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Synthesis and Properties of Optically Active α-Alkyl-γ-aryloxymethyl-γ-lactones as Chiral Dopants for Ferroelectric Liquid Crystals

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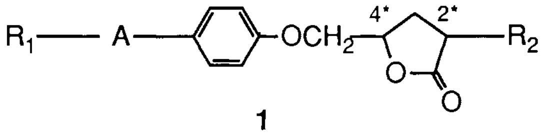
Optically active α-alkyl-γ-aryloxymethyl-γ-lactones were synthesized from chiral epichlorohydrin in short steps and found to be superior chiral dopants for ferroelectric liquid crystals (FLCs).

Since the principle of electro-optical devices using FLCs was proposed in 1980,[1)] many materials having chiral smectic C phase (SmC*) have been investigated. One of the most important factor for FLC materials is the fast response. The response time τ can be represented by $\tau = \eta / (Ps \bullet E)$, where η is the orientational viscosity, Ps is the spontaneous polarization and E is the applied electric field.[2)] In order to realize fast response, FLC materials are often prepared by doping chiral compounds having large Ps to smectic C (SmC) liquid crystalline mixtures with low viscosity. The value of Ps is closely related to partial structures possessing both dipole parts and chiral centers in chiral dopants.[3)] Recently, we designed novel molecules containing chiral α,γ-disubstituted γ-lactone rings[4)] and showed their usefulness as chiral dopants because of their large Ps's.[5,6)] This excellent property would be based on the unique γ-lactone structures; two chiral centers and a dipole part are fixed in one cyclic system. This study focuses on the synthesis of optically active α-alkyl-γ-aryloxymethyl-γ-lactones (**1**) and the effect of the molecular structure on some properties of mixtures doped with **1**.



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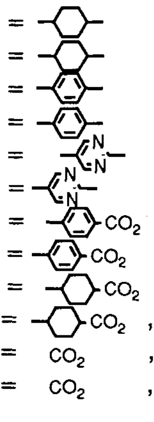
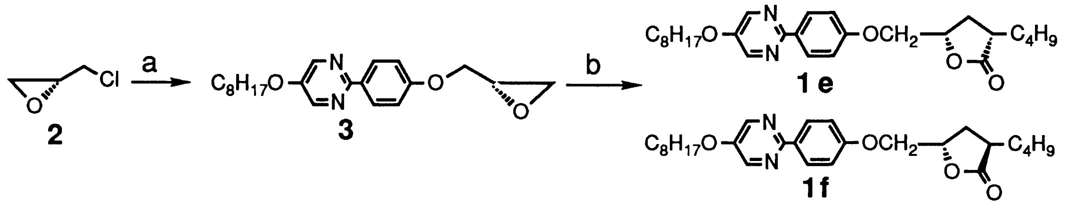
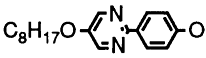
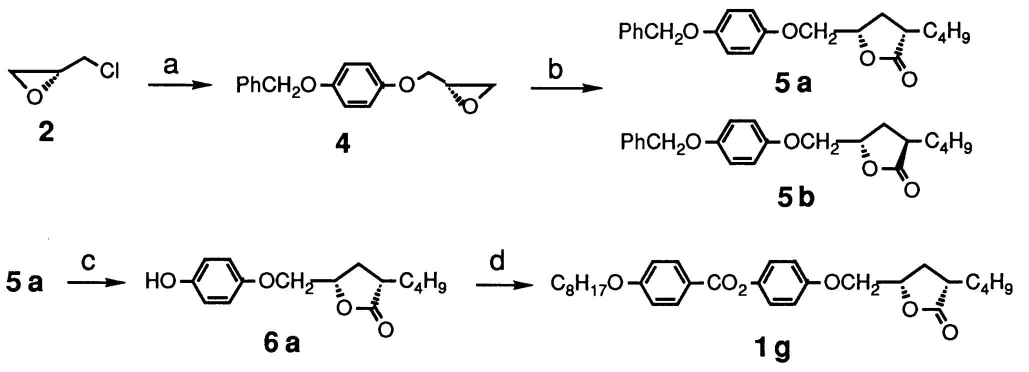
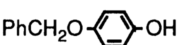


1a A = , R_1 = n-C_5H_{11}, R_2 = n-C_4H_9, 2S,4S (cis)
1b A = , R_1 = n-C_5H_{11}, R_2 = n-C_4H_9, 2R,4S (trans)
1c A = , R_1 = n-C_8H_{17}, R_2 = n-C_3H_7, 2S,4S (cis)
1d A = , R_1 = n-C_8H_{17}, R_2 = n-C_3H_7, 2R,4S (trans)
1e A = , R_1 = n-$C_8H_{17}O$, R_2 = n-C_4H_9, 2S,4S (cis)
1f A = , R_1 = n-$C_8H_{17}O$, R_2 = n-C_4H_9, 2R,4S (trans)
1g A = CO_2, R_1 = n-$C_8H_{17}O$, R_2 = n-C_4H_9, 2S,4S (cis)
1h A = CO_2, R_1 = n-$C_8H_{17}O$, R_2 = n-C_4H_9, 2R,4S (trans)
1i A = CO_2, R_1 = n-C_5H_{11}, R_2 = n-C_4H_9, 2S,4S (cis)
1j A = CO_2, R_1 = n-C_5H_{11}, R_2 = n-C_4H_9, 2R,4S (trans)
1k A = CO_2, R_1 = n-C_5H_{11}, R_2 = n-C_4H_9, 2S,4S (cis)
1l A = CO_2, R_1 = n-C_5H_{11}, R_2 = n-C_4H_9, 2R,4S (trans)



Scheme 1. a) , *t*-BuOK, *t*-BuOH; b) *n*-$C_4H_9CH(CO_2Me)_2$, *t*-BuOK, *t*-BuOH.



Scheme 2. a) , *t*-BuOK, *t*-BuOH; b) *n*-$C_4H_9CH(CO_2Me)_2$, *t*-BuOK, *t*-BuOH; c) H_2, Pd-C, AcOEt; d) , DCC, CH_2Cl_2.

The chiral γ-lactones **1e** (27%) and **1f** (23%) were prepared from (R)-epichlorohydrin[7] in a similar procedure to those of **1a**-**1d**[4] with high enantioselectivity.[8] (Scheme 1) The chiral γ-lactone (**1g**) was prepared as shown in Scheme 2. The reaction of (R)-epichlorohydrin (**2**) with hydroquinone monobenzyl ether in the presence of potassium *t*-butoxide (*t*-BuOK) in *t*-butyl alcohol (*t*-BuOH) at room temperature for 4 hours gave **4** in 87% yield based on the hydroquinone derivative. The epoxide (**4**) was treated with dimethyl *n*-butylmalonate and *t*-BuOK in *t*-BuOH under reflux for 3 hours to afford **5** in 35% yield as a mixture of diastereomers (cis (**5a**) : trans (**5b**) = 72 : 28). Each diastereomer of **5** was easily separated by silica gel column chromatography. Debenzylation of the cis isomer (**5a**) was carried out by catalytic reduction, H_2/Pd-C in ethyl acetate under 2 kg/cm^2 for 30 minutes, to afford **6a** in 86% yield. Condensation of **6a** and *p*-*n*-octyloxybenzoic acid was achieved by N,N-dicyclohexylcabodiimide (DCC) in dichloromethane at room temperature for 2 hours to give **1g** in 34% yield. **1i** and **1k** were prepared from **6a** in a similar manner, and each trans isomer (**1h**, **1j**, **1l**) was also prepared from **5b**.

The γ-lactones (**1**) did not exhibit any mesophases. Table 1 shows some physical properties and electro-optical characteristics of the FLC mixtures comprised of **1** (2wt%) and an achiral liquid crystalline mixture A (98wt%).[9] Almost all the transition temperatures of the mixtures are unaffected by doping of **1** due to the small amount (2wt%) of doping. Every mixture containing **1** showed suitable tilt angles (ca. 20 degrees) for an application in the birefringent mode. The mixtures containing cis-lactones showed large Ps's, more than 4.7 nC/cm^2 (**1a**, **1c**, **1e**, **1g**, **1i**, **1k**), and some of them exhibited fast response, less than 100 μs at room temperature (**1a**, **1c**, **1e**, **1i**). Few chiral dopants have been known so far to show such large Ps's and fast responses with such a small doping of 2wt%.[10] These observations would be explained by the unique structures of α,γ-disubstituted γ-lactone as follows: 1) two asymmetric carbon atoms are fixed in a rigid 5-membered lactone ring, thereby, free rotation of the dipole moiety (an ester group) is considerably restricted, 2) the carbonyl group and the ether group are in the same plane[11] and arranged perpendicular to the long axis of the molecule in the same direction. The mixtures containing **1g**, **1i**, or **1k** showed rather slow response time in spite of their large Ps's and showed rather large tilt angles. Since the introduction of the ester group increased the tilt angle, the rather slow response time would be attributable to their large tilt angle and high viscosity derived from the ester group. One of the most remarkable results in this research is that the mixtures containing cis-lactones exhibited larger Ps's and faster responses than those containing trans-lactones in each diastereomer pair. These phenomena would result from a conformational difference between their molecular structures in SmC*.[12]

The present study demonstrates that the α-alkyl-γ-aryloxymethyl-γ-lactones are excellent chiral dopants for FLCs. The partial rigid structure having proper mutual disposition between dipole moiety and chiral center is extremely important in order to design an excellent chiral dopant. Modifications of the γ-lactones are now in progress.

Table 1. Properties of FLC mixtures containing 2wt% of **1** and 98wt% of the mixture A[a]

Chiral dopant	Mp[b] θm/°C	Phase transition temp[c]/°C SmC* SmA	N*	I	Response time[d] μs	Ps[e] nC cm^{-2}	Tilt angle deg
1a	84	46	61	67	86	-5.3	21
1b	85	50	63	68	158	-0.9	17
1c	115	51	63	68	84	-6.5	21
1d	117	51	63	69	263	-0.8	19
1e	130	50	63	69	84	-4.7	19
1f	108	52	65	69	131	-1.7	19
1g	91	50	61	68	192	-4.7	22
1h	93	50	62	69	328	-—[f]	19
1i	85	50	62	68	94	-7.1	23
1j	100	50	63	67	228	-0.6	19
1k	72	49	59	67	152	-7.7	23
1l	56	49	58	66	291	-—[f]	23

a) See Ref. 9. b) Melting point of chiral dopant. c) SmC*: chiral smectic C Phase, SmA: smectic A phase, N*: chiral nematic phase, I: isotropic liquid phase. d) Response time was defined as the 0 to 50% change of transmission of light under the voltage of 10 V$_{p\text{-}p}$/μm at 25°C. Cells were constructed with two glass plates coated with polyimide rubbed in the same direction and their thickness was 2 μm. e) Measured by the triangular method.[13] f) The absolute value was lower than 0.5.

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7) The optical yield was more than 99%. N. Kasai, H. Shima, and K. Tsujimura, *USP*-4840907 (1989).
8) The optical yields were estimated more than 95% by the HPLC analysis using chiral column, "CHIRALCEL OD" produced by Daicel Chemical Industries, Ltd.
9) The host liquid crystalline mixture A is composed of 2-(4-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%). Cr <rt SmC 51 SmA 63 N 69 I (°C). Cr: crystalline phase, SmC: smectic C phase, SmA: smectic A phase, N: nematic phase, I: isotropic liquid phase.
10) FLC mixtures containing more than 5wt% of chiral dopants have been reported. For example, see CH. Bahr and G. Heppke, *Mol. Cryst. Liq. Cryst.*, **148**, 29 (1987); T. Sakurai, N. Mikami, R. Higuchi, M. Honma, and K. Yoshino, *Ferroelectrics*, **85**, 469 (1988); D. M. Walba, H. A. Razavi, N. A. Clark, and D. S. Parmar, *J. Am. Chem. Soc.*, **110**, 8686 (1988); H. R. Dübal, C. Escher, D. Günther, W. Hemmerling, Y. Inoguchi, I. Müller, M. Murakami, D. Ohlendolf, and R. Wingen, *Jpn. J. Appl. Phys.*, **27** (1988) L2241; T. Kusumoto, T. Hanamoto, T. Hiyama, S. Takehara, T. Shoji, M. Osawa, T. Kuriyama, K. Nakamura, and T. Fujisawa, *Chem. Lett.*, **1990**, 1615.
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