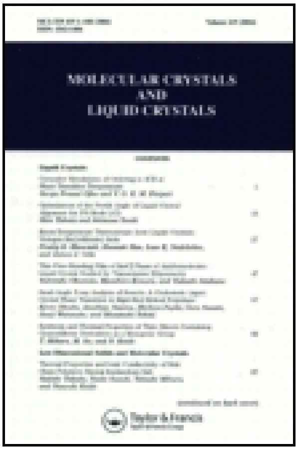

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Synthesis and Properties of Ferroelectric Liquid Crystals Derived from 5-Alkyl-δ-Valerolactones

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Synthesis and Properties of Ferroelectric Liquid Crystals Derived from 5-Alkyl-δ-Valerolactones

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New homologous FLCs (**I**–**II**-n [n=1–4]) derived from optically active 5-alkyl-6-valerolactones were synthesized. Their mesomorphic properties were systematically investigated with respect to their molecular structures, which were different in terms of the length of an alkyl group attached to a chiral centre and the direction of phenylpyrimidyl group. For compounds type **I**-n, with pyrimidyl group conjugated to the terminal position carrying chiral 5-fluoro-alkyloxy tail, elongation of the attached alkyl groups enhanced the stability of the chiral smectic C phase, while the other type, with pyrimidyl group conjugated to the terminal position carrying achiral alkyloxy tail, showed no remarkable alteration in the stability of the phase. Short optical response time (22μs, 80°C[Tc-T=10K]) was found for the FLC **II**-3 that has almost the same magnitude of spontaneous polarization (25nCcm^{-2}, 80°C[Tc-T=10K]) with that of **II**-4.

Keywords: 5-alkyl-6-valerolactones; phenylpyrimidine; ferroelectric liquid crystal

INTRODUCTION

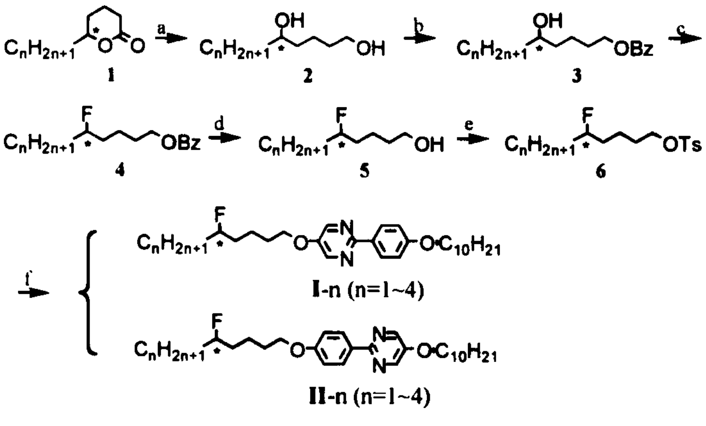
An investigation of physical properties of material, especially in the field of liquid crystals, is often based on their chemical structures. Since ferroelectricity of the liquid crystals having chiral smectic C phase was discovered by Meyer *et al.* in 1975 [1], much attention has been paid to the FLC. Moreover, since Clark and Lagerwall proposed electro optical device using surface stabilized ferroelectric liquid crystals (SSFLC) in 1980 [2], attempts to find the materials with more superior properties have been carried out extensively. However, low rotational viscosity of the FLC is generally important to develop the display devices due to their rapid switching process.

In the previous works, the FLCs with short optical response time (26μs, 75°C[Tc-T=20K]) were prepared using optically active 5-fluoro-1-decyloxy group as a chiral alkyloxy tail derived from optically active (*R*)-1,2-epoxyheptane [3,4]. In this work, effects of the molecular structure alteration in terms of the length of an alkyl group attached to the chiral centre and the direction of phenylpyrimidyl group on their mesomorphic and ferroelectric behaviors have been investigated.

Optically active 5-fluoro-1-alkanols were prepared by a new synthetic procedure starting from optically active 5-alkyl-δ-valerolactone. The lactones were obtained by optical resolution of their racemate [5].

SYNTHESIS

Scheme 1 showed a synthetic procedure of liquid crystals using optically active 5-alkyl-δ-valerolactone as a starting material. The following synthetic reactions were carried out without racemization. It was confirmed by determination of optical purity of intermediate (5-fluoro-1-alkylbenzoate) using HPLC equipped with a chiral column (Daicel Chiralcel OB-H). The lactones **1** were reduced to provide the diols **2**. The fluorinated alcohols of **5** were obtained by fluorination and deprotection of the regio-selective benzoylated of **3**. These alcohols **5** were conjugated to the appropriate phenylpyrimidyl group via tosylation. The detail preparation methods are described in the experimental section.



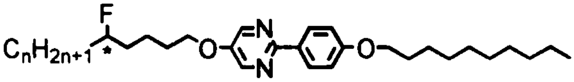
a)LiAlH$_4$,THF b)BzCl, DABCO,CH$_2$Cl$_2$ c)DAST,CH$_2$Cl$_2$ d)KOHaq, MeOH e)TsCl, Et$_3$N,CH$_2$Cl$_2$ f)core, NaH, DMF

SCHEME 1 Synthetic procedure of FLCs (I~II-n)

RESULTS AND DISCUSSION

Mesomorphic Properties

For compounds **I**-n, Table 1 showed that the stability of the smectic C phases increased significantly depending on the length of an alkyl group attached to the chiral centre. Especially for compound **I**-1, formation of the smectic C phase has perfectly been obstructed.

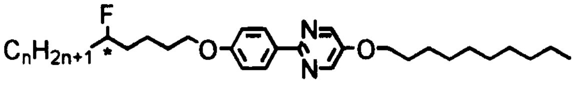


I-n (n=1~4)

TABLE 1 Phase transition temperatures of **I**-n (n=1~4).

Compounds	n	*Cr*		S_C^*		S_A		*Iso*
I-1	1	•	61			•	86	•
I-2	2	•	52	•	73	•	91	•
I-3	3	•	56	•	83	•	97	•
I-4	4	•	44	•	93	•	97	•

TABLE 2 Phase transition temperatures of **II**-n (n=1~4).



II-n (n=1~4)

Compounds	n	*Cr*		S_C^*		S_A		*Iso*
II-1	1	•	29	•	78	•	88	•
II-2	2	•	33	•	80	•	88	•
II-3	3	•	35	•	91	•	92.5	•
II-4	4	•	41	•	91.5	•	92	•

In contrast, as shown in Table 2, compounds II-n which were different from compounds I-n only in the position of the pyrimidyl group, showed no disappearence of smectic C phase depending on the lengthening of the attached alkyl group.

Electro-Optical Properties

Figure 1 showed the spontaneous polarization of the FLCs prepared, both type I-n and II-n. Except compound II-3, FLCs with a longer chiral tail showed large magnitude of the spontaneous polarization. It suggests that rotational flexibility of dipole moment will be obstructed by increasing the length of an alkyl group attached to the chiral centre.

A significant difference of optical response time between the FLCs with n=3 and 4 is shown in Figure 2. Especially for type II-n, II-3 has a shorter optical reponse time than II-4, while both II-3 and 4 have about almost the same magnitude of spontaneous polarization. It is well known that a magnitude of spontaneous polarization is in inverse

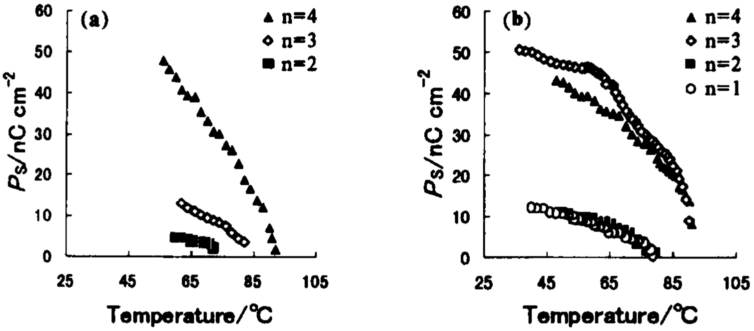


FIGURE 1 Temperature dependence of spontaneous polarization (P_S) of I-n (a) and II-n (b).

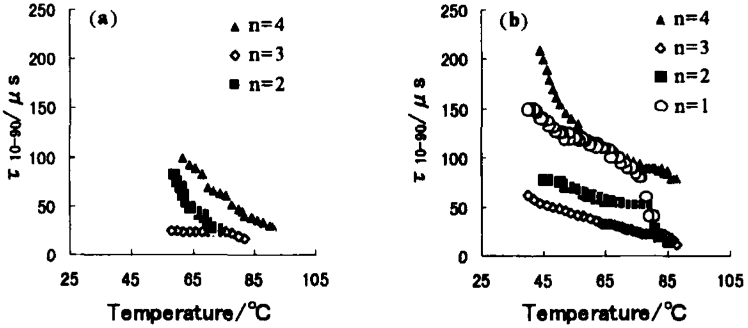


FIGURE 2 Temperature dependence of optical response time ($\tau_{10\text{-}90}$) of **I-n** (**a**) and **II-n** (**b**).

proportion to a response time, and in proportion to a viscosity [8]. It suggests that lengthening of an alkyl group attached to the chiral centre may increases its rotational viscosity. However, shortening of the length of the attached alkyl group will cause the increase of their rotational viscosity, since F-F interactions will act as a dominant factor in the molecular interaction for both types of molecules with n smaller than 3. As shown in Figure 2, the interaction will result in a longer optical response time.

Figure 3 showed the tilt angle of compounds prepared. For FLC with n=1 and 2, the tilt angle increased gradually from 0° with cooling the temperature, while that of with n ≥ 3, increased immediately from more than 10°.

The tilt angle increased with lengthening of an alkyl group attached to the chiral centre. The tilt angle reached at about 23°and 29° for the type **II** of FLCs with n=1~2 and 3~4, respectively.

CONCLUSION

New homologous FLCs (**I**~**II**-n [n=1~4]) were synthesized from optically active 5-alkyl-δ-valerolactone without racemization. These FLCs were systematically characterized with respect to their molecular structures. It was found that the length of an alkyl group attached to the chiral centre and the direction of the phenyl pyrimidyl group play an important role to characterizing their ferroelectric properties.

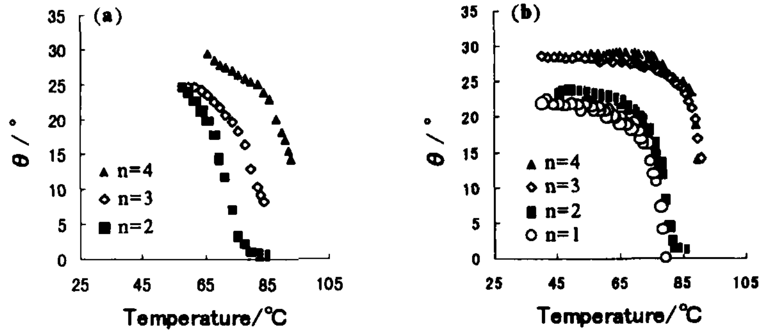


FIGURE 3 Temperature dependence of tilt angle (θ) of **I**-n (a) and **II**-n (b).

EXPERIMENTAL

The intermediates and products were determined by ^{1}H, ^{13}C, and ^{19}F NMR (Bruker AM400), and infrared (IR) spectroscopy (Perkin-Elmer FT1640). Optical rotations were measured by polarimeter (Jasco DIP360 or 370), and optical purity by high performance liquid chromatography (Jasco PU980/8071T).

The phase transition temperature was observed with a Nikon Optiphot2-POL polarizing microscope equipped with a Mettler FP82HT hot stage and a Mettler FP90 thermal control-unit, and with a differential scanning calorimeter (Mac Science DSC3100). The magnitude of the spontaneous polarization was measured using the triangular wave method under a field of ± 5 $V_{pp}\mu m^{-1}$ in an 20 μm-thick cell. The response time ($\tau_{10\text{-}90}$) was measured using a rectangular wave under the same field in a 1.4~2 μm-thick cell.

Synthesis of 5-hydroxy-1-nonanol (2 [n=4])

(The same following methods were carryed out also for n=1,2, and 3.)

To a suspended solution of $LiAlH_4$ (0.87g, 23mmol), a solution of *S*-(−) 5-nonyl-δ-valerolactone (2.3g, 15mmol) in dry THF (10ml) was slowly added. The mixture was stirred for six hours at room temperature under N_2 atmosphere. Saturated Na_2SO_4 solution, and 3M hydrochloric acid was added. The organic layer was extracted with Et_2O, and dried over anhydrous $MgSO_4$. The condensated crude product was distilled (135-150°C, 30mmHg) to yield a colourless liquid (2.26g, 14.1mmol, 94 %). Optical rotation : $[\alpha]_D^{24}$+0.49°, $[\alpha]_{435}^{22}$+1.76° (*c*1.0, MeOH); ^1H NMR($CDCl_3$): 0.89-0.92(t, 3H, CH_3), 1.29-1.61(m, 12H, CH_2), 2.63(m, 1H, OH), 3.58-3.59(m, 1H, CHO), 3.61-3.64(t, 2H, CH_2O) ; ^{13}C NMR ($CDCl_3$): 13.9(CH_3), 21.7, 22.7, 27.8, 32.4, 36.8, 37.2(CH_2), 62.3(CH_2OH), 71.6(CHOH) ; IR (neat, cm^{-1}) 3355 (OH), 2932-2862(CH_3, CH_2).

Synthesis of 5-hydroxy-1-nonyl benzoate (3 [n=4])

To a stirred solution of *S*-(+)-5-hydroxy-1-nonanol (**2** [n=4])(100mg, 0.63mmol) and benzoyl chloride (88mg, 0.62mmol) in dry CH_2Cl_2 (2ml), 1,4-diazabicyclo[2,2,2]octane (DABCO) (213mg, 1.9mmol) was added slowly. The solution was then stirred at room temperature for 3 hours under N_2 atmosphere. Dilute HCl solution was added. The organic layer was extracted with CH_2Cl_2. The extract was washed with distilled water, and dried over anhydrous Na_2SO_4. The condensated mixture was purified by thin layer chromatography (AcOEt:Hexane=1:5) to yield a light yellow liquid (126mg, 0.48mmol, 77 %). Optical rotation: $[\alpha]_D^{27}$+1.53°, $[\alpha]_{435}^{25}$+2.38° (*c*1.1, MeOH); ^{1}H NMR($CDCl_3$): 0.88-0.92(t, 3H, CH_3), 1.31-1.81(m, 12H, CH_2), 3.62(m, 1H, CHO), 4.32-4.35(t, 2H, CH_2O), 7.41-8.05(m, 5H, C_6H_4); ^{13}C NMR($CDCl_3$): 14.0(CH_3), 22.2, 22.7, 27.8, 28.8, 36.9, 37.2(CH_2), 64.9(CH_2OBzl), 71.7(CHOH), 128.3-132.8(Ph), 166.7(C=O) ; IR(neat, cm^{-1}) 3411(OH), 2932-2861(CH_3, CH_2), 1720(C=O)

Synthesis of 5-fluoro-1-nonyl benzoate (4 [n=4])

A solution of (diethylamino)sulfurtrifluoride (DAST) (320mg, 2.0mmol) in 5ml of dry CH_2Cl_2 was added to a stirred solution of *S*-(+)-5-hydroxy-1-nonyl benzoate (**3** [n=4]) (150mg, 0.6mmol) in dry CH_2Cl_2 (3ml) at −78°C under N_2 atmosphere. The mixture was stirred for 30 minutes at the same temperature. Saturated Na_2SO_4 solution was added, and the organic layer was extracted with CH_2Cl_2. The extract was washed with distilled water, and dried over anhydrous Na_2SO_4. The solvent was evaporated off, and remaining mixture was purified by thin layer chromatography (AcOEt:Hexane=1:7) to yield a light yellow liquid (81mg, 0.30mmol, 54 %). Optical rotation: $[\alpha]_D^{26}$−0.75°, $[\alpha]_{435}^{24}$−2.35°(*c*0.8, MeOH); Optical purity: 95%e.e. (determined using Chiralcel OB-H); ^{1}H NMR($CDCl_3$): 0.88-0.92(t, 3H, CH_3), 1.31-1.82(m, 12H, CH_2), 4.32-4.35(t, 2H, CH_2O), 4.40-4.57(dm, 1H, CHF, J_{H-F}=49.45Hz), 7.42-8.05(m, 5H, C_6H_4) ; ^{13}C NMR ($CDCl_3$): 13.9(CH_3), 21.8, 22.5, 27.2, 28.6, 34.7, 34.9(CH_2), 64.8(CH_2OBzl), 93.4-95.1(d, CHF, J=166.8Hz), 128.3-132.8(Ph), 166.6(C=O) ; ^{19}F NMR ($CDCl_3$): −181.2~−181.0(m, CHF) ; IR (neat, cm^{-1}) 3063(Ph), 2954-2870(CH_3, CH_2), 1720(C=O).

Synthesis of 5-fluoro-1-nonanol (5 [n=4])

To a stirred solution of *R*-(−)-5-fluoro-1-nonyl benzoate (4 [n=4]) (75mg, 0.3mmol) in MeOH (2ml), 1M KOH (1ml) was added. The *mixture was stirred at room temperature for overnight. The mixture was* extracted with Et_2O, and washed with a 5wt% Na_2CO_3 solution. The extract was dried over anhydrous $MgSO_4$. The solvent was evaporated off to yields a colourless liquid (38mg, 0.23mmol, 84%). Optical rotation: $[\alpha]_D^{27}$+0.22°, $[\alpha]_{435}^{24}$+0.76° (c1.8, Et_2O); ^1H NMR($CDCl_3$): 0.89-0.93(t, 3H, CH_3), 1.32-1.62(m, 12H, CH_2), 3.64-3.67(t, 2H, CH_2O), 4.40-4.54(dm, 1H, CHF, $J_{H\text{-}F}$=49Hz) ; ^{13}C NMR ($CDCl_3$): 13.9(CH_3), 21.4, 22.5, 27.2, 32.5, 34.7, 34.9(CH_2), 62.7(CH_2OH), 93.6-95.2(d, CHF, J=166.9Hz).

Synthesis of 5-fluorononyl-p-toluenesulfonate (6 [n=4])

A solution of *p*-toluenesulfonyl chloride (53mg, 0.3mmol) and 5-fluoro-1-nonanol (38mg, 0.23mmol) in 2ml of dry dichloromethane was stirred at ice-water temperature. Dry triethylamine (98mg, 1.0mmol) was added. The mixture was stirred for 12 hours at room temperature. To the mixture, 1M hydrochloric acid was added, and the organic layer was extracted with dichloromethane. The concentrated mixture was purified by thin layer chromatography (AcOEt:hexane=1:5) to yield a colourless liquid (43mg, 0.14mmol, 37%). Optical rotation : $[\alpha]_D^{27}$−1.02°, $[\alpha]_{435}^{25}$−1.02° (c2.1, Et_2O) ; ^1H NMR ($CDCl_3$) : 0.88-0.92(t, 3H, CH_3), 1.24-1.80(m, 12H, CH_2), 2.47(s, 3H, CH_3), 4.03(t, 2H, CH_2O), 4.4-4.8(dm, 1H, CHF, J=80Hz), 7.4-7.8(dd, 4H, C_6H_4).

Synthesis of 2-(p-decyloxy)phenyl-5-(5-fluorononyloxy)pyrimidine 1-4(n=4).

In a solution of 2-(*p*-decyloxy)phenylpyrimidyne (51mg, 0.16mmol) and NaH (60%wt, 21 mg, 0.52mmol) in dry DMF (2ml), a solution of 5-fluorononyl-*p*-toluenesulfonate (**6** [n=4]) (43mg, 0.13mmol) in dry DMF (1ml) was added at 25°C under N_2 atmosphere. The mixture was heated for 3 hours at 70°C. Distilled water was added, and the organic layer was extracted with Et_2O. The extract was washed with distilled water, and dried over anhydrous $MgSO_4$. The condensated mixture was purified by thin layer chromatography (AcOEt:hexane=1:5) to yield a white powder. Yield after recrystallization: 40mg, 0.09mmol, 68%. Optical rotation: $[\alpha]_D^{28}-1.56°$ (*c*0.9, CH_3Cl); ^1H NMR($CDCl_3$): 0.80-0.87(dt, 6H, $2CH_3$), 1.21-1.76(m, 28H, $14CH_2$), 3.93-4.04(dt, 4H, $2CH_2O$), 4.37-4.50(dm, 1H, CHF, *J*=49.6Hz), 6.88-6.92(d, 2H, $C_6H_2N_2$, *J*=9.9Hz), 8.19-8.21(d, 2H, C_6H_4, *J*=8.8Hz), 8.35(s, 2H, C_6H_4) ; ^{13}C NMR ($CDCl_3$): 13.9,14.1(CH_3), 21.6-34.9(CH_2), 68.1,68.6 (CH_2O), 93.4-95.0 (d, CHF, *J*=167.5Hz), 114.4-160.78 (C_6H_4,$C_6H_2N_2$).

References

[1] Meyer, R. B., Liebert, L., Strzelecki, L., and Keller, P., 1975, *J. Phys. Lett. Paris*, Vol. 36, 69.

[2] Clark, N. A., and Lagerwall, S. T., 1980, *Appl. Phys. Lett.*, Vol. 36, 899.

[3] Nagashima, Y., Ichihashi, T., Koji, N., Iwamoto, M., Aoki, Y., and Nohira, H., 1997, *Liquid Crystals*, Vol. 23, 537–546.

[4] Nagashima, Y., Aoki, Y., and Nohira, H., 1998, *Ferroelectrics*, Vol. 212, 333–340.

[5] Asep, R., Aoki, Y., and Nohira, H., *The 37th Symposium on Organic Synthetic Chemistry*, A-26, Tokyo, Japan, 1999.

[6] Liu, H. and Nohira, H., 1998, *Ferroelectrics*, Vol.207, 541–553.

[7] Hori, K. and Tsuji, C., 1998, *Ferroelectrics*, Vol. 212, 301–308.

[8] Goodby, J.W., Blinc, R., Clark, N.A., Lagerwall, S.T., Osipov, M.A., Pikin, S.A., Sakurai, T., Yoshino, K., and Zeks, B., *Ferroelectric Liquid Crystals*, (Gordon & Breach Science Publisher).