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SYNTHESIS OF SEMI-PERFLUORINATED FLCs AND THE EFFECT OF FLUORINATION EXTENT ON MESOMORPHIC PROPERTIES

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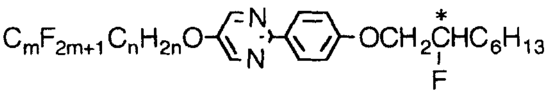
Abstract A series of semi-perfluorinated ferroelectric liquid crystals, 5-(n-perfluoro alkyl)alkyloxy-2-[p-(2-fluorooctyloxy)phenyl]pyrimidines, was synthesized and their mesomorphic properties investigated. Compared with non-fluorinated analogue , chiral smectic C phase is strongly enhanced. All of the compounds showed chiral smectic C phase enantiotropically. As fluorination extent of the achiral tail increased, tilt angle, spontaneous polarization and response time increased. Especially, when the length of the achiral tail is seven and fluorination extent is 60%, chiral smectic C phase is so stable that smectic A phase completely disappeared. What's more, its spontaneous polarization is more than $300nC \cdot cm^{-2}$. All the compounds showed little temperature dependence of response time.

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 so as to prepare desirable materials, various molecular design have been made 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 polymorphism[2]. Also, modification of the chiral end group, which is all-important in a ferroelectric liquid crystal molecule, can significantly influences both polymorphism and ferroelectric properties such as the direction and magnitude of spontaneous polarization, tilt angle and helical twist sense[3]. Recently, modification of the core such as introducing a fluoroatom to the different position of the core is actively studied[4]. What is deserved to notice here is that reports on changing the nature of the achiral tail for systematic research are few. The main reason for this is that few chemical modification are available. Except carbon, no other tetravalent elements are suitable for ferroelectric liquid crystal backbone. Hydrogens in organosilicons are reactive and tin is too large to favor mesophases. Thus, only substitution for hydrogen seems possible for modification of achiral endgroups.

In fact, only perfluorocarbon chains can be used instead of hydrocarbon ones due to steric factor and general availability[5].

It has been reported that the fluorination of the hydrocarbon strongly enhanced smectic behavior which tends to be S_A phase[6]. Recent studies revealed that at least in semi-fluorinated phenylbenzoate systems, smectic A phase is favored at low extent of fluorination, which is defined as the percentage of Fs relative to the total Fs+Hs, and chiral smectic C phase is enhanced at high extent of fluorination[7-8]. In this paper, we will report the synthesis of the fluorinated ferroelectric liquid crystals, 5-(n-perfluoroalkyl)alkyloxy-2-[p-(2-fluorooctyloxy)phenyl]pyrimidines(Scheme 1), and discuss their physical properties. Using these compounds allow us to investigate the relationship between the extent of fluorination and the liquid crystalline properties.

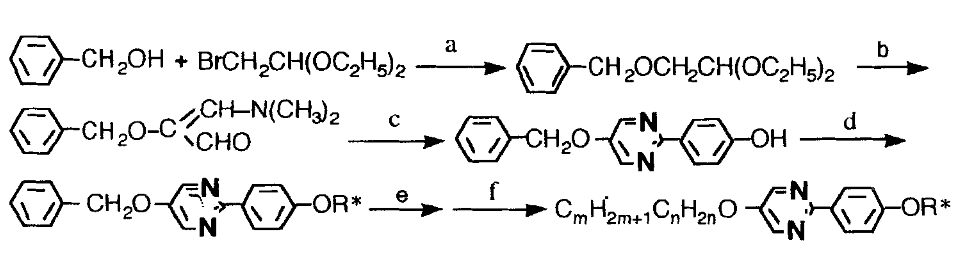


m+n=7 **1** m+n=8 **2** m+n=9 **3**

SCHEME 1

EXPERIMENTAL

Compounds **1-3** were synthesized as outlined in scheme 2. The structure of the intermediates and products were determined by ^{1}H-NMR and ^{13}C NMR(Bruker ARX 400), IR(Perkin-Elmer FT1640) and mass spectroscopy(JEOL DX303). A Nikonoptiphoto-pol polarizing microscopy in conjunction with a Mettler FP82HT hot stage and central processor was used for phase identification .Transition temperatures were determined by differential scanning calorimetry(MAC Science DSC3100). The spontaneous polarization was measured using the triangular wave method under a field of 4Vpp μm^{-1} with a thick cell.The response time was measured using a rectangular



(a) NaH, dry DMF; (b) Triphosgen, dry DMF; (c) p-Hydroxybenzamidine, dry methanol; (d) $C_6CH_{13}\overset{*}{C}H(F)CH_2OTs$, NaH, dry DMF; (e) 5% Pd/C, H2; (e) $C_mH_{2m+1}C_nH_{2n}OTs$, NaH, dry DMF.

SCHEME 2 Synthetic route of compounds **1-3** wave under a field of 4Vpp·μm^{-1} with a thick cell. The cell used was constructed from indium oxide coated glass plate. The inner surface of the cell was coated with a polyimide alignment film in order to achieve a homogeneous planar alignment.

RESULTS AND DISCUSSION

Phase diagram

Phase transition temperatures of compounds **1**-**3** are listed in table1. All of the compounds showed an entiotropic Sc* phase. At the same length of the achiral tail, liquid crystalline property, especially Sc* phase increased with increasing fluorination extent. Compared with the non-fluorinated analogues[9], although both the thermal stability of S_A and Sc* increased, the temperature range of S_A decreased while the temperature range of Sc* increased. For compound **2d**, the A-C transition temperature is 43.7℃ higher than that of **2a** and the temperature range of Sc* is more than 8 times as wide as that of **2a**. At the same time, the temperature range of S_A decreased from 20℃ to 2.9℃. And for compound **3d**, the A-C transition temperature is 55.9℃ higher than that of **3a** and the temperature range of Sc* is more than 6 times as wide as **3a**. What is fascinating is that for compound **1b**, Sc* was so strongly favored that S_A completely disappeared.

As we have suggested previously[7], the more the larger fluorine atom is introduced into an achiral endgroup, the more the molecule tends to be tilted in order to minimumize the useless space. Thus, tilted Sc* is more favored than orthogonal S_A. The results of semi-perfluorinated phenylpyimidines also support such a suggestion.

TABLE 1 Phase transition temperatures of compounds **1**-**3**

No.	m	n	Cr1	Cr2		Sc*		S_A		Iso
1a	3	4	-	·	80.7	·	109.9	·	113.3	·
1b	4	3	-	·	78.9	·	-		123.3	·
2a	0	8	-	·	70	·	74	·	94	·
2b	2	6	-	·	78.5	·	90.2	·	109	·
2c	3	5	-	·	102.5	·	110.5	·	120	·
2d	4	4	-	·	84.2	·	117.7	·	120.6	·
3a	0	9	-	·	71	·	82	·	94	·
3b	3	6	67.8	·	70.8	·	108.5	·	117.3	·
3c	4	5	-	·	94.5	·	119.2	·	126.4	·
3d	6	3	78.2	·	82.5	·	137.9	·	142.2	·

Physical properties

The physical properties of compounds **1**-**3** were summarized in table 2. The first-order transition nature of **1b** gives it a tilt angle as large as about 45°. For **3d**, although the A-

C transition is a second-order one, the tilt angle is also as large as 45°, which can be attributed to the high extent of fluorination of the achiral endgroup.

Three sets of compounds showed a similar tendency of temperature dependence of tilt angle, spontaneous polarization and response time. The temperature dependence of tilt angle of **2** is shown in figure 1. It showed that the tilt angle increased with increasing fluorination extent. This coincides with that the larger fluorine atom leads the molecule to tilt as mentioned above.

TABLE 2 Physical properties of compounds **1**-**3**

No.	m	n	θ (deg.)	Ps ($nC \cdot cm^{-2}$)	Po ($nC \cdot cm^{-2}$)	τ (μsec.)	T (°C)
1a	3	4	32.3	107.2	200.4	16.2	100
1b	4	3	44.5	202.9	289.4	21.8	100
2a	0	8	-	41.5	-	11.0	70
2b	2	6	17.6	54.1	181.4	12.5	85
2c	3	5	28.6	79.4	166.1	15.3	100
2d	4	4	37.8	130.2	212.4	18.8	100
3a	0	9	-	90.3	-	10.3	100
3b	3	6	26.3	71.0	160.6	12.6	100
3c	4	5	33.7	101.4	182.7	19.2	100
3d	6	3	45.2	170.7	241	22.6	100

The temperature dependence of spontaneous polarization P of **2** is depicted in figure 2. As shown in the figure, similar to the tilt angle, P increased with increasing fluorination extent, too. Since P is a function of the tilt angle, the tilt angle should be taken into account to allow for accurate comparison of the effect of the extent of fluorination. A normalized polarization Po was afforded by dividing Ps by sinθ. The results showed that high fluorination extent gave a large value of Po, too.

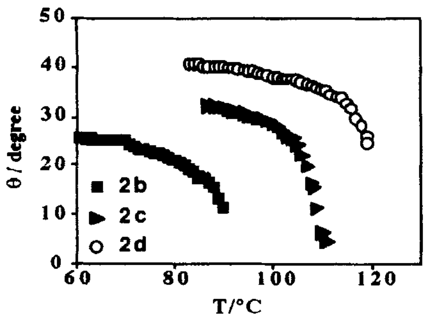


FIGURE 1 Temperature dependence of tilt angle of **2**

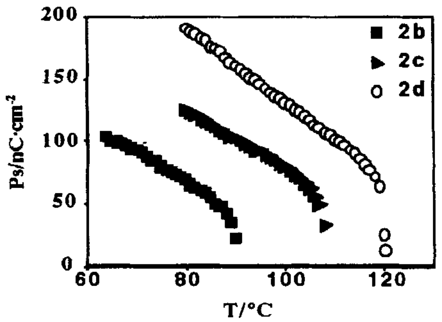


FIGURE 2 Temperature dependence of Ps of **2**

Response time is closely related to viscosity η, spontanoeus polarization Ps and applied voltage E. Large Ps and low viscosity are expected to result in a fast response according to equation (1).The fast response time and low temperature dependence of **1**-**3** can be attributed to the low viscosity by fluorination. Because of the similar structure of **1**-**3**, their viscosity can be considered as almost the same. Thus, according to equation (1), the compound with larger Ps will give a faster response. However, opposite results were obtained. As shown in table 2 and figure 3, the less fluorinated compound shows a faster response. It could be ascribed to the weight of the molecule.

$$\tau \doteqdot \eta / E \cdot Ps \tag{1}$$

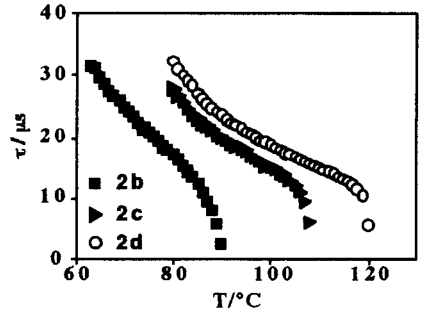


FIGURE 3 Temperature dependence of τ of **2**

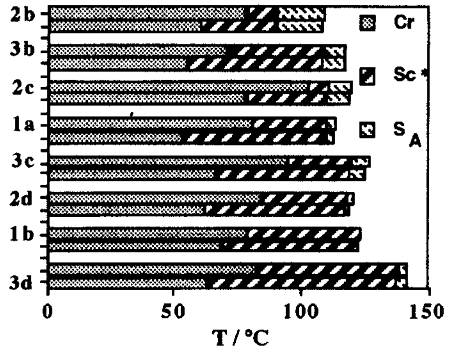


FIGURE 4 Relationship between fluorination extent and phase diagram

Usually, the heavier a molecule is, the slower it moves. Although fluorine atom has a small radius comparable with hydrogen atom, its weight is about 20 times as heavy as that of hydrogen. Thus, the higher extent of fluorination results in heavier molecule, and in spite of larger Ps, leads to slow response.

Effect of fluorination on phase diagram

Although simple change in length of the aliphatic tails can strongly influences the polymorphism in non-fluorinated systems, when fluorinated, molecular interaction greatly changes so that fluorinated systems behave quite differently from non-fluorinated ones. In non-fluorinated systems, Sc* phase becomes stable with increasing length of the aliphatic tail. But in fluorinated systems, the effect of fluorination is greater than that of the length of the tail to some extent. As described in the section of phase diagram, at the same length of the achiral endgroup, Sc* is favored with increasing fluorination extent. Without considering the length of the achiral tail, higher extent of fluorination also gives more stable and wider Sc* phase as shown in figure 4. **1b** with a short length of terminal group but high extent of fluorination showed a more stable Sc* phase than **2** and **3** except **3d** whose fluorination extent is greater than that of **1b**. Such a result suggests that an appropriate fluorination of the achiral tail is an effective way to increase the stability of Sc* phase.

CONCLUSION

(1) A series of semi-perfluorinated ferroelectric liquid crystals, 5-(n-perfluoroalkyl)alkyloxy - 2-[p-(2-fluorooctyloxy)phenyl]pyrimidines,was synthesized.

(2) The low viscosity by fluorination allows a fast response time and low temperature dependence.

(3) High fluorination extent of the achiral tail gives a large tilt angle, spontaneous polarization. Also high fluorination extent results in a heavy molecule and thus leads to a slow response.

(4) Although both smectic A phase and chiral smectic C phase is thermally stabilized by fluorination, the temperature range of chiral smectic C phase becomes wide, while the temperature range of smectic A phase becomes narrow with increasing fluorination extent.

(5) In fluorinated systems, to some extent, fluorination extent influences liquid crystalline properties more than the length of the achiral tail. A compound with a short length of the achiral tail but high fluorination extent such as **1b** shows a much more stable chiral smectic C phase than a compound with a long length of the achiral tail but low fluorination extent such as **3b**.

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