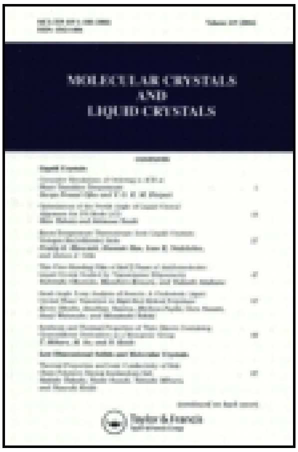

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl18

Synthesis of Fluorine-Containing Ferroelectric Liquid Crystals

Sei'Ichi Arakawa [a] , Kei'Ichi Nito [a] & Jun'Etsu Seto [a]

[a] Sony Corporation Research Center, 174 Fujitsuka-cho, Hodogaya-ku, Yokohama, 240, Japan

Version of record first published: 04 Oct 2006.

To cite this article: Sei'Ichi Arakawa , Kei'Ichi Nito & Jun'Etsu Seto (1991): Synthesis of Fluorine-Containing Ferroelectric Liquid Crystals, Molecular Crystals and Liquid Crystals, 204:1, 15-25

To link to this article: http://dx.doi.org/10.1080/00268949108046590

Mol. Cryst. Liq. Cryst., 1991, Vol. 204, pp. 15–25
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Printed in the United States of America

Synthesis of Fluorine-Containing Ferroelectric Liquid Crystals

SEI'ICHI ARAKAWA, KEI'ICHI NITO and JUN'ETSU SETO
Sony Corporation Research Center, 174 Fujitsuka-cho, Hodogaya-ku, Yokohama 240, Japan

(Received July 25, 1990)

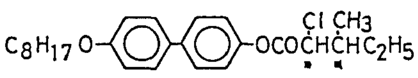
Ferroelectric liquid crystals having a fluorine atom at an asymmetric carbon were synthesized by means of a new method without hydrofluoric acid. An amino acid, L-isoleucine, is converted to (R,S)-α-fluorinated chiral carboxylic acid. Biphenyl and triphenyl type liquid crystals are easily synthesized using this fluorinated carboxylic acid, which show a large spontaneous polarization of 200 nC/cm^2 for the biphenyl type and 300 nC/cm^2 for the triphenyl type. The electro-optic properties of the mixtures consisting of the chiral compound and various non-chiral smectic C (SmC) compounds are also described.

Keywords: ferroelectrics, spontaneous polarization, synthesis, electrooptic properties, F-containing ferroelectrics

1. INTRODUCTION

The invention of the surface stabilized ferroelectric liquid crystal displays (SSFLC)[1] in 1980 initiated the search for chiral smectic C compounds.[2] Nowadays, one of the most important requirements is a fast response time, because the scanning line number of a XY-matrix SSFLC display depends on the response time.

In order to fulfill this requirement, the viscosity of the liquid crystal mixture has to be reduced, or the spontaneous polarization (Ps) has to be increased.[3] Concerning the Ps, the chlorine-containing ferroelectric liquid crystals (FLC) described below showed large Ps greater than 200 nC/cm^2.[4]



In this work, we focused on the synthesis of the fluorine-containing ferroelectric liquid crystals, because of the good stability and higher polarity of a C—F bond compared to a C—Cl bond. The fluorine-containing FLC molecules were synthesized utilizing the ring opening reaction of the chiral epoxides with hydrofluoric acid.[5] However, the synthesized compounds showed a Ps smaller than 80 nC/cm^2.

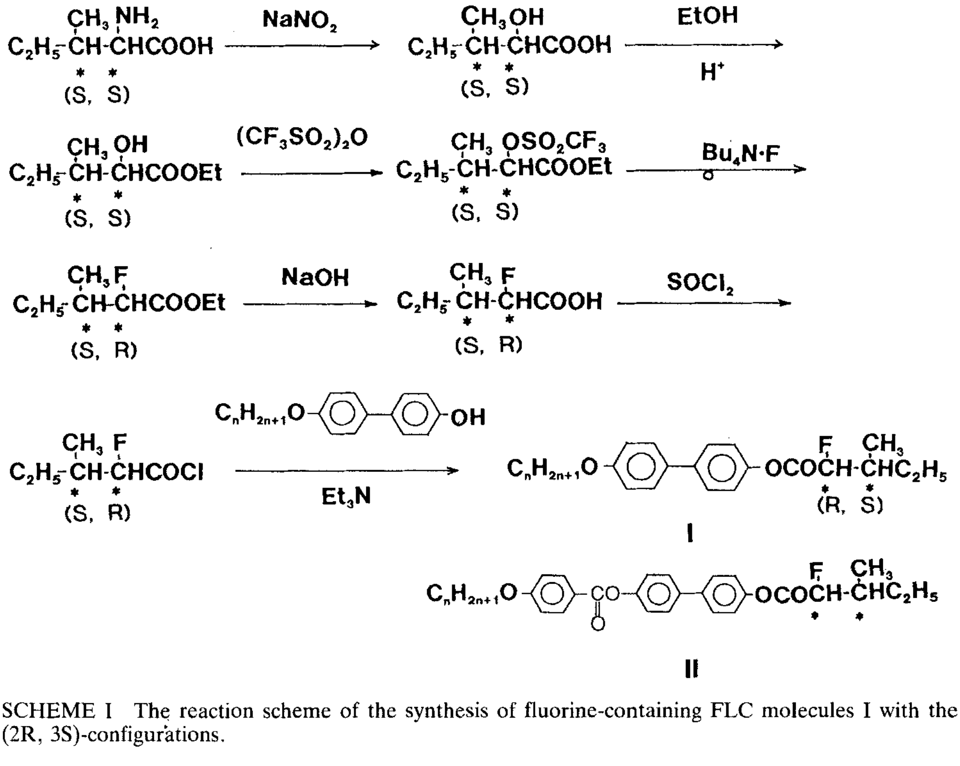
We synthesized the fluorine-containing FLC molecules with large Ps greater than 300 nC/cm^2, using a new and safe method without hydrofluoric acid. The absolute configurations of the chiral centers in the obtained liquid crystals were examined. Furthermore, the electro-optic properties of mixtures consisting of this chiral compound and various non-chiral SmC compounds were also described.

2. RESULTS AND DISCUSSION

2.1 Synthesis of the Liquid Crystals

The scheme of the synthesis of the liquid crystals is shown in Scheme I.

An amino acid, L-isoleucine, is converted to a 2-hydroxy-3-methyl-pentanoic acid ethyl ester, by the reaction with sodium nitrite in the aqueous acetic acid solution and subsequent esterification. This oxy acid ester is converted to a trifluoromethane sulfonate, followed by treatment with tetrabutylammonium fluoride to give a α-fluorinated chiral carboxylic acid ethyl ester. It is saponified and reacted with thionyl chloride or oxalyl chloride to give the corresponding acid chloride. The liquid crystal I and II are easily synthesized by the reaction of this acid chloride with 4,4′-biphenyldiol monododecyl ether or 4-(4-alkoxybenzoyloxy)biphenyl-1-ol, respectively. Although this synthetic method has a lot of reaction steps, it is a steady and effective method, because it contains no complicated process such as an optical resolution, and the yield in each step is high.



SCHEME I The reaction scheme of the synthesis of fluorine-containing FLC molecules I with the (2R, 3S)-configurations.

2.2 Determination of Absolute Configurations of Two Chiral Centers

The liquid crystals I and II have two chiral centers in a molecule. A starting material, L-isoleucine, has the (2S, 3S)-configurations at two chiral centers. The configuration at the 3-position must be retained during the reactions shown in Scheme I. Therefore, it is a most interesting point to know whether the configuration at the 2-position is retained or inversed.

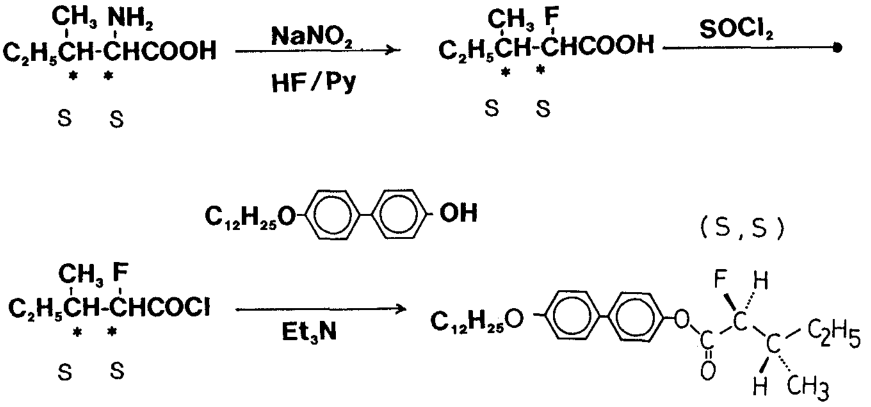
So we examined the following reaction as shown in Scheme II. The reaction of the diazonium salts of the amino acids in acidic solution is known to proceed with a retention of configuration at a chiral center. Therefore, the obtained chiral compound III in Scheme II would have the (2S, 3S)-configurations at two chiral centers. In spite of very low yield in 1–2%, we synthesized the fluorinated chiral compound III.

The proton NMR spectra of the compounds I and III are shown in Figure 1. When we compare two spectra, it is found that the chemical shifts of the proton signals at δ about 5 ppm (the proton at the 2-position, double-doublet, coupled with a fluorine nucleus and a neighbor proton) are mutually different. Therefore, the chiral compounds I and III are not enantiomeric but diastereoisomeric with each other.

Both configurations at the 3-position in the compounds I and III are the S-configurations. Therefore, difference of two compounds is in difference of the configuration at the 2-position. If the compound III has the (S, S)-configurations, the compound I would have the (R, S)-configurations.

Considering the stereochemistry in the reactions shown in Scheme I, the inversion of configuration may occur in only one step, that is, in the substitution reaction of the trifluoromethane sulfonate into a fluorine group with tetrabutylammonium fluoride. This reaction involves S_N2-like substitution with Walden inversion at the chiral center.

Therefore, it is reasonable that the chiral compound I has the (R, S)-configurations. Furthermore, if racemization could occur in the reactions shown in Scheme



III

SCHEME II The reaction scheme of the synthesis of a fluorine-containing LC molecule III with the (2S, 3S)-configurations.

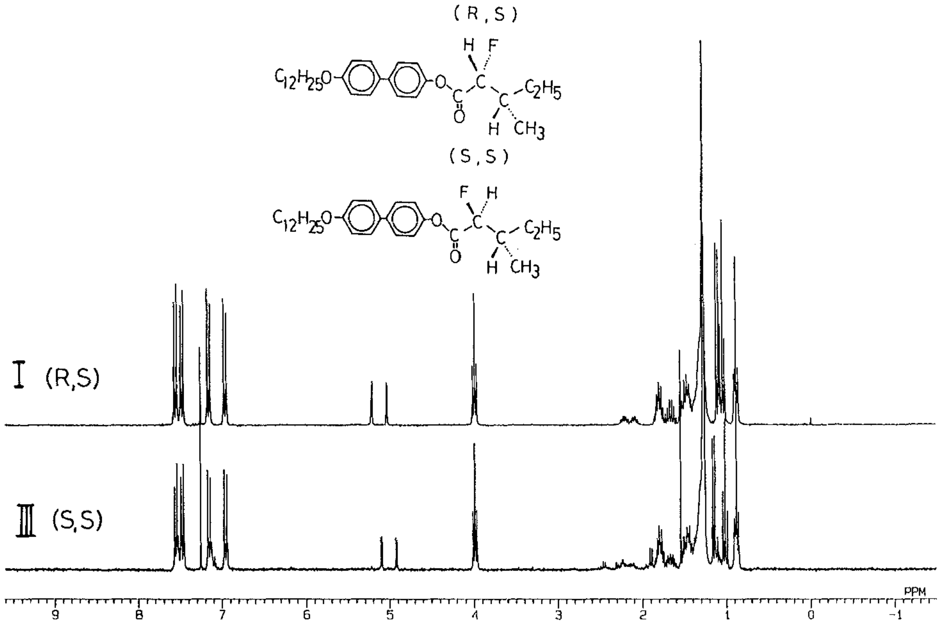


FIGURE 1 The NMR spectra of fluorine-containing LC molecules I and III.

I, the product with the (S, S)-configurations would be observed. The NMR spectrum of the chiral compound I shows no signal of the byproduct with the (S, S)-configurations. This fact indicates that the synthetic method shown in Scheme I is also excellent in a viewpoint of optical yield.

2.3 Phase Transition Temperatures and Spontaneous Polarizations of Chiral FLC Molecules

The phase transition temperatures and spontaneous polarizations of the chiral compounds I–III are shown in Table I.

Biphenyl type compounds I with the (R, S)-configurations having short alkyl chains ($n < 10$) show no chiral SmC* phase but SmA and another smectic phases of a high order. The compound I with $n = 12$ has a SmC* phase with a width of only 10°C, and show large Ps (maximum 200 nC/cm^2) as shown in Figure 2. The diastereoisomeric compound III ($n = 12$) with the (S, S)-configuration shows no SmC* phase but another smectic phase (seems to be SmA).

Triphenyl type compounds II have phase sequences, Iso-N*-SmC*-K, as shown in Table I, and have wide SmC* ranges with the width of 60–70°C, compared to the compound I ($n = 12$). As alkyl chains (n) are longer, the SmC* ranges tend to be wide. The compound II, especially in the case of $n = 8$, shows large Ps greater than 300 nC/cm^2 as shown in Figure 3.

Consequently, the compounds I and II are found to be excellent ferroelectric liquid crystals (FLC's) having large Ps.

TABLE I

The physical properties of synthesized FLC molecules

Compound	Phase transition temp (°C) K↔SmC*↔SmA↔N*↔Iso	Ps (nC/cm^2)††† Tc—30 (°C)	Max
I n=12 (R,S)†	• 71 • 81 • 93 — •	193††	200††
III n=12 (S,S)†	• 61 — • 72 — •	—	—
II n=7	• 81 • 143 — • 225 •	154	250
n=8	• 88 • 150 — • 195 •	135	313
n=9	• 91 • 160 — • 192 •	132	250
n=10	• 90 • 161 — • 190 •	114	210

†Configuration.
††At Tc—5 (°C).
†††The sense of Ps is negative, Ps(−).

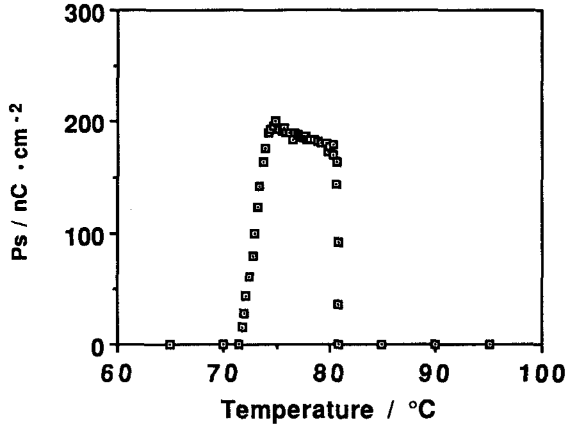


FIGURE 2 The spontaneous polarization of a FLC molecule I (*n* = 12).

2.4 Preparations of the FLC Mixtures and Electro-optic Properties

In order to exhibit the SmC* Phases over wide temperature ranges, we prepared a number of FLC mixtures by mixing of the chiral FLC molecules I or II described above with a non-chiral SmC mixture.

The non-chiral SmC mixtures consist of three types of liquid crystals; phenylpyrimidines (IV), phenylbenzoates (V), and difluorinated biphenyl cyclohexanecarboxylates (VI); their structures are shown in Figure 4. These three types of liquid crystals were mixed and an optimized mixture with a wide SmC range between −13 and 78°C was prepared. The phase sequence and transition temperatures of this mixture are shown in Table II.

The FLC mixtures are prepared by adding the chiral FLC molecules I, II or

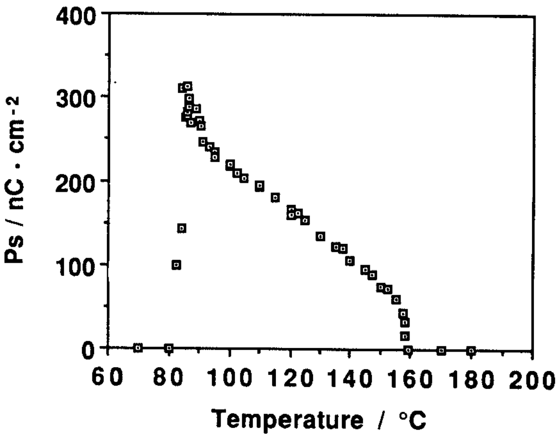
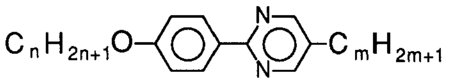
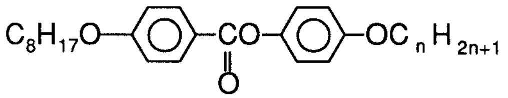


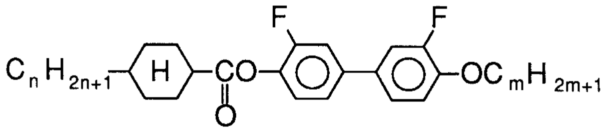
FIGURE 3 The spontaneous polarization of a FLC molecule II ($n = 8$).



IV



V



VI

FIGURE 4 The molecular structures of non-chiral SmC compounds.

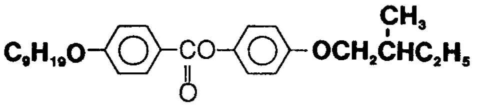
TABLE II

The optimized non-chiral SmC mixture

Liquid crystals	Content (%)	Transition temperature (°C)
IV	22 wt%	$\mathrm{Iso} \underset{105}{\longleftrightarrow} \mathrm{N} \underset{93}{\longleftrightarrow} \mathrm{SmA} \underset{77.5}{\longleftrightarrow} \mathrm{SmC^*} \underset{-12.9}{\overset{-29.2}{\rightleftarrows}} \mathrm{K}$
V	20 wt%	
VI	58 wt%	

other chiral liquid crystals for helical pitch compensation into the optimized non-chiral SmC mixture.

We used the liquid crystal VII for helical pitch compensation, which has opposite twist sense (left-handed) to I or II in both the SmC* and the N* phase. The spontaneous polarization of VII is very small (Ps = 2.7 nC/cm^2), and the sense of Ps is negative, PS(−), similar to that of I or II.



(VII)

$$\mathrm{Iso}\xrightarrow[59.6]{}\mathrm{SmA}\xrightarrow[47.4]{}\mathrm{SmC}\xrightarrow[45.5\,^{\circ}\mathrm{C}]{22\,^{\circ}\mathrm{C}}\mathrm{K}$$

As shown in Table III, the mixture A containing the compounds II (10 wt%) has wide SmC* range between −29 and 83 C and large Ps greater than 13 nC/cm^2, but has short helical pitches (about 3 μm).

In the case of the mixture B containing the compound I, the SmC* range becomes narrow comparing with the mixture A and C, because of generating other smectic phases of high order in lower temperature. The mixture C containing liquid crystal VII for pitch compensation has wide SmC* range and long helical pitches while relatively small Ps. We made 2 μm test cells filled with these FLC mixtures, and examined the electro-optic properties. An orienting layer polyimide (U-Wanisu A, made by Ube Industries Ltd.) is deposited on both glass plates and rubbed in anti-parallel directions.

In Table III, two values of the response time are shown. The chevron structure

TABLE III

The physical properties of the FLC mixtures

Property	Mixture A	Mixture B	Mixture C
Chiral content (%)	10	5	10
Chiral compound	II	I	II/VII=1
SmC* range (°C)	− 29 ~ 83	− 8 ~ 75	− 29 ~ 77
Ps (nC/cm^2)	13.2	7.3	6.5
Helical pitch (μm)			
SmC*	3.4	34.2	32.3
N*	3.2	4.7	9.3
Response time (μsec)			
Before	125	190	170
After field treatment (±30V,100Hz)	155	280	420

[1] The sense of Ps is negative, Ps(−).

[2] The twist senses are right-handed for both the SmC* and the N* phase.

is observed quite generally in SmC* phase, and an electric field applied perpendicular to the substrate plates exerts a force on the smectic layers so as to induce the bookshelf structure.[7–9] Before applying an electric field with 30 Vpp 100 Hz, the response time is fast, but the memory effect is not adequate. On the other hand, on applying an electric field for several tens of seconds, the memory states have become close to the switched states, that is, a good bistability can be generated, as shown in Figure 5. In this case, the tilt angle is 27.4° in the switched states, and 18.9° in the memory states.

The effect of an electric field results in a good contrast ratio of about 27. However, response time increases, compared with in the case of non-applying an electric field.

The relationship of response time to the spontaneous polarization is shown in Figure 6. The response time (τ) was measured, using rectangular-wave drive (10 V/μm; 100 Hz); it was taken equal to the time required for optical transmission change from 0 to 90% taking the difference between the dark and bright states as 100%. The relationship of $\tau \propto 1/Ps$ shown in Figure 6 indicates that an increase of Ps results in faster response, and as Ps is larger, the difference between two response times becomes small.

The obtained response times here are not sufficient to apply to a SSFLC flat display with a great number of scanning lines (over 400 lines).

We have already developed a new FLC mixture with a fast response (τ = 50 μsec), especially by improving the molecular structures of the chiral compounds, which will be described in the next opportunity.

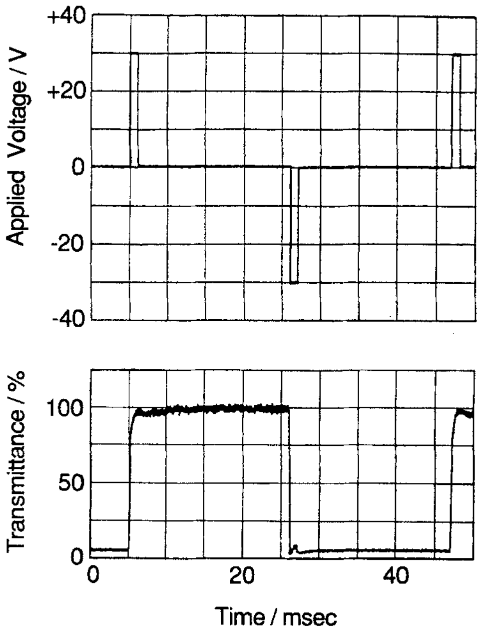


FIGURE 5 The switching behavior of the 2 μm cell filled with the FLC mixture C (±30 V, pulse width 1 ms).

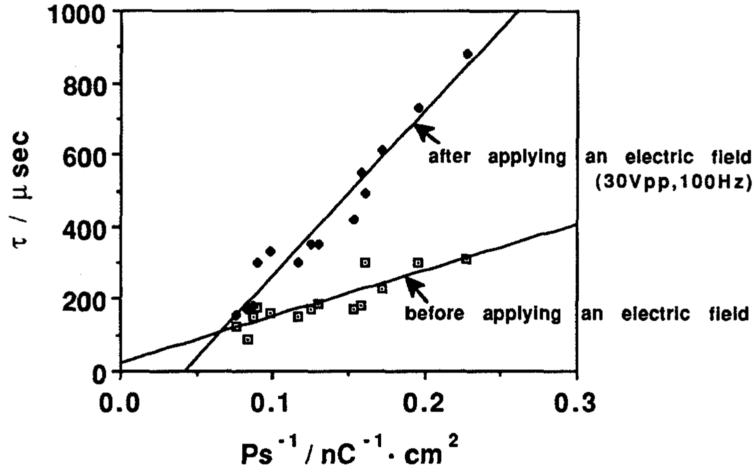


FIGURE 6 The relationship of response time (τ) to Ps.

3. CONCLUSION

We synthesized ferroelectric liquid crystals having a fluorine atom at an asymmetric carbon, by means of a new method without hydrofluoric acid. An amino acid, L-isoleucine, is converted to a chiral fluorinated carboxylic acid, via a reaction of the trifluoromethane sulfonate intermediate and tetrabutyl ammonium-fluoride. Biphenyl and triphenyl type liquid crystals are easily synthesized using this fluorinated carboxylic acid. Analysis of stereochemistry of these FLC molecules revealed that the configurations of two chiral centers were (2R, 3S), accompanying no racemic product. The FLC molecules show large Ps of 200 nC/cm^2 for the biphenyl type and 300 nC/cm^2 for the triphenyl type.

Furthermore, we prepared the FLC mixtures containing these FLC molecules with wide SmC* ranges from −29°C to about 80°C, and Ps from 6.5 to 13.2 nC/cm^2. Then we examined electro-optic properties of 2 μm thick cells filled with these FLC mixtures. On applying an electric field for several tens of seconds with a rectangular-wave of 30 Vpp 100 Hz, the smectic layers were deformed so as to take the Bookshelf structure, and a good bistability can be generated, and resulted in a good contrast ratio about 27. However, response time increased, compared with in the case of non-applying an electric field. The response time obtained here were from 150–420 μs, which are not sufficient to apply to a SSFLC flat display with a great number of scanning lines (over 400 lines). Therefore, we are now developing a FLC mixture with fast response, by improving the molecular structures of the chiral compounds.

4. EXPERIMENTAL

4.1 Synthesis of (2R, 3S)-2-Fluoro-3-methyl-pentanoic Acid

L-Isoleucine (100 g) was dissolved in 490 cc of water, 150 cc of acetic acid and 10 cc of conc. HCl. The solution of NaNO$_2$ 46 g in 350 cc of water was gradually added dropwise, during cooling with ice-water. The mixture was stirred at room temperature overnight, and extracted with ethyl ether several times. Removal of solvent gave (2S, 3S)-2-hyroxy-3-methyl-pentanoic acid. This oxy acid was esterified to give the corresponding ethyl ester (76 g, 67–72°C/2 mmHg, $[\alpha]_D^{28}$ + 5.1, neat), by an usual method.

The oxy acid ethyl ester (38 g) and lutidine (45 g) were dissolved in dichloromethane (200 ml), and cooled to 0°C. Trifluoromethanesulfonic anhydride (90 g) was added dropwise. After being stirred for 30 min, the reaction was quenched with 10% EtOAc in hexane and passed through a short silica gel column. Removal of solvent in vacuo and distillation at 75–80°C/5 mmHg gave 60 g of the trifluoromethanesulfonate (triflate); $[\alpha]_D^{28}$ − 31.3 (neat).

The triflate (60 g) was added to the solution of tetrabutylammonium fluoride ($nBu_4NF \cdot nH_2O$, 60 g) and 300 ml of acetonitrile, and the mixture was in refrigerator overnight. The mixture was then passed through a silica gel column. The solvent was removed in vacuo, and the residue was distilled at 74°C/22 mmHg to give (2R, 3S)-2-fluoro-3-methylpentanoic acid ethyl ester; colorless liquid, 18.4 g, $[\alpha]_D^{28}$ + 6.9 (neat).

This chiral ester (18.4 g) was easily saponified by reaction in 400 ml of aqueous 1N-NaOH solution at room temperature for 8 h, to give (3R, 2S)-2-fluoro-3-methylpentanoic acid, which was converted to the corresponding acid chloride (11.1 g, distilled at 58–60°C/20 mmHg), by an usual method utilizing thionyl chloride or oxalyl chloride.

4.2 Synthesis of Biphenyl Type FLC Molecules I

(2R, 3S)-2-Fluoro-3-methylpentanoyl chloride (0.65 g) was added to the solution of 4,4′-biphenyldiol monododecyl ether (1.27 g) and triethylamine (1 g) in benzene (10 ml), and the mixture was stirred for 1 h. The mixture was passed through a silica gel column (chloro-form-hexane). Removal of solvent and recrystallization from ethanol gave the FLC molecule I (n = 12); yield 1.05 g), colorless crys., NMR (270 MHz, $CDCl_3$)δ 0.88 (*t*, 3H, CH_3), 1.0–1.27 (*m*, 6H), 1.42 (*bs*, 18H), 1.50 (*m*, 1H), 1.67 (*m*, 1H), 1.78 (*m*, 2H), 2.05–2.25 (*m*, 1H), 3.99 (*t*, 2H, CH_2O), 5.03 and 5.21 (*dd*, 1H), 6.97 (*d*, 2H), 7.16 (*d*, 2H), 7.50 (*d*, 2H), and 7.55 (*d*, 2H); MS (70 eV), *m/z* (relative intensity) 470 (54), 354 (14), 302 (19), 274 (5), 186 (100); HRMS Calcd for $C_{30}H_{43}O_3F$ 470.396, Found 470.3,214.

4.3 Synthesis of the Biphenyl type Molecule III

L-Isoleucine (15 g) was dissolved in 70% polyhydrogen fluoride/pyridine (100 ml), magnetically stirred and cooled to 0°C in polyethylene flask. Sodium nitrite (11.5 g) was gradually added, and stirred at room temperature for 1 h, the mixture was quenched with ice/water and extracted with ethyl ether. The ether layer was neutralized with aqueous sodium carbonate solution and dried with magnesium sulfate. The ether was removed and crude (2S, 3S)-2-fluoro-3-methylpentanoic acid was obtained. Without purification, it was converted to the corresponding acid chloride by reaction with thionyl chloride; the yield was only 0.2 g.

The acid chloride (0.2 g) was added to the solution of 4,4′-biphenyldiol monododecyl ether (0.5 g) and triethylamine in benzene. Passing through a silica gel column, removal of solvent, and recrystallization from ethanol gave the chiral compound III; yield 0.15 g, NMR (270 MHz, $CDCl_3$)δ 0.81 (*t*, 3H, CH_3), 0.95 (*t*, 3H, CH_3), 1.08 (*d*, 3H, CH_3), 1.20 (*bs*, 18H), 1.4 (*m*, 1H), 1.65 (*m*, 1H), 1.75 (*m*, 2H), 2.0–2.2 (*m*, 1H), 3.92 (*t*, 2H, CH_2O), 4.85 and 5.03 (*dd*, 1H), 6.89 (*d*, 2H), 7.04 (*d*, 2H), 7.40 (*d*, 2H), and 7.49 (*d*, 2H); MS (70 eV), *m/z* 470 (42), 354 (37), 302 (15), 274 (3.2), 186 (100); HRMS Calcd for $C_{30}H_{43}O_3F$ 470.3196, Found 470.3180.

4.4 Synthesis of Triphenyl type FLC Molecules II

(2R, 3S)-2-Fluoro-3-methylpentanoyl chloride (1.43 g) was added to the solution of 4-(4-octyloxybenzoyloxy)biphenyl-1-ol (1 g) and triethylamine (1 ml) in benzene. Passing through a silica gel column, removal of solvent and recrystallization from ethanol gave the triphenyl type FLC molecule II ($n = 8$); yield 0.8 g, colorless crys., NMR (270 MHz, $CDCl_3$)δ 0.90 (*t*, 3H, CH_3), 1.05 (*t*, 3H, CH_3), 1.11 (*d*, 3H, CH_3), 1.4–1.5 (*m*, 11H), 1.64 (*m*, 1H), 1.83 (*m*, 2H), 2.0–2.3 (*m*, 1H), 4.05 (*t*, 2H, CH_2), 5.05 and 5.23 (*dd*, 1H), 6.99 (*d*, 2H), 7.21 (*d*, 2H), 7.28 (*d*, 2H), 7.63 (*d*, 4H), and 8.17 (*d*, 2H); MS (70 eV), *m/z* 534 (16), 302 (4), 234 (100); HRMS Calcd for $C_{33}H_{39}O_5F$ 534.2782, Found 534.2745.

4.5 Measurements of Physical Properties of FLC Molecules and FLC Mixtures

The Phase sequence behavior was monitored with DSC and polarized microscopy. The thermograms were collected on a Rigaku Denki DSC-8240 at heating/cooling rates of 2°C/min. The peak temperatures were taken to be the phase transition point and the samples were run under N_2. Phase texture observations were made with Nikon OPTIPHOT microscope equipped with a Mettler FP82 hot stage. The spontaneous polarization (Ps) was evaluated by the triangular-wave method.[10] The electro-optic effects in the cells filled with the FLC mixtures were studied by observing the change of the optical transmission through the cell during application of voltage pulses. The response time was determined by the 0 to 90% transmission change, when a rectangular wave of ± 10–15 V/μm was applied to the cells at 25°C.

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