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New Optically Active 4,4-Dialkyl-γ-lactones as Chiral Dopants for Ferroelectric Liquid Crystals

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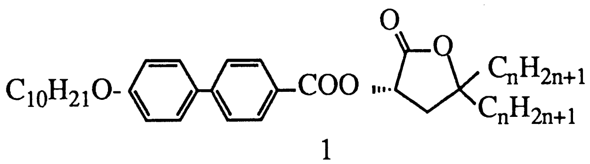
(S)-2-(4'-*n*-Decyloxybiphenyl-4-carboxy)-4,4-dialkyl-γ-butyrolactones were synthesized and shown to be good chiral dopants for ferroelectric liquid crystals.

Ferroelectric liquid crystals (FLCs) have attracted a great deal of attention since the electro-optical devices using FLCs were proposed in 1980.1) One of the most important properties for FLC materials is the response time, which is dependent upon the magnitude of spontaneous polarization (Ps), rotational viscosity, and the applied electric field.2) In order to realize a fast response, the FLC materials are often prepared by doping chiral compounds potentially posessing large Ps values to host liquid crystal mixtures showing smectic C phases around room temperature and also having low viscocity. In the last few years chiral compounds containing a γ-lactone ring have been studied as chiral dopants because they induce large Ps values.3-7) However, since they have two chiral centers, diastereomer separation is necessary to synthesize the *cis* isomers which induce large Ps values. Recently we designed and synthesized 5,5-dialkyl-δ-lactones which have only one chiral center 8) and showed that they induce large Ps values rather than corresponding δ-lactones which possess two chiral centers.9) In this letter, we report the synthesis of **1** and their properties as chiral dopants for FLCs.



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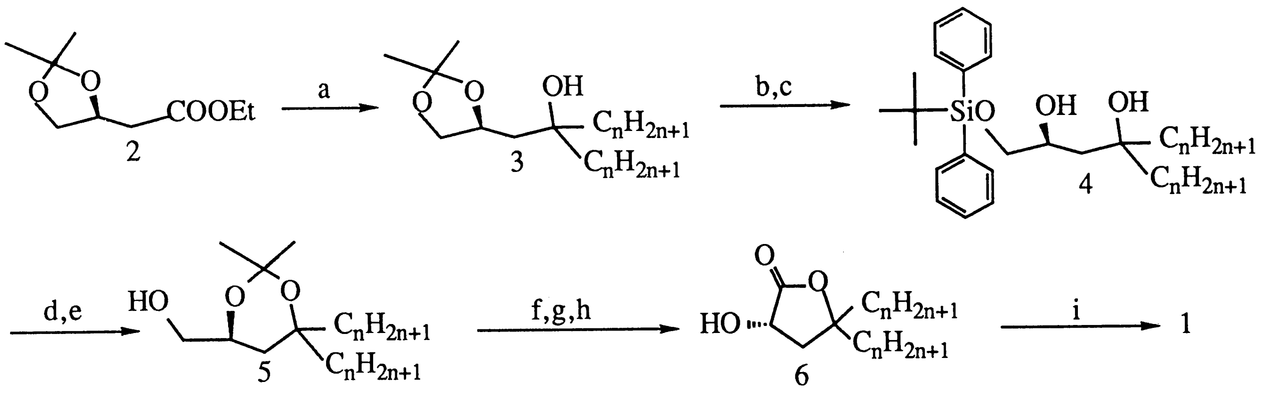
The chiral γ-lactones **1** were prepared as shown in Scheme 1. Commercially available *(S)*-(+)-2,2-dimethyl-4-ethoxycarbonylmethyl-1,3-dioxolane **2** (Wako Pure Chemical Industries, Ltd.) was added to a Grignard reagent prepared from *n*-alkyl bromide to give **3**. Deprotection of **3** was followed by silylation of primary alcohol with *t*-butyldiphenylsilyl group to afford **4**. Reprotection of **4** as acetonide and deprotection of the silyl group gave **5**. Oxidation of **5** was followed by deprotection with hydrochloric acid to give γ-lactones **6**. The optical purities of **6** were confirmed as over 90%ee respectively by analyzing the diastereomeric ratio of the corresponding *(S)*-α-methoxy-α-trifluoromethylphenylacetate 10) by HPLC. The hydroxylactones **6** were esterified in the presence of 1,3-dicyclohexylcarbodiimide and 4-dimethoxyaminopyridine to give **1**.



Scheme 1.. a) $C_nH_{2n+1}MgBr$, Et_2O b) HCl, H_2O, THF c) *t*-$BuPh_2SiCl$, Imidazole, CH_2Cl_2
d) $Me_2C(OMe)_2$, PPTS e) *n*-Bu_4NF, THF f) DMSO, $(COCl)_2$, Et_3N, CH_2Cl_2
g) $NaClO_2$, NaH_2PO_4, *t*-BuOH, H_2O h) HCl, H_2O, THF
i) $C_{10}H_{21}OPhPhCOOH$, DCC, DMAP, CH_2Cl_2

Table 1. Properties of the chiral dopants **1** in the mixture A

Chiral compounds compd. No.	 n	 Mp °C	Properties of FLC mixtures Phase transition temp /°C SmC*	 SmA	 N*	 Iso	 Ps nC cm^{-2}	 τ μs	 ρ μm	 θ deg
1a	1	118	50	60	66		+3.4	117	27	19
1b	3	91	47	61	66		+4.9	85	5.9	18
1c	5	67	45	61	65		+5.5	79	5.2	18
1d	6	72	46	60	65		+5.6	83	4.7	18
1e	8	81	46	60	65		+6.1	84	3.9	19

Table 1 shows some physical properties and electrooptical characteristics of the FLC mixtures comprised of **1** (2 mol%) and an achiral liquid crystalline mixture A.11)

Ps was measured by the triangular wave method 12) at 25 °C. Response time (τ) was defined as the 0 to 50% change of light-transmission under the square-wave voltage of ±5 V/μm at 25 °C using a polyimide rubbing cell of 2.0 μm thickness. The helical pitch (ρ) of the N* phase was measured at 63 °C using the Cano-Wedge method.13) 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 DC field applied across the sample cell.

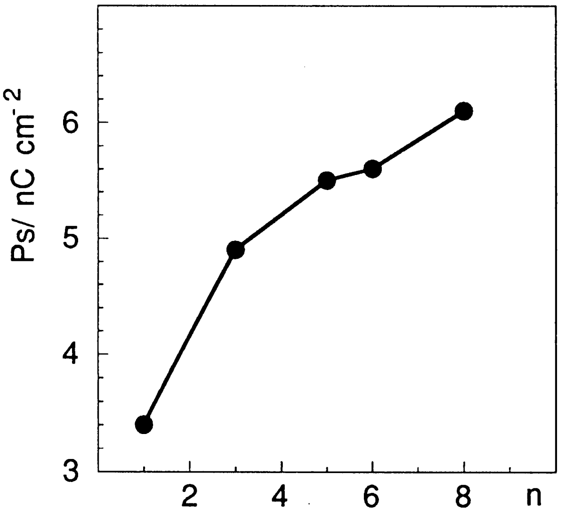


Fig.1. Ps against the carbon number n.

The γ-lactones **1** did not exhibit any mesophases. The melting point of **1** first decreases with increasing chain length n and then slightly increases from the chain length of n=5. The SmA-N* and N* -I transition temperatures of the FLC mixtures are similar, while the SmC* -SmA transition temperatures tend to decrease with increasing n.

The polarity of Ps for the mixture including γ-lactones **1** was the same as that for the mixture involving the corresponding 5,5-dialkyl-δ-lactones or 5-monoalkyl-δ-lactones, which have the *S*-configuration at the 2-position carbon atoms attached to the mesogen.8, 9) Although the magnitude of Ps did not become as large as that of the mixtures involving 5,5-dialkyl-δ-lactones, it increased with increasing n, and it showed Ps values almost as large as the mixtures involving the recently reported monoalkyl-γ-lactones which have two chiral centers.3-7) One reason for this is probably the fact that since the probability that the *cis* lactones or dialkyl lactones occupy the quasi-equatorial position with respect to the mesogen is expected to be high, the effective dipole moments would be larger than that for the *trans* lactones. Another reason is that, considering the model proposed by Koden et al,14) the alkyl chain extending toward the *trans* direction with respect to the mesogen seems to have little influence on the excluded volume effect, while the alkyl chain extending toward the *cis* direction with respect to the mesogen strongly contributes to the packing effect of the chiral dopant for the base mixture. Synthesis of the monoalkyl lactones corresponding to **1** is now under way and the relationship between the molecular structure of the γ-lactones and

Ps will be considered in further detail.

The response time, which is one of the most important properties for FLC mixtures from the practical point of view, reflects the magnitude of Ps, that is, tends to be faster with increasing alkyl chain length. However, there is no strict inverse proportional relationship between them, and it becomes rather slower from the chain length of n=5. This would be due to the influence of the increase in the rotational viscosity.

The helical pitch of the N* phase became shorter with increasing Ps values as seen in most FLC mixtures, while that of the mixtures containing 5,5-dialkyl-δ-valerolactones became longer.[8)]

In conclusion, we have shown the FLC mixtures containing optically active 4,4-dialkyl-γ-butyrolactones gave good electrooptical properties as chiral dopants for FLCs.

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11) The mixture A consists of 2-(heptyloxyphenyl)-5-heptylpyrimidine(5wt%), 2-(4-octyloxyphenyl)-5-heptylpyrimidine(10wt%), 2-(4-nonyloxyphenyl)-5-heptylpyrimidine(15wt%), 2-(4-octyloxyphenyl)-5-octylpyrimidine(20wt%), 2-(4-decyloxyphenyl)-5-octylpyrimidine(30wt%), and 2-(4-hexyloxyphenyl)-5-nonylpyrimidine(20wt%). The phase transition temperatures (T/℃) of the mixture A were Cr 4 SmC 51 SmA 62 N 68 I. M. Koden, T. Kuratate, and F. Funada, *JP*-90-110189.

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