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5,5-Dialkyl-δ-valerolactone Derivatives as New Chiral Dopants for Ferroelectric Liquid Crystals

Keiichi SAKASHITA,*†† Yuriko NAKAOKA, Tetsuya IKEMOTO, Fumiko TERADA,
Yoshitaka KAGEYAMA,* Mizuo SHINDO,††† and Kenji MORI†
Tokyo Research Laboratory, Mitsubishi Rayon Co., Ltd., 3816, Noborito, Tama-ku,
Kawasaki 214
†Department of Agricultural Chemistry, The University of Tokyo, 1-1-1, Yayoi,
Bunkyo-ku, Tokyo 113

(S)-2-(4'-Octyloxybiphenyl-4-carboxy)-5,5-dipropyl-δ-valerolactone showed interesting properties as the chiral dopant for ferroelectric liquid crystals (FLCs). The FLC mixture containing only 2% by mol of this compound exhibited the magnitude of spontaneous polarization (Ps) as large as 9.6 nC/cm^2 and the response time as fast as 75 μs at 25 ℃ in the electric field of ±5 V/μm.

Ferroelectric liquid crystals (FLCs) have been expected as a new material for application in high definition, flat panel displays and optical processing devices because of their fast response time. The response time is dependent upon the magnitude of spontaneous polarization (Ps), the effective viscosity and the applied electric field.1) It seems that the magnitude of Ps is related to the chiral environment of a chiral dopant for FLCs. In this letter, we report the synthesis of a series of chiral 2-(4'-octyloxybiphenyl-4-carboxy)-5,5-dialkyl-δ-valerolactone derivatives as new chiral dopants for FLCs.

As shown in Scheme 1, (S)-2-hydroxy-5,5-dialkyl-δ-valerolactone was prepared from (S)-γ-butyrolactone-4-carboxylic acid t-butyl ester, derived from (R)-glutamic acid, and was esterified with 4'-octyloxybiphenyl-4-carboxylic acid

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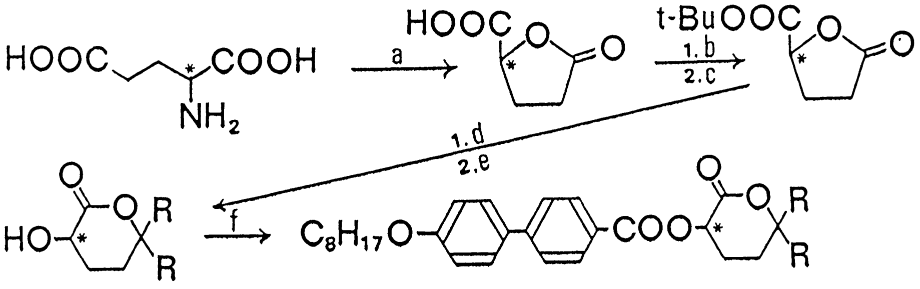
†† Present address: Central Research Laboratory, Mitsubishi Rayon Co. Ltd., 20-1, Miyuki-cho, Otake 739-06.

††† Present address: Acetate Research & Development Laboratory, Mitsubishi Rayon Co. Ltd., 3 Kaigan-dori, Toyama 931.

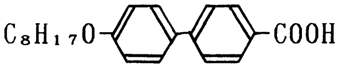
in the presence of DCC or triphenylphosphine / diethyl azo-dicarboxylate. All compounds were purified with a silica gel column chromatography followed by recrystallization from hexane and diethyl ether. According to a differential scanning calorimetry(DSC) and an optical microscopy, all compounds had no liquid crystalline phases.

The FLC mixtures were prepared by adding 2% by mol of a chiral compound into the non-chiral smectic mixture which was composed of several kinds of 2-(4-alkoxyphenyl)-5-alkylpyrimidine and had the phase transition temperature as follows;2)

$$\mathrm{SmC}\ \xrightarrow{4\ ^\circ\mathrm{C}}\ \mathrm{SmA}\ \xrightarrow{51\ ^\circ\mathrm{C}}\ \mathrm{N}\ \xrightarrow{61\ ^\circ\mathrm{C}}\ \mathrm{Iso}\quad 68\ ^\circ\mathrm{C}$$



Scheme 1. Reagents a, NaNO$_2$, H$^+$, b, SOCl$_2$, c, t-BuOH, Dimethylaniline, d, RMgBr, THF -78 °C, e, p-TsOH, Benzene reflux, f, DCC/DMAP or Pϕ_3/(NCOOEt)$_2$,



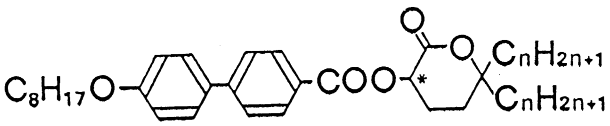
The melting point of a chiral compound and the phase transition temperatures, the magnitude of Ps, the response time (τ_{0-50}), the pitch (p) of the helical structure of chiral nematic phase (N*), and the tilt angle (θ) of these mixtures were tabulated in Table 1.

The magnitude of Ps was measured at 25 °C using a sample cell which consisted of two ITO-coated glass plates with a electrode patern. The glass surface was coated with a polyimide film which was rubbed in one direction. The thickness of the cell was 8 μm. The response time was defined to correspond to the change between 0 and 50% of the light-transmission through crossed polarizers on an application of a square-wave voltage across the sample cell with a thickness of 2 μm. The field strength was ±5 V/μm. The pitch of a helical structure of N* phase was measured at 62 °C with Cano-Wedge method. The tilt angle was equal to the half angle read from the scale on the microscope turntable between the two extreme optical state ,corresponding to the two polarities of DC-field applied across the sample cell.

The melting point of these compounds decreased with increasing the number of carbon atoms in alkyl chain at C-5 position.

The FLC mixtures showed almost the same phase transition temperatures from isotropic to N*, N* to smectic A (SmA) and SmA to chiral smectic C (SmC*). The polarity of Ps was directed by the absolute configuration at C-2 position like that of chiral 2-(4'-octyloxybiphenyl-4-carboxy)-5-alkyl -δ-valerolactone was.3) The magnitude of Ps became larger with increasing the number of carbon atoms in alkyl chain at C-5 position of the 5,5-dialkyl -δ-valerolactone derivatives. FLC mixture containing compound 4 at only 2% by mol showed the magnitude of Ps as large as +9.7 nC/cm^2. And the magnitude of Ps of this mixture was several times as large as that of a mixture containing (2R,5R)-2-(4'-octyloxybiphenyl-4-carboxy)-5-alkyl -δ- valerolactone at 2% by mol.3) The dipole moment of chiral 5,5-dialkyl -δ-valerolactone and chiral 5-alkyl-δ-valerolactone were considered to be almost the same, because the former had only a propyl group at C-5 positioninstead of hydrogen in the latter. Therefore, there would not be any difference between the magnitude of Ps of a FLC mixture containing these compounds, if they depended upon only the dipole moment of the chiral compound. We are now investigating the relationships between the magnitude of Ps

Table 1. Melting point of chiral 2-(4'-octyloxybiphenyl-4-carboxy)-5,5-dialkyl -δ-valerolactone derivatives and electrooptical properties of FLC mixtures containing these compounds.



Chiral compounds				Properties of FLC mixtures							
Compd.		Absolute	Mp	Phase transition temp /℃				Ps	τ_{0-50}	p	θ
No.	n	Confgn.	℃	SmC*	SmA	N*	Iso	nC cm^{-2}	μs	μm	deg
1	1	R	128	2	52	59	66	-5.5	92	17	22.0
2	2	R	81	3	50	59	66	-7.0	95	21	22.0
3	2	S	82	3	51	59	66	+7.2	86	-	22.0
4	3	S	66	3	55	60	66	+9.6	75	>289	21.5

and the molecular structure of these chiral dopants. In most FLC compounds or FLC mixtures examined before, it seemed that the pitch of the helical structure of N* were getting shorter with increasing the magnitude of Ps. In other words, it meaned that the helical twisting power (HTP), which was calculated from the reciprocal of the product of the concentration of a chiral compound and the pitch of the helical structure in N*, became stronger as the magnitude of Ps increased. On the contrary to these observations, in a series of 5,5-dialkyl-δ-valerolactone derivatives a pitch of the helical structure of N* were getting longer at larger magnitude of Ps. Although there are many factors directing HTP, the molecular structure would be the strongest one. But we cannot explain this extraordinary relationship between the HTP and the magnitude of Ps as the results of only steric factors. So we are now investigating the reason for this phenomenon.

The response time is one of the most important properties for an application to electrooptical devices. We measured the response time of the FLC mixtures containing 2% by mol of these chiral compounds at 25 ℃ in the electric field of ±5 V/μm. The FLC mixture containing the compound 4 showed the 0-50% response time as fast as 75 μs. But in the FLC mixture containing the compound 1 through 4, there was no inverse proportionalities between the response time and the magnitude of Ps. Considering that there was not any difference between the tilt angle of the FLC mixture containing these compound, the response time would be influenced by the increase of the rotational viscosity.

In conclusion, wesynthesized the practical chiral dopant for a FLC mixture. It gave a long pitch of the helical structure of N* and a large magnitude of Ps with only a small amount of addition.

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