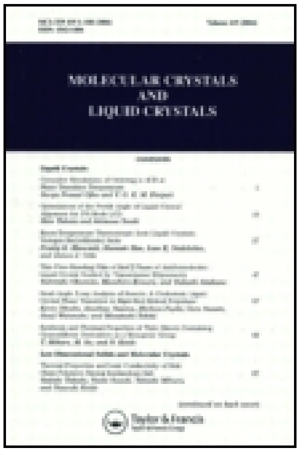


Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

First Examples Exhibiting both Double Melting Behavior and Mesomorphism in a Series of Long Chain Substituted Compounds: 1,3-Di(p-n-alkoxyphenyl)propane-1,3-dione

Kazuchika Ohta [a] , Hiromitsu Muroki [a] , Koh-Ichi Hatada [a] , Akira Takagi [a] , Hiroshi Ema [a] , Iwao Yamamoto [a] & Kei Matsuzaki [a]

[a] Department of Functional Polymer Science, Faculty of Textile Science & Technology, Shinshu University, Ueda, 386, Japan

Version of record first published: 20 Apr 2011.

To cite this article: Kazuchika Ohta , Hiromitsu Muroki , Koh-Ichi Hatada , Akira Takagi , Hiroshi Ema , Iwao Yamamoto & Kei Matsuzaki (1986): First Examples Exhibiting both Double Melting Behavior and Mesomorphism in a Series of Long Chain Substituted Compounds: 1,3-Di(p-n-alkoxyphenyl)propane-1,3-dione, Molecular Crystals and Liquid Crystals, 140:2-4, 163-177

To link to this article: http://dx.doi.org/10.1080/00268948608080150

Mol. Cryst. Liq. Cryst., 1986, Vol. 140, pp. 163–177
0026-8941/86/1404-0163/$20.00/0

First Examples Exhibiting both Double Melting Behavior and Mesomorphism in a Series of Long Chain Substituted Compounds: 1,3-Di(*p*-*n*-alkoxyphenyl)propane-1,3-dione

KAZUCHIKA OHTA†, HIROMITSU MUROKI, KOH-ICHI HATADA,
AKIRA TAKAGI, HIROSHI EMA, IWAO YAMAMOTO and KEI MATSUZAKI

Department of Functional Polymer Science, Faculty of Textile Science & Technology, Shinshu University, Ueda, 386 Japan

(*Received March 14, 1986; in final form May 22, 1986*)

A new series of β-diketones substituted by the same kind of chains, (alkoxy groups) having different lengths (C_nO-Diketone, $n = 1$–12), has been synthesized. It was found that C_nO-Diketone shows triple melting behavior for $n = 1$, double melting behavior for $n = 2$–7, and smectic mesomorphism for $n = 8$–12. It is the first example exhibiting both double (triple) melting behavior and mesomorphism in a series of long chain substituted compounds, so far as we know. Furthermore, it is noteworthy that the critical change from double melting behavior to mesomorphism occurs between $n = 7$ and $n = 8$, which is also the first example in the long chain substituted compounds, so far as we know.

Keywords: double melting behavior, smectic mesomorphism, long chain substituted compounds, β-diketone

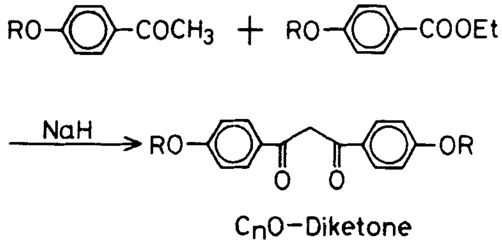
I. INTRODUCTION

In the previous paper[1] we suggested that the double melting behavior of long chain substituted compounds is a thermal behavior close to the mesomorphism. To date, we have synthesized β-diketones sub-

---

†To whom correspondence should be addressed

stituted with four different kinds of chains (1*a*,*b*,*c*,*d*) and their corresponding copper(II) complexes (2*a*,*b*,*c*,*d*) in an attempt to get new mesomorphic organic transition metal complexes.[1,2] Interestingly, we found that the ligands, 1*a* and 1*b*, show smectic mesomorphism, and that, on the other hands, the ligands, 1*c* and 1*d*, exhibit the so-called "double melting behavior."[3] Furthermore, the copper(II) complexes, 2*a* and 2*b*, show discotic mesomorphism, and the copper(II) complexes, 2*c* and 2*d*, exhibit double melting behavior. The molecular structures of these ligands and complexes are very similar to each other: all these ligands (1*a*,*b*,*c*,*d*) have the same β-diketone central parts with slightly different side chains; all these copper(II) complexes (2*a*,*b*,*c*,*d*) have the same disk-like core complex parts with slightly different side chains. Therefore, it is obvious that the double melting behavior is closely related to the mesomorphism of this type of long chain substituted compound. In the previous paper,[1] we pointed out that the chief determining factors which lead to either mesomorphism or double melting behavior are the substituent effect and the effect of central metal. For the ligands (1*a*,*b*,*c*,*d*), the determining factor must be only the substituent effect. However, this substituent effect of the four ligands is in cases where the chain lengths are the same but the kinds of the chains are different from each other: in other words, "a substituent effect of kinds." So, contrary to the case, we have synthesized here a new series of β-diketones (C_nO-Diketone in Scheme 1) substituted by the same kind of chains (alkoxy groups) having different lengths, with a view to investigating the "substituent effect of lengths" on classic mesomorphism and double melting behavior. As a result, it was found that C_nO-Diketone shows triple melting behavior for $n = 1$, double melting behavior for $n = 2$–7, and smectic mesomorphism for $n = 8$–12. It is the first example exhibiting both double (triple) melting behavior and mesomorphism in a series of long chain substituted compounds, so far as we know. So, we wish to report in this paper the multiple melting behavior and mesomorphism of C_nO-Diketone.



SCHEME 1 Synthetic route for the β-diketones, C_nO-Diketone.

II. EXPERIMENTAL

Synthesis

The synthetic route of the present β-diketone is shown in Scheme 1. The detailed procedures were almost the same as the case of the octyl substituent described in the previous paper.[2] Table I lists the yields, elemental analysis data, and the crystalline shapes obtained from recrystallization for the β-diketones; 1,3-di(*p*-*n*-alkoxyphenyl)propane-1,3-dione (alkoxy: $C_nH_{2n+1}O$ $n = 1-12$; abbreviated as C_nO-Diketone).

Measurements

The phase transformation behavior of these compounds synthesized here was observed by a polarizing microscope equipped with a heating plate controlled by a thermoregulator, Mettler FP 80 and FP 82, and measured with differential scanning calorimeter, Rigaku Denki Thermoflex TG-DSC. To distinguish between the solid polymorphs

TABLE I

Yields, elemental analysis data, and the crystalline shapes obtained from recrystallization for C_nO-Diketane

n	Yields	Elemental analysis Found(Calcd.) % C	H	Crystalline shape[a]
1	93	71.86(71.82)	5.95(5.67)	Needle(K_1)
2	89	73.21(73.06)	6.55(6.45)	Plate(K_2)
3	91	74.38(74.09)	7.11(7.11)	Needle(K_1)
4	92	74.95(74.97)	7.74(7.66)	Needle(K_2)
5	90	75.54(75.73)	8.20(8.14)	Needle(K_2)
6	93	76.09(79.38)	8.37(8.55)	Strip(K_1)
7	88	77.09(76.95)	9.00(8.91)	Needle(K_1)
8	87	77.68(77.46)	9.25(9.23)	Strip(K_2)
9	90	77.80(77.91)	9.56(9.51)	Plate(K_2)
10	91	78.49(78.31)	9.79(9.77)	Plate
11	90	78.73(78.68)	9.95(9.99)	Plate
12	93	79.30(79.01)	10.10(10.20)	Plate

[a] Each of the recrystallization solvents for the C_nO-Diketone is ethanol.

in the compounds, X-ray diffraction powder patterns were also measured with Cu-K_α radiation, using a Rigaku Geigerflex.

III. RESULTS AND DISCUSSION

In Table II the phase transitions for the β-diketones, C_nO-Diketone, are summarized. Interestingly, C_nO-Diketone shows triple melting

TABLE II

Phase transition temperatures (T_t) and enthalpy changes (ΔH_t) of C_nO-Diketone

n	$\xrightarrow[\Delta H_t\text{(kcal/mol)}]{T_t(^\circ\text{C})}$
1	$\begin{tikzcd} K_1 \arrow[rr, "\text{ca.}103"] \arrow[dr, "116.0"'] & & K_2 \arrow[rr, "\text{ca.}104"] \arrow[dr, "116.7"'] & & K_3 \arrow[r, "119.4", "11.6"'] & \text{I.L.} \\ & \text{I.L.} \arrow[ur] & & \text{I.L.} \arrow[ur] & & \end{tikzcd}$
2	$\begin{tikzcd} K_1 \arrow[r, "\text{ca.}44"] & K_2 \arrow[rr, "\text{ca.}120"] \arrow[dr, "129.5"'] & & K_3 \arrow[r, "136.9", "11.4"'] & \text{I.L.} \\ & & \text{I.L.} \arrow[ur] & & \end{tikzcd}$
3	$\begin{tikzcd} K_1 \arrow[rr, "\text{ca.}48"] \arrow[dr, "108.2"'] & & K_2 \arrow[r, "111.4", "11.0"'] & \text{I.L.} \\ & \text{I.L.} \arrow[ur] & & \end{tikzcd}$
4	$\begin{tikzcd} K_1 \arrow[rr, "\text{ca.}17"] \arrow[dr, "89.9"'] & & K_2 \arrow[r, "94.7", "12.3"'] & \text{I.L.} \\ & \text{I.L.} \arrow[ur] & & \end{tikzcd}$
5	$\begin{tikzcd} K_1 \arrow[rr, "\text{ca.}22"] \arrow[dr, "91.7"'] & & K_2 \arrow[r, "92.5", "10.8"'] & \text{I.L.} \\ & \text{I.L.} \arrow[ur] & & \end{tikzcd}$
6	$\begin{tikzcd} K_1 \arrow[rr, "\text{ca.}38"] \arrow[dr, "72.5"'] & & K_2 \arrow[r, "72.8", "9.6"'] & \text{I.L.} \\ & \text{I.L.} \arrow[ur] & & \end{tikzcd}$
7	$\begin{tikzcd} K_1 \arrow[rr, "\text{ca.}52"] \arrow[dr, "83.0"'] & & K_2 \arrow[r, "87.3", "14.8"'] & \text{I.L.} \\ & \text{I.L.} \arrow[ur] & & \end{tikzcd}$

TABLE II *Continued*

n	$\xrightarrow[\Delta H_t(\text{kcal/mol})]{T_t(^\circ C)}$	
8	$K_2 \xrightarrow[8.7]{84.1} S \xrightarrow[12.1]{86.8} \text{I.L.}$ $K_1 \xrightarrow[2.9]{77.0} S$	a
9	$K_2 \xrightarrow[7.6]{71.7} S \xrightarrow[10.9]{91.2} \text{I.L.}$ $K_1 \xrightarrow[5.7]{67.5} S$	
10	$K \xrightarrow[6.4]{61.1} S \xrightarrow[13.9]{94.8} \text{I.L.}$	
11	$K \xrightarrow[8.1]{81.3} S \xrightarrow[14.6]{93.4} \text{I.L.}$	
12	$K \xrightarrow[7.4]{73.1} S \xrightarrow[15.7]{94.0} \text{I.L.}$	

Phase nomenclatures: K = crystal, S = smectic liquid crystal, I.L. = isotropic liquid.

[a] See main text and Ref. 1.

behavior for methoxy groups (n = 1), double melting behavior for the substituents from ethoxy to hepthoxy groups (n = 2–7), and smectic mesomorphism for the substituents from octyloxy to dodecyloxy groups (n = 8–12). All transition temperatures of these β-diketones are plotted against the number of carbon atoms in the alkoxy chain in Figure 1. The detailed thermal behavior of these long chain substituted compounds is described below.

1. Triple melting behavior of the C_1O-Diketone

Triple melting behavior could be observed for the C_1O-Diketone. A sequence of the state changes of this β-diketone is shown by photomicrographs in Figure 2.

Photo No. 1: when an isotropic liquid at 120°C is cooled rapidly to room temperature, a mixture of K_1 (needle-like) crystals (upper

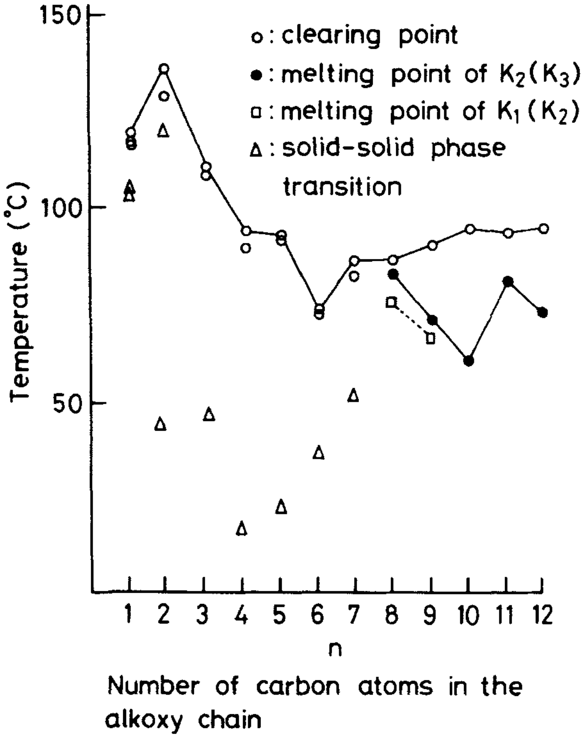


FIGURE 1 Phase transition temperatures vs. number of carbon atoms in alkoxy chain for the β-diketones, C_nO-Diketone.

side in the photo) and K_2 (strip-like) crystals (bottom side in this photo) could be obtained.

Photo No. 2: when the sample in Photo No. 1 was set on a hot plate of 116.2°C slightly over the m.p. of the K_1 crystal (116.0°C), K_1 crystals were transforming into K_2 crystals accompanied by *the melting of the* K_1, and, at the same time, K_2 crystals were transforming slowly into K_3 (plate-like) crystals.

Photo No. 3: when the sample in Photo No. 2 was heated up to 118.0°C (the temperature between the m.p.s. of K_2, 116.7°C, and K_3, 119.4°C), *the* K_2 *crystals were melting* and the K_3 (plate-like) crystals were resolidifying slowly from the melt.

Photo No. 4: by holding the temperature at 118.0°C for 1 min., the state changes in Photo No. 3 were proceeded further.

Photo No. 5: by holding the temperature at 118.0°C for more than 30 min., the K_3 crystals were growing bigger from the isotropic liquid.

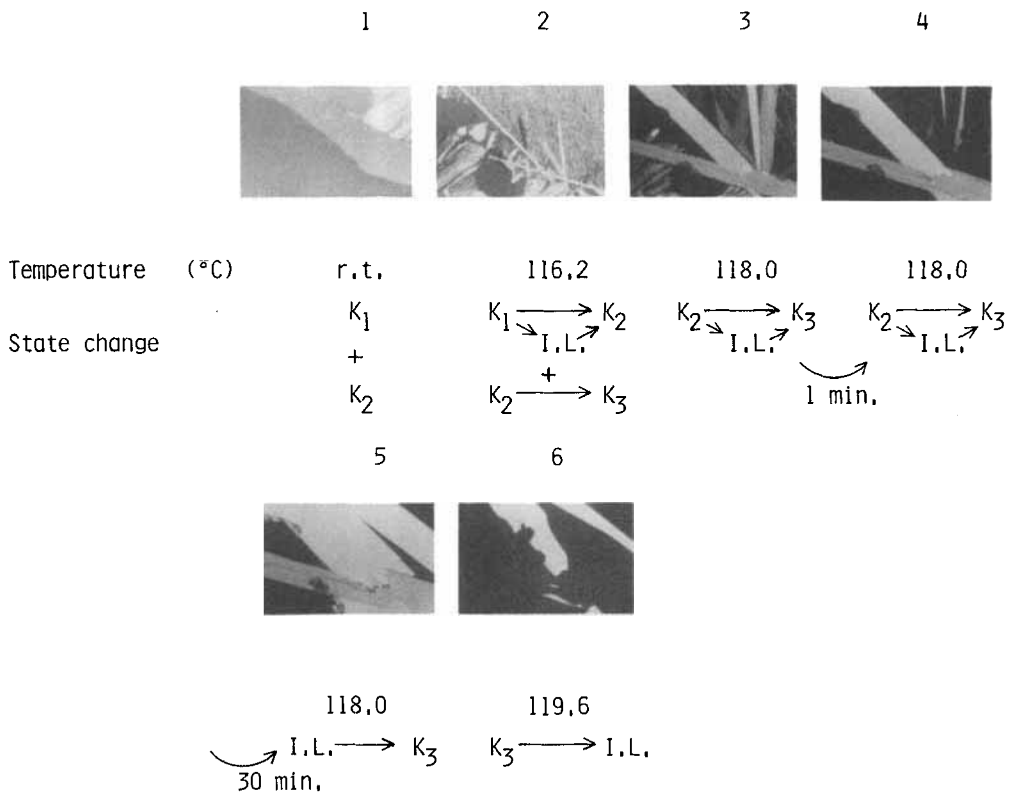


FIGURE 2 Photomicrographs of the triple melting behavior of $\mathrm{C_1O}$-Diketone.

Photo No. 6: when the sample in Poto No. 5 was heated up to 119.6°C, slightly over the m.p. of the K_3 crystal (119.4°C), *the K_3 crystals were melting.*

Thus, the triple melting behavior of the C_1O-Diketone could be observed by a polarizing microscope.

2. Double melting behavior of the C_nO-Diketone ($n = 2-7$)

Double melting behavior of the β-diketone (C_nO-Diketone) could be observed for $n = 2-7$. It is very interesting that the C_8O-Diketone exhibits smectic mesomorphism as mentioned below. The critical change from double melting behavior to mesomorphism occurs between $n = 7$ and $n = 8$ in a series of C_nO-Diketone. Such a critical change is the first example in the long chain substituted compounds, so far as we know. So, we wish to choose and report here the double melting behavior of the C_7O-Diketone.

Recrystallization of the C_7O-Diketone from ethanol gave needle-like crystals, as shown in Table I. A sequence of the state changes of this compound is shown by photomicrographs in Figure 3.

Photo No. 1: the needle-like crystals (K_1) obtained from recrystallization were set on a hot plate at room temperature.

Photo No. 2: when the sample in Photo No. 1 was heated up to 83.0°C from room temperature at the heating rate of 10°C/min, the needle-like crystals (K_1) started to melt at 83.0°C (m.p. of K_1).

Photo No. 3: by holding the temperature of the sample at 86.0°C for 5 min., small strip-like crystals (K_2) were formed from the isotropic liquid at 86.0°C.

Photo No. 4: when the temperature of the sample in Photo No. 3 was held at 86.0°C for a further 30 min., the strip-like crystals (K_2) in Photo No. 3 were growing bigger.

Photo No. 5: when the sample in Photo No. 4 was heated up to 87.3°C, the K_2 crystals were melting.

Thus, the double melting behavior of the C_7O-Diketone could be observed by a polarizing microscope.

This double melting behavior was also confirmed by DSC measurements, as shown in Figure 4. Typical DSC thermograms of the double melting behavior[4] of the K_1 crystal could be obtained at the heating rate of $\leqq 5$°C/min. Peak I (ca. 52°C), denoted in Figure 4, corresponds to the solid–solid phase transition from K_1 to K_2. The precise temperature of the solid–solid phase transition could not, however, be determined by microscopic observations, because the

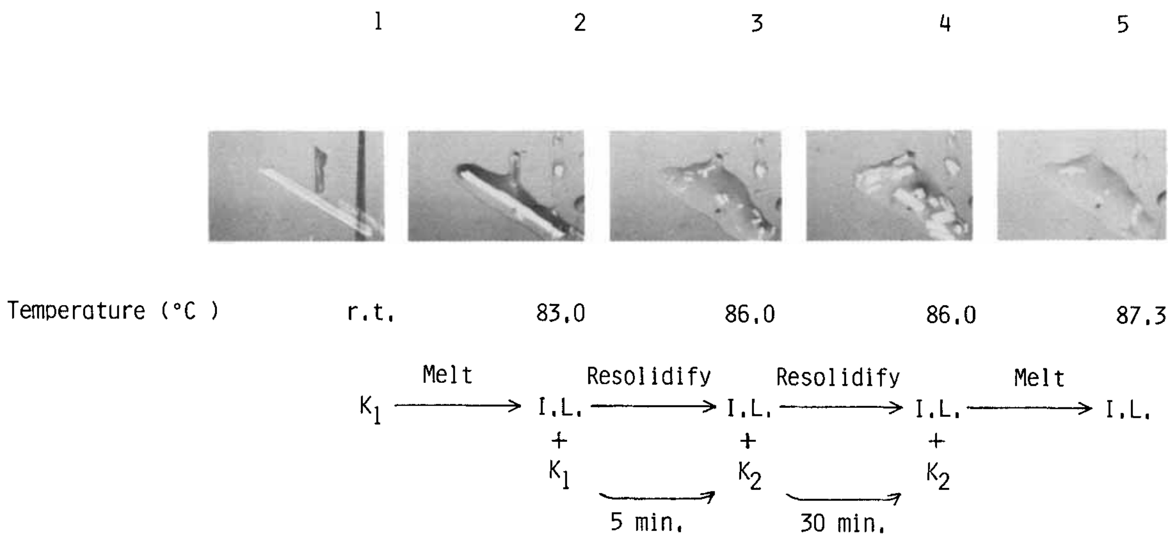


FIGURE 3 Photomicrographs of the double melting behavior of C_7O-Diketone.

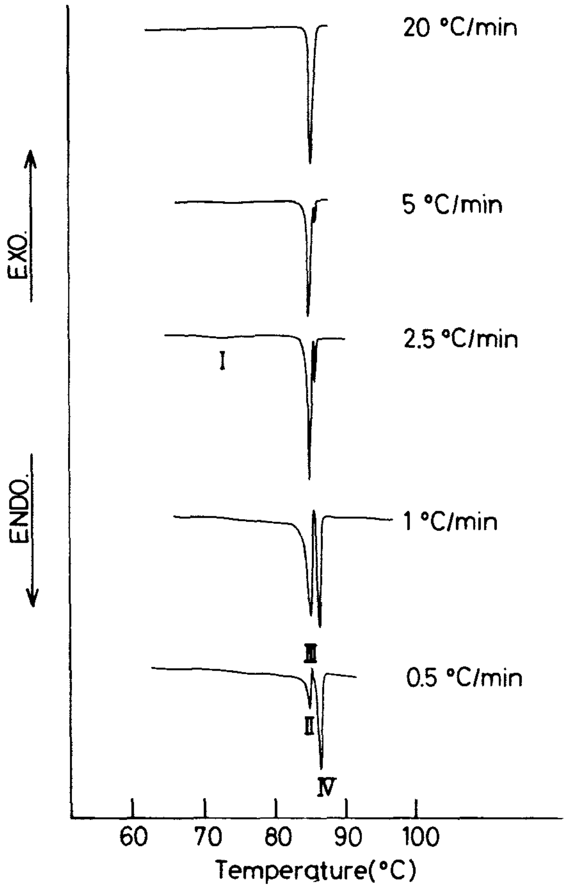


FIGURE 4 DSC thermograms of K_1 of C_7O-Diketone for different heating rates.

solid–solid phase transition is very slow and because the superheating of K_1 crystals occur easily. Although the superheating of K_1 crystals originates such double melting behavior, at the same time this makes it difficult to detect the precise temperature of the solid–solid phase transition from K_1 to K_2. Peak II and peak IV correspond to the melting of K_1 crystals and the melting of K_2 crystals, respectively. Exothermic peak III, between peak II and peak IV, corresponds to the recrystallization from the melt of K_1 crystals to K_2 crystals. The ratio of peak IV (due to the melting of the K_1 phase) to peak II (due to the melting of the K_2 phase) increases with a slower heating rate. This fact means that K_1 crystals transform largely to K_2 crystals by the solid–solid phase transition from K_1 to K_2, corresponding to peak II with a slower heating rate.

To distinguish between these two solid polymorphs, K_1 and K_2, X-ray diffraction powder patterns were observed for both of the crystals at room temperature. The diffraction data obtained are clearly different from each other. In Table III are summarized the four strongest lines in each of the solid polymorphs.

3. Smectic mesomorphism of the C_nO-Diketone (n = 8–12)

Mesomorphism of the C_8O-Diketone has already been reported in previous papers.[2] However, by further investigations, we found one more crystalline phase, denoted as K_2 in Table II. X-ray diffraction powder patterns of the K_2 crystal are clearly different from those of the K_1 crystal, as summarized in Table III. The K_2 phase melts into the smectic phase at 84.1°C (ΔH_t = 8.7 kcal/mol), and, on the other hand, the K_1 phase melts into the same smectic phase at 77.0°C (ΔH_t = 2.9 kcal/mol); on further heating, the smectic phase transforms into isotropic liquid at 86.8°C (ΔH_t = 12.1 kcal/mol). These state changes were seen in both the DSC measurements and the microscopic observations, as shown in Figure 5 and Figure 6. Photo No. 2 in Figure 6 is a photomicrograph showing the terrace structure

TABLE III

X-ray diffraction data with relative intensities (I/I_1) for the four strongest lines in each solid polymorph of C_7O-Diketone and C_8O-Diketone, respectively

n=7	K_1	dÅ	23.37	4.51	10.05	5.75
		I/I_1	100	22	21	18
	K_2	dÅ	26.77	3.62	4.62	9.21
		I/I_1	100	39	13	12
n=8	K_1	dÅ	3.66	23.25	4.23	15.24
		I/I_1	100	46	23	23
	K_2	dÅ	3.74	5.06	3.44	5.21
		I/I_1	100	51	19	17

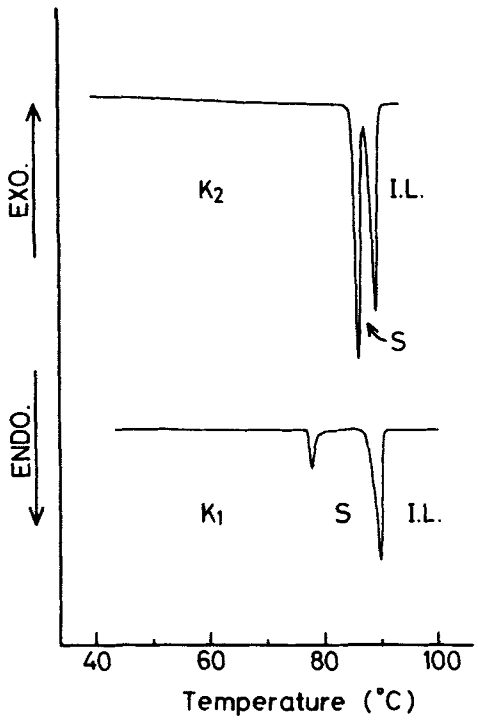


FIGURE 5 DSC thermograms of K_1 and K_2 of C_8O-Diketone. Each heating rate is 10°C/min.

of smectic characteristics. Thus, the C_8O-Diketone exhibits smectic mesomorphism. Each of the smectic phases of the other β-diketones (C_nO-Diketone, $n = 9-12$) also exhibits the same smectic texture as the C_8O-Diketone. These phase transition temperatures are summarized in Table II.

4. Relationship between tegma crystal and double melting behavior

Recently, D. Markovitsi et al. reported that an annelide-type long chain substituted copper complex exhibits triple melting behavior as per the following sequence of state changes.[5] X-ray diffraction experiments revealed that the three phases L_1, L_2, and L_3 have lamellar structures. The textures observed by a polarizing microscope are not characteristics of any organized mesophase. So, Markovitsi et al., proposed that these phases, intermediate between crystalline solid and liquid crystal, are termed "tegma crystals." Summing up the

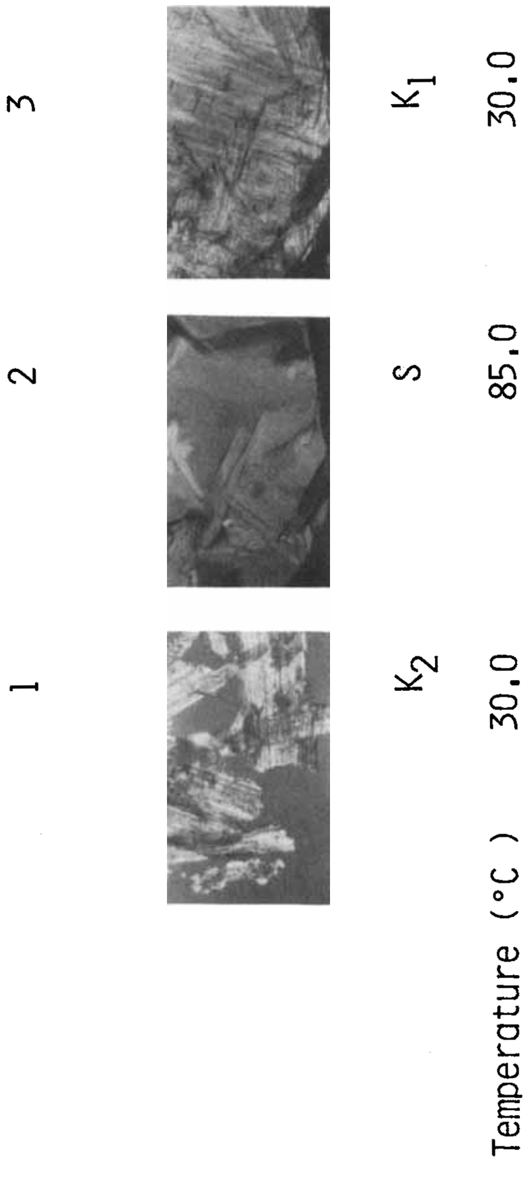
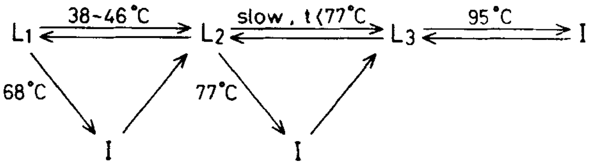


FIGURE 6 Photomicrographs of the three states, K_1, K_2, and Smectic phase, in C_8O-Diketone.



SCHEME 2 Sequence of the state changes for the annelide-type long chain substituted copper complex reported by D. Markovitsi et al. See Ref. 5.

tegma crystal, it implies two features: 1. the tegma crystal exhibits multiple melting behavior; 2. the tegma crystal resembles the liquid crystal from the standpoint of its structure. Double melting behavior of the present compound, the C_7O-Diketone, must be a thermal behavior close to mesomorphism because the critical change from double melting behavior to mesomorphism occurs between the C_7O-Diketone and the C_8O-Diketone. However, the structures of K_1 and K_2 in the C_7O-Diketone are not characteristics of any mesomorphs, as shown in Table III. Therefore, these phases are not tegma crystals. Nevertheless, the present double melting behavior of the C_7O-Diketone is thought to be close to mesomorphism. Such multiple melting behaviors of the present long chain substituted compound and the tegma crystalline compound might be close phenomena for states between crystals and liquid crystals. The new field should be studied further.

IV. CONCLUSION

A new series of β-diketones substituted by the same kind of chains (alkoxy groups) having different lengths (C_nO-Diketone, $n = 1$–12) has been synthesized. It was found that C_nO-Diketone shows triple melting behavior for $n = 1$, double melting behavior for $n = 2$–7, and smectic mesomorphism for $n = 8$–12. It is the first example exhibiting both double (triple) melting behavior and mesomorphism in a series of long chain substituted compounds, so far as we know. Furthermore, it is noteworthy that the critical change from double melting behavior to mesomorphism occurs between $n = 7$ and $n = 8$, which is also the first example in the long chain substituted compounds, so far as we know.

References

1. K. Ohta, A. Ishii, I. Yamamoto and K. Matsuzaki, *J. Chem. Soc., Chem. Comm.*, 1099 (1984); K. Ohta, A. Ishii, H. Muroki, I. Yamamoto and K. Matsuzaki, *Mol. Cryst. Liq. Cryst.*, **116**, 299 (1985).

2. K. Ohta, A. Ishii, I. Yamamoto and K. Matsuzaki, *Mol. Cryst. Liq. Cryst.*, **130**, 249 (1985).
3. The multiple melting behavior of glycerides is well known: D. Chapman, *Chem. Rev.*, **62**, 433 (1962).
4. See Figure 7 in Ref. 3.
5. D. Markovitsi, J. Andre, A. Mathis, J. Simon, P. Spegt, G. Weill and M. Ziliox, *Chem. Phys. Lett.*, **104**, 46 (1984).