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Mesomorphism and Unusual Multiple Melting Behavior via Smectic E Phase in *p*-*n*-Alkoxybiphenylbutane-1,3-dione

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4-*n*-Alkoxy-4′-acetylbiphenyl(C_nO-A: 8 ~ 12, 16, 18) and *p*-*n*-alkoxybiphenylbutane-1,3-dione(C_nO-Lig: 8 ~ 12, 16, 18) have been synthesized and characterized. The C_nO-A (n = 8 ~ 12, 16) derivatives have a smectic E mesophase. The C_nO-Lig(n = 8 ~ 12, 16, 18) have two mesophases, smectic E and smectic A mesophases. Interestingly, each of the C_nO-Lig(n = 8 ~ 12) compounds has three crystalline polymorphs. The C_nO-Lig derivatives for n = 8, 10, and 12 show two types of double melting behavior via the smectic E mesophase. The C_nO-Lig derivatives for n = 9 and 11 exhibit triple melting behavior via the smectic E mesophase.

Keywords: smectic, multiple melting behavior, β-diketone

I. INTRODUCTION

β-Diketones are useful for obtaining the mesomorphic derivatives because they are easily to be synthesized.[1–6] Furthermore, these compounds have a great ability to complex with various metal ions.[7] To date, a great variety of long chain-substituted β-diketones have been synthesized mainly by Ohta *et al.*[1–6,8–14] In these papers, the compounds show not only mesomorphism, but also so-called double melting behavior.[5,13] Moreover, they reported the first example exhibiting both double melting behavior and mesomorphism in a series of long chain-substituted β-diketones, 1,3-di(*p*-*n*-alkoxyphenyl)propane-1,3-dione.[5] They pointed out that the double melting behavior of long chain-substituted compounds is a thermal behavior close to mesomorphism.[13]

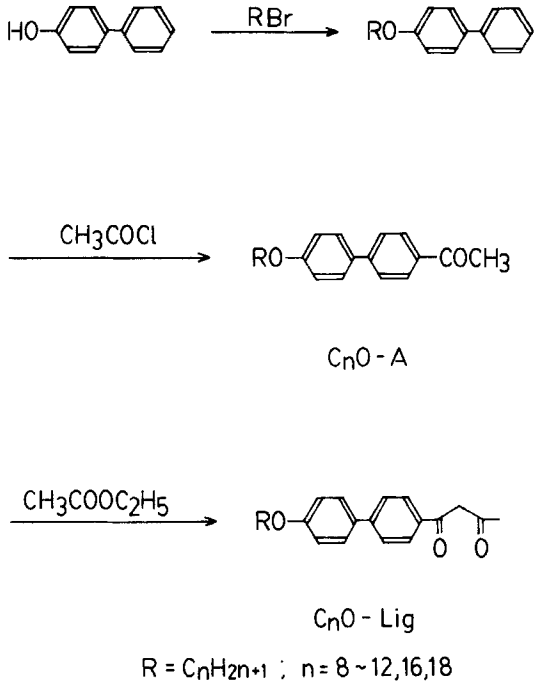
We have synthesized here a new series of the β-diketones, *p*-*n*-alkoxybiphenylbutane-1,3-dione (*n*-alkoxy: R = C_nH_{2n+1}, n = 8 ~ 12, 16, 18: abbreviated as C_nO-Lig.). All of these compounds have smectic E (S_E) and Smectic A (S_A) mesophases. Some compounds (n = 8 ~ 12) exhibited *unusual* double melting[14] behavior via the smectic E phase. We wish to report here the mesomorphism and the double melting behavior via the smectic E.

II. EXPERIMENTAL

II-1. Synthesis

The synthetic route of the present β-diketones is shown in Scheme 1. *p-n*-Alkoxybiphenyl was prepared from *p*-hydroxybiphenyl as a starting material by the same method in the literature.[5] 4-*n*-Alkoxy-4'-acetylbiphenyl (abbreviated as C_nO-A) was obtained by the method of Gray *et al.*[17] *p-n*-Alkoxybiphenylbutane-1,3-dione (abbreviated as C_nO-Lig: $n = 8 \sim 12, 16, 18$) was synthesized by the previously reported method.[10] In Table I and II are listed elemental analysis data, yields, recrystallization solvents, and the crystalline shapes obtained from recrystallization for C_nO-A and C_nO-Lig. The detailed procedures of the representative compounds, C_8O-A, and C_8O-Lig, are described in the following.

4-n-Octyloxy-4'-acetylbiphenyl (*C_8O-A*). *p-n*-Octyloxybiphenyl (2.0 g, 7.1 mmol) was dissolved in freshly distilled dry carbon disulphide (ca. 30 ml). After the solution was cooled down to $0 \sim 2°C$, anhydrous alminium chloride (1.1 g, 8.1 mmol) was quickly added to the solution with stirring. Acetyl chloride (0.72 g, 9.2 mmol) was then added slowly, and the temperature of the reaction mixture was raised gradually to the b.p. (35°C). The mixture was refluxed until the reaction was completed (1 hr). After cooling in an ice bath, ca. 10 ml of concentrated hydrochloric acid was added to the mixture. The resulting white solid was collected. The solid was chro-



SCHEME 1 Synthetic route for *p-n*-alkoxybiphenylbutane-1,3-dione, C_nO-Lig.

TABLE I

Elemental analysis data, yields, recrystallization solvents, and the crystalline shapes obtained from recrystallization for C_nO-A.

n	Elemental analysis Found(calcd.)% C	H	Yield (%)	Recrystallization solvent	Crystalline shape
8	81.44(81.61)	8.67(8.74)	30	IPA[a]	plate-like
9	81.61(81.76)	8.93(8.85)	28	IPA[a]	plate-like
10	81.77(82.05)	9.15(9.20)	23	IPA[a]	plate-like
11	81.92(81.99)	9.35(9.40)	30	IPA[a]	plate-like
12	82.06(81.97)	9.54(9.55)	27	IPA[a]	plate-like
16	82.52(82.59)	10.16(9.99)	28	IPA[a]	plate-like
18	82.70(82.76)	10.41(10.50)	29	IPA[a]	plate-like

[a]Isopropyl alcohol

matographed over a silia gel with benzene and recrystallized from isopropyl alcohol to afford 0.68 g of colorless plate-like crystals. (30%).
MS (m/e) = 324 (M^+), IR (KBr, disk, cm^{-1}) 1700 (C = O), ^{1}H-NMR ($CDCl_3$, TMS) δ (ppm) 0.9 (t, 3H, CH_3), 1.3 (m, 12H, $(CH_2)_6$), 2.6 (s, 3H, $COCH_3$), 4.0 (t, 2H, OCH_2), 6.9 ~ 8.0 (m, 8H, biphenyl)

p-n-Octyloxybiphenylbutane-1,3-dione (*C_8O-Lig*). C_8O-A (0.50 g, 1.5 mmol) was dissolved in freshly distilled dry tetrahydrofuran (THF) (ca. 20 ml). The solution was refluxed for 2 hr. in the presence of 60% sodium hydride (0.14 g, 3.1

TABLE II

Elemental analysis data, yields, recrystallization solvents, and the crystalline shapes obtained from recrystallization for C_nO-Lig.

n	Elemental analysis Found(calcd.)% C	H	Yield (%)	Recrystallization solvent	Crystalline shape
8	78.65(78.28)	8.25(8.14)	73	ethanol	powder(K_1)
9	78.91(78.92)	8.48(8.47)	86	ethanol	powder(K_3)
10	79.15(79.19)	8.69(8.72)	83	ethanol	powder(K_3)
11	79.37(79.57)	8.88(8.89)	80	ethanol	powder(K_3)
12	79.58(79.46)	9.06(9.05)	76	ethanol	powder(K_2)
16	80.29(80.20)	9.69(9.61)	71	chloroform	plate-like
18	80.58(80.42)	9.95(10.06)	84	chloroform	plate-like

mmol). Dry ethyl acetate (0.68 g, 7.7 mmol) was then added to the solution at room temperature and refluxed again for 12 hr. After cooling in an ice water bath, an aqueous hydrochloric acid solution (1N, ca. 10 ml) was added to the mixture. The product was extracted with diethyl ether. Evaporation gave a yellow solid. The solid was chromatographed over a silica gel with benzene and recrystallized from ethyl alcohol to afford 0.41 g of yellow powder (73%).
MS (m/e) = 366 (M^+), I.R. (KBr, disk, cm^{-1}) 1600 (C = C), ^{1}H-NMR ($CDCl_3$, TMS) δ (ppm) 0.9 (t, 3H, CH_3), 1.3 (m, 12H, $(CH_2)_6$), 2.2 (s, 3H, $COCH_3$), 4.0 (t, 2H, OCH_2), 6.1 (s, 1H, enol CH), 6.8 ~ 7.9 (m, 8H, biphenyl), 16.2 (s, 1H, enol OH), keto:enol = 0:100.

II-2. Measurements

Phase transition behaviors of these compounds synthesized here were observed with a polarizing microscope equipped with a heating plate controlled by a thermoregulator, Mettler FP80 and FP82, and measured with differential scanning calorimeters, Rigaku Thermoflex TG-DSC and Rigaku Thermoflex DSC-10A. The X-ray diffraction powder patterns were employed to characterize the mesophases and the crystalline polymorphs in the present compounds. The patterns were measured with Cu-Kα radiation, using a Rigaku Geigerflex equipped with a hand-made heating plate controlled by a thermoregulator.[18]

III. RESULTS AND DISCUSSION

[1]. Mesomorphism of 4-*n*-alkoxy-4′-acetylbiphenyl (C_nO-A)

The precursor compounds, C_n-A, also exhibit mesomorphism. In Table III are summarized the phase transition temperatures and phase transition enthalpy changes for C_nO-A. In Figure 1, all transition temperatures of C_nO-A are plotted against the number of carbon atoms in the alkoxy chain. Each of the C_nO-A (n = 8 ~ 12, 16) compounds has a smectic E (S_E) mesophase. The temperature range of the S_E mesophase gradually becomes narrow with increasing the number of carbon atoms from n = 8 to n = 12; at last, $C_{18}O$-A has no mesophase. All of the C_nO-A (n = 8 ~ 12, 16) compounds gave a platelet texture for the mesophases. The X-ray diffraction pattern of the mesophase of $C_{12}O$-A at 120°C corresponds to the lamellar structure, spacing = 29.4 Å and the lattice constants in a two-dimensional rectangular lattice, a = 8.08 Å, b = 5.53 Å. Therefore, this mesophase is confirmed as a smectic E phase. This result is compatible with the assignment of the S_E mesophase for the homologue of 4-ethoxy-4′-acethylbiphenyl in the literature.[19]

[2]. Mesomorphism and unusual multiple melting behavior of *p-n*-alkoxybiphenylbutane-1,3-dione (C_nO-Lig; n = 8 ~ 12, 16, 18)

All of the C_nO-Lig compounds have two mesophases of smectic E (S_E) and smectic A (S_A) mesophases. In Table IV are summarized the phase transition temperatures and their enthalpy changes of these compounds. In Figure 2, all transition temperatures of the C_nO-Lig compounds are plotted against the number of carbon

TABLE III

Phase transition temperatures (T) and enthalpy changes (ΔH) of C_nO-A.

n	Phase[a] $\xrightarrow{T^{\circ}C[\Delta H(kcal/mol)]}$ Phase
8	K $\xrightarrow{96.0[6.9]}$ S_E $\xrightarrow{136.5[3.9]}$ I.L.
9	K $\xrightarrow{104.2[8.6]}$ S_E $\xrightarrow{135.0[4.0]}$ I.L.
10	K $\xrightarrow{102.7[9.1]}$ S_E $\xrightarrow{132.1[4.2]}$ I.L.
11	K $\xrightarrow{110.5[10.2]}$ S_E $\xrightarrow{130.6[4.0]}$ I.L.
12	K $\xrightarrow{109.8[10.3]}$ S_E $\xrightarrow{129.9[3.9]}$ I.L.
16	K $\xrightarrow{116.8[14.2]}$ S_E $\xrightarrow{122.5[4.2]}$ I.L.
18	K $\xrightarrow{119.4[17.1]}$ I.L.

[a]Phase nomenclature: K = crystal, S_E = smectic E mesophase, and I.L. = isotropic liquid.

atoms in the alkoxy chain. The two mesophases S_E and S_A are established for $C_{16}O$-Lig.

(2-1). Mesomorphism of *p-n*-hexadecyloxybiphenylbutane-1,3-dione ($C_{16}O$-Lig)

$C_{16}O$-Lig was recrystallized from chloroform to afford plate-like crystals. When the virgin crystals are heated from room temperature (r.t.), they melt to a S_E mesophase at 118.9°C, followed by a S_A mesophase at 139.1°C; on further heating,

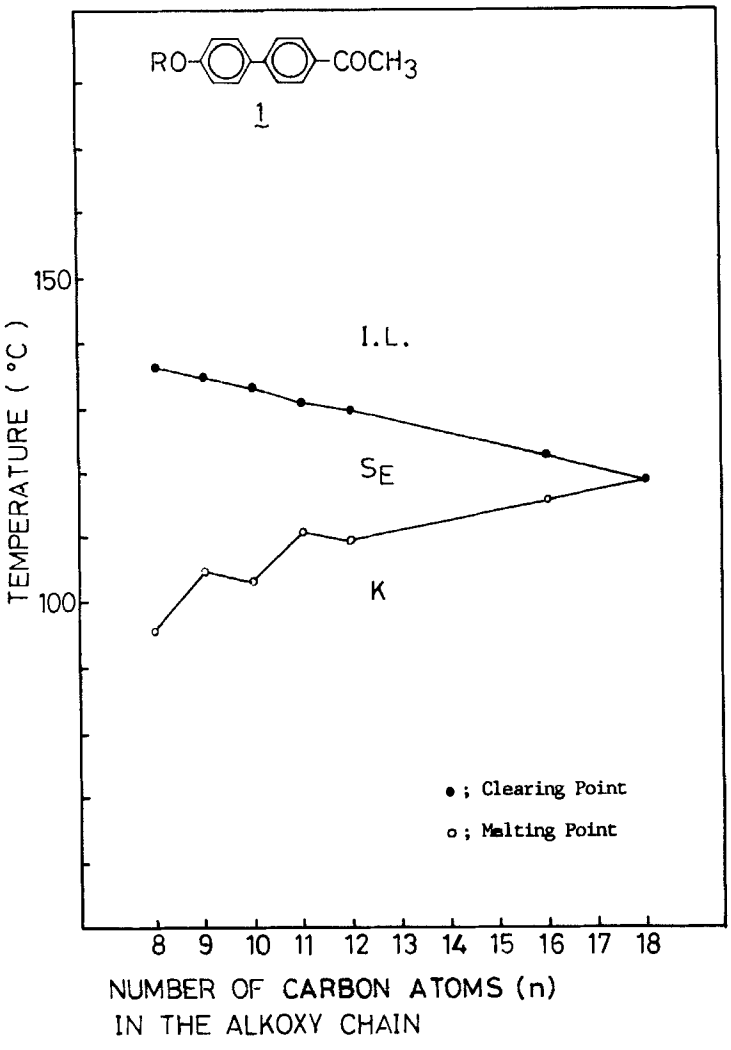


FIGURE 1 Phase transition temperatures vs. number of carbon atoms in the alkoxy chain of C_nO-A.

the S_A mesophase clears to an isotropic liquid (I.L.) at 162.0°C. The textures of the two mesophases are shown in Figure 3. When the I.L. was cooled down to 156.5°C, a focal conic texture in Figure 3a appeared: this texture is a characteristic of S_A mesophases. When the sample in Figure 3a was cooled to 133.0°C, a platelet texture of a characteristic of S_E mesophases was growing in the focal-conic texture of the S_A mesophase (Figure 3b): on further cooling to 132.0°C, the texture completely transformed to the platelet texture as shown in Figure 3c. These S_E and S_A mesophases were confirmed also by powder X-ray diffraction. The X-ray diffraction powder patterns of the mesophases are shown in Figure 4. The pattern of the S_A mesophase at 150°C is illustrated in Figure 4a. It gave a diffuse band around 2θ

TABLE IV

Phase transition temperatures (T) and enthalpy changes (ΔH) of C_nO-Lig.

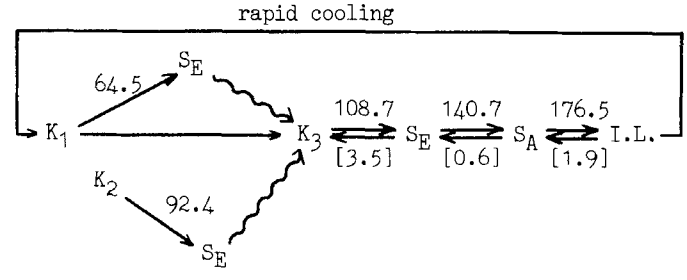
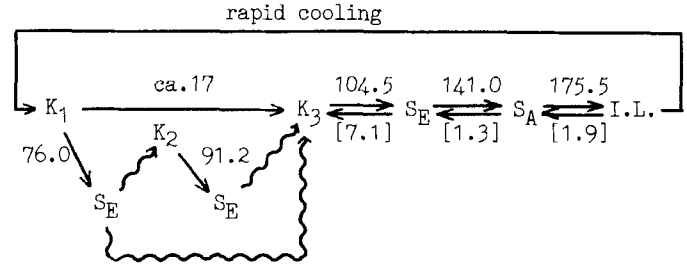
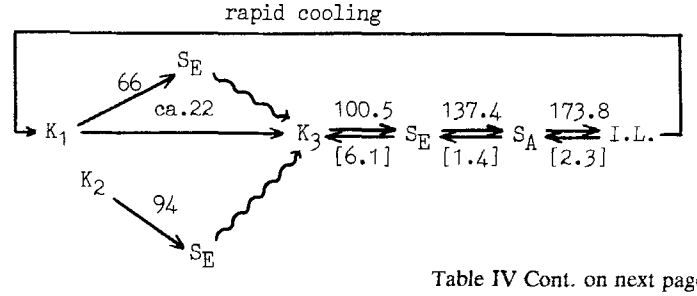
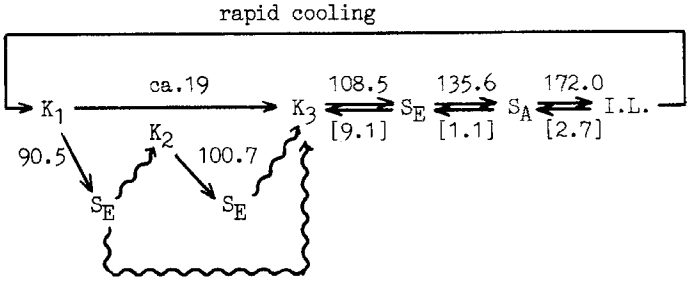
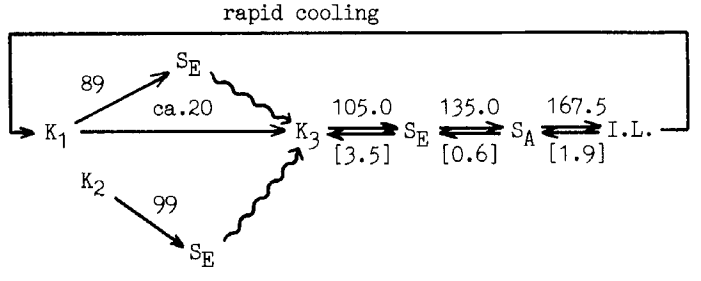
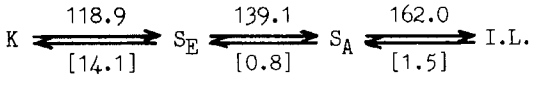
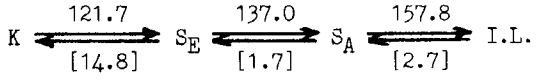
n	Phase[a] $\xrightarrow[\Delta H[kcal/mol]]{T^oC}$ Phase
8	
9	
10	

Table IV Cont. on next page

= 20° in the X-ray wide-angle region, corresponding to the melt of the alkoxy chains. It also gave three narrow reflections in the low-angle region, which correspond to the (001), (002) and (004) planes, respectively, for a layered structure, the interlayer distance = 35.0 Å. Therefore, the mesophase was confirmed as a S_A mesophase. The X-ray diffraction powder pattern of the S_E mesophase at 130°C

TABLE IV

(Continued)

11	
12	
16	
18	

[a]Phase nomenclature: K = crystal, S_E = smectic E mesophase, S_A = smectic A mesophase, and I.L. = isotropic liquid.

is shown in Figure 4b. It gave three narrow reflections in the low-angle region, which correspond to the (001), (002), and (004) planes; the interlayer distance = 35.7 Å. It also gave three narrow reflections in the wide-angle region, which correspond to (110), (200), and (210) in a two-dimensional rectangular lattice, respectively, lattice constants a = 8.06 Å, b = 5.49 Å. Thus, the lower temperature mesophase was confirmed as a S_E mesophase.

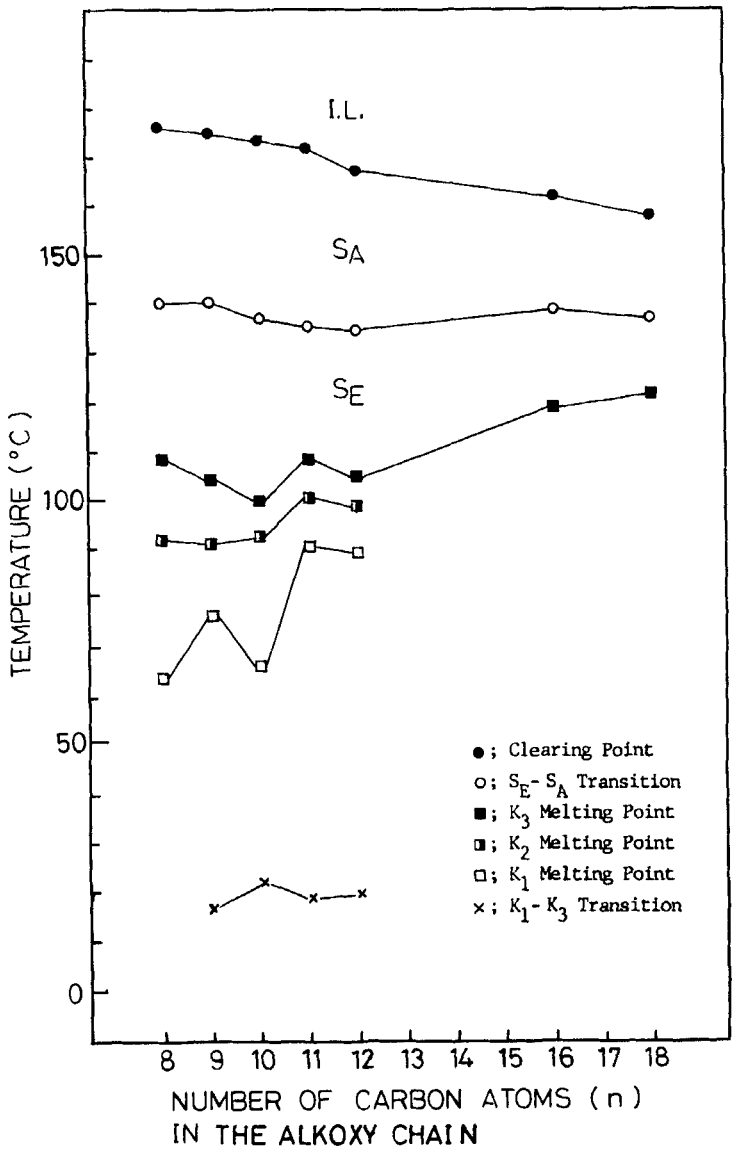


FIGURE 2 Phase transition temperatures vs. number of carbon atoms in the alkoxy chain of C_nO-Lig.

(2-2). Unusual double melting behavior via the S_E mesophase of $C_{12}O$-Lig

Two types of unusual double melting behavior were revealed for $C_{12}O$-Lig.

a). *Generality of two types of double melting behavior.* Generally, usual double melting behavior is observed via an isotropic liquid having high fluidity.[15] Recently, Ohta *et al.* reported unusual double melting behavior via a mesophase (via a discotic mesophase[14]; via a nematic phase[16]). Double melting behavior is

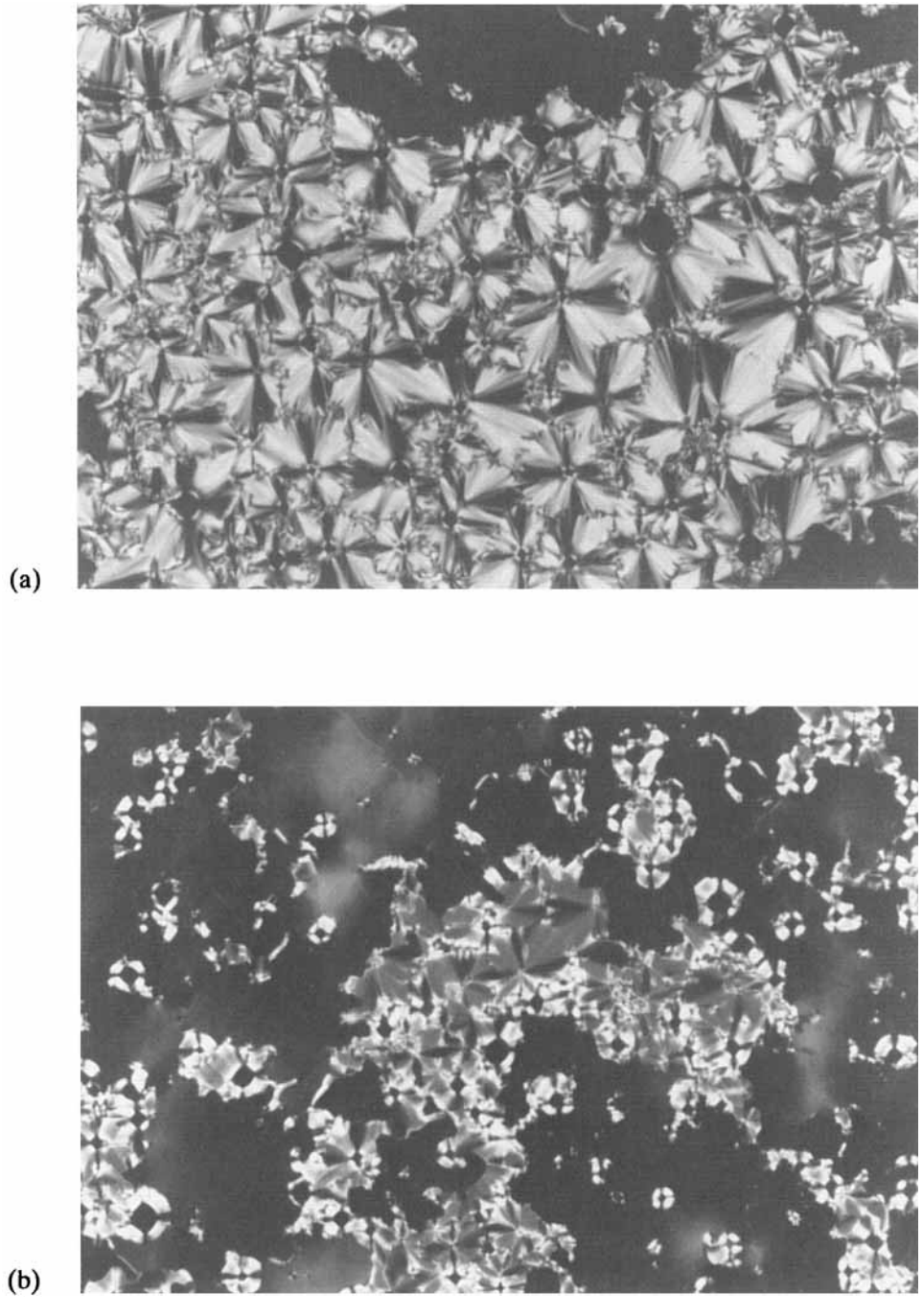
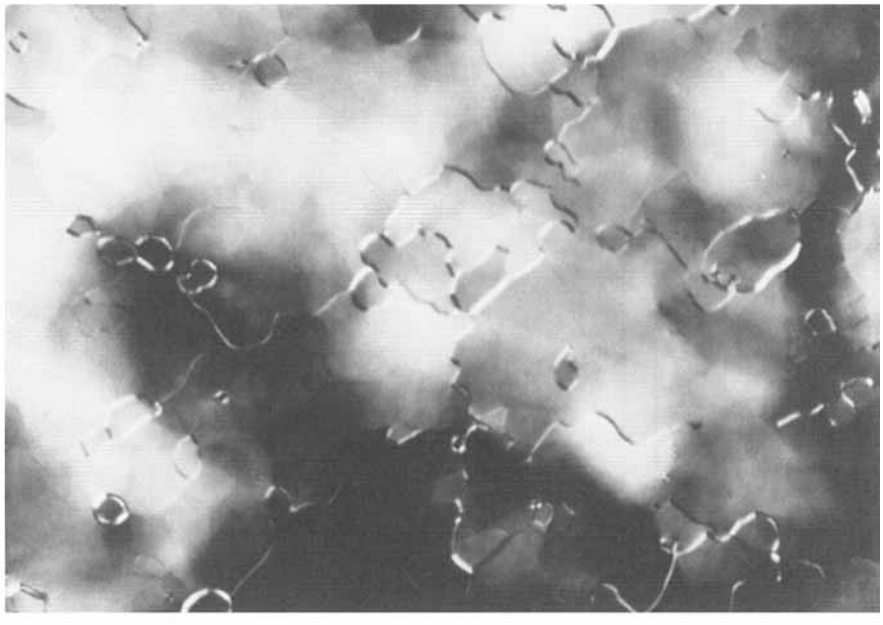


FIGURE 3 The textures of the smectic A mesophase of *p-n*-hexadecyloxybiphenylbutane-1,3-dione (C_{16}O-Lig); (a) the focal-conic texture of the smectic A mesophase obtained from the isotropic liquid on cooling to 156.5°C, (b) the platelet growth of the smectic E mesophase in the focal-conic texture of the smectic A mesophase at 133.0°C, (c) the platelet texture of the smectic E *mesophase at 132.0*°C. See Color Plate II.



(c)

FIGURE 3 (continued)

classified into two types (Figure 5). When we assume that a compound has two crystalline polymorphs, K_1 and K_2, one type of the double melting behavior can be observed for a monotropic relation between K_1 and K_2 (Case A in Figure 5); the other type for an enantiotropic relation between K_1 and K_2 (Case B in Figure 5). The method to distinguish these two types is to observe the heating rate dependence of differential scanning calorimeter (DSC) thermograms.[5,10,13,14] In the former (Case A), the DSC thermograms show two endothermic peaks (Peaks I and III) and one exothermic peak (Peak II). Peak I and Peak III correspond to the meltings of K_1 and K_2, respectively. Peak II between Peaks I and III corresponds to a recrystallization from the melt of K_1 to the K_2 crystalline phase. The ratio of Peak III (due to the melting of K_2) to Peak I (due to the melting of K_1) decreases with a faster heating rate. Hence, the *slower* the heating rate, the more clearly double melting behavior can be observed for Case A. In the latter (Case B), the DSC thermograms exhibit three endothermic peaks (Peaks I, II and IV) and one exothermic peak (Peak III). Peak I corresponds to the crystal-crystal phase transition from K_1 to K_2: however, it is not clear in most of the cases because Peak I is often observed as a very broad peak. Peak II and Peak IV correspond to the meltings of K_1 and K_2, respectively. Peak III between Peak II and Peak IV corresponds to the recrystallization from the melt of K_1 to the K_2 crystalline phase. The ratio of Peak II (due to the melting of K_1) to Peak IV (due to the melting of K_2) increases with a faster heating rate. Hence, the *faster* the heating rate, the more clearly double melting behavior can be observed for Case B. The heating rate dependence of Case B is quite opposite to that of Case A. Therefore, these two types of the double melting behaviors are distinguishable from the heating rate dependence.

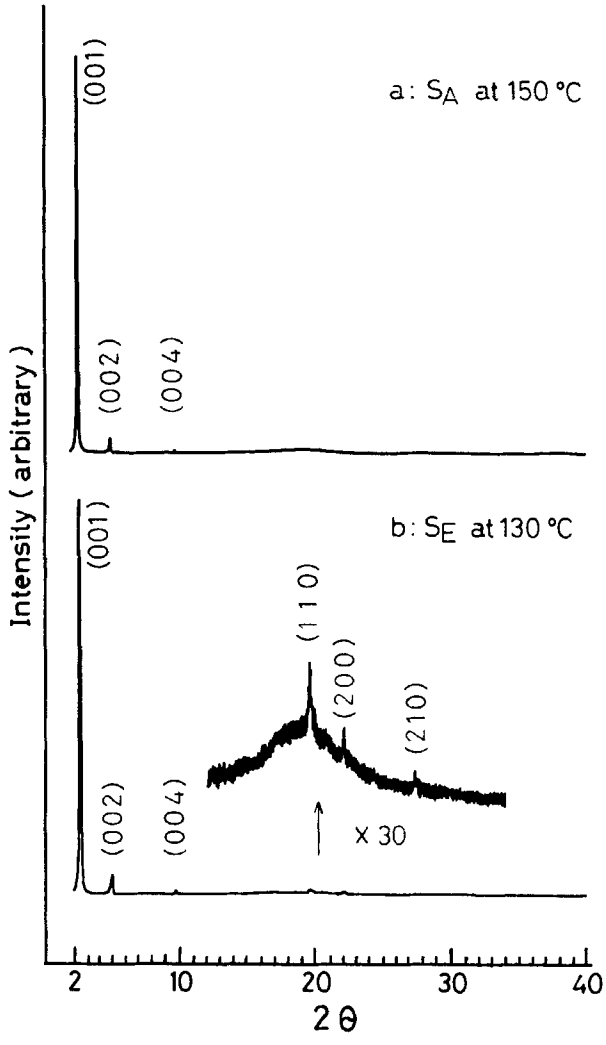


FIGURE 4 X-Ray diffraction powder patterns of C_nO-Lig: (a) the smectic A(S_A) mesophase at 150°C, (b) the smectic E(S_E) mesophase at 130°C.

b). *Preparation of crystallographically pure crystals, K_1, K_2, and K_3 of $C_{12}O$-Lig.* It is apparent from generality above-mentioned that a compound exhibiting double melting behavior necessarily has at least two crystalline polymorphs. Crystallographically pure crystals of the K_1, K_2, and K_3 states in $C_{12}O$-Lig could be obtained as follows.

The K_2 crystals were obtained from recrystallization in ethanol at −20°C. The K_1 crystals appeared when an I.L. at 180°C was cooled *rapidly* by placing it onto a stainless steel plate at ca. 5°C. The K_3 crystals could be obtained when an I.L. at 180°C was cooled *slowly* to room temperature over 1 hr. To distinguish these three crystalline polymorphs in the $C_{12}O$-Lig compounds, X-ray diffraction powder

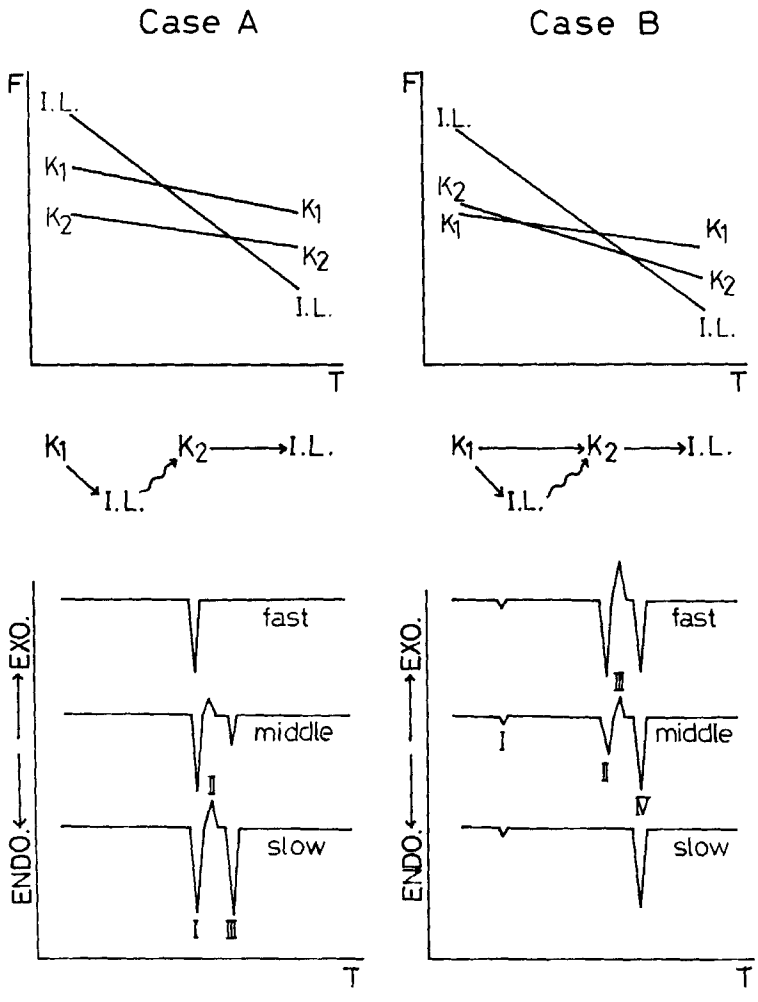


FIGURE 5 The two types of double melting behavior, Case A: a monotropic relation between K_1 and K_2; Case B: an enantioptropic relation between K_1 and K_2.

patterns were recorded. The X-ray powder patterns of the two crystalline polymorphs of K_2 and K_3 could be obtained at room temperature as illustrated in Figure 6. The two patterns of the K_2 and K_3 polymorphs were completely different. Hence, the K_2 and K_3 crystals are different crystalline polymorphs. The pattern of the pure K_1 could not be obtained, because the K_1 transformed to the K_3 during X-ray radiation at room temperature, and because the K_1 crystals gradually transform by the crystal-crystal phase transition from K_1 to K_3 at ca. 20°C. Therefore, we always obtained a mixed pattern of K_1 and K_3. Nevertheless, the pattern gave the reflections characteristic of the K_1 crystalline form at d = 3.13, 3.79, 15.5, and 26.7 Å for the four strongest reflections.

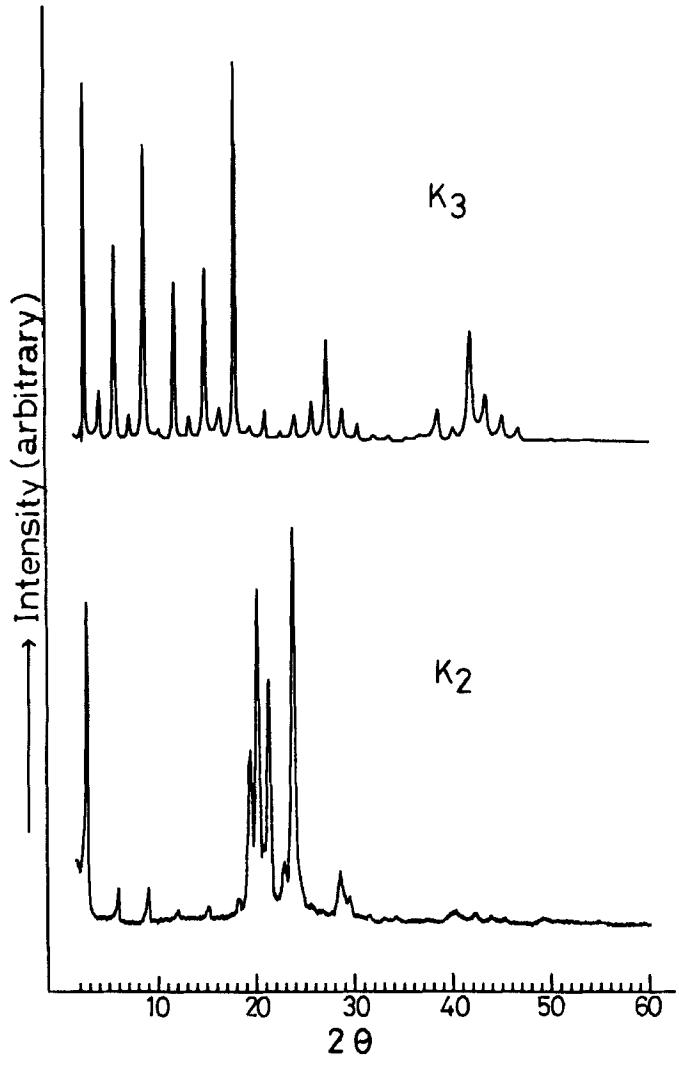


FIGURE 6 X-Ray diffraction powder patterns of C_{12}O-Lig: (a) the virgin crystals (K_2) at r.t., (b) the K_3 obtained when the I.L. at 180°C was cooled slowly to r.t. over 1 hr.

c). *Heating rate dependence of the DSC thermograms of the K_1 crystals.* It is apparent from generality above-mentioned that double melting behavior can be estimated by heating dependence of the DSC thermograms.

Figure 7 shows the DSC thermograms of the K_1 crystals for different heating rates, 2.5, 10, and 40°C/min. The thermogram for 10°C/min. exhibits six peaks (Peaks I, II, III, IV, V, and VI). Peak I could be observed especially for heating the sample from −10°C. Peak I corresponds to the crystal-crystal phase transition from K_1 to K_3 at ca. 20°C. Peak II and Peak IV correspond to the melting of K_1 to the S_E mesophase at 89°C and the melting of K_3 to the S_E mesophase at 105.0°C,

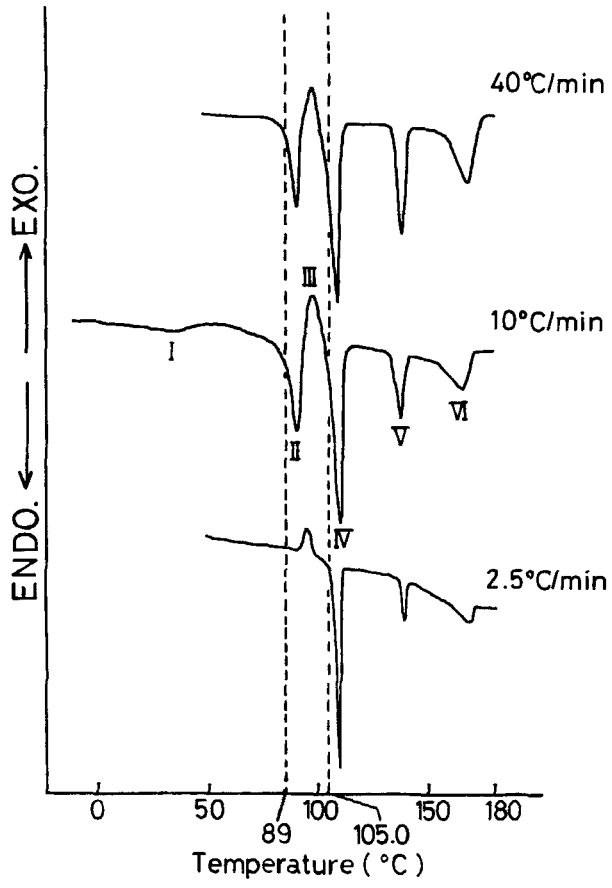


FIGURE 7 DSC thermograms of K_1 of $C_{12}O$-Lig for different heating rates.

respectively. Exothermic Peak III between Peak II and Peak IV corresponds to the recrystallization from the melt of K_1 to the K_3 crystals. Peak V and Peak VI correspond to the phase transition from the S_E mesophase to the S_A mesophase at 135.0°C and the clearing from the S_A mesophase to I.L. at 167.5°C, respectively. The ratio of Peak II (due to the melting of K_1) to Peak IV (due to the melting of K_3) increases with a faster heating rate. Therefore, the $C_{12}O$-Lig compound shows a double melting behavior via the S_E mesophase with an enantiotropic relation between K_1 and K_3, which corresponds to Case B in Figure 5.

d). *Heating rate dependence of the DSC thermograms of the K_2 crystals.* Figure 8 shows three DSC thermograms of the K_2 crystal for different heating rates, 2.5, 10, and 40°C/min. These thermograms exhibit five peaks (I, II, III, IV, and V). Peak I and Peak III correspond to the melting of K_2 to the S_E mesophase at 99°C and the melting of K_3 to S_E mesophase at 105.0°C, respectively. Exothermic Peak II between Peak I and Peak III, which is relatively ambiguous in this figure, corresponds to the recrystallization from the melt of K_2 to the K_3 crystals. The

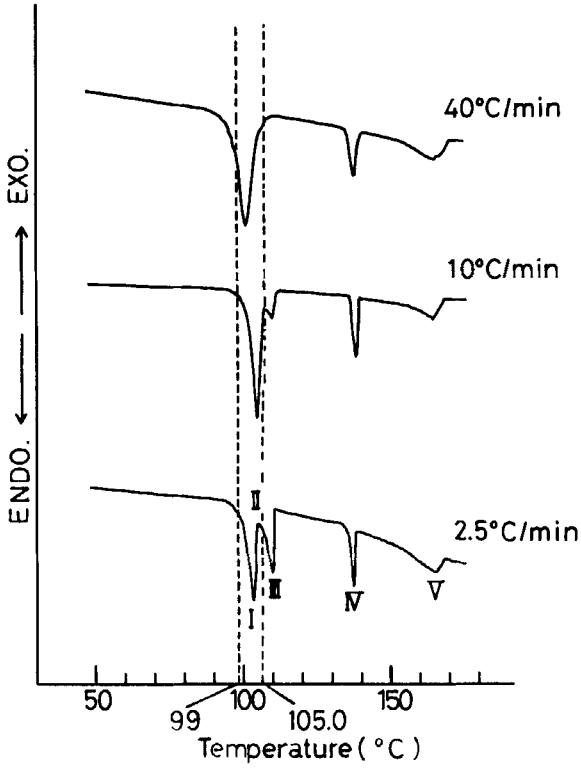


FIGURE 8 DSC thermograms of K_2 of $C_{12}O$-Lig for different heating rates.

ratio of Peak III (due to the melting of K_3) to Peak I (due to the melting of K_2) decreases with a faster heating rate. Therefore, the $C_{12}O$-Lig compound exhibits a double melting behavior via the S_E mesophase with a monotropic relation between K_2 and K_3, which corresponds to Case A in Figure 5.

e). *Heating rate dependence of the DSC thermograms of the K_3 crystals.* Figure 9 shows three DSC thermograms of the K_3 crystals for different heating rates, 2.5, 10, and 40°C/min. All the thermograms were the same for the different heating rates; i.e., no heating rate dependence was observed. Therefore, it can be elucidated that K_3 is the most stable crystalline phase in the three polymorphs.

The complicated melting behavior discussed above can be readily explained by the schematic free-energy (F) vs. temperature (T) diagram in Figure 10. When the K_1 is heated from 0°C, the crystal-crystal phase transition from K_1 to K_3 partially occurs at the intersection of the K_1 line and the K_3 line at ca. 20°C. However, since the crystal-crystal phase transition is very slow, the superheating of K_1 readily occurs along the K_1 line until the K_1 melts into the S_E mesophase at the intersection of the K_1 line and the S_E line at 89°C followed by the recrystallization from the S_E mesophase to the K_3 crystals due to relaxation†: all portions of the S_E mesophase

†Theoretically, it is possible to transform from the superheated K_1 to the metastable K_2 at the intersection of the K_1 line and the K_2 line. However, it was not observed for this compound by a polarizing microscope and a DSC.

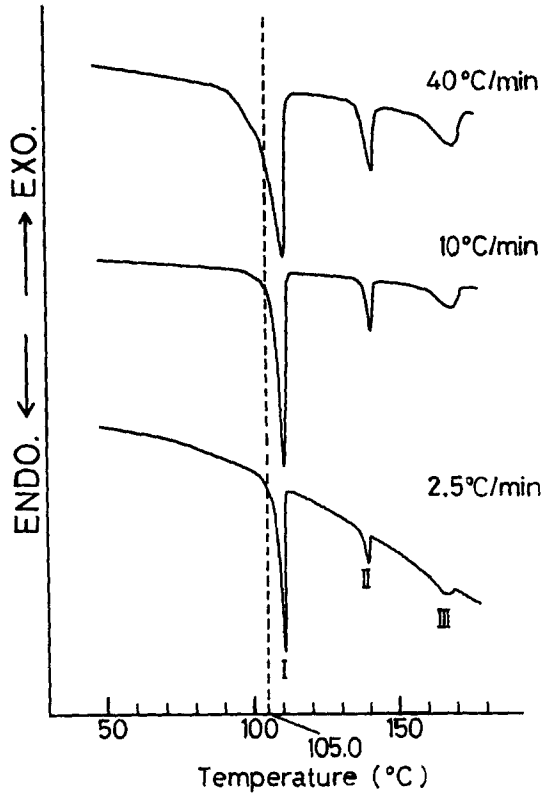


FIGURE 9 DSC thermograms of K_3 of $C_{12}O$-Lig for different heating rates.

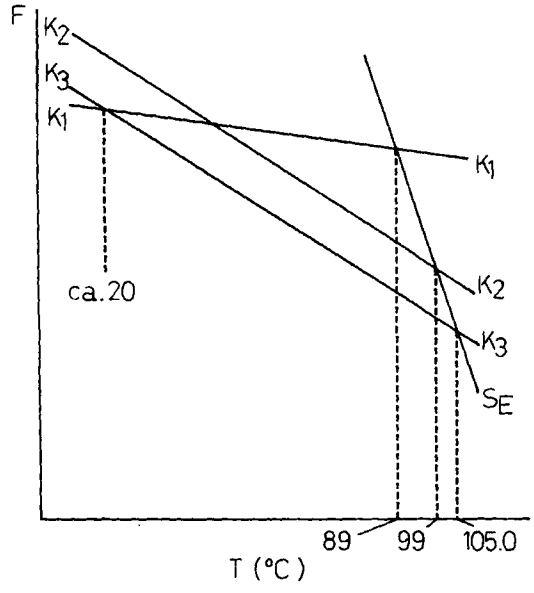


FIGURE 10 The schematic free-energy (F) vs. temperature (T) diagram of $C_{12}O$-Lig.

change into K_3 crystals. On further heating, the K_3 melts again into the S_E mesophase at the intersection of the K_3 line and the S_E line. This corresponds to Case B in Figure 5 which is the double melting behavior with the *enantiotropic* relation between K_1 and K_3. When the K_2 is heated from room temperature, it melts to the S_E mesophase at 99°C followed by the recrystallization from the S_E mesophase to K_3 due to relaxation. On further heating the K_3 melts again into the S_E mesophase at 105.0°C. This corresponds to Case A in Figure 5 which is the double melting behavior with the *monotropic* relation between K_2 and K_3. When the K_3 is heated from room temperature along the K_3 line, it exhibits only single melting from the K_3 to the S_E mesophase at the intersection of the K_3 line and the S_E line at 105.0°C.

Thus, these complicated two types of unusual double melting behavior via the S_E mesophase of $C_{12}O$-Lig can be readily explained by the schematic F-T diagram.

(2-3). Unusual triple melting behavior via the S_E mesophase of C_9O-Lig

The C_nO-Lig (n = 9, 11) compounds exhibit unusual triple melting behavior. The unusual triple melting behavior was revealed in detail for C_9O-Lig. C_9O-Lig has three crystalline polymorphs, K_1, K_2, and K_3 (the same case as $C_{12}O$-Lig). The results of the microscopic observations and the DSC measurements supported that a schematic F-T diagram of C_9O-Lig is the same as that of $C_{12}O$-Lig (Figure 10). Nevertheless, C_9O-Lig shows a triple melting behavior. This results from the relaxation from the S_E mesophase to a mixture of the K_2 and K_3 phases at the m.p. of the K_1.

When the K_1 of C_9O-Lig is heated from 0°C, a crystal-crystal phase transition from K_1 to K_3 partially occurs at ca. 17°C. The superheated K_1 melts to the S_E mesophase at 76.0°C (the first melting). When the S_E mesophase is held at 84°C, the recrystallization from the S_E mesophase into a mixture of the K_2 and K_3 crystals occurs due to the relaxation. The K_2 melts again to the S_E mesophase at 91.2°C (the second melting). When the S_E mesophase is held at 98.0°C, the recrystallization from the S_E mesophase into the K_3 occurs. The K_3 melts again to the S_E mesophase at 104.5°C (the third melting). This is the unusual triple melting behavior via the S_E mesophase of C_9O-Lig. In this case of C_9O-Lig, the recrystallization from the S_E mesophase into *a mixture of the K_2 and K_3 crystals* at the melting point of K_1 occurs, whereas, in the case of $C_{12}O$-Lig, the recrystallization from the S_E mesophase *only to* K_3 occurs. Therefore, the additional melting of the K_2 could be observed for C_9O-Lig. As a result, the unusual triple melting behavior could be observed for C_9O-Lig.

[3]. Is smectic E phase a mesophase or a crystalline phase?

At present, it is currently believed that S_E phase is a crystalline phase rather than a mesophase.[20] The multiple melting behavior of the present C_nO-Lig (n = 8 ~ 12) compounds protests against this tendency. Generally, multiple melting behavior can be observed via liquid with high fluidity, as with an isotropic liquid.[15] When a metastable crystalline polymorph with lower m.p. is heated up to its m.p., it melts to an isotropic liquid. The isotropic liquid is so fluid that the molecules readily rearrange into a more stable crystalline phase due to the relaxation phenomenon (see Figure 10). If the smectic E phase is so solid (like a crystal) that the molecules

cannot move, a rapid rearrangement of the molecules, i.e., rapid relaxation from the S_E phase to K can not occur. In other words, if the S_E phase is a true crystalline phase without fluidity, such rapid rearrangement of the molecules and recrystallization do not occur; consequently, the multiple melting behavior via S_E should not be observed.

The present C_nO-Lig ($n = 8 \sim 12$) exhibits the multiple melting behavior via the S_E mesophase. Therefore, this indicates that S_E mesophases are not crystals but liquids with fluidity. In other words, S_E mesophase is a liquid crystal rather than a crystal.

IV. CONCLUSION

We have synthesized here C_nO-A and C_nO-Lig ($n = 8 \sim 12, 16, 18$). C_nO-A ($n = 8 \sim 12, 16$) has a S_E mesophase. C_nO-Lig ($n = 8 \sim 12, 16, 18$) has two mesophases, S_E and S_A mesophases. Interestingly, three crystalline polymorphs exist in each of the C_nO-Lig ($n = 8 \sim 12$) compounds. C_nO-Lig for $n = 8, 10, 12$ shows two types of double melting behavior via the S_E mesophase. C_nO-Lig for $n = 9, 11$ exhibits the triple melting behavior via the S_E mesophase.

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