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Synthesis and Properties of Optically Active Phenoxypropionates Having Various Cores

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Optically active phenoxypropionates having a variety of cores were synthesized and the effect of the different core structures on the spontaneous polarization (Ps) values was investigated. The results indicate that the core structure has a great influence on the Ps value and compound **3** in which a chiral group attached to the 5-phenyl side of the 2,5-diphenylpyrimidine core showed the largest Ps of 240 nC/cm^2. The ability as a chiral dopant for ferroelectric liquid crystal (FLC) were also evaluated. It was found that compound **3** was the most interesting, because the doping of compound **3** induced large Ps and wide tilt angle and this FLC mixture showed short response time. Moreover, the Sc range of host liquid crystal mixture are slightly extended by doping of compound **3**.

Keywords: Ferroelectric liquid crystal, chiral dopant, phenoxypropionate

1. INTRODUCTION

Since the discovery of ferroelectricity in the chiral smectic C (Sc*) phase by R. Meyer[1] and the proposal of electro-optical devices using ferroelectric liquid crystals by Clark and Lagerwall in 1980,[2] extensive studies have been done on ferroelectric liquid crystal materials and their applications. One of the most important features of FLC is fast switching. To realize fast switching, the FLC material needs to show large spontaneous polarization and low rotational viscosity.[3] In order to obtain FLC with large Ps, the efforts have been mainly done on the synthesis of a new chiral part, and little has been elucidated on the effects of the core structures. Therefore, we synthesized several compounds having various cores and investigated the effect of the core structure on the Ps value. In this paper we describe the synthesis and the Ps values of some phenoxypropionates having various cores. Moreover, we also describe the ability as a chiral dopant of these compounds.

2. SYNTHESIS

The synthesis was carried out as outlined in Scheme 1. The secondary hydroxy group of ethyl lacate was converted into its tosylate, after which the tosyl group was displaced by para-substituted phenolate anions. This reaction involves the Walden inversion at the asymmetric C-atom and thus leads to (R) absolute configuration. The final products were purified by column chromatography on silica-gel using hexane and ether as the eluent followed by recrystallization from ethanol. The optical purity of the compound is very important. So, we measured the enantiomeric excess of **3** as a representative by HPLC with a chiral column and obtained e.e. of 94.7%.

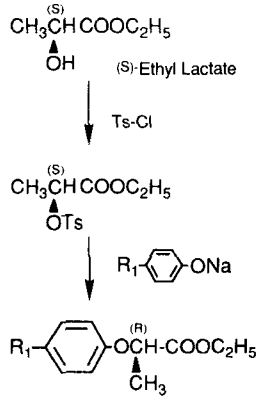
3. MEASUREMENT OF PHYSICAL PROPERTIES

Measurement was carried out on 2 μm thick cells consisting of two ITO glass slides coated with polyimide rubbed in the same direction. The spontaneous polarization (Ps) was measured by the triangular wave method.[4] The sense of Ps was determined by the field reversal method by optical observation of the director motion.[5] The response time (τ) was defined as the time difference between voltage reversal and a 90% change in optical transmission by applying a rectangular wave. The tilt angle (θ) was measured from the scale on the microscope turntable between the two extreme optical states, corresponding to the two polarities of a DC field applied across the sample cell.

4. RESULTS AND DISCUSSION

4.1. Physical Properties of Compounds 1–6

The molecular structures of the compounds studied here are shown in Figure 1. The phase transition temperatures and Ps values of compounds **1–6** are listed in



SCHEME 1 Synthesis route of optically active phenoxypropionates.

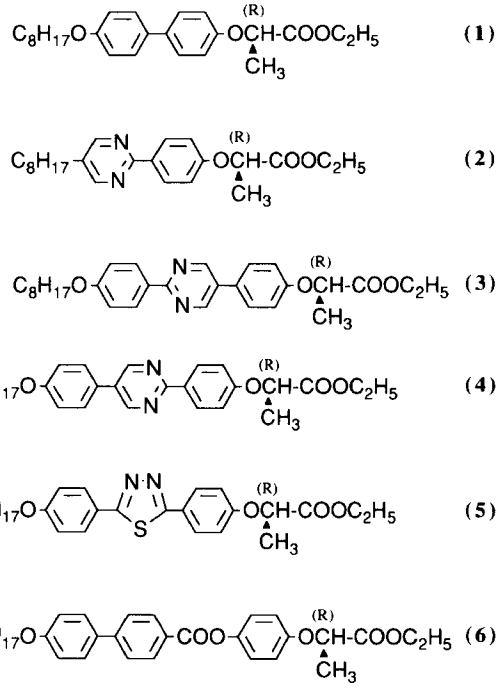


FIGURE 1 The molecular structures of optically active phenoxypropionates.

TABLE I

Transition temperatures and Ps values of compounds **1–6**

Compound	Phase transition Temperature (℃)[a]							Ps (nC / cm²)	
	Cr	Sx	Sc*	SA	N*	I		$T_{AC-10℃}$	max.
1	· 31.0	—	—	—	—	·		—	—
2	· 18.0	—	—	—	—	·		—	—
3	· 51.0	(· 46.0)[b]	· 69.0	—	· 91.5	·		+220	+240
4	· 65.5	—	· 84.0	· 105.0	—	·		+ 24	+ 45
5	· 88.5	—	(· 76.5)[b]	(· 81.5)[b]	· 92.0	·		+ 3.0	+ 65
6	· 66.0	(· 60.0)[b]	· 93.0	—	· 134.0	·		+ 47	+141

a) Cr: crystalline solid, Sx: unidentified smectic phase, Sc*: chiral smectic C phase, SA: smectic A phase, N*: chiral nematic phase, I: isotropic liquid phase.
b) ( ) indicates a monotropic phase transition.

Table I. The temperature dependencies of the Ps values of compounds **3–6** are shown in Figure 2. Compounds **1** and **2** having two aromatic rings as a core do not exhibit any mesophase and compounds **3–6** which have three aromatic rings as a core exhibit the Sc* phase. It is interesting that the Ps values of these compounds (**3–6**) are so different from one another, though these compounds have the same chiral structure. In these compounds, compound **3** having 2,5-diphenylpyrimidine as a core, showed the largest Ps of 240 nC/cm^2. In the case of the compounds with 2,5-diphenylpyrimidine as a core (**3** and **4**), the position of the chiral part also has a great influence on the Ps value, that is, the Ps value of compound **3** in which the chiral group attached to the 5-phenyl side of the 2,5-diphenylpyrimidine core is much larger than that of the compound **4** in which the chiral group attached to the 2-phenyl side of the 2,5-diphenylpyrimidine core. It is clear that the core structure has a great influence on the Ps value.

4.2. Properties as Chiral Dopant for FLC

For practical use, the properties in non-chiral host liquid crystal mixtures are important. Therefore, we next investigated the ability as a chiral dopant of these compounds. FLC mixtures were made by doping 5 wt.% of compound to a non-chiral Sc host liquid crystal mixture being composed of 2-(4-hexyloxyphenyl)-5-nonylpyrimidine (33.3 wt.%), 2-(4-octyloxyphenyl)-5-octylpyrimidine (33.3 wt.%) and 2-(decyloxyphenyl)-5-octylpyrimidine (33.3 wt.%). The physical properties of the resulting FLC mixtures are shown in Table II. The Ps's of these FLC mixtures are smaller than the values expected from their own Ps values. For example, the FLC mixture containing 5 wt.% of **6** exhibited Ps of only 0.5 nC/cm^2, though compound **6** showed maximum Ps of 140 nC/cm^2 by itself. We suppose the reason for this is that the free rotation of the chiral compound is promoted by diluting with the host liquid crystal mixture. The FLC mixtures of compounds **1**, **2** and **3**

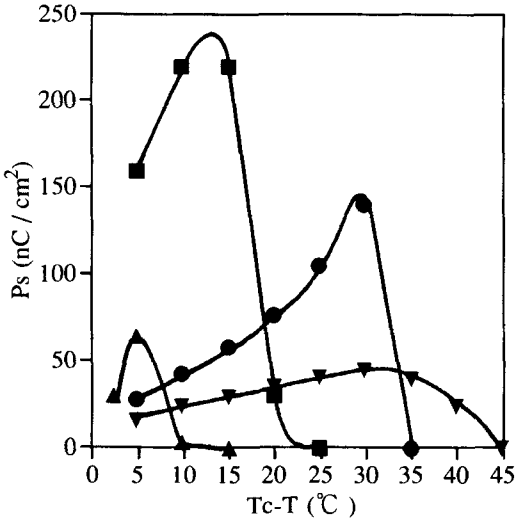


FIGURE 2 Temperature dependence of the Ps value of (■), (▼), (▲), (●).

TABLE II

Properties of compounds **1–6** in non-chiral liquid crystal mixture[a)]

Compound	Ps (nC/cm^2)	τ (μ sec.)	θ (deg)	Phase transition Temp.(℃)[b)] Sc*	SA	N*	I
1	+1.0	110	15.5	· 43	· 57	· 64	·
2	+0.4	100	10.5	· 44	· 57	· 63	·
3	+2.5	110	19.5	· 55	· 62	· 68	·
4	+0.6	170	8.0	· 42	· 66	· 68	·
5	+—[c)]	630	15.5	· 50	· 67	· 69	·
6	+0.5	260	12.5	· 50	· 64	· 68	·
Host[d)]	—	—	—	· 53	· 60	· 65	·

a) Chiral compound was added 5wt.% to the host liquid crystal mixture. b) Sc*: chiral smectic C phase, SA: Smectic A phase, N*: chiral nematic phase, I: isotropic liquid phase. c) Very small (below detection limit) d) Consisted of 2-phenylpyrimidines.

showed similar switching times of about 100 μ seconds, though the Ps value of **3** is several times larger than that of **1** and **2**. As the response time (τ) can be represented by $\tau = \eta/(Ps \times E)$, where η is the rotational viscosity, Ps is the spontaneous polarization and E is the applied electric field,[3] the above result suggests that the rotational viscosity of compound **3** is higher than that of **1** and **2**. About the phase transition temperature, the I-N* and N*-SA transition temperatures of the host liquid crystals were not so much affected by adding 5 wt.% of these compounds. But the SA-Sc* transition temperatures dropped by doping. Only the mixture containing **3** showed slightly higher SA-Sc* transition temperature than that of host liquid crystal mixture. From the results shown in Table II, compound **3** is considered most useful as a chiral dopant for FLC, because the doping of compound **3** induced large Ps and wide tilt angle and this FLC mixture showed a short response time. Moreover, the Sc range of the host liquid crystal mixture is slightly extended by doping compound **3**. In addition to the above feature, good alignment was obtained.

4.3. Conclusion

We thus conclude that the core structure of the ferroelectric liquid crystal has a great influence on the Ps value. In these compounds, **3** in which a chiral group attached to the 5-phenyl side of the 2,5-diphenylpyrimidine core showed the largest Ps of 240 nC/cm^2. Compound **3** is also most useful as a chiral dopant for FLC.

5. EXPERIMENTAL

IR, ^{1}H NMR and mass spectra were recorded on a Shimadzu IR-408, Varian EM-360 and Hitachi M-80, respectively, under standard conditions. Final products were

purified by column chromatography on silica-gel followed by recrystallization from ethanol. Optical purity was measured by HPLC with a chiral column: "CHIRALCEL OD" Produced by Daicel Chemical Industries, Ltd. The phase transition temperatures were determined by using a Rigaku Denki DSC-8230 apparatus and texture observations were made using a Nikon XTP-II polarizing microscope in conjunction with a Mettler FP-82 hot stage and FP-80 control unit. The preparation of **3** as a representative is given below.

5.1. (S)-Ethyl 2-*p*-Toluenesulfonyloxypropionate

To a solution of (S)-ethyl lactate (12.0 g) in pyridine (70 ml) was added *p*-toluenesulfonylchloride (20.0 g) in several portions at 0°C and the resulting slurry was stirred for 15 hours at 5°C. The reaction mixture was poured into 10% HCl and extracted twice with ether. The combined organic layer was washed several times with water, dried over anhydrous magnesium sulfate and concentrated in vacuum. The resulting residue (25.0 g) was used without further purification.

IR (neat): 2930, 1745, 1590, 1445, 1360, 1180 cm^{-1} ^1H NMR ($CDCl_3$): 1.20 (3H, *t*, *J* = 7 Hz), 1.50 (3H, *d*, *J* = 7 Hz), 1.43 (3H, s), 4.12 (2H, *q*, *J* = 7 Hz), 4.94 (1H, *q*, *J* = 7 Hz), 7.35 (2H, *d*, *J* = 9 Hz), 7.73 (2H, *d*, *J* = 9 Hz).

5.2. (R)-5-{4-(1-Ethoxycarbonyl)ethoxyphenyl}-2-(4-octyloxyphenyl)pyrimidine (3)

A suspension of sodium hydride (176 mg) in dry *N*,*N*′-dimethylformamide (5 ml) was cooled to 0°C. A solution of 5-(4-hydroxyphenyl)-2-(4-octyloxyphenyl)pyrimidine (1.54 g) in dry DMF (10 ml) was added during 30 minutes and the resulting mixture was stirred at 0°C for one hour. The tosylate (1.4 g) was added dropwise and the mixture was stirred at room temperature for 2 hours. The reaction mixture was poured into 5% HCl and extracted twice with ether. The extract was washed several times with water and dried over anhydrous magnesium sulfate. The solvent was evaporated and the resulting solid was purified by column chromatography on silica-gel with hexane-ether as eluent, followed by recrystallization from ethanol to yield **4** (1.0 g).

IR (Nujol): 2900, 2840, 1742, 1727, 1603, 1578 cm^{-1} ^1H NMR ($CDCl_3$): 0.89 (3H, *t*, *J* = Hz), 1.2–1.5 (18H, *m*), 4.04 (2H, *t*, *J* = 7 Hz), 4.25 (2H, *q*, *J* = 7Hz), 4.81 (1H, *q*, *J* = 7 Hz), 7.00 (2H, *d*, *J* = 9 Hz), 7.01 (2H, *d*, *J* = 9 Hz), 7.53 (2H, *d*, *J* = 9 Hz), 8.41 (2H, *d*, *J* = 9 Hz), 8.91 (2H, *s*) Mass: *m*/*z* 476 (M^+).

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