  Bull. Chem. Soc. Jpn., 61, 2573—2578 (1988)

Thermal and Ferroelectric Properties of Novel Ferroelectric Liquid Crystals Containing α-Methylcinnamoyl Moiety in the Core Structure

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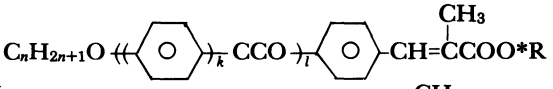
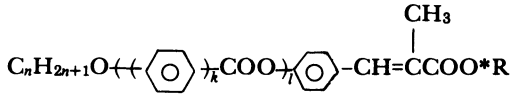
(Received February 10, 1988)

Six homologous series of novel ferroelectric liquid crystals containing α-methylcinnamoyl moiety in the core structure:



(IA: k=1, l=1, *R=-$CH_2^*CHC_2H_5$, n=8—16; IB: k=1, l=1, *R=$^*CHC_6H_{13}$, n=8—16; IIA: k=1, l=2, *R=-$CH_2^*CHC_2H_5$, n=9—16; IIB: k=1, l=2, *R=$^*CHC_6H_{13}$, n=8—14; IIIA: k=2, l=1, *R=-$CH_2^*CHC_2H_5$, n=9—16; IIIB: k=2, l=1, *R=$^*CHC_6H_{13}$, n=9—16) have been synthesized and their thermal and ferroelectric properties have been investigated. The mesomorphic transition temperatures and the spontaneous polarization for the homologous series (IA, IB, IIA, IIB, IIIA, and IIIB) depend on the core structure, the chiral group, and the terminal alkoxyl chain length. These homologous series show the chiral smectic C phase over wide temperature ranges including room temperature and the values of their maximum spontaneous polarization are in the range of 30 to 800 μC m^{-2}. The thermal stability of the mesophase and the magnitude of the spontaneous polarization have been discussed from the view point of the molecular structure and the local molecular interactions.

It was recently shown that the thin cell containing ferroelectric liquid crystals was applied to high-speed switching devices.[1] Since then, much attention has been given to the synthesis of ferroelectric liquid crystals which show the chiral smectic C (Sm*C) phase over a wide temperature range including room temperature and have large spontaneous polarization.[2-6] However, there are few liquid crystals which exhibit the Sm*C phase in the region of lower temperature than room temperature and have large spontaneous polarization. Therefore, eutectic mixtures which show the enantiotropic Sm*C phase over a wide temperature range covering room temperature have been prepared by mixing several compounds.[7-10] In addition to such practical approach, the synthesis of novel compounds and the investigation of the correlation between the physical properties and the molecular structure are necessary in order to design the materials with higher quality than those reported so far. In the previous paper,[11] we reported that the homologues with longer alkoxyl chain of (*S*)-2-methylbutyl esters or 4-(4-*n*-alkoxybenzoyloxy)-α-methylcinnamic acid (IA homologues shown below) show enantiotropic Sm*C phase around room temperature. In addition to these homologues (IA), we have synthesized other five homologous series (IB, IIA, IIB, IIIA, and IIIB) as shown in the following general formula:



IA: k = 1, l = 1, *R = -$CH_2^*CHC_2H_5$, n = 8—16,

IB: k = 1, l = 1, *R = $^*CHC_6H_{13}$, n = 9—16,

IIA: k = 1, l = 2, *R = -$CH_2^*CHC_2H_5$, n = 9—16,

IIB: k = 1, l = 2, *R = $^*CHC_6H_{13}$, n = 8—14,

IIIA: k = 2, l = 1, *R = -$CH_2^*CHC_2H_5$, n = 9—16,

IIIB: k = 2, l = 1, *R = $^*CHC_6H_{13}$, n = 9—16,

In the present paper, we discuss the effect of the core, the chiral part, and the terminal alkoxyl chain in the molecular structure on the mesomorphic transition temperatures and the magnitude of the spontaneous polarization in the Sm*C phase.

Experimental

Preparation of Materials. All the reagents purchased from Tokyo Kasei Co., Ltd. were used without further purification. *p*-Hydroxy-α-methylcinnamic acid was prepared by a Perkin reaction according to the literature.[12] (*S*)-2-Methylbutyl or (*R*)-1-methylheptyl ester of *p*-hydroxy-α-methylcinnamic acid were synthesized by an esterification reaction of *p*-acetoxy-α-methyl-cinnamoyl chloride with (*S*)-2-methyl-1-butanol or (*R*)-1-methyl-1-heptanol using triethylamine as a base, followed by the hydrolysis of the acetoxyl group selectively in the mixed solvent of tetrahydrofuran and methanol (volume ratio : 9/1) containing equimolar 1 mol dm^{-3} LiOH. The specific rotations $[\alpha]_D$ measured in chloroform at 23 °C were 3.56° and −26.73° for the (*S*)-2-methylbutyl ester and the (*R*)-1-methylheptyl ester, respectively. 4′-Alkoxy-1-biphenylcarboxylic acids were synthesized by the hydrolysis of the 4′-alkoxy-4-cyanobiphenyls, which were synthesized by a reaction or 4′-cyanobiphenyl-4-ol with the corresponding alkyl bromides in cyclohexanone containing K_2CO_3, in NaOH–H_2O–ethylene glycol solution. (*S*)-2-Methylbutyl or (*R*)-1-methylheptyl esters of *p*-hydroxybenzoyloxy-α-methylcinnamic acid were synthesized by an esterification reaction of *p*-acetoxybenzoyl chloride with (*S*)-2-methylbutyl or (*R*)-1-methylheptyl esters of *p*-hydroxy-α-methylcinnamic acid using triethylamine as a base, followed by the hydrolysis of the acetoxyl group selectively in the mixed solvent of tetrahydrofuran and methanol (volume ratio: 9/1) containing equimolar 1 mol dm^{-3} LiOH at room temperature.

The homologous series (IB, IIA, IIB, IIIA, and IIIB) were prepared by an esterification reaction of the *p*-hydroxy-α-methylcinnamates or the 4-(4-hydroxybenzoyloxy)-α-methylcinnamates with the corresponding *p*-alkoxybenzoyl chlorides or 4′-alkoxy-1-biphenylcarboxylic acid chlorides using triethylamine as a base. The products were purified by column chromatography (silica gel, benzene–hexane), followed by the recrystallization from ethanol.

Their elementary analysis data are listed in Table 1.

Table 1. Elemental Analyses for Homologous Series IB, IIA, IIB, IIIA, and IIIB

(IB Homologues)

Carbon No. *n*	Calcd (%)		Found (%)	
	C	H	C	H
9	76.08	9.01	75.84	9.21
10	76.33	9.15	76.33	9.32
11	76.56	9.28	76.49	9.55
12	76.78	9.40	76.91	9.40
14	77.19	9.63	77.17	9.64
16	77.38	9.78	77.32	10.02

(IIA Homologues)

Carbon No. *n*	Calcd (%)		Found (%)	
	C	H	C	H
9	74.23	7.55	74.22	7.69
10	74.50	7.69	74.38	7.66
11	74.72	7.85	74.71	8.04
12	74.96	7.98	75.16	8.27
14	75.39	8.25	75.20	8.33
16	75.80	8.49	75.63	8.79

(IIB Homologues)

Carbon No. *n*	Calcd (%)		Found (%)	
	C	H	C	H
8	74.74	7.84	74.95	7.97
9	74.97	7.98	75.25	8.15
10	75.19	8.11	75.02	8.38
11	75.41	8.24	75.59	8.44
12	75.61	8.36	75.70	8.54
14	76.00	8.60	76.00	8.77

(IIIA Homologues)

Carbon No. *n*	Calcd (%)		Found (%)	
	C	H	C	H
9	77.85	8.13	77.84	8.29
10	78.05	8.27	78.32	8.49
11	78.23	8.42	78.43	8.44
12	78.40	8.55	78.68	8.78
14	78.71	8.81	78.86	8.98
16	79.00	9.04	78.93	9.23

(IIIB Homologues)

Carbon No. *n*	Calcd (%)		Found (%)	
	C	H	C	H
9	78.40	8.55	78.67	8.59
10	78.54	8.64	78.68	8.94
11	78.71	8.81	78.84	8.82
12	78.86	8.93	78.89	9.10
14	79.14	9.16	79.04	9.31
16	79.38	9.36	79.25	9.60

Measurement of Physical Properties. An identification of the mesophase was carried out using a Nikon polarizing microscope equipped with a Mettler FP-52 heating stage. Transition temperatures were measured using a Daini Seikosha SSC-560 differential scanning calorimeter (DSC) at a scanning rate of 2.5 °C min^{-1} under N_2 atmosphere. The spontaneous polarization (Ps) was determined by a triangular wave method reported by Miyasato et al.[13] The frequency, the maximum amplitude, and the cell thickness were 10 Hz, 150 V, and 50 μm, respectively.

Results and Discussion

The melting points and the mesomorphic transition temperatures for the homologous series (IA, IB, IIA, IIB, IIIA, and IIIB) are summarized in Table 2. All the homologous series except a IA homologue with terminal octyloxyl chain and IB homologues with shorter alkoxyl chains (n=8—10) exhibit the enantiotropic Sm*C phase. Their phase sequences above Sm*C are isotropic (Iso)-smectic A(SmA)-Sm*C for the homologues (IA, IB, IIB, IIIA, and IIIB) and IIA homologues with longer alkoxyl chains (n=14,16) and are Iso-cholesteric(Ch)-SmA-Sm*C for IIA homologues with shorter alkoxyl chains (n=9—12). The IB homologues with longer alkoxyl chains (n=11—16) and the IIIA and IIIB homologues with shorter alkoxyl chains (n=9—12) exhibit other smectic phases (Sm 3) below the Sm*C. However, these phases have not been determined at this stage, yet. As is

Table 2. Phase Transition Temperatures for Homologous Series (IA—IIIB)

Series	Carbon No. (n)	Mp θ_m/°C	Phase transition temperature (°C)[a] Sm3–Sm*C	Sm*C–SmA	SmA–Iso(Ch)	Ch–Iso
IA	8	34.2	—	—	72.1	—
	9	30.4	—	31.0	72.3	—
	10	32.9	—	36.0	74.2	—
	11	33.9	—	41.0	74.2	—
	12	29.4	—	44.6	75.6	—
	14	41.9	—	44.7	74.4	—
	16	44.9	—	50.2	74.4	—
IB	8	29.8	—	—	37.8	—
	9	7.3	—	(5.5)[b]	35.3	—
	10	20.6	—	(14.7)	38.2	—
	11	22.2	(6.0)	26.4	35.8	—
	12	22.0	(6.2)	27.0	37.8	—
	14	16.7	(7.7)	29.2	35.5	—
	16	30.5	24.2	34.0	37.0	—
IIA	9	78.5	—	93.1	178.9	189.4
	10	77.5	—	117.0	178.2	185.0
	11	76.7	—	128.0	177.1	181.7
	12	78.1	—	139.0	176.7	179.4
	14	76.7	—	142.0	173.1	—
	16	72.6	—	141.0	170.3	—
IIB	8	54.8	—	53.5	155.3	—
	9	63.5	—	94.1	151.6	—
	10	62.6	—	105.9	149.3	—
	11	73.5	—	116.5	144.7	—
	12	62.6	—	117.1	142.9	—
	14	60.3	—	119.6	136.0	—
IIIA	9	51.6	62.1	159.8	196.3	—
	10	52.6	64.6	151.5	196.5	—
	11	64.4	(59.8)	152.9	192.7	—
	12	64.8	(60.2)	150.0	189.0	—
	14	74.4	—	150.0	197.7	—
	16	80.4	—	152.0	193.6	—
IIIB	9	27.4	62.1	128.1	160.2	—
	10	57.4	58.8	131.8	157.6	—
	11	48.4	(47.5)	128.3	156.6	—
	12	56.2	(41.6)	131.9	148.4	—
	14	62.1	—	122.3	140.2	—
	16	70.3	—	126.0	138.8	—

a) Sm3; unidentified smectic phase, Sm*C; chiral smectic C, SmA; smectic A, Ch; cholesteric, Iso; isotropic liquid.
b) ( ); monotropic transition.

evident from the table, the transition temperatures from the SmA phase to the Sm*C one for IB homologues are very low and the temperature range of the enantiotropic Sm*C phase for the homologous series IIA and IIIA is significantly wide. Such mesomorphic properties are comparable with those for the well-known MORE series with broad-band Sm*C phase, although their values of the spontaneous polarization are very small.[14,15] The IB homologue with terminal nonyloxyl chain exhibits the lowest transition temperature from SmA phase to Sm*C at 5°C monotropically, and the IIIA homologue with the terminal nonyloxyl chain exhibits the widest temperature range of the enantiotropic Sm*C phase from 62.1 to 159.8 °C. These results indicate that the α-methylcynnamoyl moiety is a suitable structure for the appearance of the Sm*C phase.

The transition temperatures from SmA phase to Iso or from SmA phase to Ch against the carbon number in terminal alkoxyl chain are plotted in Fig. 1. Compared with the transition temperatures for the homologous series IIA, IIB, IIIA, and IIIB, those for the homologous series IA and IB are little dependent on the terminal alkoxyl chain length. This result can be interpreted as follows: the thermal stability of SmA phase of the IA and IB homologues is a little affected by the thermal motion of the flexible alkoxyl chain because of their transition temperatures much lower than those for the other homologous series. Another characteristic feature is the effect of the chiral groups

on the transition temperatures. On changing a 2-methylbutyl group to a 1-methylheptyl group, the Ch phase observed in the homologous series IIA disappears in the homologous series IIB, and the transition temperatures for the homologous series IB, IIB, and IIIB become about 30—50 °C lower than those for the corresponding homologous series IA, IIA, and IIIA. The effects of the chain branching on the thermal stability of the mesophase have been investigated on the Schiff base compounds with branched alkylcinnamate moieties by Gray and Harrison and have been discussed in terms of a steric effect between the branched methyl group and the ester group.[16] Our results are similar to those reported previously[16] and can be interpreted in terms of the difference of the steric hindrance between the 1-methyl branch and the 2-methyl branch. The former interacts with the carbonyl oxygen much stronger than the latter and lies out of the plane of the mesogen, thus leading to decrease greatly both Ch and SmA thermal stabilities.

The transition temperatures from Sm*C phase to SmA against the carbon number in the terminal alkoxyl chain are plotted in Fig. 2. As is pointed out by McMillan,[17] de Jue,[18] and Patel and Goodby,[19] the transition temperatures from Sm*C to SmA depend strongly on the core structure with local dipole moments and the terminal chain length. As seen in Fig. 2, the transition temperatures for IA and IB homologues gradually increase with the terminal alkoxyl chain length and those for IIA and IIB homologues increase steeply with the terminal alkoxyl chain length in the range of lower carbon number and are approaching to the constant value in the region of higher carbon number. On the other hand, the transition temperatures for IIIA and IIIB homologues slightly decrease with the terminal alkoxyl chain length. These facts indicate that the effect of the terminal alkoxyl chain on the thermal stability of the Sm*C phase is quite different if the compounds have different core structures. The effect of the chiral group on the thermal stability of the Sm*C is a little different from that of the SmA phase, that is, the degree of depression of the transition temperature from Sm*C to SmA by replacing the 2-methylbutyl group into the 1-methylheptyl group is not so large as that from Iso or Ch phase to SmA and depends on the core structures. These facts also indicate that the position of the bulky methyl branch

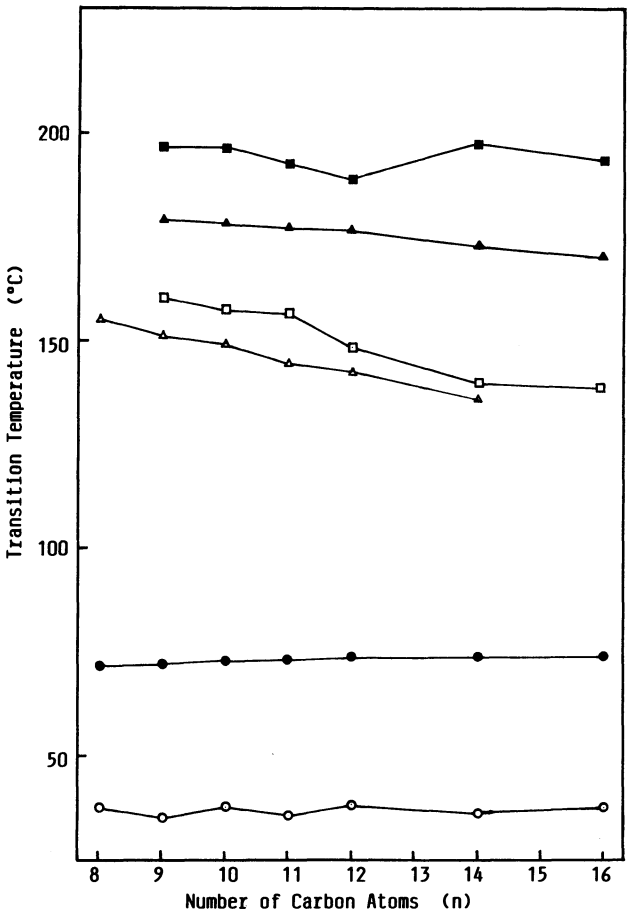


Fig. 1. Plots of the transition temperatures from SmA phase to Iso or Ch phse against the number of carbon atoms in the *n*-alkoxyl chain of the homologous series IA(-●-), IB(-○-), IIA(-▲-), IIB(-△-), IIIA(-■-), and IIIB(-□-).

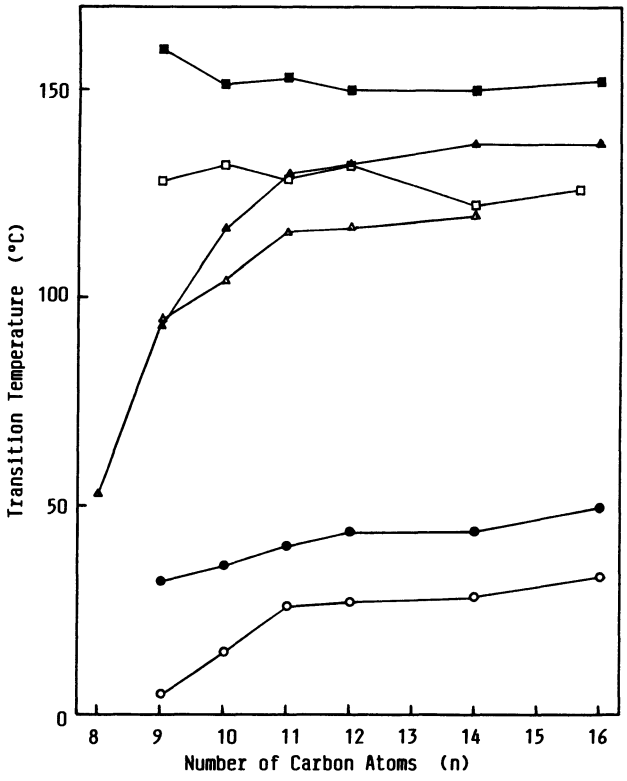


Fig. 2. Plots of the transition temperatures from Sm*C phase to SmA against the number of carbon atoms in the *n*-alkoxyl chain of the homologous series IA(-●-), IB(-○-), IIA(-▲-), IIB(-△-), IIIA(-■-), and IIIB(-□-).

and the chain length of the chiral group play some role for the appearance of Sm*C phase as well as the core structure and the terminal alkoxyl chain length.

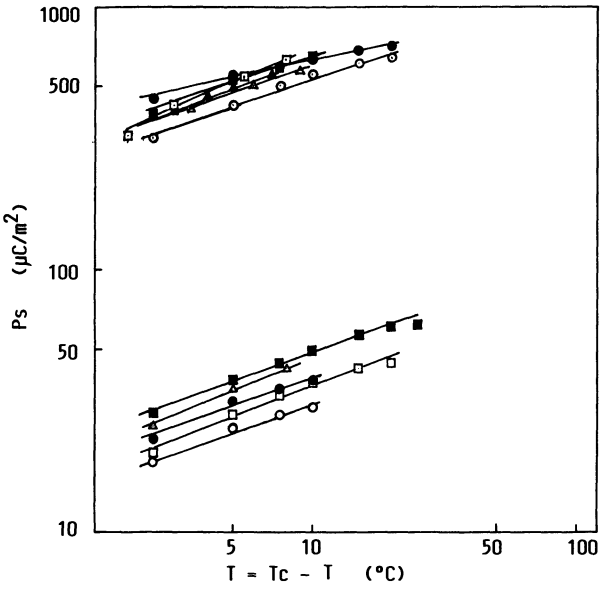


Fig. 3. Logarithmic plots of the temperature dependence of the spontaneous polarization for the homologous series IA and IB: n=9(-○-); n=10(-●-); n=11(-□-); n=12(-■-); n=14(-△-); n=16(-▲-). The cell thickness, the frequency, and the maximum amplitude of applied voltage are 50 μm, 10 Hz, and 150 V, respectively.

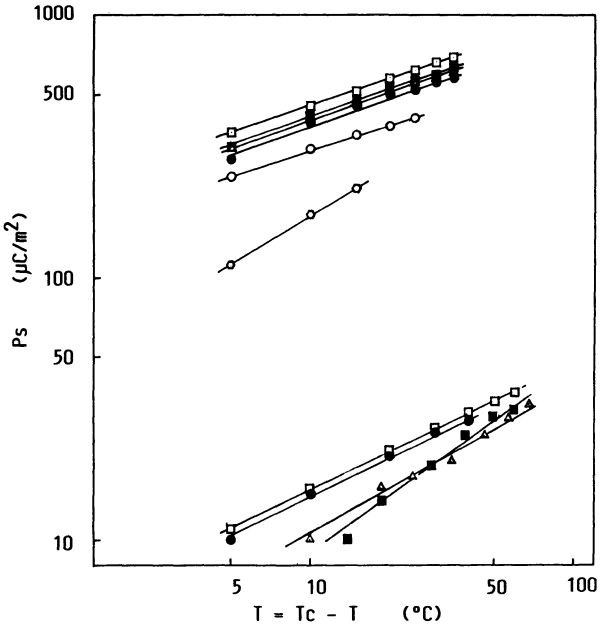


Fig. 4. Logarithmic plots of the temperature dependence of the spontaneous polarization for the homologous series IIA and IIB: n=8(-⬡-); n=9(-○-); n=10(-●-); n=12(-■-); n=14(-△-). The cell thickness, the frequency, and the maximum amplitude of applied voltage are 50 mm, 10 Hz, and 150 V, respectively.

The temperature dependence of the spontaneous polarization in the Sm*C phase for a number of the homologues in the homologous series (IA and IB), (IIA and IIB), and (IIIA and IIIB) are shown in Figs. 3, 4, and 5, respectively. It is clearly shown that the temperature dependence of the measured values for all the IA, IB, IIA, IIB, and IIIB homologues except that for IIIA homologues is represented by the expression $P_s=A(\Delta T)^{\alpha}$. The log-log plots of P_s vs. ΔT for the IIIA homologues form nonlinear curve, which could be divided into two linear lines with different gradient. This fact may indicate that two processes concerned with the temperature dependence of the spontaneous polarization exist in the Sm*C phase of the IIIA homologues.

As is expected from the effect of the position or the asymmetric carbon in the chiral part on the spontaneous polarization reported so far,[20,21] the magnitude of the spontaneous polarization for the homologous series IB, IIB, and IIIB with 1-methylheptyl group is one order higher than that for the corresponding homologous series IA, IIA, and IIIA with 2-methylbutyl group. Some relation between the spontaneous polarization and the core structure is also seen among the homologous series (I, II, and III), that is, the values of the spontaneous polarization for the homologous series I, II, and III are approximately in the order of III>I>II. Additionally, in each homologous series, the magnitude of the spontaneous polarization shows the maximum value at a certain length of the terminal alkoxyl chain.

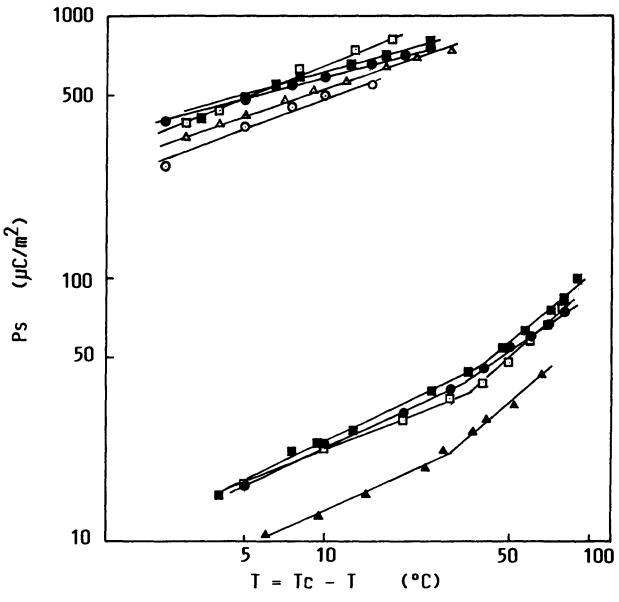


Fig. 5. Logarithmic plots of the temperature dependence of the spontaneous polarization for the homologous series IIIA and IIIB: n=9(-○-); n=10(-●-); n=11(-□-); n=12(-■-); n=14(-△-); n=16(-▲-). The cell thickness, the frequency, and the maximum amplitude of applied voltage are 50 μm, 10 Hz, and 150 V, respectively.

The magnitude of the spontaneous polarization is considered to depend on the size of the lateral component of dipole moment of the ester group adjacent to the chiral part and on the degrees of the restriction of a rotation about the molecular long axis and of an internal rotation around the bond between the chiral part and the core. The effect of the restriction of the internal rotation around the bond between the chiral part and the core on the spontaneous polarization is clearly seen in the homologous series A with the 1-methyl branch and in the series B with the 2-methyl branch. In comparison with the 2-methyl branch in the chiral group, the 1-methyl branch restricts the internal rotation around the bond between the chiral part and the core more strongly due to the steric hindrance. The difference of the values of the spontaneous polarization among the homologous series (I, II, and III) with the same chiral group is not so large. This result may be attributed to the reason that the core structure near the chiral part for the homologous series I, II, and III is identical, and then, the size of the net dipole moment related to the spontaneous polarization is considered to be almost same. However, the effect of the core and the terminal alkoxyl chain length on the magnitude of the spontaneous polarization cannot be well explained at this stage, because the temperature range of Sm*C phase among these homologous series is quite different one another, therefore the degree of the restriction of the rotation about the molecular long axis cannot be estimated.

More detailed study on the molecular motion and the structure in the Sm*C phase must be necessary in order to elucidate the correlation between the spontaneous polarization and the molecular structure.

The authors thank Dr. Toshio Yoshihara for his helpful discussion and also thank Mrs. Mioko Uematsu and Mr. Yoshihiro Sako for their assistance of experiments.

References

1) N. A. Clark and S. T. Lagewall, *Apll. Phys. Lett.*, **36**, 899 (1980).

2) T. Sakurai, N. Mikami, R. Higuchi, M. Honma, M. Ozaki, and K. Yoshino, *J. Chem. Soc., Chem. Commum.*, **1986**, 979.

3) T. Sakurai, N. Mikami, M. Ozaki, and K. Yoshino, *J. Chem. Phys.*, **85**, 585 (1986).

4) T. Inukai, S. Saitoh, H. Inoue, K. Miyazawa, K. Terashima, and K. Furukawa, *Mol. Cryst. Liq.Cryst.*, **141**, 251 (1986).

5) K. Terashima, M. Ichihashi, M. Kikuchi, K. Furukawa, and T. Inukai, *Mol. Cryst. Liq. Cryst.*, **141**, 237 (1986).

6) K. Yoshino, M. Ozaki, H. Taniguchi, M. Ito, K. Satoh, N. Yamasaki, and T. Kitazume, *Jpn. J. Appl. Phys.*, **26**, L-77 (1987).

7) K. Kondo, S. Era, M. Isogai, and A. Mukoh, *Jpn. J. Appl. Phys.*, **24**, 1389 (1985).

8) J. P. Le Pesant, J. N. Perbert, B. Mourey, M. Hareng, G. Decobert, and J. C. Dubois, *Mol. Cryst. Liq. Cryst.*, **129**, 61 (1985).

9) W. Kuczynski, S. T. Lagerwall, M. Matuszezyk, K. Skarp, B. Stebler, and J. Wahl, *Mol. Cryst. Liq. Cryst.*, **146**, 173 (1987).

10) K. Mohr, S. Köhler, K. Worm, G. Pelzl, S. Diele, H. Zaschke, D. Demus, G. Andersson, I. Dahl, S. T. Lagerwall, K. Skarp, and B. Stebler, *Mol. Cryst. Liq. Cryst.*, **146**, 151 (1987).

11) J. Nakauchi, Y. Kageyama, M. Uematsu, and S. Minami, *Bull. Chem. Soc. Jpn.*, **60**, 4239 (1987).

12) J. R. Johnson, "Organic Reaction" ed by R. Adams, W. E. Bachman, J. R. Johnson, L. F. Fieser, H. R. Snyder, Robert E. Krieger Pub., Huntington, New York (1978), Vol. 1, p. 210.

13) K. Miyasato, S. Abe, H. Takezoe, A. Fukuda, and E. Kuze, *Jap. J. Appl. Phys.*, **2**, L-661 (1983).

14) A. Hallsby, M. Nilsson, and B. Otterholn, *Mol. Cryst. Liq. Cryst.*, **82**, 61 (1982).

15) K. Skarp, K. Flatischler, K. Kondo, Y. Sato, K. Miyasato, H. Takezoe, A. Fukuda, and E. Kuze, *Jpn. J. Appl. Phys.*, **22**, 566 (1982).

16) G. W. Gray and K. J. Harrison, *Sym. Faraday Soc.*, **5**, 54 (1971).

17) W. L. McMillan, *Phys. Rev. A*, **8**, 1921 (1973).

18) W. H. de Jeu, *J. Phys.(Paris)*, **38**, 1265 (1977).

19) J. S. Patel and J. W. Goodby, *Mol. Cryst. Liq. Cryst.*, **144**, 117 (1987).

20) R. B. Meyer, L. Liebert, L. Strzelecki, and P. Keller, *J. Phys.(Paris)*, **36**, L-69 (1975).

21) T. Sakurai, K. Sakamoto, M. Honma, K. Yoshino, and M. Osaki, *Ferroelectrics*, **58**, 21 (1984).