of component stucture on other specific properties of FLC mixtures such as viscosity, spontaneous polarization, etc. These effects have been achieved by the addition of both non-mesogenic dopants and smectic molecules which are known to augment the desired properties.

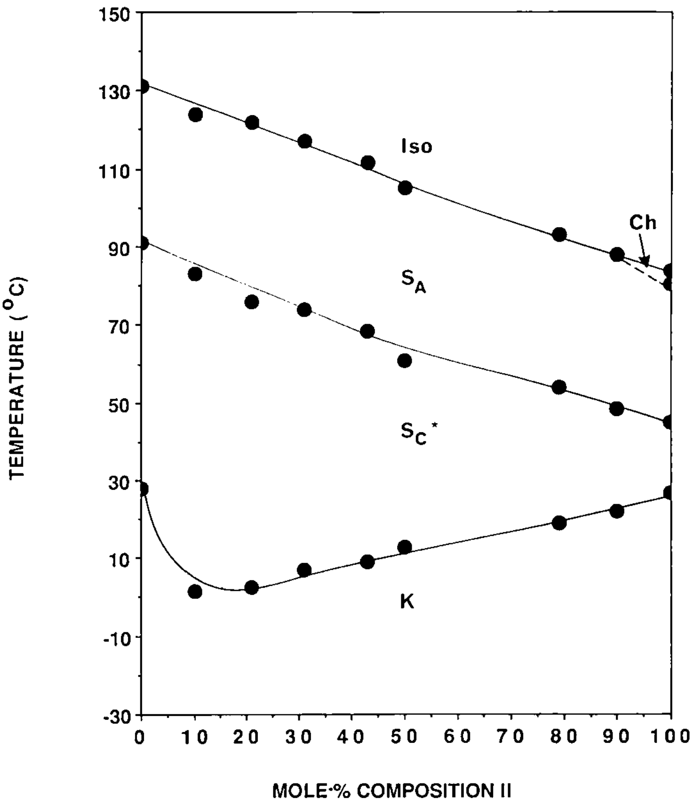
In this limited study, only S_c^* exhibiting molecules were used in order to establish a broad range mixture. Three of the four compounds are enantiotropic with the exception being III. The strategy employed here was to first identify binary mixtures which formed eutectics. The third component was then added in order to adjust the upper and lower ends of the S_c^* range.

Figure 2 depicts the binary phase diagram for the FLC mixture of I and II. The presence of the fluorine atom in II significantly narrows the width of the smectic phases relative to I. This substitution effect has also been observed in other LC structures.[20] A eutectic is exhibited when the mole percentage of II is between 10–20%; the S_c^* range at 10 mole-% of II is 0 to 83°C. The fact that the minimum is somewhat shallow is probably related to the structural similarity of I and II. Above this composition the $S_c^* \rightarrow K$ transition rises monotonically up to 100 mole-% II, while the $S_c^* \rightarrow S_A$ and $S_A \rightarrow$ Iso transitions decrease as the mole-% of II increases. The cholesteric phase exhibited by compound II disappears after the addition of just 10% of I.

A very different situation arises when compound II is mixed with III (see Figure 3). The plot of the DSC (heating cycle) phase transition temperatures versus composition shows the profound effect of the monotropic nature of III. Above approximately 50 mole-% of the reversed core compound II the S_c^* phase is lost. The cholesteric phase in this case is maintained across the compositional range probably because both compounds exhibit this phase in the same temperature regime. This is important since the presence of a cholesteric phase is generally believed to be necessary in order to obtain good alignment of the S_c^* phase. A shallow eutectic is also formed in this system at about 80 mole-% with a S_c^* phase width of 40°C.

FIGURE 2

Phase diagram for mixtures containing compounds I and II (heating cycle).



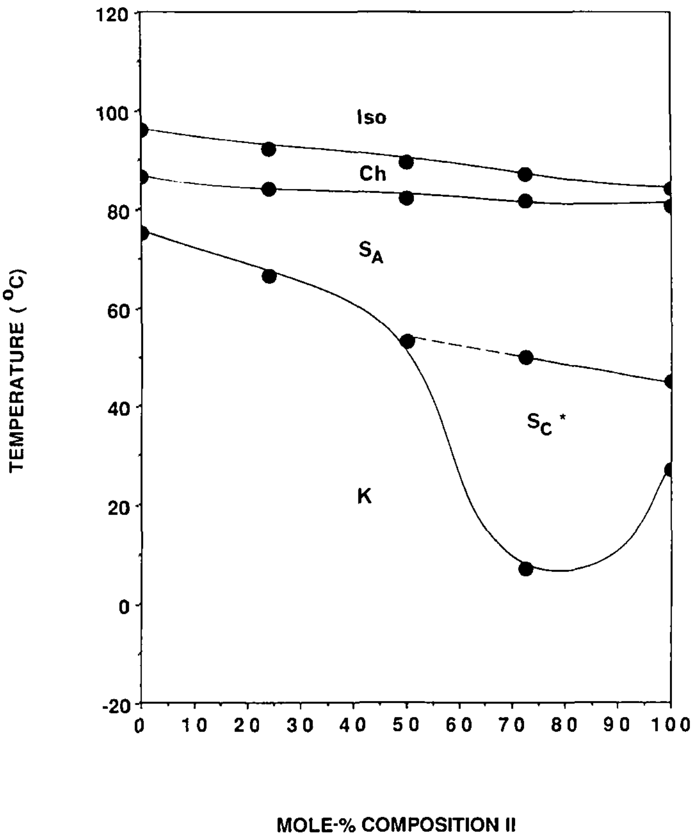
When compound I is added to III somewhat different results are obtained (see Figure 4). Firstly, due to the increased S_c^* phase breadth of I, the phase is maintained at higher concentrations of III. It is lost between 70–80 mole-% of III. The most striking feature of Figure 4 is the deep eutectic point formed at the ratio of approximately 65/35 mole-% (I/III).

The temperature range of the S_c^* phase of this binary mixture (−34°C to 74°C) is wide enough to meet LC device operation specifications. The cooling curves (DSC) at these compositions do not display any crystallization exotherms (down to −50°C), and it should be noted that the points plotted on Figure 4 were obtained by holding the samples at −50°C (for 12–24 hr) before heating (10°C/min). Above 35–38 mole-% of compound III the K → S_c^* transition increases precipitiously with a concomitant narrowing of the S_c^* range.

In practice one would not want to operate in a region of the phase diagram which is so sensitive to compositional variations. The compositional tolerance as well as the S_c^* range can be increaed by the addition of a third component to the 65/35 mixture of I/III (Mix A). For example, the addition of FLC II to Mix A is depicted

FIGURE 3

Phase diagram for mixtures containing compounds II and III (heating cycle).

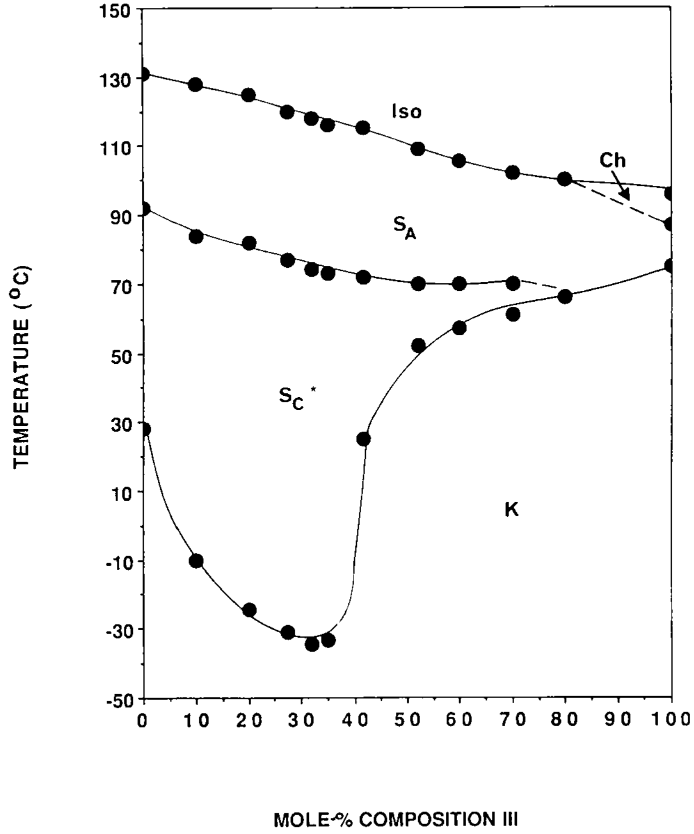


in Figure 5. In this diagram Mix A is treated as a single component with the left side of the axis representing 100 mole-%. Upon the addition of II the eutectic well is broadened while still maintaining most of the S_c^* range. A much more dramatic effect is caused by the addition of compound IV to Mix A. In this case, the low end of the S_c^* range is maintained (-30 to -35°C) for up to 70 mole-% of IV added. This is unexpected since the $K \rightarrow S_c^*$ transition of IV is 75°C. Here again no $S_c^* \rightarrow K$ peaks were recorded upon cooling and the heating cycle peak temperatures represent samples that were held at low temperatures for extended periods of time. In addition to the broadening of the eutectic well, compound IV also raises the $S_c^* \rightarrow S_A$ transition temperature to 100°C. It should be noted here that when compound IV is mixed with one of the other three FLC's alone, comparable broad range mixtures are not realized.

We have demonstrated that broad-range S_c^* mixtures which encompass ambient

FIGURE 4

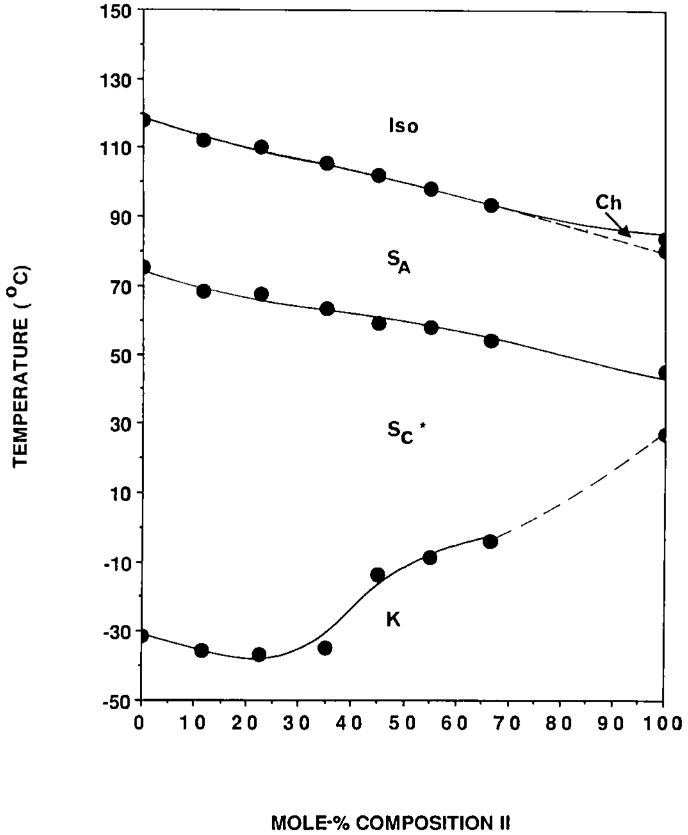
Phase diagram of mixtures containing compounds I and III (heating cycle).



temperatures may be formulated from just two or three components. The determination of eutectic points of binary mixtures of structurally similar FLC's has proven to be helpful in the development of ternary mixtures. To our knowledge the S_c^* range of the ternary mixtures illustrated in this project (−35°C → 100°C) represent the widest range mixtures reported to date. It is recognized that these particular mixtures may not be suitable for device applications since their electrooptic properties have not been fully explored. However, if any of these other properties (rotational viscosity, birefringence, P_s, etc.) should require manipulation, other compounds may be added. Since the S_c^* range of mixtures is so wide, they will be able to tolerate larger amounts of dopants and other FLC's and still be able to meet device temperature specifications. The other alternative to improve the electrooptic parameters of these mixtures would be to make minor molecular variations to the individual compounds, but this approach is known to be very risky in so far as maintaining an S_c^* phase.

FIGURE 5

Phase diagram for ternary mixtures of Mix A and II (heating cycle).



References

1. S. T. Lagerwall, B. Otterholm and K. Skarp, *Mol. Cryst. Liq. Cryst.*, **152**, 503 (1987).
2. L. A Beresnev, L. M. Blinov, M. A. Osipov and S. A. Pikin, *Mol. Cryst. Liq. Cryst.*, **158A**, 3 (1988).
3. S. T. Lagerwall and I. Dahl, *Mol. Cryst. Liq. Cryst.*, **114**, 151 (1984).
4. N. A. Clark and S. T. Lagerwall, *Appl. Phys. Lett.*, **36**, 899 (1980).
5. T. M. Leslie, *Ferroelectrics*, **58**, 9 (1984).
6. P. Keller, *Mol. Cryst. Liq. Cryst.*, **102**, (Lett.) 295 (1984).
7. K. Furukawa, K. Terashima, M. Ichihashi, H. Inoue, S. Saito and T. Inukai, *6th Liq. Cryst. Conf. Soc. Count.*, Halle (GDR), (1985) Abstracts, A37.
8. K. Furukawa and K. Terashima, Eur. Pat. Appl. EP 178,647 (1986).
9. R. Higuchi, Eur. Pat. Appl. EP 159,872 (1985).
10. K. Furukawa and K. Terashima, Eur. Pat. Appl. EP 192,267 (1986).
11. D. Coates, P. A. Gemmell, G. W. Gray, D. Lacey, K. J. Toyne and D. J. S. Young, UK Patent Appl. GB 2,166,754 (1986).
12. H. Inoue, T. Inukai, K. Ohno, K. Miyazawa and S. Saito, Eur. Pat. Appl. EP 228,303 (1986).

13. W. Kuczynski, S. T. Lagerwall, M. Matuszczyk, K. Skarp, B. Stebler and J. Wahl, *Mol. Cryst. Liq. Cryst.*, **146**, 173 (1987).
14. C. H. Bahr and G. Heppke, *Mol. Cryst. Liq. Cryst.*, **148**, 29 (1987).
15. C. Escher, H. -R. Dubal, W. Hemmerling, I. Muller, D. Ohlendorf and R. Wingen, *Ferroelectrics*, **84**, 89 (1988).
16. W. Cumming, R. Gaudiana, C. McGowan, R. Minns and A. Naiman, United States Patent Application No. 887620.
17. Results from this laboratory to be published.
18. T. Kitamura, A. Mukoh and S. Era, *Mol. Cryst. Liq. Cryst.*, **112**, 319 (1984).
19. J. D. Magerum, A. M. Lackner, J. E. Jensen, L. J. Miller, W. H. Smith, Jr., S. -M. Wong and C. I. van Ast, *Fifth International Symp. on Liq. Cryst. and Ordered Fluids*, ACS Meeting, St. Louis (1984).
20. G. W. Gray, D. Lacey, J. E. Stanton and K. J. Toyne, *Liq. Cryst.*, **1(5)**, 407 (1986).