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Relationship between Molecular Structure and Induced Spontaneous Polarization for Chiral Dopants Containing an Optically Active Lactone

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A series of new optically active γ-lactones were synthesized. The relationship between molecular structures and induced spontaneous polarization of optically active γ-lactones and δ-lactones has been investigated. The molecular shapes of chiral dopants, especially the alkyl chains extending from a lactone ring, were found to play important roles in the generation of spontaneous polarization.

Keywords: Ferroelectric liquid crystal, spontaneous polarization, chiral smectic C phase, chiral dopants, γ-butyrolactone, δ-valerolactone

INTRODUCTION

Ferroelectric liquid crystal (FLC) displays[1] are in the process of being developed for commercial applications. One of the important factors for the commercialization of these displays is the response time of the FLC mixtures. It is difficult to determine an acceptable chiral smectic C (Sc*) phase temperature range with a sufficiently high spontaneous polarization (Ps) and low viscosity. Therefore, FLC materials are often prepared by doping chiral compounds potentially possessing large Ps values into host liquid crystal mixtures showing a smectic C (Sc) phase around room temperature and also having a low viscosity. In the last few years, chiral compounds containing a lactone ring have been avidly studied as chiral dopants;[2–10] however, they were not suitable for large scale synthesis because they have two chiral centers, thus sometimes necessitating a diastereomer separation to synthesize them. Recently we designed and synthesized 5,5-dialkyl-δ-lactones **1**, which have only one chiral center, and also demonstrated that they induce large Ps values[11,12] compared to the corresponding δ-lactones **2** and **3**,

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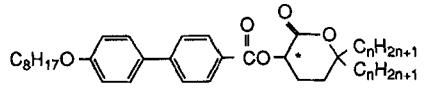
which possess two chiral centers.[9,10] In a previous letter, we reported that 4,4-dialkyl-γ-lactones **4** were also found to induce large Ps values.[13] In this paper, we report the synthesis of the corresponding monoalkyl γ-lactones **5** and **6**, and discuss the relationship between the molecular structure of the lactones and induced spontaneous polarization.



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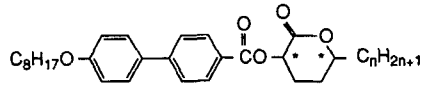
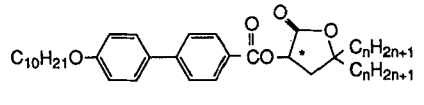


2 (cis) **3** (trans)



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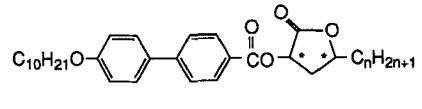


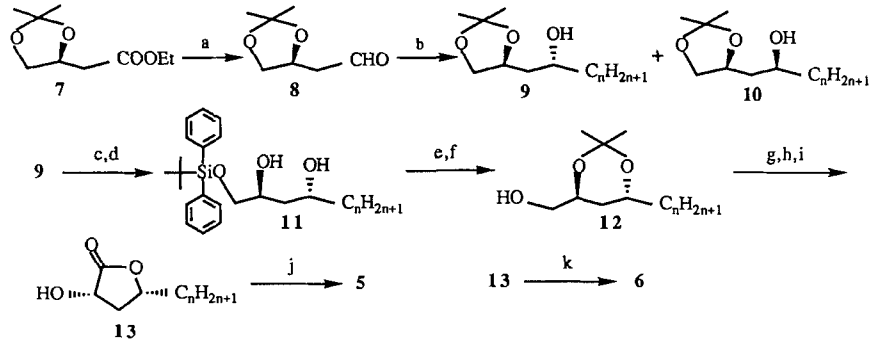
5 (cis) **6** (trans)

EXPERIMENTAL

Measurement of Physical Properties

FLC mixtures were prepared by adding 2 mol% of a chiral compound into a non-chiral Sc mixture[14] whose transition temperatures (T/°C) were Cr 4 SmC 51 SmA 62 N 68 I. Ps values were measured by the triangular wave method[15] at 25°C. The sign of the Ps was determined by observing the tilt direction in the DC field as defined by Lagerwall *et al.*[16] The response time (τ) was defined as the 0 to 50% change in light-transmission under a 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.[17] 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 the DC field applied across the sample cell.

Synthesis of New Compounds 5 and 6



SCHEME 1 a) *i*-Bu_2AlH, CH_2Cl_2; b) $C_nH_{2n+1}MgBr$; c) HCl, H_2O, THF; d) *t*-$BuPh_2SiCl$, Imidazole, CH_2Cl_2; e) $Me_2C(OMe)_2$, PPTS; f) *n*-Bu_4NF, THF; g) DMSO, $(COCl)_2$, Et_3N, CH_2Cl_2; h) $NaClO_2$, NaH_2PO_4, *t*-BuOH, H_2O; i) HCl, H_2O, THF; j) $C_{10}H_{21}OC_6H_4{\cdot}C_6H_4COOH$, DCC, DMAP, CH_2Cl_2; k) $C_{10}H_{21}OC_6H_4{\cdot}C_6H_4COOH$, DEAD, PPh_3, Benzene.

(*S*)-2,2-Dimethyl-4-formylmethyl-1,3-dioxolane 8

DIBAL-H solution (0.93M in hexane, 90 ml) was added dropwise to a stirred solution of commercially available (S)-2,2-dimethyl-4-ethoxycarbonylmethyl-1,3-dioxolane **7**[18] (15 g) in dry CH_2Cl_2 (150 ml) at $-78°C$ under Ar. The mixture was stirred for 20 min. Methanol (18 ml) was added to the stirred mixture at $-78°C$. The stirring was continued for 45 min after the addition with a gradual raise in the reaction temperature to room temperature. The mixture was filtered and concentrated *in vacuo*. Methanol (20 ml) was added to the residue again and concentrated *in vacuo*. The residue was filtered through a column of SiO_2 (100 g) to yield 6.8 g (59%) of **8**, ν_{max} (neat) 2750 (w), 1730(s) cm^{-1}; δ ($CDCl_3$) 1.36 (3H, s), 1.41 (3H, s), 2.48–3.00 (2H, m), 3.59 (1H, dd, $J = 8$ Hz, $J = 6$ Hz), 4.19 (1H, dd, $J = 8$ Hz, $J = 6$ Hz), 4.35–4.67 (1H, m), 9.81 (1H, s). This was employed in the next step without further purification.

(4*S*, 2′*R*)-2,2-Dimethyl-4-(2′-hydroxy)decyl-1,3-dixolane 9

The aldehyde **8** (2.5 g) in dry Et_2O (20 ml) was added to a stirred and cooled solution of n-$C_8H_{17}MgBr$ in dry Et_2O prepared from n-$C_8H_{17}Br$ (5.7 g) and Mg (0.72 g) in dry Et_2O (30 ml) at 0°C under Ar. The stirring was continued for 2 hr at 0°C. The mixture was poured into a saturated NH_4Cl solution and extracted with Et_2O. The extract was washed with water and brine, dried over $MgSO_4$ and concentrated *in vacuo*. The residue was chromatographed over SiO_2 (150 g). Elution with n-hexane-EtOAc (5:1) gave 2.14 g (48%) of **9**, n_D^{21} 1.4469; $[\alpha]_D^{22} - 3.4°$ ($c =$ 0.80, Et_2O); ν_{max} (neat) 3450 (br) cm^{-1}; $\delta(CDCl_3)$ 0.70–1.00 (3H, m), 1.10–1.80 (16H, m), 1.37 (3H, s), 1.42 (3H, s), 2.18 (1H, d, $J = 6$ Hz, $-OH$), 3.58 (1H, t, $J =$ 8 Hz), 3.70 – 4.00 (1H, m) 4.09 (1H, dd, $J = 8$ Hz, $J = 6$ Hz), 4.16 – 4.50 (1H, m). (Found: C, 69.56; H, 11.66. Calc. for $C_{15}H_{30}O_3$: C, 69.72; H, 11.70%). In this step, 1.43 g (32%) of its diastereomer **10** (nonpolar compared to **9**) was also produced.

(2*S*, 4*R*)-1-*t*-Butyldiphenylsilyloxy-2,4-undecanediol 11

Ten ml of 4N HCl was added to a stirred and cooled solution of **9** (1.6 g) in THF (15 ml) at 0°C. This mixture was stirred for 1 hr at 0°C and then the mixture was poured into a saturated $(NH_4)_2SO_4$ solution and extracted with EtOAc repeatedly. The extract was dried over K_2CO_3 and concentrated *in vacuo*. The residue was dissolved into DMF (15 ml), and then imidazole (0.91 g) and TBDPSCl (1.74 g) were added to the solution at 0°C. The stirring was continued for 16 hr after the addition with a gradual raise in the reaction temperature to room temperature. The mixture was poured into ice–water and extracted with Et_2O. The extract was washed with brine, dried over $MgSO_4$ and concentrated *in vacuo*. The residue was chromatographed over SiO_2 (50 g). Elution with n-hexane-EtOAc (5:1) gave 2.34 g (83%) of **11**, n_D^{21} 1.5190; $[\alpha]_D^{22} - 5.6°$ ($c = 0.75$, Et_2O); ν_{max} (neat) 3400 (br) cm^{-1}; $\delta(CDCl_3)$ 0.70 – 1.00 (3H, m), 1.07 (9H, s), 1.10 – 1.63 (16H, m), 2.36 (1H, d, $J = 5$ Hz, —OH), 2.81 (1H, d, $J = 3$Hz, —OH), 3.60 (1H, d, $J =$ 8Hz), 3.62 (1H, d, $J = 4$ Hz), 3.65 – 4.20 (2H, m), 7.30 – 7.75 (10H, m). (Found: C, 73.61; H, 9.71. Calc. for $C_{28}H_{44}O_3Si$: C, 73.63; H, 9.71%).

(4*S*, 6*R*)-2,2-Dimethyl-4-hydroxymethyl-6-*n*-octyl-1,3-dioxane 12

A solution of **11** (1.78 g), 2,2-dimethoxypropane (20 ml) and PPTS (60 mg) was stirred for 18 hr at room temperature. The mixture was poured into $NaHCO_3$ solution and extracted with Et_2O. The extract was then washed with $NaHCO_3$ solution and brine, dried over $MgSO_4$ and concentrated *in vacuo*. The residue was dissolved into THF (10 ml), and then TBAF solution (1.0 M in THF, 10 ml) was added to the solution at 0°C. The mixture was then stirred for 1 hr, poured into water and extracted with Et_2O. The extract was washed with brine, dried over $MgSO_4$ and concentrated *in vacuo*. The residue was chromatographed over SiO_2 (30 g). Elution with *n*-hexane-EtOAc (5:1) gave 0.89 g (88%) of **12**, n_D^{22} 1.4503; $[\alpha]_D^{22} - 22.3°$ ($c = 1.21$, Et_2O); ν_{max} (neat) 3450 (br) cm^{-1}; $\delta(CDCl_3)$ 0.70 – 1.00 (3H, m) 1.00 – 2.50 (22H, m), 3.45 – 4.10(4H, m). (Found: C, 69.50; H, 11.85. Calc. for $C_{15}H_{30}O_3$: C, 69.72; H, 11.70%).

(2*S*, 4*R*)-2-Hydroxy-4-*n*-octyl-γ-butyrolactone 13

A solution of DMSO (0.58 ml) in CH_2Cl_2 (1.8 ml) was added dropwise to a cooled (– 70°C) and stirred solution of oxalyl chloride (0.54 ml) in CH_2Cl_2 (31 ml) under Ar. The mixture was stirred for 2 min at – 70°C, and then a solution of **12** (0.75 g) in CH_2Cl_2 (10 ml) was added dropwise with stirring. After 45 min, Et_3N (3.2 ml) was added dropwise and the stirring was continued for 15 min. The mixture was allowed to warm to 0°C, stirred for 30 min at this temperature, and then NH_4Cl solution (12 ml) was added to the mixture. The organic layer was washed with brine, dried over $MgSO_4$ and concentrated *in vacuo*. The residue was filtered through a column of SiO_2 (10 g) to yield crude aldehyde (0.54 g). $NaClO_2$ (0.63 g) was added to a solution of the crude aldehyde (0.54 g), *t*-BuOH (15 ml), H_2O (4 ml), 2-methyl-2-butene (0.65 g) and NaH_2PO_4 (0.28 g) at room temperature. The mixture was stirred for 1 hr at room temperature, poured into saturated $(NH_4)_2SO_4$ solution and extracted with EtOAc. The extract was washed with brine and concentrated *in vacuo*. The residue was dissolved into THF (3 ml) and then 6N HCl (3 ml) was added to the solution. The mixture was stirred for 30 min and poured into saturated $(NH_4)_2SO_4$ solution and extracted with EtOAc repeatedly. The extract was washed with brine and concentrated *in vacuo*. The residue was chromatographed over SiO_2 (12 g). Elution with *n*-hexane-EtOAc (3:1) gave 0.36 g (58%) of **13**, m.p. 78°C; $[\alpha]_D^{22} + 4.2°$ ($c = 0.84$, Et_2O); ν_{max} (neat) 3420 (br), 1745 (s) cm^{-1}; $\delta(CDCl_3)$ 0.70 – 1.00 (3H, m) 1.00 – 1.80 (14H, m), 1.80 – 2.07 (1H, m), 2.55 – 2.84 (1H, m), 2.95 (1H, d, $J = 3$ Hz, —OH), 4.23 – 4.63 (2H, m). (Found: C, 67.15; H, 10.21. Calc. for $C_{12}H_{22}O_3$: C, 67.25; H, 10.35%).

(2*S*, 4*R*)-2-(4′-*n*-Decyloxybiphenyl-4-carboxy)-4-*n*-octyl-γ-butyrolactone 5c

DMAP (0.06 g) was added to a solution of **13** (0.10 g), 4′-*n*-decyloxybiphenyl-4-carboxylic acid (0.17 g) and DCC (0.10 g) in CH_2Cl_2 (3 ml) at room temperature. After being stirred overnight, the mixture was concentrated *in vacuo*. The residue was chromatographed over SiO_2 (5 g). Elution with benzene gave **5c**. This was recrystallized from *n*-hexane-EtOAc to yield 0.21 g (82%) of pure **5c**, m.p. 136°C; $[\alpha]_D^{22} + 6.3°$ ($c = 1.65$, $CHCl_3$); ν_{max} (KBr) 1760 (s), 1720 (s) cm^{-1}; $\delta(CDCl_3)$ 0.70 – 1.00 (6H, m) 1.00 – 1.95 (30H, m), 1.95 – 2.22 (1H, m), 2.76 – 3.09 (1H, m), 4.01 (2H, t, $J = 6$ Hz), 4.30 – 4.65 (1H, m). 5.72 (1H, dd, $J = 10$ Hz, $J = 9$ Hz), 6.99 (2H, d, $J = 8$ Hz), 7.57

TABLE I

Properties of Mixtures Containing 2 mol% of γ-Lactone Derivatives 5 and 6

No.	n	abc. config	m.p (°C)	Transition temp. (°C) Sc*	S_A	N^*I	τ (μsec)	Ps (nC/cm²)	θ (deg)	N^* pitch (μm)
5a	3	(2*S*, 4*R*) *cis*	144	51	61	67	114	+4.4	20	5.8
5b	5	(2*S*, 4*R*) *cis*	142	52	61	67	82	+4.9	20	5.1
5c	8	(2*S*, 4*R*) *cis*	136	51	60	67	112	+4.8	20	4.7
6a	3	(2*R*, 4*R*) *trans*	119	53	61	67	212	−1.6	19	12
6b	5	(2*R*, 4*R*) *trans*	119	53	61	68	229	−1.2	18	10
6c	8	(2*R*, 4*R*) *trans*	118	53	61	67	302	−0.8	19	8.1

(2H, d, J = 8 Hz), 7.63 (2H, d, J = 8 Hz), 8.12 (2H, d, J = 8 Hz). (Found: C, 76.22; H, 9.06. Calc. for $C_{35}H_{50}O_5$: C, 76.32; H, 9.15%).

(2*R*, 4*R*)-2-(4′-*n*-Decyloxybiphenyl-4-carboxy)-4-*n*-octyl-γ-butyrolactone 6c

Ph_3P (0.13 g) was added to a solution of **13** (0.10 g), 4′-*n*-decyloxybiphenyl-4-carboxylic acid (0.17 g) and DEAD (0.09 g) in benzene (2 ml) at room temperature. After being stirred overnight, the mixture was concentrated *in vacuo*. The residue was chromatographed over SiO_2 (5 g). Elution with benzene gave **6c**. This was recrystallized from *n*-hexane-EtOAc to yield 0.20 g (80%) of pure **6c**, m.p. 118°C; $[\alpha]_D^{22}$ + 30.6° (c = 1.09, $CHCl_3$); ν_{max} (KBr) 1780 (s), 1705 (s) cm^{-1}; δ($CDCl_3$) 0.70 − 1.00 (6H, m) 1.00 − 2.00 (30H, m), 2.50 (2H, t, J = 7 Hz), 4.01 (2H, t, J = 6 Hz), 4.60 − 4.90 (1H, m) 5.66 (1H, t, J = 8 Hz), 6.99 (2H, d, J = 8 Hz), 7.57 (2H, d, J = 8 Hz), 7.63 (2H, d, J = 8 Hz), 8.12 (2H, d, J = 8 Hz). (Found: C, 76.62; H, 9.12. Calc. for $C_{35}H_{50}O_5$: C, 76.32; H, 9.15%).

RESULTS AND DISCUSSION

Figure 1 shows the plots of the induced Ps values against the carbon number for δ-lactones and γ-lactones respectively.[12,13] In the case of γ-lactone derivatives, the *cis*-γ-lactones and dialkyl-γ-lactones induce large Ps values, although the *trans*-γ-lactones do not. On the other hand, in the case of δ-lactone derivatives, the dialkyl-δ-lactones induce extremely large Ps values, although there is little difference in the induced Ps values between the *cis*-δ-lactones and *trans*-δ-lactones.

Figure 2 shows the model proposed by Koden *et al.*,[19,20] which is applied to our *cis*, *trans* and dialkyl γ-lactones, respectively. The dipole moment of a lactone ring for a right conformer is in the opposite direction of that for a left conformer. Here, the volume occupied by each conformer for the nonchiral Sc mixtures is considered (Figure 3). If the occupied volume for one conformer is as small as the nonchiral molecule showing an Sc phase, the conformer can easily fit in the nonchiral Sc mixtures. If the occupied volume of the other conformer is not as small, it will be difficult for the conformer to fit into it. Consequently, a difference in the probability of each conformer existing in the Sc phase results. The bigger the difference in the probability, the larger the remaining dipole moment becomes; consequently, the Ps value is thought to become larger also.

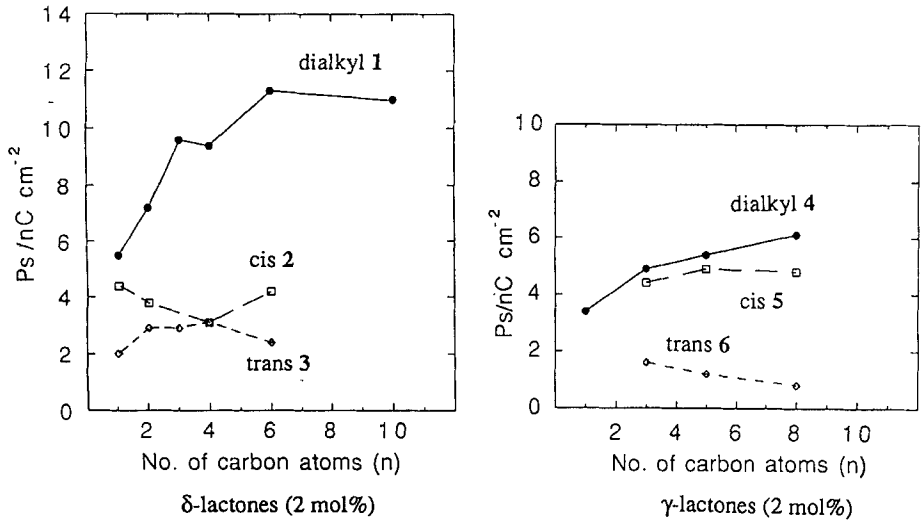


FIGURE 1 Plots of the induced Ps values against the number of carbon atoms.

When this is considered, a right conformer of the *cis*-γ-lactones is advantageous for the packing of the nonchiral Sc mixtures compared to a left conformer, although the contribution of both conformers of the *trans* lactones to the packing effect is not very different. Here, when we consider the occupied volume of each conformer of the *cis* and *trans* lactones, it is found that the alkyl chain extending toward the *cis* direction with respect to the mesogen determines the occupied volume, while the alkyl chain toward the *trans* direction has little influence on it; that is, the alkyl chain toward the *trans* direction with respect to the mesogen has little influence on the difference in the probability of each conformer existing in the Sc phase. The dialkyl γ-lactones, which have alkyl chains toward both the *cis* and *trans* directions, have the same advantage of the packing effect as the *cis* lactones. Consequently, the *cis*-γ-lactones and dialkyl-γ-lactones are expected to induce almost the same large Ps values, which is actually consistent with empirical data (Figure 1).

Similarly, for the δ-lactone derivatives the alkyl chain extending toward the *cis* direction with respect to the mesogen determines the occupied volume. Therefore *cis*-δ-lactones and dialkyl-δ-lactones are expected to induce large Ps values, while *trans*-δ-lactones are expected to induce small Ps values because there is not much difference in the volume effect between right and left conformers (Figure 4). Actually, the Ps values are large for the dialkyl lactones and small for the *trans* lactones; however, for the *cis* lactones the Ps value is as small as that of the *trans* lactones. This is probably due to the fact that the conformation of *cis*-δ-lactones is not necessarily the "pseudo–chair" form but could be the "boat" form.[12] For the *trans* and dialkyl derivatives, the "chair" form must be the stable form, but for the *cis* derivatives, when the mesogen is supposed to be in an equatorial orientation with respect to the δ-lactone ring, the "boat" form can be rather advantageous especially in the liquid crystal phase because the alkyl chain becomes equatorially oriented even though the "boat" form is not advantageous for the

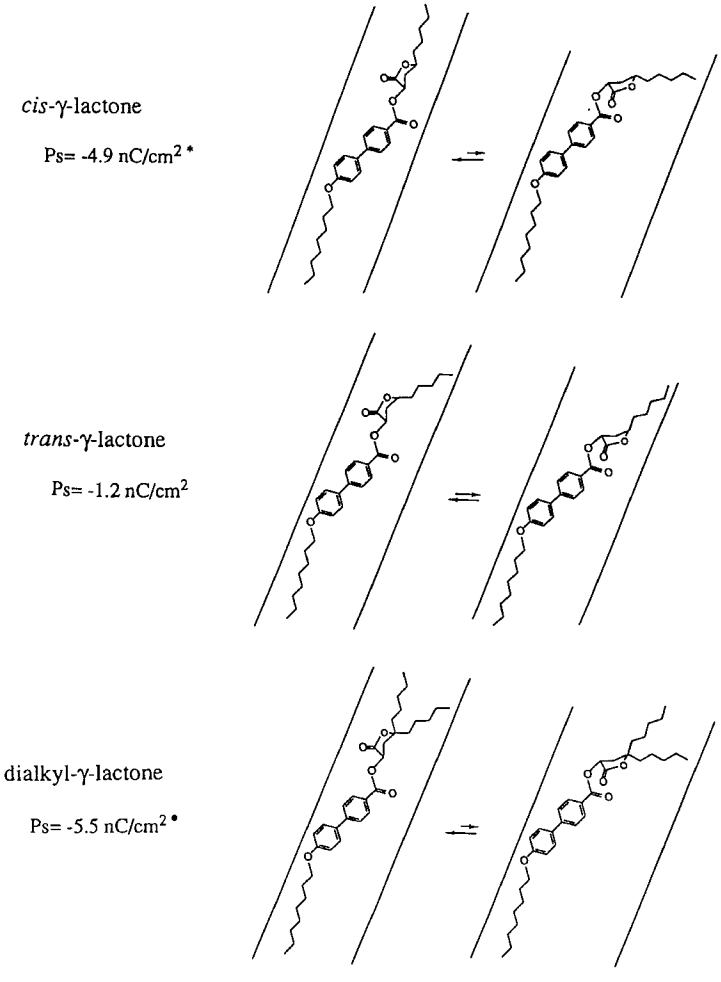


FIGURE 2 Molecular conformational model for the γ-lactones ($n = 5$) in the Sc phase.

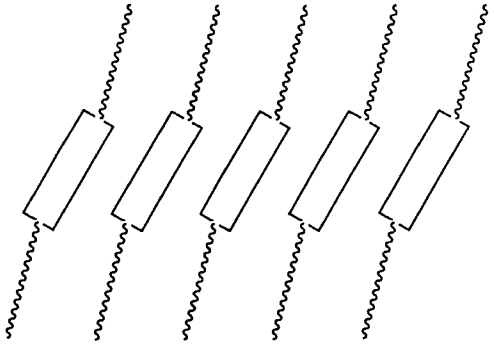


FIGURE 3 The model for the nonchiral Sc mixtures.[21,22]

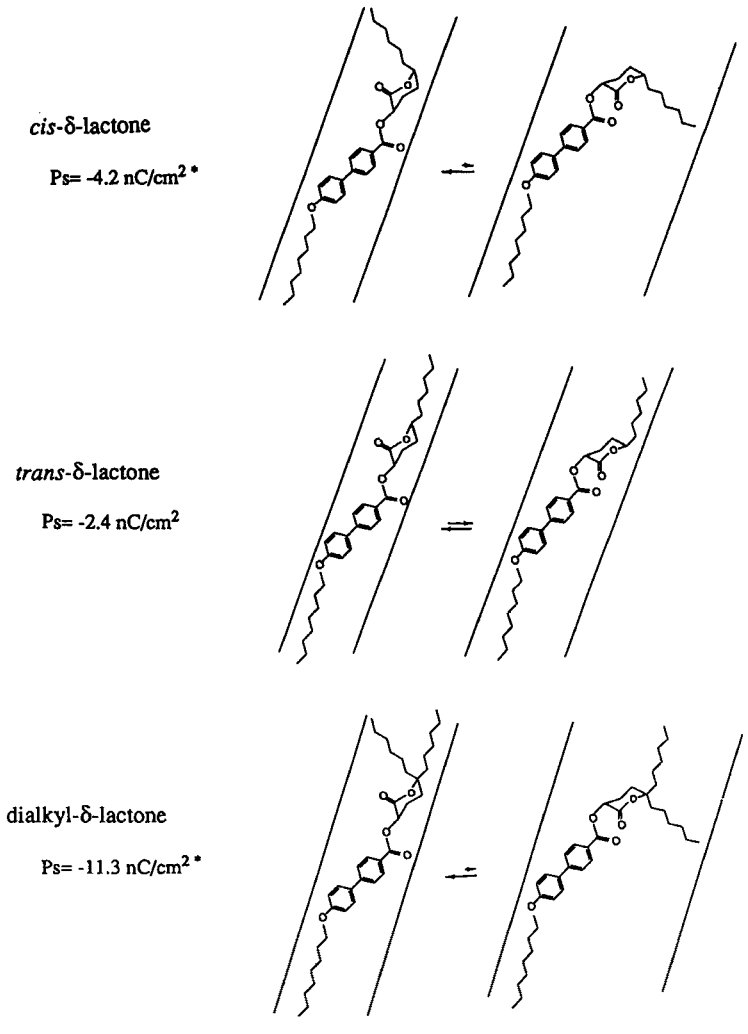


FIGURE 4 Molecular conformational model for the δ-lactones ($n = 6$) in the Sc phase.

ring energy. If so, the alkyl chain from a lactone ring extends toward the direction of the molecular axis, the difference in the probability between the two conformers whose dipole moment of the lactone ring are opposite is expected to be small, similar to the *trans* lactones (Figure 5).

When this is considered, the reason why chiral dopants containing a lactone ring induce large Ps values would not be because a chiral lactone ring itself fixes the dipole moment but because the lactone ring fixes the alkyl chain extending from the ring. The alkyl chain determines the molecular shape of each conformer whose direction of dipole moment is different.

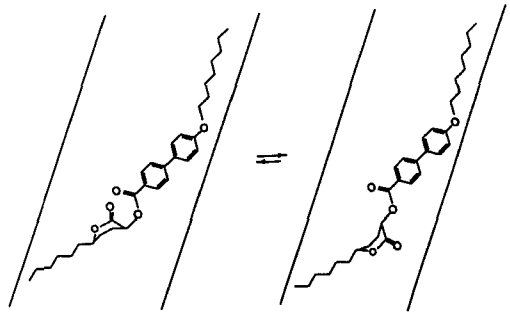


FIGURE 5 Molecular conformational model for the *δ-cis*-lactones (boat form) in the Sc phase.

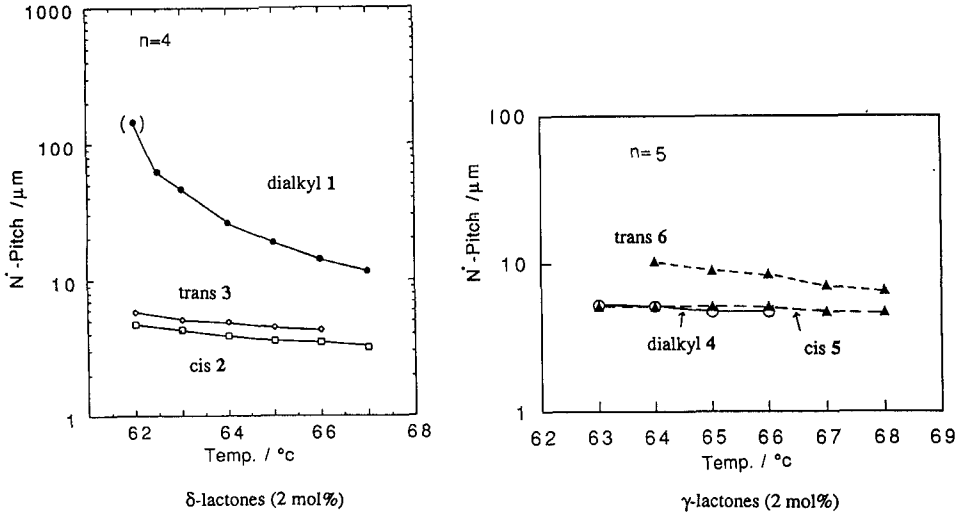


FIGURE 6 Temperature dependence of the helical pitch in the N^* phase.

Finally, interesting results concerning the helical pitch of the chiral nematic phase are shown in Figure 6. The helical pitches induced by dialkyl-*δ*-lactones are very long in spite of induced large Ps values, although those of *cis* and *trans* *δ*-lactones are rather short. On the other hand, for *γ*-lactones those of dialkyl lactones were short, similar to most general chiral dopants, that is, the helical pitch becomes shorter as the Ps becomes larger. The reason for this interesting result is now under investigation.

In conclusion, we investigated the relationship between molecular structures and induced spontaneous polarization for optically active lactones. We also investigated molecular shapes of chiral dopants, especially the alkyl chains extending from a lactone ring which were found to play important roles in the generation of spontaneous polarization.

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