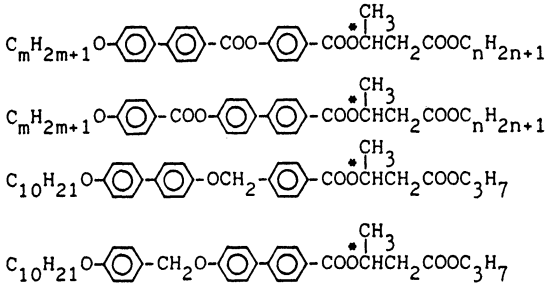
  Bull. Chem. Soc. Jpn., 62, 1011—1016 (1989) 

# Novel Ferroelectric Liquid Crystals Derived from Normal Alkyl Esters of (*R*)-3-Hydroxybutanoic Acid. The Correlation between Molecular Structure and Mesomorphic Properties

Jun NAKAUCHI,* Keiichi SAKASHITA, Yoshitaka KAGEYAMA, Seiji HAYASHI, and Kenji MORI†
Tokyo Research Laboratory, Mitsubishi Rayon Co., Ltd., Noborito, Tama-ku, Kawasaki, Kanagawa 214
†Department of Agricaltural Chemistry, The University of Tokyo, Yayoi 1-1-1, Bunkyo-ku, Tokyo 113
(Received Sepetmber 16, 1988)

The following series of novel ferroelectric liquid crystals, derived from normal alkyl esters of (*R*)-3-hydroxybutanoic acid, have been synthesized, and several factors determining their mesomorphic properties have been investigated:



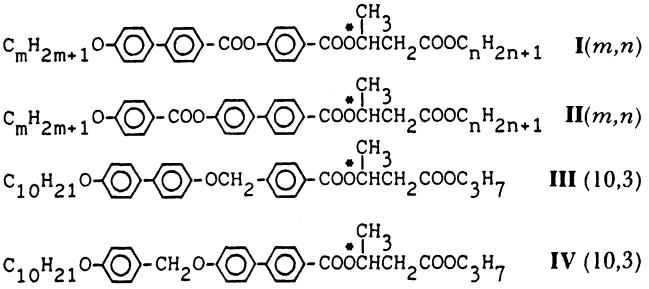

The smectic polymorphism for these compounds with three aromatic rings is strongly affected by the position and kind of the linkage groups in the core. The effects of the lengths of the two terminal chains (*m*,*n*) and the linkage groups in the core on the thermal stability of the smectic A and chiral smectic C phases have been discussed from the structural points of view.

Very many compounds with a chiral smectic C(Sm*C) phase have been synthesized since the invention of high-speed switching devices based on these compounds' ferroelectric properties.[1] Their common structural features are a rigid core consisting of at least two aromatic rings and two terminal chains at the ends of the core, one of which contains at least one chiral group.

There have been many studies of the effects of molecular structure of the core and the length of the achiral terminal chain on the mesomorphic properties of the liquid crystals.[2] However, the correlation between the molecular structure and the mesomorphic properties still remains insufficiently understood. Especially, there have been few investigations of the effect of the length of terminal chain at the chiral part on the mesomorphic properties because of the limited number of chiral reagents used in experiments.

Systematic investigations of the effect of the lengths of the two terminal chains on the mesomorphic properties have been made by Goodby and Gray employing homologues of the normal alkyl esters of 4′-alkoxy-1-biphenylcarboxylic acids. They have shown that the SmC phase appears when both the terminal chains have an appropriate chain length,[3] although these compounds do not have chiral groups in their molecular structures.

We have selected normal alkyl esters of (*R*)-3-hydroxybutanoic acid as chiral reagents and have synthesized novel ferroelectric liquid crystals with three aromatic rings in the core. Their general molecular structures are as follows:



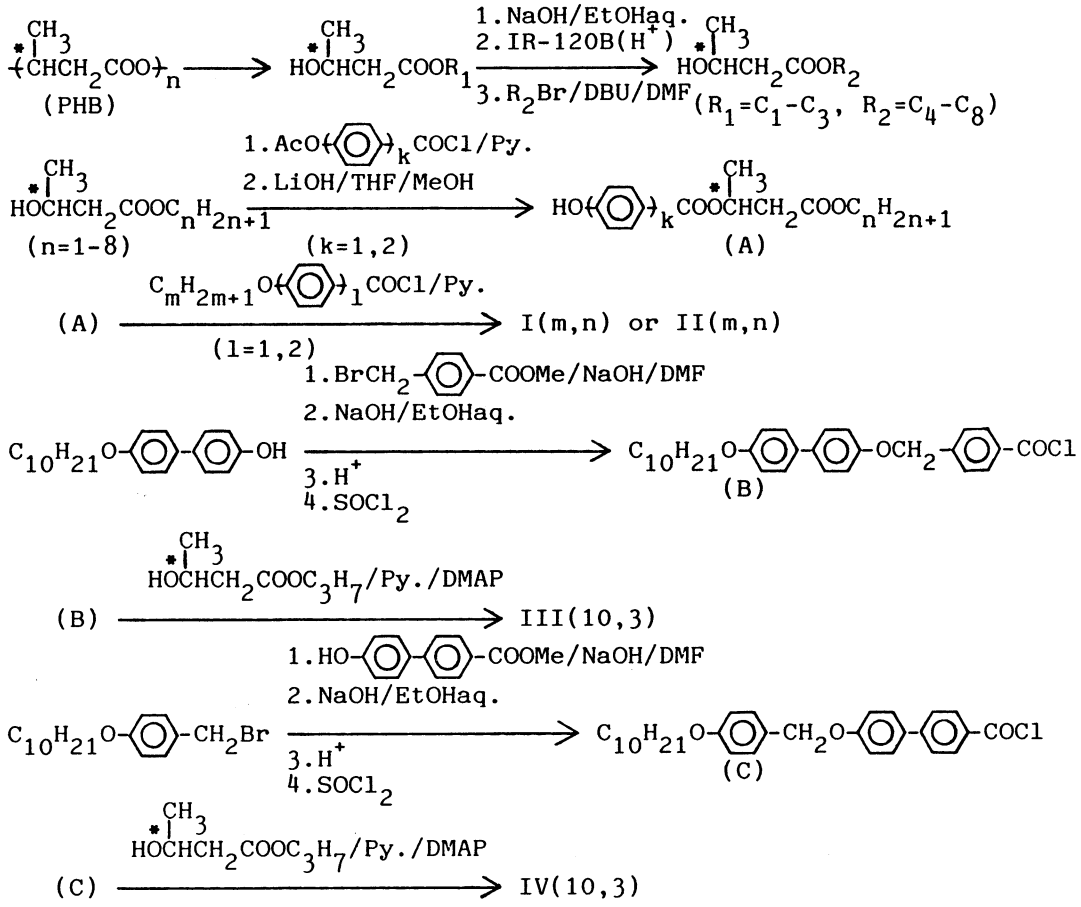

One of these compounds **I**(8,2) has already been synthesized and its ferroelectric property reported by Taniguchi et al.;[4] however, no systematic investigations of the mesomorphic properties of the homologous series have yet been done.

In the present paper, we discuss the effect of the lengths of two terminal chains and of the position and kind of the linkage groups in the core on the thermal stability of the mesophase.

## Experimental

**Preparation of Materials.** The homologous series, **I**(*m*,*n*) and **II**(*m*,*n*), and the analogues, **III**(10,3) and **IV**(10,3), were synthesized by Scheme 1.

In order to obtain highly optically pure reagents, poly-((*R*)-3-hydroxybutanoic acid) (PHB) (Imperial Chemical Industry Co., Ltd.) was chosen as the starting material. The normal alkyl esters of (*R*)-3-hydroxybutanoic acid were eas-



Scheme 1.

ily prepared by the following method. The lower alkyl ($R_1$: methyl, ethyl, propyl) esters of (*R*)-3-hydroxybutanoic acid were synthesized by the alkolysis of PHB in the corresponding dry alcohols, using conc. $H_2SO_4$ as the catalyst. Sugai et al. reported that the optical purity of ethyl (*R*)-3-hydroxybutanoate synthesized by a similar method was 100% e.e. ($[\alpha]_D^{21}=-43.4°$ in $CHCl_3$).[5] The specific rotation $[\alpha]_D^{23}$ of the ethyl (*R*)-3-hydroxybutanoate prepared by our method was −44.7°; therefore, its optical purity was estimated to be 100% e.e. The higher alkyl ($R_2$: butyl, pentyl, octyl) esters of (*R*)-3-hydroxybutanoic acid were prepared by an esterification reaction of (*R*)-3-hydroxybutanoic acid obtained by the hydrolysis of the ethyl (*R*)-3-hydroxybutanoate with the corresponding alkyl bromides in *N*,*N*-dimethylformamide (DMF), using 1,8-diazabicyclo[5.4.0.]-7-undecene (DBU) as the catalyst. The esters of 4-hydroxybenzoic acid or 4′-hydroxy-1-biphenylcarboxylic acid with the normal alkyl esters of (*R*)-3-hydroxybutanoic acid were prepared by reacting 4-acetoxybenzoyl chloride or 4′-acetoxy-1-biphenylcarbonyl chloride with normal alkyl (*R*)-3-hydroxybutanoates in dry pyridine, followed by the hydrolysis of acetoxyl group selectively in a mixed solvent of tetrahydrofuran (THF) and methanol containing equimolar 1 mol dm$^{-3}$ LiOH. The homologous series, **I**(*m*,*n*) and **II**(*m*,*n*), were synthesized by esterifying the (A) compounds with the corresponding 4-alkoxybenzoyl chlorides or 4′-alkoxy-1-biphenylcarbonyl chlorides in dry pyridine. Compounds **III**(10,3) and **IV**(10,3) were prepared by reacting propyl (*R*)-3-hydroxybutanoate with Compounds **B** and **C** respectively in dry pyridine containing 10 wt% 4-dimethylaminopyridine (DMAP). All the final products were purified by silica-gel column chromatography, followed by two recrystallizations from ethanol.

Their elementary analysis data are listed in Table 1.

**Measurement of Thermal Properties.** The mesophase was identified using a Nikon polarizing microscope equipped with a Mettler FP-52 heating stage. the 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 $N_2$ atomosphere.

## Results and Discussion

The melting points and the mesomorphic transition temperatures for the homologous series, **I**(*m*,*n*) and **II**(*m*,*n*), are summarized in Table 2. The mesomorphic trends of **I**(*m*,3) and **II**(*m*,3) are shown in Figs. 1 and 2. As can be seen in the figures, both of the series show the phase sequence of isotropic(Iso)-smectic A(SmA)-chiral smectic C(Sm*C)-unidentified smectic phase(Sm3)-crystal(Cryst). The Sm3 phase for **I**(*m*,3) appears monotropically below the Sm*C in the homologues with shorter alkoxyl chains (*m*=7—11). This phase shows a broken and banded focal-conic fan texture or a pseudo-homeotropic or schlieren texture which resembles photomicrographs of the reference sample reported by Gray and Goodby.[6] The transi-

Table 1. Elemental Analyses for the **I**(*m*,*n*), **II**(*m*,*n*), **III**(10,3), and **IV**(10,3) Homologous Series

| Homologous series | Carbon No. (*m*,*n*) | Calcd (%) | | Found (%) | |
|---|---|---|---|---|---|
| | | C | H | C | H |
| **I**(*m*,*n*) | (7,3) | 72.83 | 7.19 | 72.97 | 7.25 |
| | (8,3) | 73.15 | 7.37 | 72.87 | 7.53 |
| | (9,3) | 73.44 | 7.53 | 73.55 | 7.30 |
| | (10,3) | 73.73 | 7.69 | 74.01 | 7.82 |
| | (11,3) | 74.00 | 7.84 | 74.12 | 7.85 |
| | (12,3) | 74.26 | 7.99 | 74.26 | 8.25 |
| | (14,3) | 74.74 | 8.26 | 74.75 | 8.12 |
| | (16,3) | 75.19 | 8.51 | 75.14 | 8.59 |
| | (10,1) | 73.15 | 7.37 | 73.18 | 7.54 |
| | (10,2) | 73.44 | 7.53 | 73.58 | 7.66 |
| | (10,4) | 74.00 | 7.84 | 73.86 | 7.86 |
| | (10,5) | 74.26 | 7.99 | 74.48 | 7.99 |
| | (10,8) | 74.97 | 8.39 | 75.14 | 8.63 |
| **II**(*m*,*n*) | (7,3) | 72.83 | 7.19 | 72.82 | 7.24 |
| | (8,3) | 73.15 | 7.37 | 73.00 | 7.40 |
| | (9,3) | 73.44 | 7.53 | 73.61 | 7.67 |
| | (10,3) | 73.73 | 7.69 | 73.66 | 7.72 |
| | (12,3) | 74.26 | 7.99 | 74.44 | 7.98 |
| | (14,3) | 74.74 | 8.26 | 74.97 | 8.48 |
| | (16,3) | 75.19 | 8.51 | 75.46 | 8.72 |
| | (10,2) | 73.44 | 7.53 | 73.66 | 7.59 |
| | (10,4) | 74.00 | 7.84 | 74.08 | 8.03 |
| | (10,6) | 74.50 | 8.13 | 74.23 | 8.25 |
| | (10,7) | 74.74 | 8.26 | 74.68 | 8.34 |
| | (10,8) | 74.97 | 8.39 | 75.12 | 8.44 |
| **III**(10,3) | (10,3) | 75.48 | 8.22 | 75.87 | 8.44 |
| **IV**(10,3) | (10,3) | 75.48 | 8.22 | 75.23 | 8.42 |

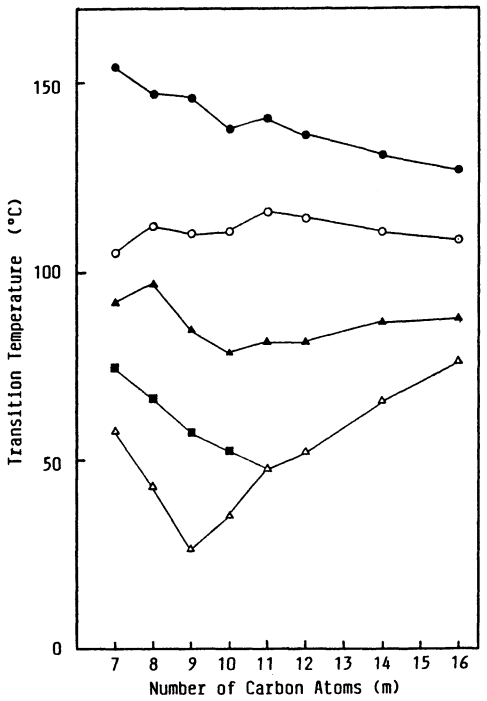



Fig. 1. Plots of transition temperatures against the number of carbon atoms (*m*) in the alkoxyl chain of homologous series **I** (*m*,3): mp (—▲—); Iso-SmA (—●—); SmA-Sm*C (—○—); Sm*C-Sm3 (—■—); Sm3-Cryst (—△—).

Table 2. Phase-Transition Temperatures for the **I**(*m*,*n*) and **II**(*m*,*n*) Homologous Series

| Homologous series | Carbon No. (*m*,*n*) | Phase-transition temperatures(°C)[a] | | | | |
|---|---|---|---|---|---|---|
| | | Mp | Sm4-Sm3 | Sm3-Sm*C | Sm*C-SmA | SmA-Iso |
| **I**(*m*,*n*) | (7,3) | 91.8 | — | (74.9)[b] | 105.0 | 154.3 |
| | (8,3) | 96.8 | — | (66.6) | 112.0 | 147.0 |
| | (9,3) | 84.5 | — | (57.1) | 110.0 | 146.1 |
| | (10,3) | 78.6 | — | (52.5) | 110.5 | 137.9 |
| | (11,3) | 81.2 | — | — | 115.9 | 140.6 |
| | (12,3) | 81.3 | — | — | 114.1 | 136.1 |
| | (14,3) | 86.3 | — | — | 110.5 | 130.1 |
| | (16,3) | 87.2 | — | — | 108.2 | 126.9 |
| | (10,1) | 78.5 | (64.0) | 102.8 | 120.0 | 155.7 |
| | (10,2) | 88.1 | — | (58.0) | 120.0 | 146.1 |
| | (10,4) | 68.0 | — | (50.2) | 111.1 | 136.5 |
| | (10,5) | 70.9 | — | (49.2) | 95.9 | 129.6 |
| | (10,8) | 74.5 | — | — | 83.5 | 123.7 |
| **II**(*m*,*n*) | (7,3) | 68.7 | — | (30.7) | (57.8) | 127.6 |
| | (8,3) | 77.7 | — | — | (67.5) | 131.5 |
| | (9,3) | 92.2 | — | — | (80.0) | 129.2 |
| | (10,3) | 85.8 | — | (56.6) | (84.0) | 126.5 |
| | (12,3) | 77.2 | — | — | 93.0 | 122.8 |
| | (14,3) | 72.1 | — | (49.3) | 96.1 | 118.7 |
| | (16,3) | 72.2 | — | — | 96.5 | 116.0 |
| | (10,2) | 75.8 | — | (58.9) | 82.9 | 131.0 |
| | (10,4) | 63.9 | — | (53.9) | 65.5 | 124.0 |
| | (10,6) | 72.2 | — | (44.3) | (64.6) | 110.5 |
| | (10,7) | 76.3 | — | (46.3) | (62.5) | 110.5 |
| | (10,8) | 76.3 | — | (46.1) | (63.9) | 110.9 |

a) Mp; melting point, Sm3, Sm4; unidentified smectic phase, Sm*C; chiral smectic C, SmA; smectic A, Iso; isotropic liquid. b) ( ); monotropic transition.

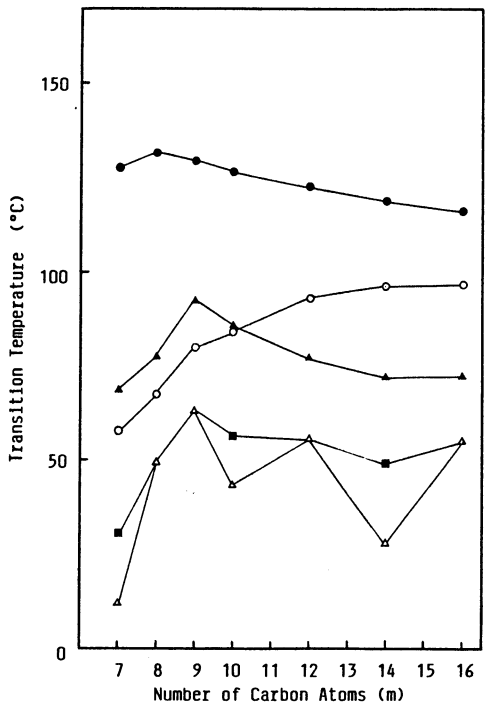



Fig. 2. Plots of transition temperatures against the number of carbon atoms ($m$) in the alkoxyl chain of homologous series **II** ($m$,3): mp (—▲—); Iso-SmA (—●—); SmA-Sm*C (—○—); Sm*C-Sm3 (—■—); Sm3-Cryst (—△—).

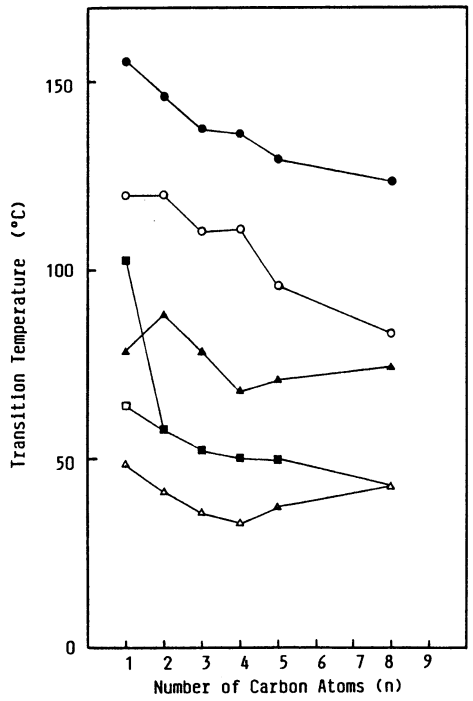



Fig. 3. Plots of transition temperatures against the number of carbon atoms ($n$) in the alkyl ester chain of homologous series **I** (10,$n$): mp (—▲—); Iso-SmA (—●—); SmA-Sm*C (—○—); Sm*C-Sm3 (—■—); Sm3-Sm4 (—□—); Sm3,Sm4-Cryst(—△—).

tion enthalpies measured by DSC are about 0.86—1.5 kJ mol$^{-1}$. On the other hand, the Sm3 phase for **II**($m$,3) appears monotropically below the Sm*C in the homologues with heptyloxyl, decyloxyl, and tetradecyloxyl chains and shows a focal-conic fan texture or a homeotropic texture formed from the broken focal-conic fan or the schlieren textures of the Sm*C phase, respectively. Moreover, the transition bars across the backs of the fans are observed at the transition from the Sm3 phase to the Sm*C. The transition enthalpies are about 1.5—4.5 kJ mol$^{-1}$. From these findings, we speculate that the Sm3 phases of **I**($m$,3) and **II**($m$,3) may be chiral smectic **I**(Sm*I) and smectic B(SmB), respectively; however, more detailed study by the X-ray diffraction method and the misibility test will be necessary for the assignment of these phases.

The Iso-SmA transition temperaturs for **I**($m$,3) and **II**($m$,3) show normal trends, that is, an odd-even alternation and a gentle falling as the series ascend. On the other hand, the SmA-Sm*C transition temperatures show significantly different features. The Sm*C phase for **I**($m$,3) appears enantiotropically, and the SmA-Sm*C transition temperatures do not change very much in respect to the length of the terminal alkoxyl chain, whereas the Sm*C phase for **II**($m$,3) appears monotropically in the region of the shorter alkoxyl chains ($m$=7—10) and becomes enantiotropic in the region of the longer alkoxyl chains ($m$=12—16). Their transition temperatures gradually increase with the length of the terminal alkoxyl chain, leading to the decrease in the temperature range of the SmA phase.

There are some characteristic features in the phase transition from the Sm*C phase to the Sm3 phase for **I**($m$, 3) and **II**($m$, 3). The Sm*C-Sm3 transition for **I**($m$,3) appears as a monotropic transition in the homologues with shorter alkoxyl chains ($m$=7—10), and the transition temperatures decrease with the length of the terminal alkoxyl chain. On the other hand, the Sm*C-Sm3 transition for **II**($m$,3) appears as a monotropic one, and the transition temperatures seem to increase with the length of the terminal alkoxyl chain in the region of the shorter chains and to slightly decrease in the region of the longer chains. However, the correlation between the molecular structure and these Sm3 phases cannot be found at this stage because the assignment of these phases has not yet been accomplished.

Figures 3 and 4 present the mesomorphic trends of the homologous series, **I**(10,$n$) and **II**(10,$n$). These homologous series show phase sequences similar to those of the corresponding homologous series **I**($m$,3) and **II**($m$,3). The Sm3 phases again appear monotropically in all the homologues except **I**(10,8). All the Sm3 phases for **I**(10,$n$) and **II**(10,$n$) except that for **I**(10,1) exhibit a texture similar to those of the **I**($m$,3) and **II**($m$,3); therefore, the Sm3 phases of **I**(10,$n$) and **II**(10,$n$) may be Sm*I and SmB, respectively. The Sm3 phase of the **I**(10,1) homologue shows a broken focal-

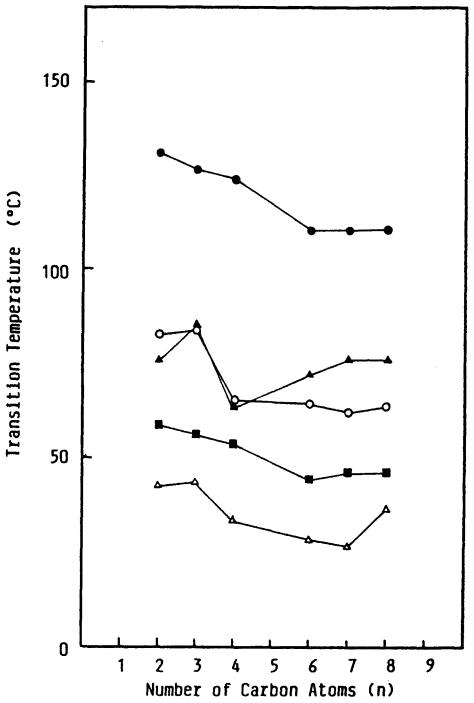



Fig. 4. Plots of transition temperatures against the number of carbon atoms ($n$) in the alkyl ester chain of homologous series **II** (10,$n$): mp(—▲—); Iso-SmA (—●—); SmA-Sm*C (—○—); Sm*C-Sm3 (—■—); Sm3-Cryst (—△—).

conic fan whose back is "L"-shaped and which has highly coloured patches or pseudo-homeotropic textures. The transition enthalpy is too small to be estimated from the DSC chart. From these findings, we speculate that this phase may be chiral smectic F(Sm*F); however, more detailed studies employing the X-ray diffraction method will be necessary for the assignment of this phase.

The effects of the terminal chain length for the chiral part on the thermal stability of the mesophase are a little different from those of the other terminal alkoxyl chain. The Iso-SmA transition temperatures for **I**(10,$n$) and **II**(10,$n$) show a gentle falling with the terminal chain length ($n$), although the odd-even alternation is not clear. The SmA-Sm*C transition temperatures for **I**(10,$n$) and **II**(10,$n$) also decrease with the terminal chain length ($n$), unlike those of the corresponding homologous series, **I**($m$,3) and **II**($m$,3) where the other terminal chain varies. This tendency probably means that the thermal stability of the Sm*C phase is reduced as the difference in length between the two terminal chains is small. Such a tendency has also been reported by Goodby and Gray in the homologous series of $n$-alkyl esters of 4-alkoxy-1-biphenylcarboxylic acids, in which the SmC phase has been observed only with the alkoxyl chain from hexyloxyl to tetradecyloxyl and with the alkyl ester chains from propyl to decyl. However, in comparison with the homologous series of the normal alkyl esters of 4-alkoxy-1-biphenyl carboxylic acids, there are some differences in

Table 3. Phase Sequence and Transition Temperature

| Analogues | Phase sequence and transition temperature (°C) |
|---|---|
| **I**(10,3) | Cryst $\xrightarrow{78.6}$ Sm*C $\xleftrightarrow{110.5}$ SmA $\xleftrightarrow{137.9}$ Iso; Cryst $\xleftarrow{35.6}$ Sm3 $\xleftarrow{52.5}$ Sm*C |
| **II**(10,3) | Cryst $\xrightarrow{85.8}$ SmA $\xleftrightarrow{126.5}$ Iso; Cryst $\xleftarrow{43.4}$ Sm3 $\xleftarrow{56.6}$ Sm*C $\xleftarrow{84.0}$ SmA |
| **III**(10,3) | Cryst $\xrightarrow{85.4}$ Sm2 $\xleftrightarrow{110.5}$ Sm*C $\xleftrightarrow{127.0}$ Iso; Cryst $\xleftarrow{35.6}$ Sm3 $\xleftarrow{85.4}$ Sm*C |
| **IV**(10,3) | Cryst $\xrightarrow{90.0}$ SmA $\xleftrightarrow{93.6}$ Iso; Cryst $\xleftarrow{72.6}$ Sm*C $\xleftarrow{84.0}$ SmA |

the effects of the terminal chains on the thermal stability of the Sm*C phase for the homologous series, **I**($m$,$n$) and **II**($m$,$n$), with three aromatic rings in the core. According to McMillan,[7] de Jeu,[8] and Patel and Goodby,[9] the thermal stability of the Sm*C phase is strongly affected by the polar groups in the core. In the cases of **I**($m$,$n$) and **II**($m$,$n$), the only structural difference between them is the position of -COO- linkage in the core. This means that the effects of the terminal chain length on the thermal stability of Sm*C phase are quite different only if the position of the linkage group is changed in the core.

To investigate the effects of the linkage groups in the core with three aromatic rings on the mesomorphic properties in more detail, the mesomorphic properties of two further analogues with the same terminal chains will be examined (Table 3).

In comparison with **I**(10,3) and **II**(10,3), the **III**(10,3) and **IV**(10,3) analogues with a $-CH_2O-$ linkage in the core have the phase sequences of Iso-Sm*C-Sm2-Sm3-Cryst and of Iso-SmA-Sm*C-Cryst, respectively. The Sm2 phase of **III**(10,3) shows a broken-fan or a schlieren texture under a polarizing microscope, and the transition enthalpy is 1.4 kJ mol$^{-1}$; therefore, this phase may be Sm*I. The microscopic texture of the Sm2 phase changes slightly at the Sm2-Sm3 transition and turns into another broken-banded fan or schlieren texture in the Sm3 phase, and the transition enthalpy is 2.1 kJ mol$^{-1}$; however, this phase cannot be speculated on at this stage. As is evident from these results, the smectic polymorphism for the homologous series with three aromatic rings in the core is strongly influenced by the position and kind of the linkage groups in the core.

There are also some characteristic tendencies for the mesomorphic transition temperatures among these four analogues. The Iso-SmA or Iso-Sm*C transition are in the order of: **I**(10,3)>**II**(10,3)≈**III**(10,3)>**IV**(10,3). As is to be expected from Gray's report,[2] the thermal stability of the smectic phase depends on the rigidity and planarity of the central linkage in the core. Con-

traty to the -COO- linkage, the $-CH_2O-$ linkage has no double-bond character; therefore, the Iso-Sm*C and Iso-SmA transition temperatures for **III**(10,3) and **IV**(10,3) should be lower than those for **I**(10,3) and **II**(10,3). Judging from the data, this speculation seems to be valid; however, the Iso-SmA transition temperature for **II**(10,3) (126.5 °C), is almost the same as the Iso-Sm*C transition temperature for **III**(10,3) (127.0 °C), and the difference in the Iso-smectic transition temperature between **I**(10,3) and **II**(10,3) is only 11.4 °C, whereas that between **III**(10,3) and **IV**(10,3) is 33.4 °C. These facts cannot be explained only by the difference in the flexibility of the linkage groups. In the core moiety containing three aromatic rings, the biphenyl ring is known greatly to enhance the thermal stability of the smectic phase because of its lath-like shape. On the other hand, the chiral part with a protruding 1-methyl branch in the molecule significantly reduces the thermal stability of the smectic phase. If the biphenyl ring is connected to the chiral part with 1-methyl branch through the -COO- linkage, as is **II**(10,3) and **IV**(10,3), they could not form a parallel arrangement with one another because of the steric hindrance of the 1-methyl branch. In the cases of **I**(10,3) and **III**(10,3), the biphenyl ring is connected to the chiral part through the $-COO-C_6H_4-COO-$ or the $-OCH_2-C_6H_4-COO-$ linkage. In these two analogues, the biphenyl rings could be packed parallel with one another more easily than those in **II**(10,3) and **IV**(10,3), because the effect of the protruding 1-methyl branch on the packing of the biphenyl ring is diluted through the linkage groups, thus leading to Iso-smectic transition temperatures higher than the corresponding analogues **II**(10,3) and **IV**(10,3). Additionally, compared with the biphenyl ring in **I**(10,3), that in **III**(10,3) is connected to the $-C_6H_4-COO^{*}CH(CH_3)-CH_2COOC_3H_7$ through the $-OCH_2-$ linkage, which is more flexible than the -COO- linkage, so that the biphenyl ring in **III**(10,3) could form the parallel arrangement most easily in the smectic phase, with the result that **III**(10,3) has a comparatively higher Iso-Sm*C transition temperature among these four analogues.

The authors would like to thank Dr. Hiroshi Sato for his hearty encouragement throughout this work and also to thank Dr. Toshio Yoshihara for his useful suggestions. The authors also wish to thank Mr. Teruyuki Yamada, Mr. Shigeo Kamimura, Mr. Yoshihiro Sako, and Mrs. Mioko Uematsu for their assistance in the experiments.

**References**

1) N. A. Clark and S. T. Lagerwall, *Appl. Phys. Lett.*, **36**, 899 (1980).
2) G. W. Gray, "Advances in Liquid Crystals," ed by G. H. Brown, Academic press, New York, San Francisco, London (1976), Vol. 2, p. 1.
3) J. W. Goodby and G. W. Gray, *Mol. Cryst. Liq. Cryst.*, **48**, 127 (1978).
4) H. Taniguchi, M. Ozaki, and K. Yoshino, *Jpn. J. Appl. Phys.*, **26**, Suppl. 26-2 101 (1987).
5) T. Sugai, M. Fujita, and K. Mori, *Nippon Kagaku Kaishi*, **1983**, 1315.
6) G. W. Gray and J. W. Goodby, "Smectic Liquid Crystals—Textures and Structures," Leonard Hill, Glasgow and London (1984).
7) W. L. McMillan, *Phys. Rev. A*, **8**, 1921 (1973).
8) W. H. de Jeu, *J. Phys. (Paris)*, **38**, 1265 (1977).
9) J. S. Patel and J. W. Goodby, *Mol. Cryst. Liq. Cryst.*, **144**, 117 (1987).