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Effects of fluorination extent and direction of ester group in semiperfluorinated phenyl benzoate FLCs on mesomorphic properties

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An achiral semiperfluorinated chain has been introduced into classical phenyl benzoate mesogenic moieties in which the other terminal chain is chiral. The consequences of this modification on the mesomorphic properties are discussed. At a low fluorination extent, the smectic A phase is strongly favoured, while at high extents of fluorination the chiral smectic C phase is enhanced. The direction of the central ester linkage influences not only the phase diagram, but also the spontaneous polarization induction power.

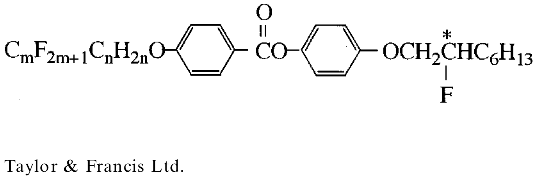
1. Introduction

A conventional model for a ferroelectric liquid crystal is a rod-like molecule formed by a rigid core with two flexible hydrocarbon tails, at least one of which is chiral. To study the correlation between molecular structure and mesomorphic properties with the aim of preparing desirable materials, various molecular designs have been used and a great number of ferroelectric liquid crystals have been synthesized [1]. It was initially found that a simple change in the length of the aliphatic tails can strongly influence the liquid crystal polymorphism [2]. Also, modification of the chiral end group, which is all-important in a ferroelectric liquid crystal molecule, can significantly influence both the polymorphism and the ferroelectric properties such as the direction and magnitude of the spontaneous polarization, tilt angle and helical twist sense [3–11].

Recently, modifications of the core by introducing a fluoro-substituent into different positions has been actively studied [12–16]. What deserves to be noticed here is that reports on changing the nature of the achiral tail have been few. The main reason for this is that few chemical modifications are available. Except for carbon, no other tetravalent elements are suitable for the spine of terminal chains of ferroelectric liquid crystals. The hydrogens in organosilicons are reactive and tin is too large to favour mesophases. Thus, only substitution of the hydrogens seems possible for modification of achiral end groups. In fact, only perfluorocarbon chains can be used instead of hydrocarbon chains due to the steric factor and general availability [17].

Fluorine is known to have the largest electronegativity, a small atomic radius comparable with hydrogen, and a small polarizability leading to very low surface energy [18]; hence perfluorinated liquid crystals are expected to be of low viscosity, low birefringence and good chemical stability [19]. Recent studies show that fluorination of the hydrocarbon chain strongly enhances smectic phases [20] and this has inspired the study of fluorinated liquid crystals [21–25]. Enhancement of smectic phases by fluorination is attributed to the fact that fluorocarbon chains are incompatible with both saturated and aromatic hydrocarbon moieties [26]; they prefer to aggregate with their companions to form a layer structure, somewhat like amphiphilic molecules [27].

Interest in the influence of fluorination on mesomorphic properties led us to synthesize two series of semiperfluorinated ferroelectric liquid crystals [28], 4-(2-fluoro-octyloxy)phenyl 4-[(*n*-perfluoroalkyl)-alkyloxy]benzoates (structure **1**) and 4-[(*n*-perfluoroalkyl)-alkyloxy]phenyl 4-(2-fluoro-octyloxy)benzoates (structure **2**) (see below). Using these semiperfluorinated compounds allowed us to study systematically the effects of fluorination extent, which is defined as the percentage of fluorine atoms relative to the total number of fluorine atoms and hydrogen atoms, on the liquid crystalline behaviour.



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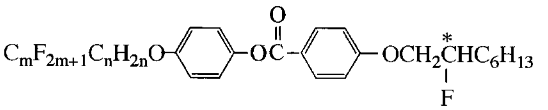
$C_mF_{2m+1}C_nH_{2n}O{-}C_6H_4{-}O\overset{O}{\overset{\|}{C}}{-}C_6H_4{-}OCH_2\underset{F}{\overset{*}{C}}HC_6H_{13}$

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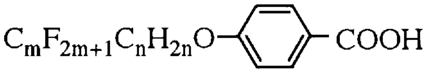
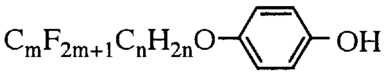
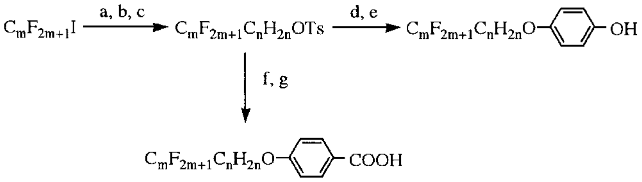
2. Materials

The following semiperfluoroalkyloxybenzoic acids and phenols were used as the essential intermediates to synthesize compounds **1** and **2**.





These benzoic acids and phenols were prepared as shown in the following scheme [28].



(a) AIBN, $CH_2{=}CH(CH_2)_{n-2}OH$;
(b) $LiAlH_4$, dry ether;
(c) TsCl, DABCO, dry CH_2Cl_2;
(d) 4-benzyloxyphenol, NaH, dry DMF;
(e) 5% Pd/C, H_2, methanol
(f) Ethyl 4-hydroxybenzoate, NaH, dry DMF;
(g) KOH, ethanol, H_3O^+.

Compounds **1** and **2** were readily obtained by esterification of the semiperfluoroalkyloxybenzoic acids and phenols with 4-(2-fluoro-octyloxy)phenol and 4-(2-fluoro-octyloxy)benzoic acid, respectively, using dicyclohexylcarbodiimide (DCC).

3. Results and discussion

The mesomorphic properties of liquid crystals are known to depend strongly on the nature of the terminal groups [29]. The replacement of hydrogen atoms of terminal groups with fluorine atoms must cause a change in intermolecular interactions and consequently in the mesomorphic properties, due to electronic and steric effects.

The transition temperatures of the compounds **1**, whose central ester linkages are conjugated with the terminal position carrying the non-chiral perfluoroalkyloxy tail, are summarized in table 1. As shown in table 1, the stability of the smectic phase increases with increasing fluorination extent (see equation (1) below) for the same length of the achiral tail. The tendency is similar for the compounds with different chain lengths. The non-fluorinated compound ($m=0$, $n=8$) *[3]* shows a cholesteric phase above the smectic A phase and a chiral smectic C phase below the smectic A. When only two carbons are perfluorinated (**1c**, $m=2$, $n=6$), the smectic A phase becomes so stable thermally that the chiral smectic C phase and the cholesteric phase disappear. Accompanying the increase in fluorination extent, the chiral smectic C phase appears again. Compound **1d** shows a monotropic chiral smectic C phase and **1e**, with a higher fluorination extent, shows an enantiotropic chiral smectic C phase. It has been reported [30] that a fluorinated terminal group is linear and more rigid than a non-fluorinated one because the larger fluorine atom favours an almost all *trans*-conformation (table 2). The thermal stability of a mesophase is known to be influenced by the effective molecular length/breadth ratio. The linear and rigid nature of the fluorinated tail may result in a large molecular length/breadth ratio and therefore in a very stable smectic phase compared with the non-fluorinated system.

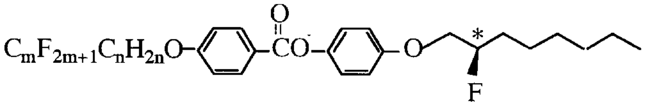
$$\text{Fluorination extent } (\%) = \frac{2m+1}{2(m+n)+1} \times 100 \quad (1)$$

It has been reported that a simple change in the length of an aliphatic tail group can stronly influence the polymorphism in non-fluorinated systems [2]. But when fluorinated, the molecular interactions greatly change, so that fluorinated systems behave quite differently from non-fluorinated systems. In fluorinated systems, the length of the tail still has an effect on the polymorphism, but the fluorination dominates the mesomorphic behaviour. Transition temperatures are plotted against the fluorination extent without considering the length of the achiral tail in figure 1. **1c**, with a fluorination extent of 29·4% showed no chiral smectic C phase, but with the fluorination extent increased to 36·8% (**1f**), a monotropic chiral smectic C phase appeared. When the fluorination extent is raised to 46·7% or over, the chiral smectic C phase becomes enantiotropic.

It has long been known [31] that for phase transitions of normal chain molecular crystals, the greater the density of the unit cell, the more stable is the crystal. And when the molecules tend to be tilted, the density of the unit cell tends to increase. The behaviour of the compounds **1** can be explained reasonably in such a way. The more we introduce larger fluorine atoms into the achiral end group, the more useless space is created in an orthogonal packing, owing to steric and electronic effects. Thus, the tilted chiral smectic C phase is favoured.

The transition temperatures of the compounds **2**, whose central ester groups are directed oppositely to

Table 1. Transition temperatures of 4-(2-fluoro-octyloxy)phenyl 4-[(*n*-perfluoroalkyl)alkyloxy]-benzoates (compounds **1**).



Compound	$m+n$	m	n	Cr		S_X		S_C^*		S_A		I
1a	7	3	4	•	85·7	—		•	93	•	106·3	•
1b	7	4	3	•	62·6	•	65·3	•	103	•	119·6	•
1c	8	2	6	•	97	—		—		•	101·2	•
1d	8	3	5	•	85·6	—		(•	84)	•	113	•
1e	8	4	4	•	93·8	—		•	107	•	119·4	•
1f	9	3	6	•	88·7	—		(•	85)	•	111·2	•
1g	9	4	5	•	76·1	(•	43·8)	•	98·4	•	120·4	•
1h	9	6	3	•	74·1	—		•	121·2	•	141·6	•

Note: transition temperatures for 4-(2-fluoro-octyloxy)phenyl (4-octyloxy)benzoate [3] are Cr 66 S_C^* 76 S_A 83 N* 89 I.

Table 2. Conformational energies of butane and decafluorobutane and their ratio of *trans* to *gauche* [30].

Compound	Energy *trans*→*gauche*/kJ mol^{-1}	Ratio *trans*/*gauche*
C_4H_{10}	3·4	69/31
C_4F_{10}	9·1	95/05

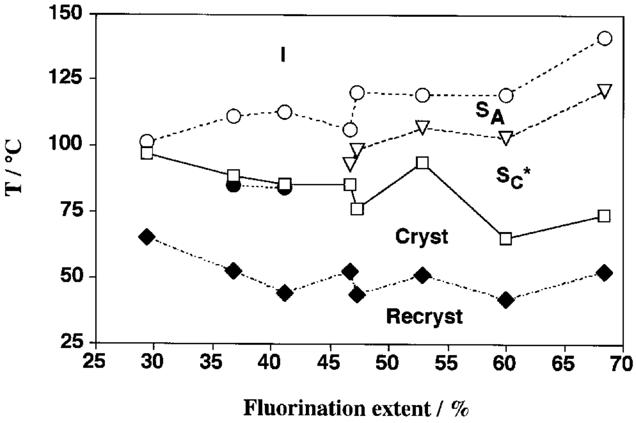


Figure 1. Transition temperatures of the compounds **1** plotted against fluorination extent.

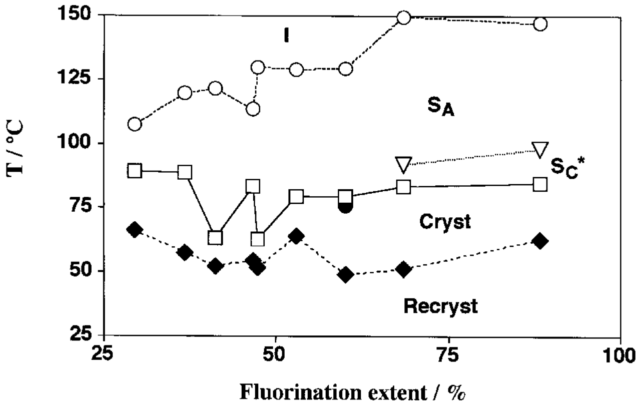
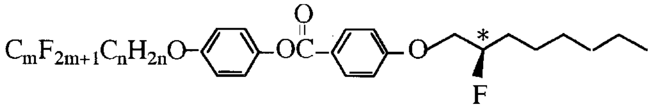


Figure 2. Transition temperatures of the compounds **2** plotted against fluorination extent.

that in the compounds **1**, are listed in table 3. Compared with the compounds **1**, the liquid crystalline properties of the compounds **2** are better, but the stability of the chiral smectic C phase is not as good as that of the compounds **1**. At the same fluorination extent (46·7% ~ 60%), the compounds **1** show a stable smectic A phase and a chiral smectic C phase, while the compounds **2** exhibit only stable smectic A phases. Although it is unknown why the direction of the central ester linkage makes such a big difference to mesophase sequences, it is certain that the conjugation of the ester group with the terminal position plays an important role here. For the same reasons mentioned above for the compounds **1**, the chiral smectic C phase becomes stable with increase in fluorination extent as shown in figure 2. When the fluorination extent increases to 68·4%, **2h** also exhibits an enantiotropic chiral smectic C phase like the compounds **1**.

Although we do not have all the requisite compounds (such as those with fluorination extents from 10% to 20%), it is clear that the fluorination extent of the achiral terminal group must be carefully optimized to obtain desirable mesophases. As has been pointed out, the replacement of hydrogen atoms with fluorine atoms generally results in enhanced smectic behaviour, which tends to be smectic A in type [32], but in semi-perfluorinated systems, at least in phenyl benzoate systems, it seems that at a low fluorination extent, the

Table 3. Transition temperatures of 4-[(*n*-perfluoroalkyl)alkyloxy]phenyl 4-(2-fluoro-octyloxy)benzoates (compounds **2**).



Compound	$m+n$	m	n	Cr		S_C^*		S_A		I
2a	7	3	4	•		—	83·5	•	113·3	•
2b	7	4	3	•	(76·0	•)	79·4	•	129·2	•
2c	8	2	6	•		—	89·3	•	107·2	•
2d	8	3	5	•		—	63·4	•	121·1	•
2e	8	4	4	•		—	79·8	•	128·8	•
2f	9	3	6	•		—	89·0	•	119·5	•
2g	9	4	5	•		—	62·8	•	129·7	•
2h	9	6	3	•	83·7	•	92	•	149·5	•

Note: transition temperatures for (4-octyloxy)phenyl 4-(2-fluoro-octyloxy)benzoate [3] are Cr 85 (S_C^* 82) S_A 96 I.

smectic A phase is favoured and at a high fluorination extent, the chiral smectic C phase is enhanced.

The influence of fluorination extent on spontaneous polarization **P** for the compounds **1** is depicted in figure 3. The spontaneous polarization decreases slightly with increasing fluorination extent. Contrary to the trend in spontaneous polarization, the tilt angle increases with increasing fluorination extent (figure 4). This agrees with the idea that the larger fluorine atoms lead the molecules to tilt as mentioned above. Since **P** is a function of tilt angle, the tilt angle needs to be taken into account in making any accurate comparison of the effect of fluorination extent on spontaneous polarization. A normalized polarization P_0 was obtained by dividing the polarization by sin θ. The reults are shown in figure 5.

The compounds **1** and **2** were also doped at 5 wt% concentration into a host liquid crystal [28]. The ferroelectric liquid crystal mixtures were then evaluated for their mesomorphic properties. The data are summarized in table 4.

As shown in table 4, neither the direction of the central ester linkage nor the fluorination extent significantly affects the transition temperatures of the FLC mixtures. Also, the mesomorphic properties change little with fluorination extent. However, the direction of the central ester linkage does make a great difference to the induced spontaneous polarizations as between compounds **1** and **2**. The compounds **1**, whose central ester linkage is conjugated with the terminal position carrying the achiral perfluoroalkyloxy tail, impart a comparatively large induced spontaneous polarization to the mixtures, while the compounds **2**, whose central ester group is conjugated with the terminal position carrying the chiral tail, have such a small spontaneous polarization induction power that a measurable induced spontaneous polarization was not observed for the FLC

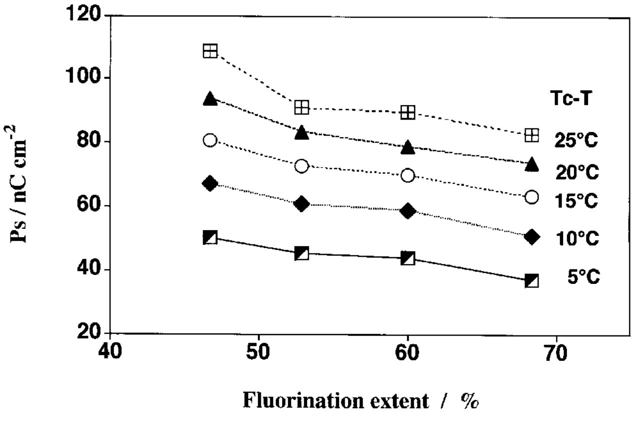


Figure 3. Relationship between **P**s and fluorination extent of the compounds **1**.

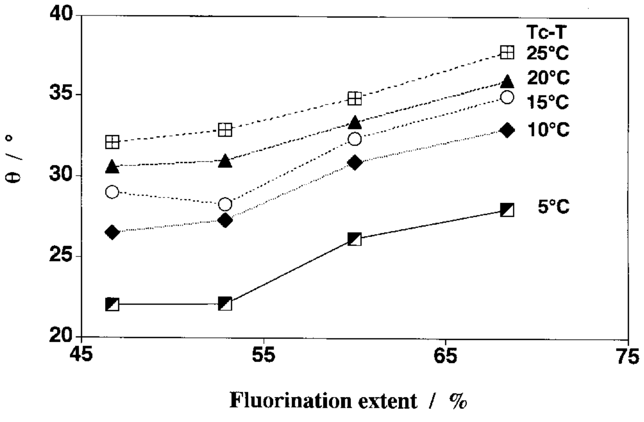


Figure 4. Relationship between tilt angle and fluorination extent of the compounds **1**.

Table 4. Physical properties of ferroelectric liquid crystal mixtures. The host liquid crystal is a mixture of phenylpyrimidine homologues [28] with transition temperatures: Cr<r.t. S_C^* 64 S_A 72·5 N 78 I.

Compounds No.	*m*	*n*	wt %	Transition temperatures Cr		S_C^*		S_A		N*		I	P_s[a] nCcm^{-2}	τ_{10-90}[b] μs	θ[c] degrees
1	3	5	5	•	0·2	•	63·4	•	73·0	•	77·0	•	3·20	250	19·6
	3	4	5	•	0·4	•	65·7	•	73·9	•	77·7	•	2·95	230	20·8
	4	4	5	•	0·2	•	65·7	•	73·9	•	77·6	•	3·59	170	20·2
	4	3	5	•	0·2	•	65·7	•	73·8	•	77·6	•	3·35	130	20·5
2	3	4	5	•	0	•	64·1	•	72·8	•	77·2	•	~0	890	17·0
	4	4	5	•	0·3	•	64·8	•	73·6	•	77·7	•	~0	490	19·5
	4	3	5	•	0·3	•	64·8	•	74·4	•	78·3	•	~0	2380	18·6
	6	3	5	•	0·5	•	64·0	•	75·1	•	77·8	•	~0	/	18·2

[a] P_s was measured using a triangular field of 4 V pp μm^{-1} and an 18 μm cell. $T_c - T = 20$°C.
[b] τ_{10-90} was measured using a rectangular field of 10 V pp μm^{-1} and a 1·4 μm cell. $T_c - T = 20$°C.
[c] θ was measured using a field of ±24 V and a 1·4 μm cell. $T_c - T = 20$°C.

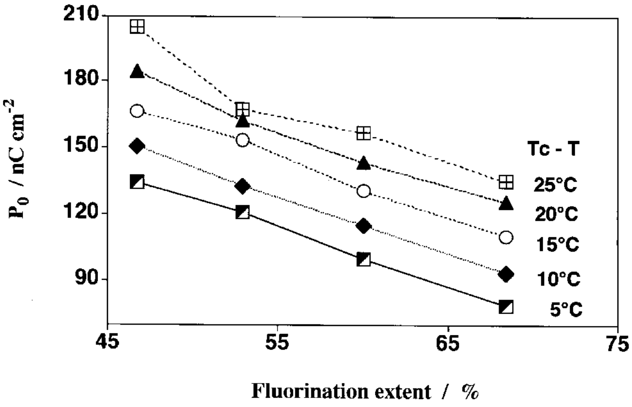


Figure 5. Relationship between normalized polarization and fluorination extent of the compounds **1**.

mixtures doped with the compounds **2**. The result is a very slow response.

It has been reported that the direction of the central ester group of phenyl benzoates influences phase diagrams greatly [1]. But up to now the reason is unclear. In this work, we have found that not only the phase diagram, but also the spontaneous polarization induction power are strongly influenced by the direction of the central ester group of phenyl benzoates. To find the explanation for this, further study is needed.

4. Conclusions

(1) In fluorinated systems, the fluorination extent affects the phase diagrams greatly. At low fluorination extent, the smectic A phase is strongly favoured, while at high fluorination extent, the chiral smectic C phase is especially favoured.
(2) The tilt angle increases with increasing fluorination extent and P_0 decreases with increasing fluorination extent for the compounds **1**.
(3) The direction of the central ester group influences both phase diagrams and liquid crystalline properties. When the ester group is conjugated with the terminal position carrying the chiral tail, the spontaneous polarization induction power decreases to such a small extent that no measurable spontaneous polarization was obtained for a ferroelectric liquid crystal mixture.

5. Experimental

A Nikon Optiphoto-pol polarizing microscope in conjunction with a Mettler FP82HT hot stage and central processor was used for phase identification and transition temperature determination. Differential scanning calorimetry (DSC) was performed using a MAC Science DSC3100 system. The spontaneous polarization was measured using the triangular wave method using a field of 4 V μm^{-1} and a thick cell. The response times for ferroelectric liquid crystal mixtures were measured using a rectangular wave at a field of 10 V μm^{-1} and with a 1·4 μm cell. The cell used was constructed from indium oxide coated glass plates. The inner surfaces of the plates were coated with a polyimide alignment film in order to achieve a homogeneous planar alignment.

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