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Influence of fluorination extent on liquid crystalline properties of semi-perfluorinated phenylpyrimidine ferroelectric liquid crystals

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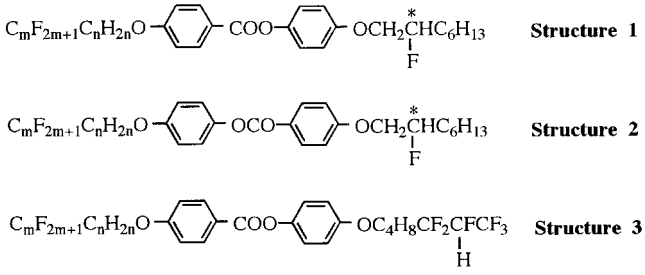
A series of semi-perfluorinated ferroelectric liquid crystals, 2-[4-(2-fluoro-octyloxy)phenyl]-5-(ω-*n*-perfluoroalkylalkyloxy)pyrimidines were prepared and their physical properties evaluated. All of the fluorinated phenylpyrimidines exhibited a chiral smectic C phase enantiotropically. The results showed that high fluorination extent favours the tilted chiral smectic C phase. Also, highly fluorinated compounds exhibited a large cone tilt angle and large spontaneous polarization. However, the response became slow as the fluorination extent increased. Although the compounds showed a large spontaneous polarization in the pure state, their spontaneous polarization power as chiral dopants was so small that very little spontaneous polarization could be measured.

1. Introduction

In non-fluorinated liquid crystal systems, a simple change in the length of the achiral terminal chain strongly influences their polymorphism [1]. Usually the long terminal chain favours smectic modifications. When the carbon chain length is greater than six atoms, tilted phases are promoted over orthogonal phases. When the terminal chain is fluorinated, the mesomorphic phase sequence is expected to change greatly due to the change of the nature of the terminal chain. It is known that smectic modifications, especially smectic A phase, are favoured by fluorination of the terminal chain [2, 3]. Our systematic investigation on partially perfluorinated phenylbenzoates (scheme 1) revealed that the smectic A phase is strongly favoured at low fluorination and chiral smectic C phase is especially favoured at high fluorination [4–7]. For example, the non-fluorinated analogue of structure **1** showed an enantiotropic chiral smectic C phase. However, when only two carbons were fluorinated, the chiral smectic C phase disappeared completely; only a smectic A phase appeared. As the fluorination extent increased, the chiral smectic C phase reappeared. Such an interesting phenomenon was also found in another phenylbenzoate series with a partially perfluorinated chiral tail (structure **3**) [8].

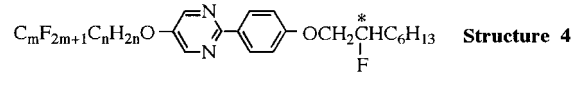


Scheme 1.

Since not all of the compounds with structures **1** or **2** exhibited a chiral smectic C phase, the relationship between ferroelectric properties and fluorination extent could not be investigated systematically. For such a purpose, phenylpyrimidine could be a good choice. Hence, we have prepared 2-[4-(2-fluoro-octyloxy)phenyl]-5-(ω-*n*-perfluoroalkylalkyloxy)pyrimidines (structure **4**). In this paper, we will report their synthesis and mesomorphic and physical properties and elucidate the relation of the fluorination extent to these properties.

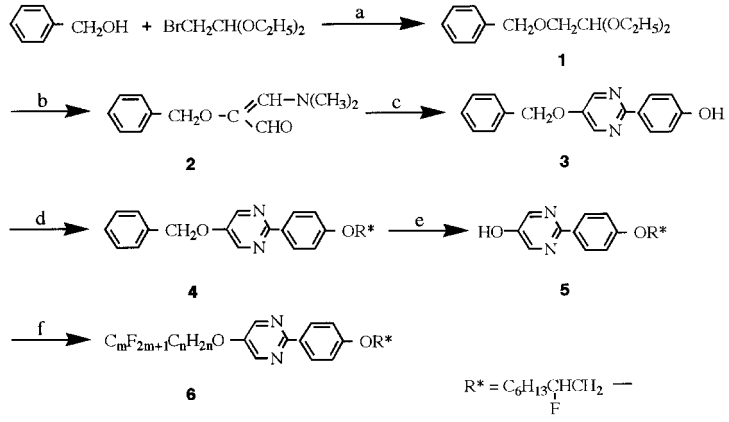
2. Synthesis

The target compounds, **6**, 2-[4-(2-fluoro-octyloxy)-phenyl]-5-(ω-*n*-perfluoroalkylalkyloxy)pyrimidines, were prepared according to the route shown in scheme 3. Starting from bromoacetaldehyde diethyl acetal and benzyl alcohol, benzyloxyacetaldehyde diethyl acetal (**1**)



Scheme 2.

*Author for correspondence.



(a)Dry DMF, NaH; (b)Dry DMF, triphosgen; (c)p-Hydroxybenzamidine, dry methanol;
(d)Dry DMF, NaH, R*OTs; (e) 5%Pd/C, H_2, methanol/ethyl acetate;
(f)Dry DMF, NaH, $C_mF_{2m+1}C_nH_{2n}OTs$

Scheme 3. Synthetic route for 2-[4-(2-fluoro-octyloxy)phenyl]-5-(ω-*n*-perfluoroalkylalkyloxy)pyrimidines (**6**).

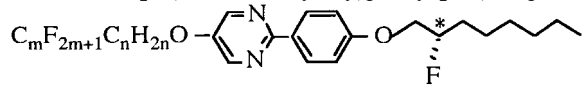
was synthesized. The following Vilsmeier reaction afforded 2-benzyloxy-3-dimethylaminoacrolein (**2**), which was then treated with 4-hydroxybenzamidine to afford 5-benzyloxy-2-(4-hydroxyphenyl)pyrimidine (**3**). Williamson etherification of **3** with 2-fluoro-octyl *p*-toluenesulphonate gave 5-benzyloxy-2-(2-fluoro-octyloxy)pyrimidine (**4**), which was then deprotected to give 2-[4-(2-fluoro-octyloxy)-phenyl]-5-hydroxypyrimidine (**5**). The target compounds were finally obtained by etherification of **5** with *n*-perfluoroalkylalkyl *p*-toluenesulphonates. The synthesis of *n*-perfluoroalkylalkyl *p*-toluenesulphonates has been reported previously [5].

3. Results and discussion

3.1. *Mesomorphic properties*

The phase behaviour and the transition temperatures of compounds **6** together with two reference compounds are listed in table 1. All the compounds show an enantiotropic chiral smectic C phase. Except for **6b** ($m = 4, n = 3$), all the compounds also exhibited a smectic A modification enantiotropically. Compared with the non-fluorinated analogues [**ref** (**8**) and **ref** (**9**)], the melting points and clearing points increased greatly with fluorination. Comparison of compounds with the same achiral terminal chain length showed that the stability of both smectic A and chiral smectic C phases increases with fluorination extent of the achiral terminal chain (defined as the percentage of fluorine atoms relative to the total number of fluorine atoms and hydrogen atoms) [6]. However, the temperature range of the chiral smectic C phase becomes wide, while the temperature range of the smectic A phase becomes narrow. This tendency can be clearly seen in figure 1. The temperature ranges of the smectic A and chiral smectic C phases for

Table 1. Phase transition temperatures of 2-[4-(2-fluoro-octyloxy)phenyl]-5-(ω-*n*-perfluoroalkylalkyloxy)pyrimidines (**6**).



Compound	$m+n$	m	n	Cr		SmC*		SmA		I
6a	7	3	4	•	80·7	•	109·9	•	113·3	•
6b	7	4	3	•	78·9	•		—	123·3	•
6c	8	2	6	•	78·5	•	90·2	•	109·0	•
6d	8	3	5	•	102·5	•	110·5	•	120·0	•
6e	8	4	4	•	84·2	•	117·7	•	120·6	•
6f	9	3	6	•	70·8	•	108·5	•	117·3	•
6g	9	4	5	•	94·5	•	119·2	•	126·4	•
6h	9	6	3	•	82·5	•	137·9	•	142·2	•
ref (**8**)	8	0	8	•	69·9	•	79·6	•	96·2	•
ref (**9**)	9	0	9	•	63·9	•	89·0	•	96·2	•

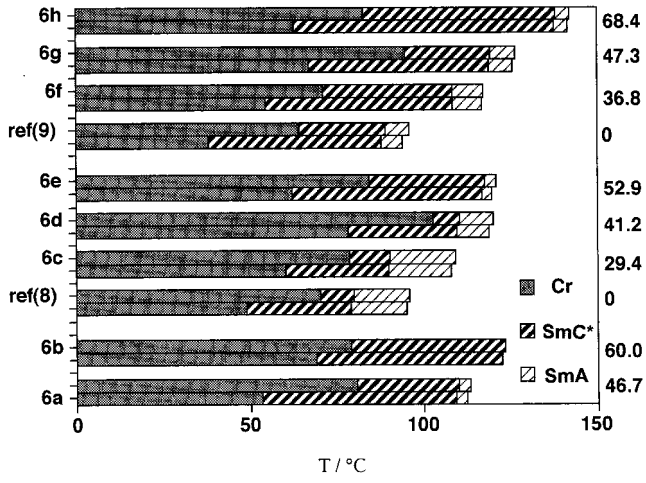


Figure 1. Phase diagram for compounds with the same achiral terminal chain length. The numbers on the right represent the fluorination extent of the achiral terminal chain.

6c are 18·8°C and 11·7°C, respectively. As the fluorination extent was raised to 52·9%, the temperature range of the chiral smectic C phase increased to 33·5°C, while that of the smectic A phase decreased to 2·9°C.

The phase diagram in relation to fluorination extent of the achiral terminal chain irrespective of chain length is shown in figure 2. Similarly to the results for compounds with the same chain length, the thermal stability of the smectic A and the chiral smectic C phases increased with increase of fluorination extent. The temperature range of the chiral smectic C phase also increased, while the temperature range of the smectic A phase decreased irrespective of the terminal chain length.

As would be expected, the terminal chain length greatly affects polymorphism. The achiral chain length of **ref** (**9**) is only one carbon longer than that of **ref** (**8**),

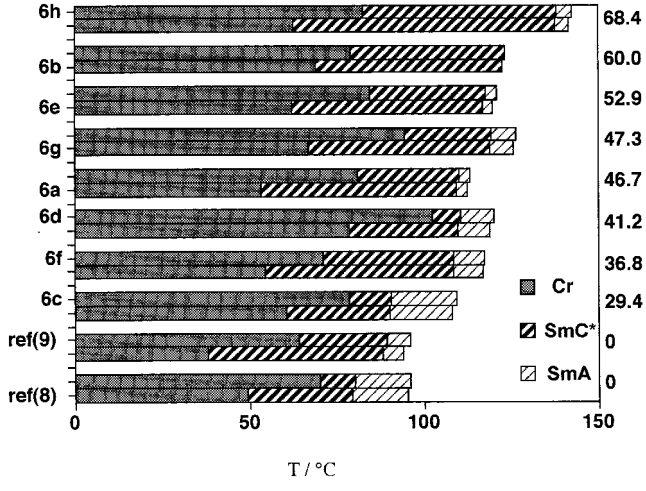


Figure 2. Phase diagram for compounds **6** irrespective of the terminal chain length. The numbers on the right represent the fluorination extent of the achiral terminal chain.

however, the difference in thermal stability of the chiral smectic C phases is 10·6°C. Such a conclusion holds for non-fluorinated systems; however, the situation is expected to be different in fluorinated systems. Let us first compare non-fluorinated and fluorinated compounds with the same achiral terminal chain length. When the achiral terminal chain length is eight atoms, the difference in the thermal stability of the chiral smectic C phase between non-fluorinated **ref** (**8**) and the least fluorinated **6c** is 10·6°C. As the fluorination extent increased, the difference was raised to 30·9°C and 38·1°C when comparing **ref** (**8**) with **6d** and **6e**, respectively. A similar result, that the thermal stability increases with the increasing fluorination extent, is obtained for compounds with an achiral terminal chain length of nine. The thermal stability difference in the chiral smectic C phase between the non-fluorinated **ref** (**9**) and the least fluorinated **6f** is 19·5°C. The difference was raised to 30·2°C and 48·9°C when comparing **ref** (**9**) with **6g** and **6h**, respectively. Secondly, compare **ref** (**9**) with **6a** and **6b**, whose achiral terminal chain lengths are seven, two carbons shorter than that of **ref** (**9**). The result clearly shows that **6a** and **6b** exhibit much more stable chiral smectic C phases than does **ref** (**9**). The thermal stability difference is 20·9°C and 34·3°C for **6a** and **6b**, respectively.

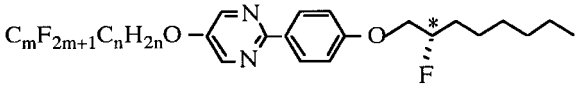
It is clear from this that the effect of fluorination extent of the achiral chain on the stability of the chiral smectic C phase is much greater than that of the length of the achiral tail for fluorinated compounds. In other words, fluorination dominates the phase behaviour in fluorinated systems.

3.2. *Physical properties*

The physical properties are summarized in table 2. Almost all the compounds **6** exhibited a cone tilt angle (θ) greater than 30°; **6b** showed a cone tilt angle as large as 45° due to the first-order nature of the transition [9]. It is noteworthy that **6h** also showed a cone tilt angle as large as 45° in spite of the second-order nature of the A–C transition. This could be due to the high extent of fluorination of **6h**. As described in § 3.1, the chiral smectic C phase is favoured as the extent of fluorination increases. In other words, molecules are prone to tilt with increase in fluorination. Thus, a high level of fluorination produces a large cone tilt angle.

The measurement results of the cone tilt angles of **6f**, **6g** and **6h**, whose achiral terminal chain lengths are 9, are depicted in figure 3. As predicted, a compound with a higher fluorination extent showed a larger cone tilt angle than did a compound with lower fluorination. Similar behaviour was seen in compounds **6a** and **6b**, whose terminal chain lengths are 7, and for **6c**, **6d** and **6e**, whose achiral terminal chain lengths are 8.

Table 2. Physical properties of 2-[4-(2-fluoro-octyloxy)-phenyl]-5-(ω-*n*-perfluoroalkylalkyloxy)pyrimidines (**6**).



Compound	$m+n$	m	n	P_s nC cm^{-2}	τ μs	θ deg	T °C
6a	7	3	4	107·2	16·2	32·3	100
6b	7	4	3	202·9	21·8	44·5	100
6c	8	2	6	54·1	12·5	17·6	85
6d	8	3	5	79·4	15·3	28·6	100
6e	8	4	4	130·2	18·8	37·8	100
6f	9	3	6	71·0	12·6	26·3	100
6g	9	4	5	101·4	19·2	33·7	100
6h	9	6	3	170·7	22·6	45·2	100
ref (**8**)	8	0	8	80·1	15·1	—	70
ref (**9**)	9	0	9	104	17·9	—	70

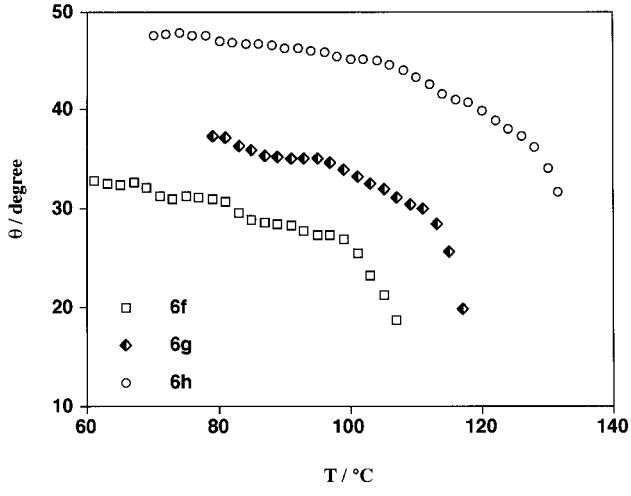


Figure 3. Temperature dependence of tilt angles of compounds **6f**, **6g** and **6h**.

The above discussion indicates that the tilted chiral smectic C phase becomes more stable with the fluorination extent irrespective of the terminal chain length. Thus, the cone tilt angle also increases with fluorination irrespective of the terminal chain length. The results given in figure 4 are coincident with prediction, and therefore strongly support the conclusion that high fluorination extent favours tilting and thus favours the chiral smectic C phase.

The spontaneous polarization ($\mathbf{P}_s$) was also found to increase with increase in fluorination (table 2). The magnitude of $\mathbf{P}_s$ of **6h** is twice that of **6f**. The temperature dependence of **6f**, **6g** and **6h** is shown in figure 5. Similarly to the tilt angles, the increase of spontaneous polarization with increase of fluorination is also

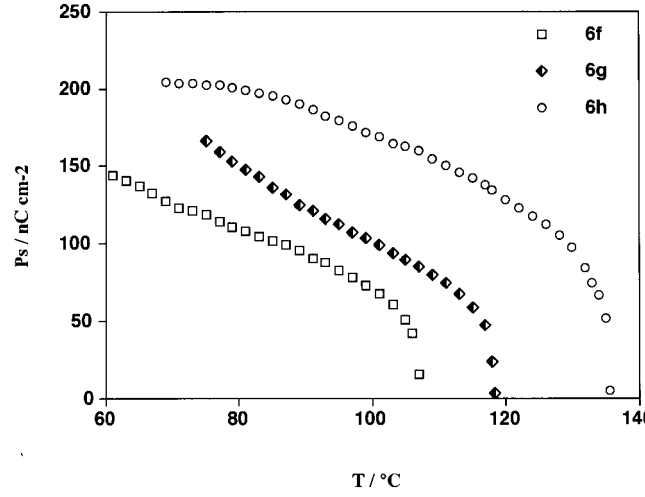


Figure 5. Temperature dependence of spontaneous polarizations of compounds **6f**, **6g** and **6h**.

independent of the achiral terminal chain length, as shown in figure 6.

The response speed is determined by rotational viscosity η, spontaneous polarization $\mathbf{P}_s$ and applied voltage E. For a given viscosity, the larger the spontaneous polarization and applied voltage, the faster the switching speed. The rotational viscosity of the fluorinated homologues **6** could be supposed as the same. Thus, a compound with a large spontaneous polarization could be expected to switch faster than a compound with a lower value. However, the results of measurement of response time (τ) showed an opposite effect (figures 7 and 8). The compound with the lowest fluorination extent, **6c**, which has the smallest spontaneous polarization, shows the

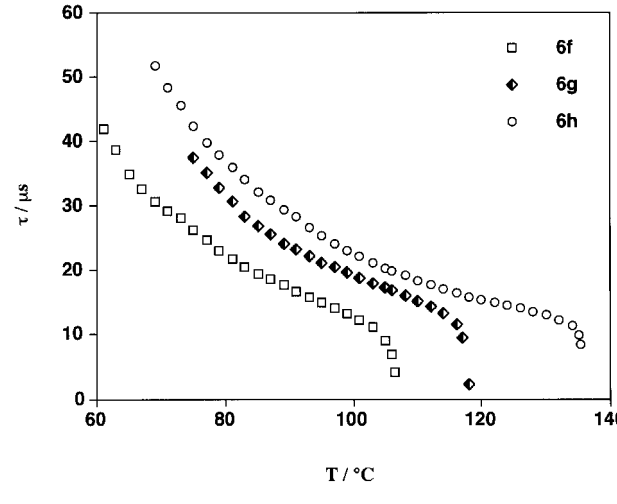


Figure 7. Temperature dependence of response times of compounds **6f**, **6g** and **6h**.

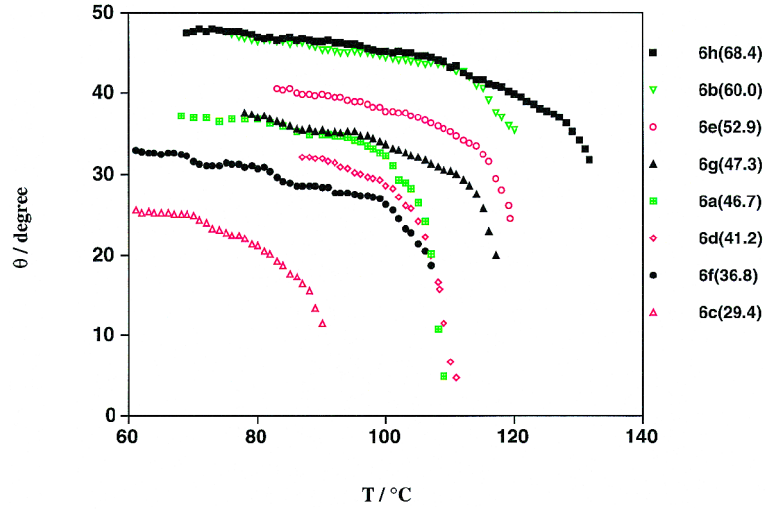


Figure 4. Temperature dependence of tilt angles of compounds **6**. The same colour represents compounds with the same achiral terminal chain length. The numbers on the right represent the fluorination extent of the achiral terminal chain.

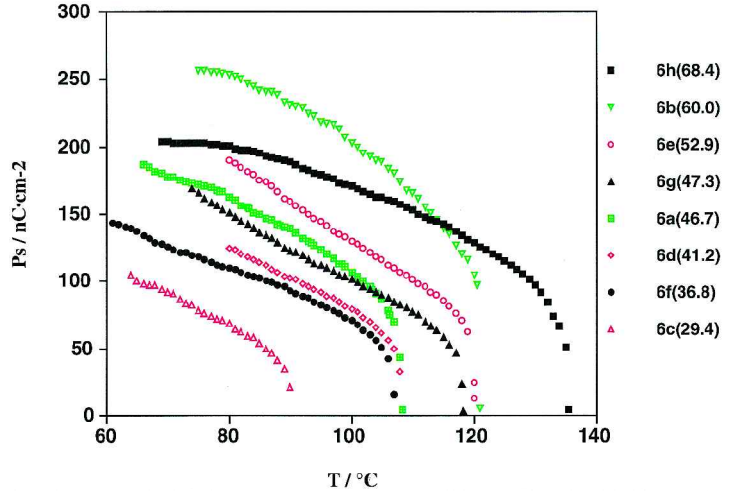


Figure 6. Temperature dependence of $\mathbf{P}_s$ of compounds **6**. The same colour represents compounds with the same achiral terminal chain length. The numbers on the right represent the fluorination extent of the achiral terminal chain.

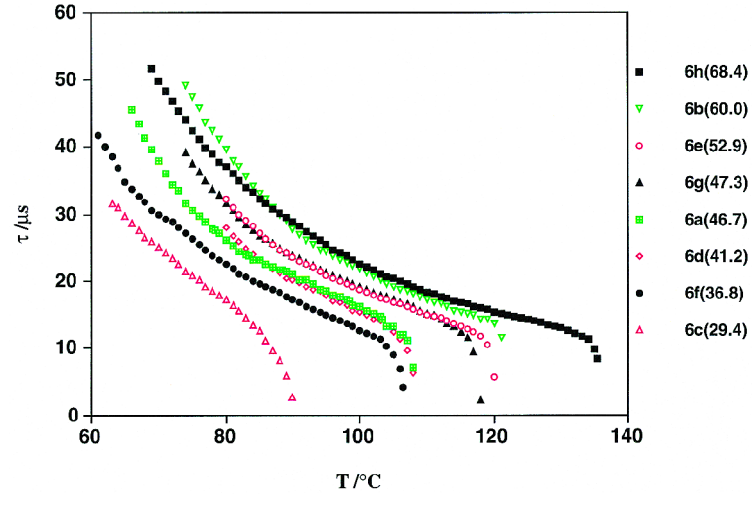


Figure 8. Temperature dependence of response time of compounds **6**. The same colour represents compounds with the same achiral terminal chain length. The numbers on the right represent the fluorination extent of the achiral terminal chain.

fastest response; the compound with the highest fluorination extent, **6h**, which has the largest spontaneous polarization, shows the slowest response. The higher the fluorination extent, the heavier the molecule; it can be imagined that a more massive molecule will reorient more slowly than a light molecule.

All the compounds showed a low temperature dependence of response time, as shown in figure 8.

Table 3. Physical properties of ferroelectric liquid crystal mixtures doped with compounds **6**.

Compound	*m*	*n*	wt %	Cr		SmC*		SmA		N*		I	$\mathbf{P}_s$ / nC cm^{-2}	τ_{10-90} / μs	θ / deg
6a	3	4	2·3	•	<r.t.	•	65·9	•	72·0	•	77·8	•	1·65	520	20·6
6b	4	3	2·0	•	<r.t.	•	65·9	•	72·2	•	78·0	•	~0	900	20·3
6c	2	6	3·1	•	<r.t.	•	65·4	•	74·2	•	79·4	•	~0	230	20·0
6d	3	5	2·3	•	<r.t.	•	65·5	•	74·2	•	78·8	•	2·90	250	19·4
6e	4	4	2·0	•	<r.t.	•	64·1	•	72·8	•	77·2	•	~0	—	—
6f	3	6	2·1	•	<r.t.	•	63·3	•	72·0	•	78·0	•	~0	1370	18·2
6g	4	5	2·0	•	<r.t.	•	63·9	•	72·0	•	79·0	•	~0	1630	18·0
6h	6	3	2·0	•	<r.t.	•	64·3	•	71·5	•	78·0	•	~0	1070	18·5
ref (**8**)	0	8	2·1	•	<r.t.	•	63·0	•	71·0	•	77·4	•	1·0	1200	18·5
ref (**9**)	0	9	2·1	•	<r.t.	•	63·5	•	71·5	•	78·0	•	~0	>2000	17·5

3.3. *Ferroelectric liquid crystal mixtures doped with compounds* ***6***

Compounds **6** were mixed with a host liquid crystal† to prepare FLC mixtures. The phase transition temperatures and physical properties, together with those of the reference compounds, are summarized in table 3. Compounds **6** themselves showed a large spontaneous polarization. However, examination of the physical properties of the ferroelectric liquid crystal mixtures doped with **6** showed that the spontaneous polarization induction power of **6** was so small that almost none was observed for the FLC mixtures. Such a result may be argued to be due to bad compatability between the fluorinated dopants and the base liquid crystal. However, as shown in table 3, the two non-fluorinated reference compounds also afforded an unmeasurable induced spontaneous polarization. It is not yet clear why one compound induces a large $\mathbf{P}_s$, while another compound induces only a very small $\mathbf{P}_s$. The experimental data showed that the spontaneous polarization induction power of a compound seemed to have no direct relationship to the magnitude of its spontaneous polarization in the pure state.

4. Conclusion

We have prepared a series of novel semi-perfluorinated ferroelectric liquid crystals, 2-[4-(2-fluoro-octyloxy)-phenyl]-5-(ω-*n*-perfluoroalkylalkyloxy)pyrimidines and investigated their mesomorphic and ferroelectric properties in detail. The experimental results showed that:

(1) The liquid crystalline mesophases, especially smectic A and chiral smectic C phases, are stabilized by fluorination of the achiral terminal chain.

(2) Although both smectic A and chiral smectic C phases are thermally stabilized by fluorination, the temperature range of the chiral smectic C phase becomes wide, while that of the smectic A phase becomes narrow with increase of the fluorination extent.

(3) Compounds **6** show a short response time with low temperature dependence.

(4) The higher the fluorination extent of the achiral tail, the larger the cone tilt angle and spontaneous polarization, but the slower the response.

(5) In fluorinated systems, fluorination extent influences liquid crystalline properties more greatly than does the length of the achiral tail. A compound with a short achiral tail but high fluorination, such as **6b**, shows a much more stable chiral smectic C phase than a compound with a long achiral tail but low fluorination extent, such as **6f**.

(6) Although compounds **6** showed a large spontaneous polarization themselves, their spontaneous polarization induction power was quite low.

5. Experimental

The structures of chemical intermediates and products were confirmed by ^{1}H NMR and ^{13}C NMR (Bruker ARX400), infrared (IR) spectroscopy (Perkin-Elmer FT1640) and mass spectroscopy (JEOL DX303). The progress of reactions was monitored frequently using gas chromatography or thin layer chromatography. The purity of each final compound was checked by HPLC analysis. Transition temperatures were measured by differential scanning calorimetry (MAC Science DSC 3100) and phase identification was made using a NIKONOPTIPHOTO-POL polarizing microscope in conjunction with a Mettler FP82HT hot stage and central processor. The $\mathbf{P}_s$ was measured using the triangular wave method under a field of 4 V μm^{-1} with a 18 μm cell. The response time τ_{10-90} was measured using a rectangular wave under a field of 10 V μm^{-1} with a 1·4 μm cell and τ was measured using a rectangular wave under a field of 4 V μm^{-1} with a 18 μm cell.

† The host liquid crystal is a mixture of phenylpyrimidines, whose transition temperature is Cr 15 SmC 64 SmA 72·5 N 78 I (°C).

5.1. *Benzyloxyacetaldehyde diethyl acetal (**1**)*

Benzyl alcohol (8·51 g, 78·8 mmol) was added carefully to a suspension of sodium hydride (4·7 g, 117·5 mmol) in DMF at 0°C. The mixture was stirred at 0°C for 30 min and then at ambient temperature for 1 h. Bromoacetaldehyde diethyl acetal (10·35 g, 52·5 mmol) was added to the mixture after the evolution of hydrogen ceased. The mixture was then heated to 120°C for 8 h. After cooling to room temperature, ice water and brine were added to the mixture and the product was extracted into ether (×4). The combined ethereal extracts were dried over sodium sulphate for one night. After removal of the solvent by evaporation, the crude product was distilled at reduced pressure to remove low boiling and high boiling impurities. The distillate at 140°C/7 mmHg was then purified by column chromatography (silica gel/*n*-hexane-ethyl acetate, 3 : 1, $R_f = 0{\cdot}58$). 5·94 g of colourless liquid was obtained. Yield: 50·5%; IR (cm^{-1}, neat): 3088, 3063, 3031, 2975, 2928, 1724, 1705, 1603, 1584, 1496, 1452, 1374, 1115, 1028, 746, 714, 699; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 1·19 (t, $J = 7{\cdot}10$ Hz, 6H), 3·49–3·57 (m, 4H), 3·63–3·70 (m, 2H), 4·55 (s, 2H), 4·65 (t, $J = 5{\cdot}20$ Hz, 1H), 7·21–7·31 (m, 5H, aromatic); ^{13}C NMR (100 MHz, $CDCl_3$) *d* (ppm): 15·6, 62·4, 71·0, 73·7, 101·5, 127·9, 128·0, 128·6, 138·5.

5.2. *2-Benzyloxy-3-dimethylaminoacrolein (**2**)*

Dimethyl formamide (9·05 g, 122·5 mmol) and 1,2-dichloroethane (10 ml) were added to a two-necked flask and then cooled to 0°C. To the mixture was added dropwise a solution of triphosgen (7·63 g, 25·7 mmol) in 1,2-dichloroethane (50 ml) at 0°C (note: poisonous! Use fume cupboard). The mixture was then moved from the ice bath and stirred at room temperature for 1 h. A solution of benzyloxyacetaldehyde diethyl acetal (5·49 g, 24·5 mmol) in 1,2-dichloroethane was added to the mixture. After stirring at room temperature for 1 h, the mixture was heated at 70°C for 2 h. After cooling to ambient temperature, a small amount of ice water was added carefully. Saturated aqueous sodium carbonate was then added at 0°C to decompose the remaining triphosgen. After the evolution of CO_2 had ceased, the mixture was heated to 90°C to remove 1,2-dichloroethane. The product was extracted into a mixed solvent of benzene/ethanol, 2 : 1 (×6); the combined extracts were dried over sodium carbonate. After removal of the solvent, the crude product obtained was twice purified by column chromatography. A mixed solvent of benzene/ethyl acetate (2 : 1) was used as eluent first time. The less polar impurities were eluted and the product remained near the starting point. The product containing polar impurities was then eluted with a mixed solvent of benzene and 99% ethanol (2 : 1). Removal of the solvent gave a brown viscous liquid, which was purified by column chromatography (benzene/ethanol, 8 : 1); 2·24 g (10·9 mmol) of light brown viscous liquid was finally obtained. Yield: 44·5%; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 3·13 (s, 6H), 4·94 (s, 2H), 6·21 (s, 1H), 7·21–7·4 (m, 5H, aromatic), 8·59 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 32·01, 37·07, 74·5, 128·5, 128·9, 129·2, 134·7, 138·1, 150·0, 163·1, 184·2.

5.3. *5-Benzyloxy-2-(4-hydroxyphenyl)pyrimidine (**3**)*

Dry methanol (8 ml) was added to a two-necked flask; finely cut sodium (660 mg) was added under a nitrogen atmosphere. When the evolution of hydrogen ceased, 4-hydroxybenzamidine hydrochloride (2·26 g, 13·1 mmol) was added, and then a solution of 2-benzyloxy-3-dimethylaminoacrolein (2·24 g, 10·9 mmol) in 10 ml dry methanol. The mixture was then heated to 70°C for 6 h. The mixture was cooled to room temperature after partially removing methanol by distillation. Acetic acid (5 ml) and distilled water (10 ml) were added and the product was extracted into ether (×4). The combined ethereal extracts were then washed with saturated sodium bicarbonate and distilled water. After drying over sodium sulphate for one night, the ether was removed by evaporation. Purification by column chromatography, twice (silica gel; benzene/ethyl acetate, 3 : 1), gave 1·03 g (3·71 mmol) of white crystals, m.p. 160·5–162·0°C. Yield: 34·0%; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 5·18 (s, 2H), 5·32 (s, 1H), 6·87–6·92 (m, 2H), 7·36–7·46 (m, 5H), 8·21–8·25 (m, 2H), 8·48 (s, 2H); ^{13}C NMR (400 MHz, $CDCl_3$) δ (ppm): 71·4, 115·9, 128·1, 129·1, 129·3, 129·9, 135·9, 144·8, 151·3, 157·8, 158·4.

5.4. *2-[4-(2-Fluoro-octyloxy)phenyl]-5-hydroxypyrimidine (**5**)*

5-Benzyloxy-2-(4-hydroxyphenyl)pyrimidine (1·03 g, 3·71 mmol) was added to a suspension of sodium hydride (190 mg) in 2 ml DMF. The mixture was stirred at room temperature for an hour. A solution of 2-fluoro-octyl *p*-toluenesulphonate (1·16 g, 3·84 mmol) in DMF was then added and the mixture heated to 120°C for 10 h. After cooling to room temperature, distilled water and brine were added. The resulting white power in the organic layer was purified by filtration and washing with ether. 1·10 g (2·70 mmol) of white solid was obtained.

The 5-benzyloxy-2-(2-fluoro-octyloxy)pyrimidine obtained was then dissolved in a mixed solvent of methanol and ethyl acetate (1 : 2, 90 ml) and 5% palladium carbon (300 mg) was added. The mixture was then stirred at room temperature for 48 h under a hydrogen atmosphere. After filtration of palladium carbon, the solvent was removed by evaporation. Purification on a short column gave a white solid (0·752 g, 2·36 mmol), m.p. 162–164°C. Yield: 87·6%; IR (cm^{-1}, KBr): 3422, 2921, 2856, 1611, 1586, 1560, 1519, 1433, 1306, 1280,

1258, 1179, 1132, 1039, 847, 790; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 0·90 (t, $J = 6{\cdot}8$ Hz, 3H), 1·31–1·75 (overlap peaks, 10H), 4·06–4·20 (m, 2H), 4·76–4·94 (dm, 1H), 5·61 (s, 1H), 6·98–7·02 (m, 2H), 8·24–8·28 (m, 2H), 8·41 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 70·5 (d, $^2J_{C-F} = 23{\cdot}8$ Hz), 92·6 (d, $^1J_{C-F} = 172{\cdot}6$ Hz), 115·2, 116·6, 129·8, 131·2, 145·4, 148·9, 160·8; MS *m/z*: 319 (M^+), 188, 159, 119.

5.5. *2-[4-(2-Fluoro-octyloxy)phenyl]-5-(4-perfluoropropyl)butyloxypyrimidine (**6b**)*

2-[4-(2-Fluoro-octyloxy)phenyl]-5-hydroxypyrimidine (80 mg, 0·25 mmol) was added to a suspension of sodium hydride (20 mg) in 2 ml DMF at room temperature. After the mixture was stirred for 1 h, a solution of 3-perfluorobutylpropyl *p*-toluenesulphonate (109 mg, 0·28 mmol) in DMF was added and the mixture heated to 120°C for 10 h. The mixture was cooled to room temperature, and distilled water and brine were added. The product was extracted into ether (×3), and the combined ethereal extracts were dried over sodium sulphate. The crude 2-[4-(2-fluoro-octyloxy)phenyl]-5-(4-perfluoropropyl)-butyloxypyrimidine was purified by thin layer chromatography and recrystallization from *n*-hexane/ethanol; 123 mg (0·23 mmol) of white crystals was obtained. Yield: 90·8%; IR (cm^{-1}, KBr): 2939, 2858, 1608, 1436, 1358, 1302, 1278, 1251, 1224, 1174, 1134, 1071, 1023, 848, 790, 722; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 0·90 (t, $J = 6{\cdot}7$ Hz, 3H), 1·26–1·43 (overlap peaks, 10H), 1·82–1·94 (m, 2H), 2·16–2·18 (m, 2H), 4·06–4·19 (m, 4H), 4·78–4·91 (dm, 1H), 6·96–7·02 (m, 2H), 8·19–8·31 (m, 2H), 8·41 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 14·7, 17·8, 23·2, 25·5 (d, $^3J_{C-F} = 4{\cdot}6$ Hz, $CDCl_3$) δ (ppm): 14·7, 17·8, 23·2, 25·5 (d, $^3J_{C-F} = 4{\cdot}6$ Hz), 29·3, 29·7, 30·4, 31·0 (t, $^2J_{C-F} = 22{\cdot}3$ Hz), 32·1, 32·3, 68·8, 70·5 (d, $^2J_{C-F} = 23{\cdot}6$ Hz), 92·6 (d, $^1J_{C-F} = 171{\cdot}9$ Hz), 115·2, 129·8, 131·3, 144·4, 151·6, 158·5, 160·8; MS *m/z*: 542 (M^+), 522, 412, 318, 188.

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References

[1] Smith, G. W., Garlund, Z. G., and Curtis, R. T., 1973, *Mol. Cryst. liq. Cryst.*, **19,** 527.
[2] Titov, V. V., Zverkova, T. I., Kovshev, E. I., Fialkov, Yu. N., Shelazhenko, S. V., and Yagupolski, L. M., 1978, *Mol. Cryst. liq. Cryst.*, **47,** 1.
[3] Twieg, R. J., Betterton, K., Dipietro, R., Gravert, D., Nguyen, C., Nguyen, H. T., Babeau, A., and Destrade, C., 1991, *SPIE*, **1455,** 86.
[4] Liu, H., and Nohira, H., 1995, 21st Liquid Crystal Conference, 2C15, Sendai, Japan.
[5] Liu, H., and Nohira, H., 1996, *Liq. Cryst.*, **20**, 581.
[6] Liu, H., and Nohira, H., 1997, *Liq. Cryst.*, **22,** 217.
[7] Liu, H., and Nohira, H., 1996, 16th International Liquid Crystal Conference, D3P.03, Kent, U.S.A.
[8] Liu, H., and Nohira, H., 1998, *Ferroelectrics* (in press).
[9] Goodby, J. W., Blinc, R., Clark, N. A., Lagerwall, S. T., Osipov, M. A., Pikin, S. A., Sakurai, T., Yoshino, K., and Zeks, B., 1991, *Ferroelectric Liquid Crystals* (Gordon & Breach Science Publisher).