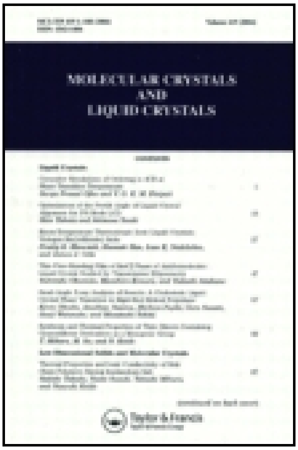

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Novel Ferroelectric Liquid Crystalline δ-Valerolactone Derivatives with Very Large Spontaneous Polarization

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Novel Ferroelectric Liquid Crystalline δ-Valerolactone Derivatives with Very Large Spontaneous Polarization

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A series of new chiral compounds with a δ-valerolactone ring were synthesized and the physical properties of these compounds as well as the electrical properties of their ferroelectric liquid crystal (FLC) mixtures were investigated. The magnitude of spontaneous polarization (*Ps*) in the chiral smectic C phase (SmC*) was found to be as high as 384 nC/cm^2 for (2R, 5R)-2-(4'-octyloxybiphenyl-4-carboxy)-5-butyl-δ-valerolactone at $\Delta T = Tc - T = 5$°C, where *Tc* is the temperature of transition from the isotropic phase to the SmC* phase and *T* is the temperature at which the experiments were carried out. An FLC mixture containing 2% by weight of the optical isomer, (2S, 5R)-2-(4'-octyloxy-biphenyl-4-carboxy)-5-hexyl-δ-valerolactone exhibited a response time as fast as 96 μ seconds at 25°C, for an applied square-wave voltage of ±10 volts. The relationship between the structural properties and the thermal properties, magnitude and polarity of *Ps* as well as the response times for their FLC mixtures are discussed.

Keywords: Ferroelectric liquid crystal, chiral smectic C, spontaneous polarization, δ-valerolactone, response time, configuration, conformation, thermal stability

I. INTRODUCTION

Over the past several years, a great deal of attention has been focused upon ferroelectric liquid crystals (FLCs) because of their potential as materials for applications in high definition, flat panel displays and optical processing devices. One of the most important properties in FLC mixtures for such applications is the response time, which is dependent upon the magnitude of spontaneous polarization (*Ps*), the rotational viscosity, and the applied electric field.[1] Although major efforts have been attempted by organic chemists to synthesize new compounds with high

Ps, none of the FLCs prepared to date have been able to satisfy all the requirements specified in the development of these applications.

A series of compounds with an optically active δ-valerolactone ring have been synthesized in order to meet the requirements suggested by the device developers. FLC mixtures then were prepared by doping a mixture of nonchiral compounds with these new compounds. A number of the new compounds and their FLC mixtures were found to display extremely high values of *Ps* and also short switching times.

In this paper, the basic physical properties of these new compounds and the ferroelectrical properties of their FLC mixtures are reported.

II. EXPERIMENTAL

II-1. Preparation of Materials

Typical synthetic routes of the new compounds used in this paper were shown in Scheme I. (2S, 5R)-2-Hydroxy-5-alkyl-δ-valerolactone was synthesized by the Kolbe electrolysis of a mixture of optically active β-hydroxy carboxylic acid and (*S*)-2-acetoxy-butandioic acid-1-ethyl ester followed by treatment with *p*-toluensulfonic acid (*p*-TsOH) in benzene after removal of the protective groups. Detailed synthetic procedure was reported in the previous paper.[2]

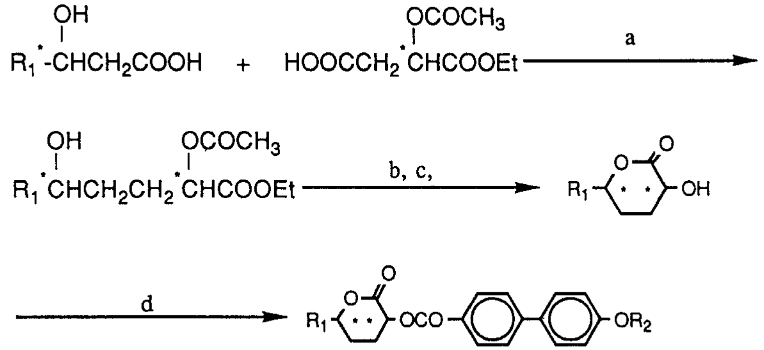
The FLC mixtures were prepared by adding 2% by weight of the chiral compound into a nonchiral smectic C mixture which was a mixture of several kinds of 2-(4-alkoxyphenyl)-5-alkylpyrimidine and had the phase transition temperatures as follows[3];

$$\mathrm{SmC} \xrightarrow{} \mathrm{SmA} \xrightarrow{} \mathrm{N} \xrightarrow{} \mathrm{Iso}$$

$$51°\mathrm{C} \qquad 61°\mathrm{C} \quad 68°\mathrm{C}$$

II-2. Measurements of Physical Properties

Measurements of phase sequence, transition temperatures, spontaneous polarization, polarity, and tilt angle for the new compounds and their FLC mixtures were carried out in accordance with the procedures reported previously.[2]



a. e^-, NaOH; b. NaOH, $EtOH/H_2O$; c. p-TsOH, Benzene; d. $(NCO_2Et)_2$, $Pø_3$, Benzene, R_2O-ø-ø-COOH.

SCHEME I Synthesis of (2R, 5R)-2-(4′-alkoxybiphenyl-4-carboxy)-5-alkyl-δ-valerolactone

The specimen was placed between two indium-tin oxide (ITO) glass plates to form a cell. The glass surface was coated with a polyimide. The polyimide film thus formed was rubbed in one direction. The cell thickness was 2 μ meters and the applied square-wave voltage was ±10 volts. The response time was measured at 25°C. The response time used in this paper is defined as the time required for the optical transmittance through the cell to change from 0% to 50% when voltage was applied to the cell.

III. RESULTS AND DISCUSSIONS

III-1. Thermal Properties

The phase transition temperatures for the homologous series of 2-(4′-alkoxybiphenyl-4-carboxy)-5-alkyl-δ-valerolactones are tabulated in Table I.

All compounds having a (2R, 5R)-δ-valerolactone ring except the homologue with the propyl group in the 5 position (Compound 9) displayed the SmC* phase, whereas those with the (2S, 5R)-δ-valerolactone ring did not exhibit any mesophases. This can partly be attributed to the difference in the conformation of the chiral portion between the (2R, 5R) derivatives and the (2S, 5R) derivatives. This can also be attributed to higher melting point of the latter than that of the former.

In other words, the former has a quasi-chair conformation which maintains the linear and lath-like shape over the whole molecule required to form mesophase, while the latter has a quasi-boat conformation which may distort the shape of the molecule to decrease their tendency to form mesophase or may enhance the aggregation of molecules to raise its melting point.

It is also noteworthy to mention that the N* phase appears in the homologues having shorter alkoxy groups in the 4′ position or shorter alkyl groups in the 5 position of the lactone ring, even though this tendency has been often observed in other analogous series.

Comparing the phase sequence and transition temperatures for (2R, 5R)-2-(4′-octyloxybiphenyl-4-carboxy)-5-hexyl-δ-valerolactone (Compound 3) with those of (S, S)-1-methylheptyl 2-(4′-octyloxybiphenyl-4-carboxy)-propionate (abbreviated as (S, S)-MOBCP) which had the chiral group with an open-ring structure for the δ-valerolactone, the thermal stability of a mesophase in (S, S)-MOBCP was much lower than that of Compound 3 as shown in Table II. This means that the δ-valerolactone ring enhances the thermal stability of a mesophase by working as a part of mesogen.

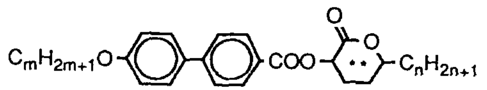
The phase transition temperatures of compounds having a (2R, 5R)-δ-valerolactone ring and various linkage groups (*X*, *Y*) are given in Table III.

Clearing point of these compounds decreases in the order of the linkage (*Y*): single bond > —OOC— > —COO— > —OCH_2—. It is thought that the thermal stability of a mesophase is associated with the flexibility of the linkage and the anisotropic polarizability of the core.

In the case of compounds with a central —OCH_2— linkage (Compound 11, 12, 13, 14, 15), the Iso-SmC* transition temperature decreases in the order of the terminal linkage (*X*): —COO— > —O— > —OOC—. This may indicate that the

TABLE I

Phase transition temperatures for a series of 2-(4′-alkoxybiphenyl-4-carboxy)-5-alkyl-δ-valerolactone

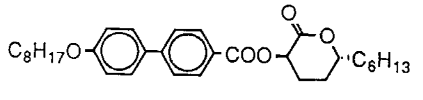
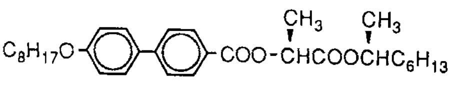
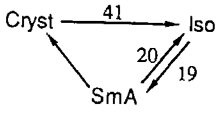


Compound No.	m	n	Absolute configuration	Phase Transition Temperatures(℃) Cryst.		SmC*		N*		Iso
1	6	6	(2R, 5R)	•	115	•	120	–	123	•
2	7	6	(2R, 5R)	•	118	•	125	–		•
3	8	6	(2R, 5R)	•	111	•	128	–		•
4	8	6	(2S, 5R)	•	152	—		–		•
5	10	6	(2R, 5R)	•	107	•	131	–		•
6	12	6	(2R, 5R)	•	107	•	131	–		•
7	16	6	(2R, 5R)	•	111	•	128	–		•
8	8	4	(2R, 5R)	•	116	(•	114)	•	118	•
9	8	3	(2R, 5R)	•	124	—		(•	119)	•
10	8	1	(2S, 5R)	•	132	—		–		•

( ) Indicates a monotropic phase transition.

TABLE II

Comparison of thermal stability between the compound having a δ-valerolactone ring and the compound having an open-ring structure

	$\text{Cryst} \xleftrightarrow{111} \text{SmC}^* \xleftrightarrow{128} \text{Iso}$
	

magnitude and the direction of the terminal outboard dipole moment may play an important role in the appearance of the SmC* phase.[4,5]

The N* phase appeared only in compounds having a central ester linkage (—COO— or —OOC—) in the case of compounds with a terminal —O— linkage (Compound 14, 15, 16, 17, 18). Moreover, the compound with —COO— linkage which induced a larger dipole moment along the molecular axis through conjugation with its adjacent benzene rings compared to —OOC— linkage didn't show any smectic phases. This would indicate that the ester linkage repress the formation of layer structure and the central dipole moment along the molecular axis may not always work to advantage in forming a smectic phase.

III-2. Ferroelectrical Properties

The magnitude and polarity of Ps for two compounds (Compounds 3 and 8) and six FLC mixtures containing 2% by weight of these compounds are summarized in Tables IV and V.

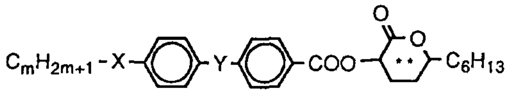
As shown in these tables, Compounds 3 and 8 exhibit extremely high Ps values with negative polarity. In particular, Compound 8 shows a Ps value as high as 384 nC/cm^2 at ΔT = 5°C. Two factors would contribute to high Ps values of these compounds, i.e.,[1] (1) large dipole moment (4.1 Debye) of δ-valerolactone,[6] (2) restricted internal rotation of the dipole moment derived from the ring structure of the chiral portion.

Compared with the Ps values for the FLC mixtures doped with 2% by weight of either Compound 3 or Compound 8, FLC mixtures prepared with chiral dopants such as Compounds 4, 5, 9 and 10 may be considered to exhibit very high Ps values. In particular, Compound 10 may render the highest Ps value to a FLC mixture although this chiral dopant does not show any mesophase by itself.

It is also noteworthy to mention that both Compound 4 and Compound 10 with a (2S, 5R)-δ-valerolactone ring show a positive polarity as opposed to compounds with a (2R, 5R)-δ-valerolactone ring which exhibit a negative polarity. From the

TABLE III

Phase transition temperatures of chiral compounds with various mesogen



Compound No.	m	X	Y	Absolute configuration	Phase Transition Temperatures(℃)			
					Cryst.	SmC*	N*	Iso
11	10	-COO-	$-OCH_2-$	(2R, 5R)	• 108	• 116	–	•
12	13	-COO-	$-OCH_2-$	(2R, 5R)	• 111	• 118	–	•
13	12	-OOC-	$-OCH_2-$	(2R, 5R)	• 100	(• 88)	–	•
14	12	-O-	$-OCH_2-$	(2R, 5R)	• 107	(• 102)	–	•
15	8	-O-	$-OCH_2-$	(2R, 5R)	• 106	(• 101)	–	•
16	8	-O-	$-CH_2O-$	(2R, 5R)	• 110	(• 100)	–	•
17	8	-O-	-OOC-	(2R, 5R)	• 106	• 115	• 123	•
18	8	-O-	-COO-	(2R, 5R)	• 108	—	• 117	•

( ) Indicates a monotropic phase transition.

TABLE IV

Spontaneous polarization for Compound 3 and Compound 8

No.	Ps (nC/cm²) at △T=5℃
3	-268
8	-384

data, one can speculate that their enantiomers, compounds with (2R, 5S) or (2S, 5S)-δ-valerolactone rings, will exhibit opposite polarities because these enantiomers are optical antipodes of compounds with (2S, 5R) or (2R, 5R)-δ-valerolactone rings, respectively. We can conclude that the polarity of Ps in these FLC compounds and FLC mixtures is dominated by the absolute configuration of 2 position in δ-valerolactone and that of 5 position does not affect the polarity of Ps in this study.

Also summarized in Table V are the response times and the tilt angles for the various FLC mixtures. It is evident from the table that the mixture doped with Compound 4 exhibits the fastest response time of 96 μ seconds. When one compares the values of the tilt angle, one may surmise that the response time for mixtures doped with Compounds 3, 5, 8 or 9, which all have a (2R, 5R)-δ-valerolactone ring and exhibit a SmC* phase, increases as the value of Ps decreases. This means that the rotational viscosities for these mixtures are not so different.

On the other hand, the response times for mixtures doped with Compound 4 or Compound 10, both having a (2S, 5R)-δ-valerolactone ring, cannot be explained by comparing the magnitude of Ps because the mixture with the lower Ps value has a faster response time than the mixture with the higher Ps value. These two mixtures have approximately the same tilt angle, 20 degrees and 21 degrees. The difference in response time between these two mixtures can therefore be attributed to the difference in the rotational viscosity.

IV. SUMMARY

The results of the present study are summarized as follows.

(1) The δ-valerolactone ring had particularly attractive properties such as

- enhancing the thermal stability of the mesophases,
- fixing the dipole moment around the chiral center,
- exhibiting extremely high spontaneous polarization.

(2) The polarity of Ps in FLC compounds and FLC mixtures with δ-valerolactone depended on the absolute configuration of 2 position in δ-valerolactone ring.

(3) The response time for the FLC mixtures doped with the lactone derivatives of (2S, 5R)-configuration (cis) was faster than that of (2R, 5R)-configuration (trans).

TABLE V

Response time of ferroelectric liquid crystal mixtures with 2 wt% of chiral additive

Additive No.	Absolute Configuration	Phase Transition Temperatures (℃)					Response time (μs)	Ps (nC/cm²)	Tilt Angle (deg.)
		Cryst.	SmC*	SmA	N*	Iso			
3	(2R, 5R)	• 2.5	• 53	• 60	• 67	•	173	-1.8	19
4	(2S, 5R)	• 2.6	• 53	• 59	• 67	•	96	+2.7	20
5	(2R, 5R)	• 2.4	• 52	• 58	• 66	•	137	-2.5	19
8	(2R, 5R)	• 1.4	• 54	• 60	• 67	•	149	-2.5	21
9	(2R, 5R)	• 3.1	• 52	• 60	• 67	•	155	-2.4	21
10	(2S, 5R)	• 2.4	• 50	• 59	• 67	•	108	+4.5	21

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