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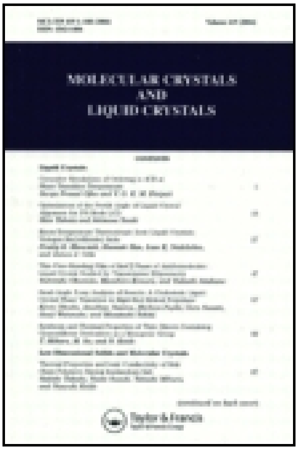

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New Ferroelectric Liquid Crystals Having 2-Fluoro-2-Methyl Alkanoyloxy Group

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New Ferroelectric Liquid Crystals Having 2-Fluoro-2-Methyl Alkanoyloxy Group

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(Received August 25, 1990)

We have prepared ferroelectric liquid crystals with newly designed chiral part, 2-fluoro-2-methyl alkanoyloxy group. The physical properties of the ferroelectric liquid crystals having this chiral part are compared with those of other ferroelectric liquid crystals having 2-fluoro alkanoyloxy group, 2-trifluoromethyl alkanoyloxy group, 2-fluoro-2-trifluoromethyl alkanoyloxy group and 2-methyl alkanoyloxy group. The ferroelectric liquid crystals having 2-fluoro-2-methyl alkanoyloxy group show large spontaneous polarization, compared with other fluorinated ferroelectric liquid crystals. We have investigated the effect of the core structures on the spontaneous polarization. Introduction of a pyrimidine ring in the core part extremely enhances spontaneous polarization, over 400 nC/cm^2. Moreover, we have also investigated the effect of chiral dopants of the compound having this chiral part.

1. INTRODUCTION

Recently, various ferroelectric liquid crystals with large spontaneous polarization, Ps, have been prepared to establish a fast response for electrooptic device.[1, 2] In order to obtain ferroelectric liquid crystals with large spontaneous polarization, a few design points are reported in terms of chemical structures. The points are as follows: (1) The first point on the appearance of the large Ps value is introduction of a large dipole moment close to the chiral carbon, preferably directly to the chiral carbon. (2) The second point is introduction of a bulky group connecting to the chiral carbon.[3–5] (3) The third point is a structure design of the core part of the molecule. However, very little has been elucidated on the effect of the core structures, although they seem to contribute to the Ps value. Therefore, in order to investigate the effect of the core structures, a new chiral part which fulfills the design points (a) and (b) should be designed, and a series of compounds having a various core and together with this chiral part must be prepared.

In this paper, we wish to report a newly designed chiral part, 2-fluoro-2-methyl alkanoyloxy group, and new ferroelectric liquid crystals having this chiral part, and

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discuss the effect of the core structures on the Ps value. Moreover, we wish to report the effect as chiral dopants of the ferroelectric liquid crystals having this chiral part.

2. EXPERIMENTAL

The synthetic route of new ferroelectric liquid crystals having 2-fluoro-2-methyl alkanoyloxy group is shown in Figure 1. The optical active 2-fluoro-2-methyl alkanoic acids were prepared from corresponding commercially available optical active 2-methyl-1,2-epoxyalkane which has been developed recently. That is, optical active 2-fluoro-2-methyl-1-alkanol were prepared by a reaction between optical active 2-methyl-1,2-epoxyalkane and SiF_4 or $(i-Pr)_2NH.4HF$.[6] Next optical active 2-fluoro-2-methyl alkanoic acid was prepared by a oxidation of optical active 2-fluoro-2-methyl-1-alkanol. The phase transition temperatures were obtained using a polarizing optical microscope with a hot stage (Metter FP-82) at a rate of 2.0 deg/min. The spontaneous polarization was measured by the triangle wave method.[7] Homogeneously aligned cells of 3.0 μm in thickness were prepared by rubbing thin polyimide films coated with substrate plates. The optical purities of these compounds in this study were inferred from the optical purities of the starting compounds. The optical purities of the starting compounds are determined by GC analysis of optical active phenetylamine derivatives of the starting compounds. The optical purities of the starting compounds are shown in Table I. The Ps value of

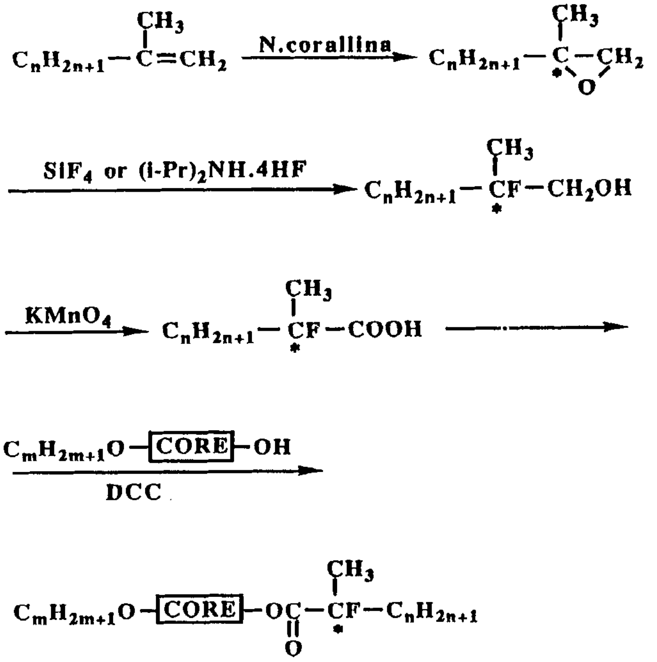

FIGURE 1 Synthetic route of ferroelectric liquid crystals having 2-fluoro-2-methyl alkanoyloxy group.

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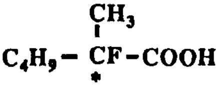
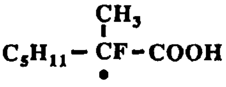
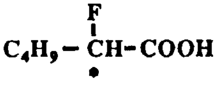
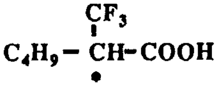
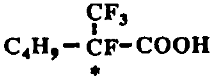
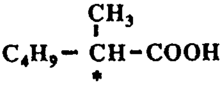
TABLE I

Optical purity of starting compounds

Compound	**Optical purity (%ee)**
 $\mathrm{C_4H_9-\underset{*}{\overset{CH_3}{C}}F-COOH}$	76
 $\mathrm{C_5H_{11}-\underset{*}{\overset{CH_3}{C}}F-COOH}$	80
 $\mathrm{C_4H_9-\underset{*}{\overset{F}{C}}H-COOH}$	71
 $\mathrm{C_4H_9-\underset{*}{\overset{CF_3}{C}}H-COOH}$	95
 $\mathrm{C_4H_9-\underset{*}{\overset{CF_3}{C}}F-COOH}$	93
 $\mathrm{C_4H_9-\underset{*}{\overset{CH_3}{C}}H-COOH}$	70

all compounds are corrected to take into account the optical purities of the corresponding starting compounds. Generally, the spontaneous polarization was determined with a voltage 30 Vpp at a frequency of 100 Hz. The tilt angle was microscopically observed by a field reversal method in which a rotation angle of the sample was measured to achieve extinction between crossed polarizer for the two state with oppositely directed polarization. The response time was measured by applying the rectangular wave of 10 V/μm. We defined response time, τ, as the time when 0–90% of the transmission values detected by a photodiode.

3. RESULTS AND DISCUSSION

3.1 Effect of New Chiral Part on Physical Properties

3.1.1 Phase transition temperature. The molecular structures of compounds **1**–**5** used in this section are shown in Figure 2. The phase transition temperatures of compounds **1**–**5** are shown in Table II. The S_C^* phase thermal stability, defined by the S_A–S_C^* phase transition temperature, of compounds **1** slightly decreases,

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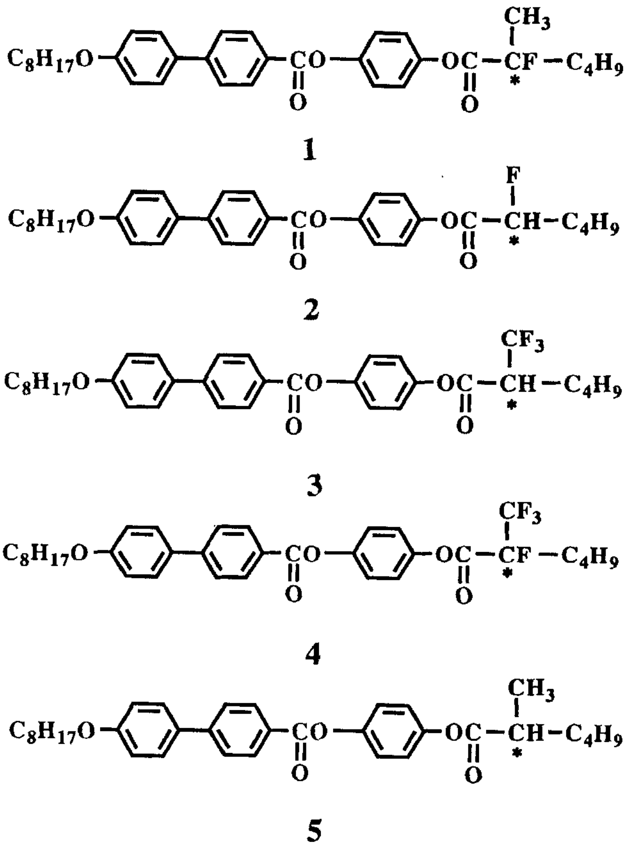

FIGURE 2 Chemical structures of compounds **1**–**5**.

compared with that of non-fluorinated analogous compound **5**. On the other hand, the S_C^* phase thermal stability of compounds **3** and **4** having —CF_3 attached to the chiral carbon greatly decreases, compared with compound **5**. These results suggest that the difference of the size between fluorine (van der waals radius 1.47Å) and hydrogene (1.20Å), or the difference of electrostatic interaction between fluorinated substituents and non-fluorinated substituents attached to the chiral carbon have greatly influence on the S_C^* phase thermal stability.

3.1.2 The Ps Value. The temperature dependence of the Ps value of compounds **1**–**5** are shown in Figure 3. The Ps value increases by introduction of various fluorinated chiral parts. However, the Ps value depends on the structures of the fluorinated chiral parts. The order of the Ps value of the compounds being,

$$\mathbf{5} < \mathbf{4} < \mathbf{2} < \mathbf{3} < \mathbf{1}.$$

The relationship between the structure of the fluorinated chiral parts and the Ps value is summarized as follows: (1) Introduction of —F and that of —CF_3 to the

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TABLE II

Phase transition temperature of compounds 1–5

Compound	**C**	**Sx**	**Sc***	**S_A**	**I**
1	• **115**		• **129**	• **162**	•
2	• **119**	• **125**	• **149**	• **207**	•
3	• **91**	(• **80**)	• **110**	• **154**	•
4	• **83**	(• **82**)	• **108**	• **151**	•
5	• **96**		• **143**	• **167**	•

C, crystalline solid; Sx, unidentified smectic phase; Sc*, a chiral smectic phase; S_A, a smectic A phase; I, isotropic liquid.

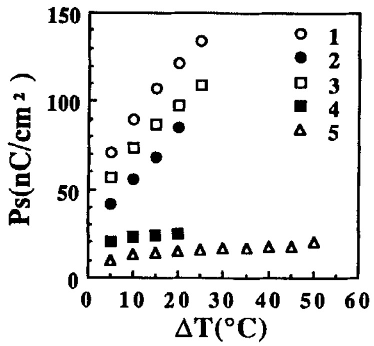

FIGURE 3 Temperature dependence of Ps value of compounds **1**–**5**. The Ps value of all compounds are corrected to take into account the optical purities of the corresponding starting compounds.

chiral carbon in compounds **2** and **3** greatly increases the Ps value. The difference of the Ps value between compounds **2** and **3** depends on the difference of the dipole moments between —F (1.85debye) and —CF_3 (2.35debye).[8] (2) Introduction of —F and —CF_3 to the chiral carbon in compound **4** are scarcely effective on the appearance of the large Ps value because the dipole moments of —F, —CF_3 and —C=O may cancell each other, that is, the Ps value of compound **4** is only 2 times larger than that of compound **5**. (3) Introduction of —F and additional introduction of methyl group to the chiral carbon cooperatively enhance the Ps value, that is, the Ps value of compound **1** is larger than those of other compounds **2**–**4** having various fluorinated chiral parts.

This cooperative effect can be attributable to the bulkiness of the methyl group, that is, the bulky group attached to the chiral carbon suppresses the intra-molecular rotation around the longitudial axis of the molecules as Yoshino *et al.* reported,[3] and help both dipoles of —F and —C=O align in the same direction. Consequently, the dipole moment of —F of compound **1** work very effectively to produce the large Ps value.

3.1.3 Tilt angle. The temperature dependence of the tilt angle of compounds **1–5** are shown in Figure 4. The tilt angle of compounds **1**, **3**, **4** and **5** is almost the same value. However, the tilt angle of compound **2** is smaller than that of other compounds. These results suggest that total size of substituents attached to the chiral carbon has influence on the tilt angle.

3.2 The Effect of Core Structures on the Ps Value

Although there are several reports of the effects of the core structures on the Ps value, most of them have been discussed very small variety of core structures.[9, 10] In order to study the effect of the core structure on the spontaneous polarization systematically, we have synthesized ferroelectric liquid crystals **6–10** having various core structures besides compound **1**. The chemical structures of these compounds are shown in Figure 5. The phase transition temperature and the Ps value of compounds **6–10** are shown in Table III. The Ps value greatly depends on the position and number of the ester groups in the core part. The order of the Ps value of the compounds being,

$$\mathbf{6} < \mathbf{7} < \mathbf{8} < \mathbf{9} < \mathbf{10}.$$

It is clear that the core structure results in a drastic change of the Ps value. The relationship between the core structure and the Ps value will be summarized as following tendencies: (1) Introduction of ester groups in the core decreases the Ps value. (2) The position of the ester groups in the core has an influence on the Ps value in comparison between compounds **7** and **8**. (3) Introduction of a pyrimidine ring in the core part greatly increases the Ps value. The Ps value of compound **10** shows over 400 nC/cm^2.

In this report, we found that this new chiral part is useful to prepare ferroelectric liquid crystals with the large Ps value. However, the core structure also plays an important role in enhancing the spontaneous polarization. The discussion of the

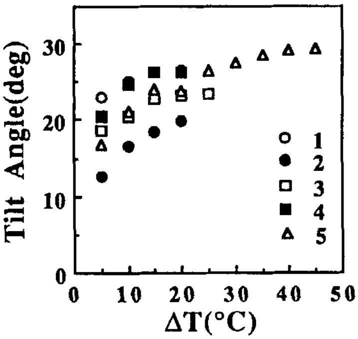

FIGURE 4 Temperature dependence of tilt angle of compounds **1–5**.

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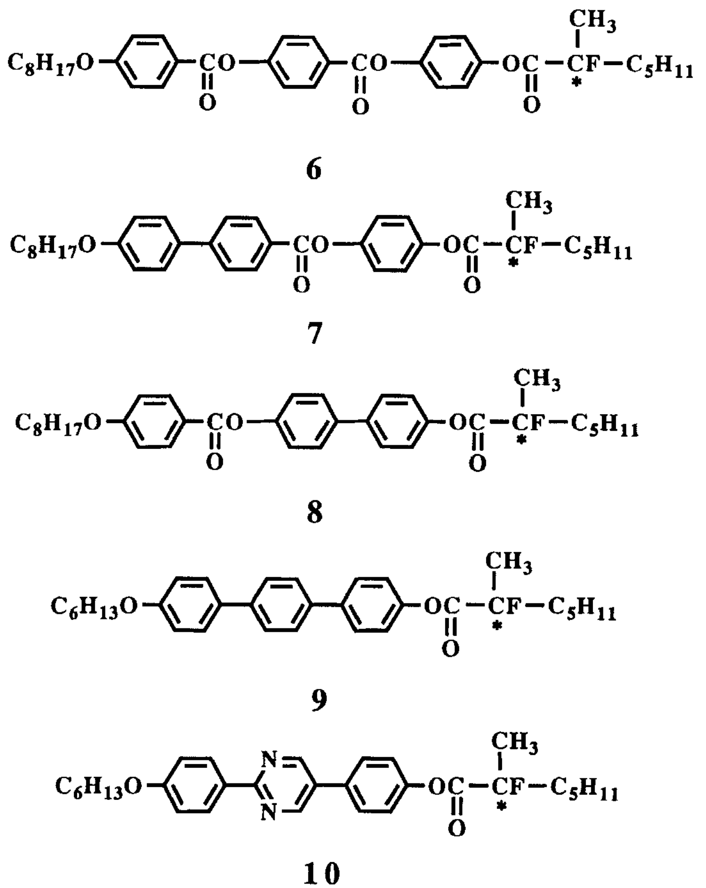

FIGURE 5 Chemical structures of compounds **6**–**10**.

Ps value v.s. the core structure have been made mostly from the standpoint of dipole moment. However, our results suggest that the magnitude of the dipole moments in the core may scarcely affect on the Ps value. Yoshizawa *et al.* reported on the ^{13}C NMR of molecular motions at the S_A-S_C^* phase transition in optical active 4-(2-methyloctanoyl)phenyl 4′-nonylbiphenyl-4-carboxylate.[11, 12] This compound has keto and ester groups as the dipole moments in the molecule. They reported that overall motion of keto carbon are suppressed at the S_A-S_C^* phase transition, although ester carbon in the core are not suppressed. That is, ester group in the core scarcely contribute to the appearance of the Ps Ps value.

Therefore, another factors, which contribute to producing Ps, of the core structure other than dipole moment should be considered, for example, size and shape of the core part, intermolecular interaction between core parts of neighboring molecules. The Ps value of compound **10** is extremely larger than that of compound **9**, which implies that the pyrimidine ring greatly contribute to promoting the interaction between core parts of the molecules.

TABLE III

Phase transition temperature and the Ps value of compounds **6–10**

Compound	Temp(°C)							Ps(nC/cm^2)	
	C		Sc*		S_A		I	T_{AC}-2°C	maximum
6	*	103	(*	100)	*	141	*	5	15
7	*	104	*	136	*	156	*	33	146
8	*	108	*	113	*	130	*	76	176
9	*	172	*	174	*	191	*	87	87
10	*	88	*	130				250	438

C, crystalline solid; Sc*, a chiral smectic C phase; S_A, a smectic A phase; I, isotropic liquid.

4. THE EFFECT AS CHIRAL DOPANT

In previous section, we found the compound with the large Ps value, 5-(4-(2-fluoro-2-methylheptanoyloxy)phenyl)-2-(4-hexyloxy-phenyl)pyrimidine. Next we investigate about the effect as chiral dopant of this compound. In order to elucidate the effect as chiral dopant of this compound, we synthesized other ferroelectric liquid crystals having various fluorinated chiral parts with the same core structures. The molecular structures in this section are shown in Figure 6, and the physical properties of compounds **10–14** are shown in Table IV. We compared the physical properties of compound **10** as chiral dopant with those of other compounds **11–14** having various chiral parts. A non-chiral S_C host (phase transition temperature: Cr 2 C S_C 47 C S_A 62 C N 67 I) being composed of phenylpyrimidines is doped with 11 wt% of chiral dopants under investigation. The physical properties of compounds **10–14** as chiral dopants are shown in Figure 7. The phase transition temperatures of the resulting mixtures are compared with that of host; spontaneous polarization, tilt angle and response time are measured as a function of temperature. The experimental data shown in Figure 7 were obtained at 25°C. We defined response time, τ, as the time when 0–90% of the transmission value was detected by a photodiode. Moreover, the temperature dependence of the response time of compound **10** and **11** is shown in Figure 8. The characteristics of compound **10** having 2-fluoro-2-methyl heptanoyloxy group as chiral dopant will be summerized as follows: (1) The S_C range of host is greatly expanded by doping compound **10**. (2) The doping of compound **10** induces appropriate spontaneous polarization and tilt angle, and this FLC mixture show short response time.

Moreover, the bulkiness of the substituent, —CH_3, attached to the chiral carbon scarcely affect on the increase of the rotational viscosity because the Ps value and the tilt angle is almost the same, and the temperature dependence of the response time is also almost the same in compounds **10** and **11** (see Figure 7 and 8). Consequently, the ferroelectric liquid crystals having 2-fluoro-2-methyl alkanoyloxy

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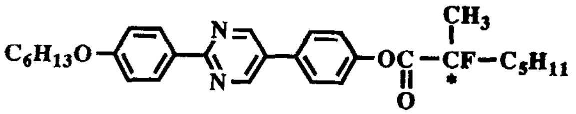

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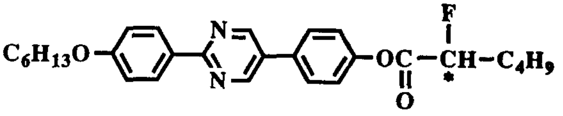

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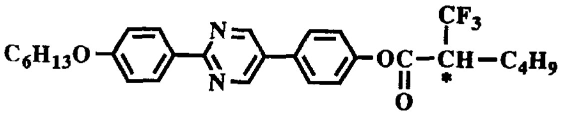

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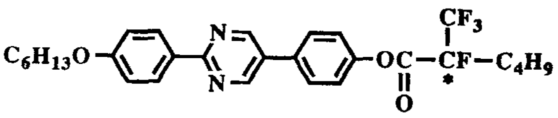

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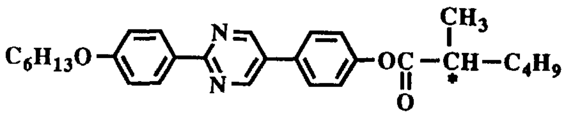


14

FIGURE 6 Chemical structures of compounds 10–14.

group are very useful to preparing ferroelectric liquid crystal mixtures with short response time.

5. FERROELECTRIC LIQUID CRYSTAL MIXTURE

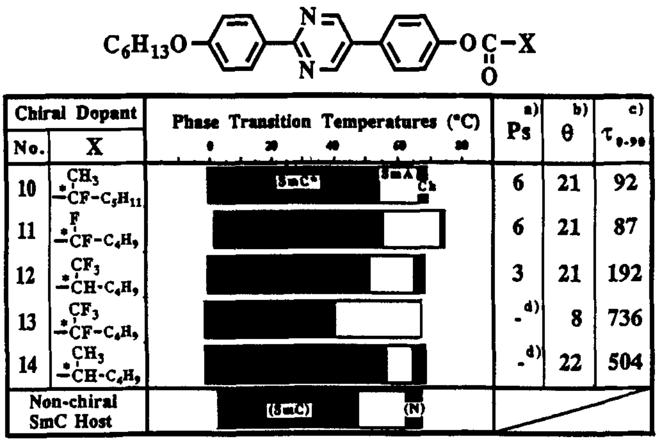
Utilizing ferroelectric liquid crystal having 2-fluoro-2-methyl alkanoyloxy group as chiral dopant, we have prepared new ferroelectric liquid crystal mixtures (see Table V). The mixture, NF-3101, is characterized by phase transition of Cr-S_C^*-S_A-I, spontaneous polarization of 21 nC/cm^2, tilt angle of 24 degree and response time of 27 μsec, and the mixture, NF-3102, is characterized by phase transition of Cr-S_C^*-S_A-Ch-I, spontaneous polarization of 6 nC/cm^2, tilt angle of 21 degree and response time of 55 μsec at 25°C and 10 V/μm. New designed FLC mixtures containing the compounds having 2-fluoro-2-methyl alkanoyloxy group can show very short response time.

TABLE IV

Phase transition temperature and the Ps value of compounds **10–14**

	Temp(°C)									Ps(nC/cm^2)
Comp.	C		Sx		Sc*		S_A		I	T_{AC}-10°C
10	•	88	•		•	130	•		•	269
11	•	134	•		•	183	•	204	•	192
12	•	94	•		•		•		•	—
13	•	92	•		•		•		•	—
14	•	82	•	90	•	150	•		•	32

C, crystalline solid; Sx, unidentified smectic phase; Sc*, a chiral smectic C phase; S_A, a smectic A phase.



Chiral Dopant No.	X	Phase Transition Temperatures (°C)	Ps$^{a)}$	θ$^{b)}$	$\tau_{0\text{-}90}$$^{c)}$
10	$-\overset{CH_3}{\overset{*}{C}}F-C_5H_{11}$		6	21	92
11	$-\overset{F}{\overset{*}{C}}F-C_4H_9$		6	21	87
12	$-\overset{CF_3}{\overset{*}{C}}H-C_4H_9$		3	21	192
13	$-\overset{CF_3}{\overset{*}{C}}F-C_4H_9$		-$^{d)}$	8	736
14	$-\overset{CH_3}{\overset{*}{C}}H-C_4H_9$		-$^{d)}$	22	504
Non-chiral SmC Host					

FIGURE 7 Physical properties of FLC mixtures containing compounds **10–14**. a) spontaneous polarization (nC/cm^2) measured by the triangular wave method at 25°C. b) apparent tilt angle (deg) under application of DC field at 25°C. c) response time (usec) measured by application of rectangular wave of 10 V/μm at 25°C. d) very small (below detection limit).

6. CONCLUSION

Newly designed chiral part, 2-fluoro-2-methyl alkanoyloxy group, is greatly useful to preparing ferroelectric liquid crystals with the large Ps value. The core structure of the ferroelectric liquid crystal compound also has a great influence on the Ps value. This effect of core structure should be attributable to the inter-molecular interaction between the core parts of the neighboring molecules. Moreover, we

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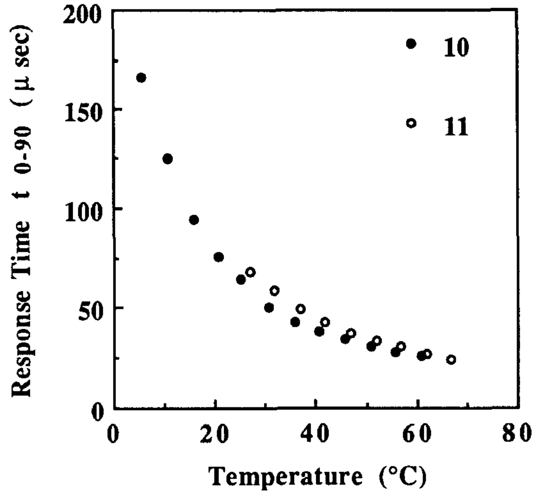

FIGURE 8 Temperature dependence of response time of FLC mixtures containing compounds **10** and **11**. Non-chiral Sc host was doped with 11 wt% of chiral dopants. The response time, τ_{0-90}, was measured by applying the rectangular wave of 10 V/μm.

TABLE V

Physical properties of FLC mixtures, NF-3101 and NF-3102

Code	Phase Transition Temperatures (°C) Cr	Sc*	S_A	Ch	I	τ_{10-90} (μs)[a]	Ps (nC/cm²)[b]	θ (°)[c]
NF-3101	• -9	• 72	• 82		•	27	21	24
NF-3102	• -11	• 64	• 74	• 81	•	55	6	21

[a] Application of rectangular wave of 10 Vpp/μm at 25°C.
[b] The triangular wave method at 25°C.
[c] Apparent tilt angle measured by microscopic observation under application of DC field at 25°C.

could prepare new ferroelectric liquid crystal mixtures with short response time, and 30 μsec.

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