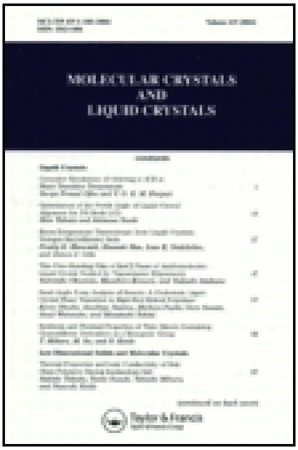

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

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

Remarkable Influence of Fluorination in Smectic and Ferroelectric Liquid Crystals

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Version of record first published: 04 Oct 2006.

To cite this article: R. Twieg , K. Betterton , R. Dipietro , D. Gravert , C. Nguyen , H. T. Nguyen , A. Babeau , C. Destrade & G. Sigaud (1992): Remarkable Influence of Fluorination in Smectic and Ferroelectric Liquid Crystals, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 217:1, 201-206

To link to this article: http://dx.doi.org/10.1080/10587259208046901

Mol. Cryst. Liq. Cryst. 1992, Vol. 217, pp. 201–206
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Printed in the United States of America

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Abstract Liquid crystals possess a wide variety of interesting and useful properties which are strongly correlated to their structure. In order to modify and enhance certain useful properties we have examined the effects of systematic introduction of fluorine. Especially interesting examples are the influences on the phase range and type including ferroelectric properties and on miscibility leading to phase separation via spinodal decomposition of the anisotropic LC phase.

INTRODUCTION

Liquid crystals play an important and growing role in a wide variety of electrooptical devices such as displays and modulators. Their utility hinges on subtle relationships amongst a variety of molecular properties, their colligative mesogenic behavior and interaction with external electrical and optical fields. By now a wide variety of liquid crystal structures have been prepared and related to physical properties of interest. Recently, the introduction of fluorine into mesogens has become much more intensively examined.[1-3] The requisite chemistry to accomplish such fluorinations has simplified and as the number of fluorinated mesogens has grown so in proportion has some predictive capability of its influences. Yet, many surprises have already been encountered and many more are in store from this group of fluorine containing materials.

Prior to discussing any specific examples it is useful to briefly examine how fluorine introduction might influence the properties of a liquid crystal. Table 1 contains selected comparisons broken down into atomic, single carbon bonded and molecular properties between fluorine vs. hydrogen and their respective derivatives. On the atomic level it is the

TABLE 1. *Selected Properties of*
Fluorine vs. Hydrogen and Their Derivatives

– *F*		– *H*
4.0	electronegativity (Pauling)	2.1
3.399	electron affinity (ev)	0.754
1.35	Van der Waals radii (Å)	1.10
C – *F*		*C* – *H*
1.38	sp^3 bond length (Å)	1.11
451	sp^3 bond strength (Δ_f^{298} kj/mol)	338-422
1.70	sp^3 group dipole (Debye)	0.30
$F(CF_2)_6F$		$H(CH_2)_6H$
1.699	density (gm/cm^3, 20°C)	0.660
198.9	molar volume (cc/mol, 20°C)	130.52
12.1	Hildebrand Parameter δ ($MPa^{1/2}$, 25 °C)	14.9
17.76	surface tension (γ, dyne/cm,25°C)	50.32
2.1	dielectric constant (22°C) (data for PTFE and PE)	2.26
1.2515	refractive index n_D^{20}	1.3751

large electronegativity and electron affinity of fluorine which is most influential. Also important to LC modifications, which are so sensitive to space filling, is the fact the fluorine is not much larger than hydrogen. At the single bond level we find again that the group dipole of the C-F bond is much larger than that of C-H reflecting the relative differences of electron affinity of these elements vs. carbon. Notably, again, the bond lengths and strengths of the fluorinated materials are generally comparable or somewhat larger than their hydrogen counterparts. The colligative properties of the perfluorinated materials and their hydrocarbon analogs is of ultimate interest. Here perfluorohexane and hexane are compared; the fluorinated material has consistantly lower Hildebrand parameter, surface tension, dielectric constant and refractive index. All these properties result from the diminished interaction the fluorinated compounds with their environment, i.e., neighboring molecules and even incident electromagnetic radiation and electric fields.

There are numerous ways to introduce fluorine into liquid crystals but here we limit this brief discussion to smectic materials in which one of the tails has been modified by introduction of a block of fluorinated carbon atoms. Three recent examples include the following: mesomorphic properties of the semifluorinated alkoxybenzoic acids, modification of the ferroelectric S_C^* properties of mesogens containing these semifluorinated structures and, finally, the novel consolute critical point in a binary liquid crystal mixture which relies on a fluorine containing component.

RESULTS

The 4-alkoxybenzoic acids are classical mesogenic materials. In the mesogenic state they exist as hydrogen bonded dimers; at short tail lengths only a nematic phase is found, at intermediate lengths both nematic and S_C phases are found, at long tail lengths only an S_C phase is found. We have studied the influence of replacing hydrocarbon blocks with fluorocarbon blocks at the end of the alkoxy chain. That is, in the generic structure $H/F(CF_2)_n(CH_2)_mOPhCOOH$ different size fluorinated blocks (n units) and hydrocarbon blocks (m units) are incorporated and the effects of the ratio n/m and the sum n+m is examined. The matrix of compounds studied to date is incomplete not only due to both synthetic challenges (especially lack of commercially available precursors at n = 5,9,11 and m = 0,1,2,7,9) but also due to the sheer magnitude of the

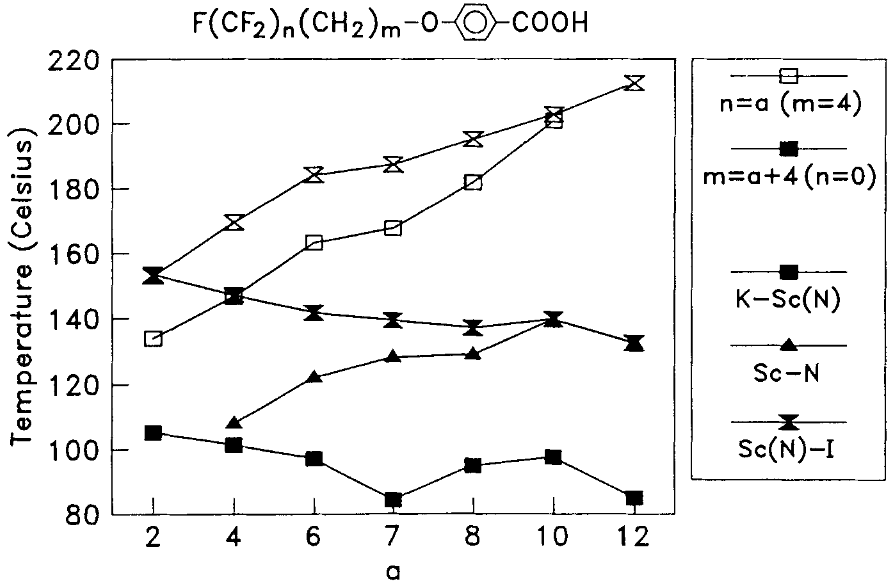
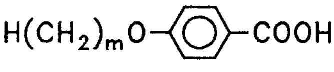


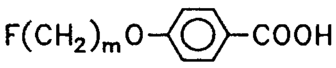
FIGURE 1. The influence of fluorocarbon block introduction on the mesomorphism of selected alkoxybenzoic acids

undertaking (144 compounds just for $n+m \leq 12$). Nonetheless, clear trends are evident from selected series which have been prepared. Take, for example, the series with the hydrocarbon block constant at $m=4$ and varying the appended fluorocarbon block between $n=2\text{-}12$ as shown in Fig 1. In the fluorinated compounds we find two trends: first, the absence of a nematic phase and second, enhanced clearing points with generally diminished mesogenic range in all cases.

Clearly, introduction of these fluorocarbon blocks has a profound influence on the mesomorphic properties of these materials. Even more remarkable is the influence of a *single fluorine atom* at the end of the alkoxy chain as can be found in the Table 2. A change in just this one single atom (out of about fifty total) has not significantly influenced the overall mesomorphic range but in each case the S_C is now an S_A phase! These phase assignments made by polarizing microscopy are being checked by X-ray analysis; preliminary results confirm the assignments.

TABLE 2. Influence of a Single Fluorine Atom on the Mesogenic Properties of Alkoxybenzoic Acids (T in °C)





m	K	S_C	S_A	N	I	K	S_C	S_A	N	I
10	. 97	.122	-	.142	.	.102	-	.125	.134	.
11	. 84	.128	-	.139	.	. 82	-	.125	.128	.
12	. 95	.129	-	.137	.	. 86	.102	.128	.129	.

Now let us examine the influence of installing the fluorinated block containing alkoxybenzoic acids in some ferroelectric liquid crystals. The goal here is to ultimately enhance the function of these materials in an SSFLC type device by changing the ferroelectric phase range, polarization density, etc.. We have modified some chiral α-chloroester thiobenzoate core materials studied earlier and a partial series is given in Fig 2.[4] As can be seen, the fluorinated materials have higher and broader temperature ferroelectric phases with larger spontaneous polarization. Such behavior has only been obtained previously by making the core larger, i.e., changing to a biphenyl system.[5]

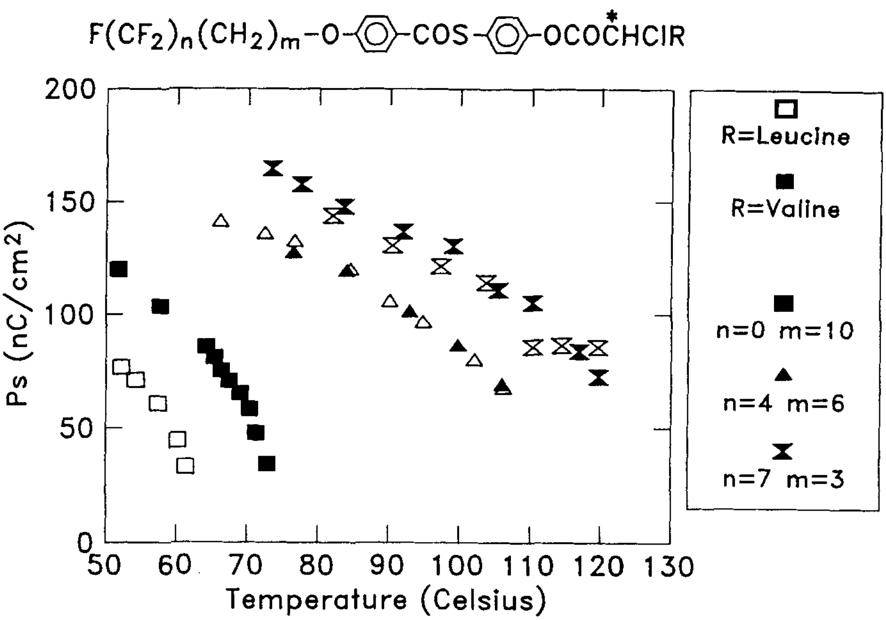


FIGURE 2. The influence of fluorocarbon block introduction on the ferroelectric temperature range and spontaneous polarization in some selected thiobenzoate core chiral chloroester FLC's.

The final example involves the remarkable phase separation found in a binary mixture of a polar liquid crystal and a fluorinated liquid crystal. We have previously described such a binary mixture with a critical temperature at 95°C.[6] New mixtures have now been identified which are composed of somewhat more readily accessible components which lower this phase separation to a more experimentally accessible temperature. For example, the commercially available decyloxycyanobiphenyl M30 (component A) has the phase sequence *K* 59.5 S_A 84 *I* while the 4-perfluorobutyl-4-butoxyphenylthiobenzoate (component B) has the phase sequence *K* 52 S_A 113 *I*. A phase diagram as a function of composition and temperature for the binary mixture has been obtained as found in Fig. 3. For example, a critical composition mixture of 41 mol% fluorinated component upon cooling from the isotropic first passes through a short *N* range into a single S_A phase and then at the critical temperature of 52° two coexisting and immiscible S_A phases are obtained. The special properties of this phase separation phenomena are presently being studied in detail.

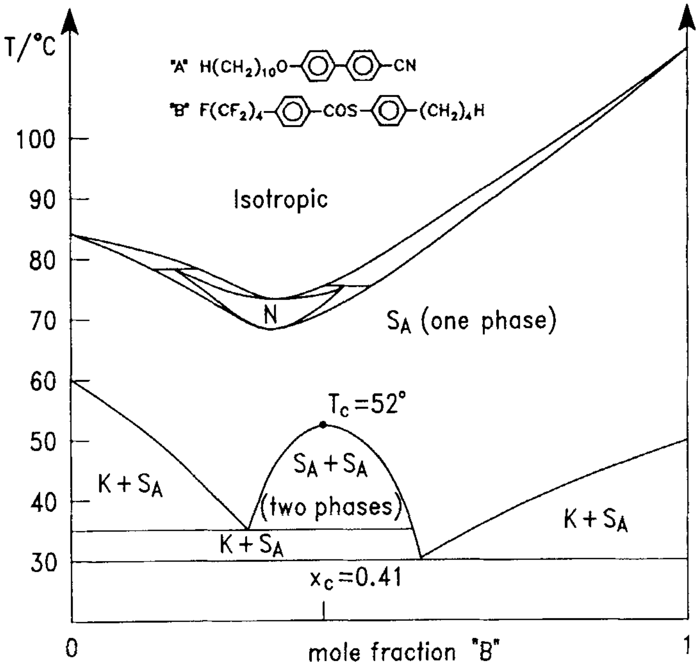


FIGURE 3. Phase diagram of a binary mixture exhibiting phase separation

CONCLUSIONS

Fluorination imparts unique and useful properties to liquid crystals. As such, in the future significantly more attention will be given to chemistry and physics of these materials.

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