

Thermal behaviour of dimesogenic liquid crystal compounds under pressure

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Abstract

Thermal behaviour of two dimesogenic liquid crystal compounds, KI5 and KI5A, was investigated under atmospheric and hydrostatic pressure by a differential scanning calorimeter and a high-pressure DTA apparatus. The enantiotropic phase transitions of crystal – multiple mesophases – isotropic liquid for both compounds were observed under atmospheric pressure. On the other hand, only two major peaks of crystal – smectic (melting) and cholesteric – isotropic (isotropization) transitions were observed under hydrostatic pressure up to 300 MPa. Not all the multiple mesophasic transitions of the KI5 compound between the incommensurate smectic A (S_{Ainc}) and cholesteric (N^*) phases could be detected because of their very small heat of transitions and the low sensitivity of the high-pressure DTA apparatus. A pressure-induced crystal polymorph of the KI5 compound appears at pressure above about 20 MPa and the crystal polymorph is formed preferentially under pressure above 100 MPa. The polymorph has a melting temperature higher than that of the normal crystal and it is thermodynamically stable. Enantiotropic phase transitions of crystal – S_{Ainc} -(TGB- N^*)-I of the KI5A compound is unchanged at pressures up to 160 MPa, but double or triple peaks are observed at the crystal – S_{Ainc} transition under high pressure above about 180 MPa. This phenomenon is ascribed to the formation of a pressure-induced crystal polymorph and a high-pressure mesophase. The incomplete T vs. P phase diagrams of the KI5 and KI5A compounds were constructed. © 1998 Elsevier Science B.V.

1. Introduction

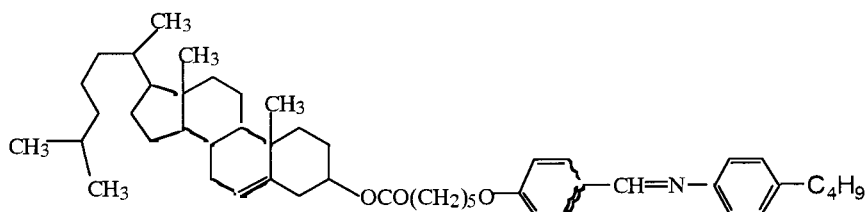
Typical low molar mass liquid crystals (l.c.) are composed of two blocks of different chemical nature; in their molecules a rigid core is covalently bonded to one or two alkyl chains in a rod-like configuration. Such l.c. compounds are no longer unique for nematic and smectic mesophase. Clarification of specific roles played by three-block molecules is one of the fascinating questions in the l.c. science. There are two main ways in tailor-making dimesogenic l.c. compounds

which contain three distinct and amphiphilic parts. First, one can introduce alternative sequences with a different chemical nature of the spacer with respect to the tails (or reciprocally). For instance, it has already been reported that the mesomorphic behaviour is quite different in dimeric compounds having highly flexible siloxane containing spacer and aliphatic tails [1–5]. Polymethylene spacers also are frequently included in those compounds [6–10]. Secondly, there are novel supramolecular systems with compounds consisting of two chemically different mesogenic rigid units. The dimesogenic l.c. compounds containing two different mesogenic cores, joined by a central flexible alkylene

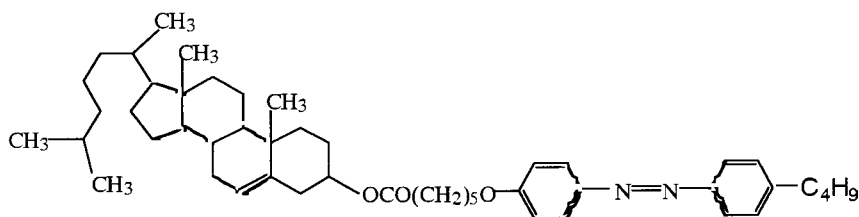
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spacer, are expected to show unique phase transitions because of possible formation of a wide variety of mesomorphic phases. When the two mesogenic units are not same, phase transition behaviour of such compounds are very complex and are rather unpredictable. This peculiarity arises much scientific interests for the study of the structure–property relationship of this type l.c. compounds. Jin et al. [11,12] first synthesized such a dimesogenic l.c. compounds containing cholesteryl and smectogenic units, i.e., *N*-[4-(6-cholesteryloxycarbonyl)pentyl]oxy)-benzylidene]-4-*n*-butylaniline and *N*-[4-(6-cholesteryloxycarbonyl)pentyl]oxy]-4-*n*-butylazobenzene, called as KI5 and KI5A, respectively. The chemical structure of both compounds are drawn below.

KI5

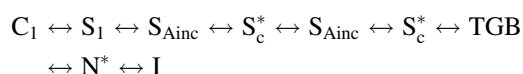


KI5A



The KI5 compound exhibits many polymorphisms including two incommensurate S_A (S_{Ainc}) phases as well as helical smectic phases (TGB and S_c^*) and cholesteric phase (N^*) between the normal crystal (C_1) and isotropic liquid (I) [13,14]. We also tried the thermal characterization of the KI5 compound by DSC [15]. Fig. 1 illustrates the typical DSC heating curve with the morphological characteristics. There are six endothermic peaks of the mesomorphic transitions between the two strong peaks of the normal crystal (C_1) – unknown mesophase transition (melting)

at 82°C and the N^* –I transition (isotropization) at about 192°C. Five enantiotropic transitions at intermediate temperatures are already characterized by Hardouin et al. [13]. In addition, a very small enantiotropic transition is observed at about 98°C [15]. This transition is detected only by DSC at present, while any other evidence for the nature of the mesophase is not available due to its very weak transition. The unknown mesophase may be a smectic phase (S_1), intermediate between the C_1 and the first S_{Ainc} phases. Accordingly the Hardouin et al.'s phase assignment of the KI5 compound should be corrected followingly.



Pressure-induced mesomorphism has been found for the first time by Shashidhar et al. [16,17] in 4-methoxybenzoic acid and 4-ethoxybenzoic acid. High pressure investigation of the phase behaviour of liquid crystals [18–28] helps us to understand the structure–property relationship of crystal and mesophase polymorphs. High-pressure differential thermal analysis and wide-angle X-ray scattering have been used for our own experiments since these methods were found to be more informative for the high-pressure investigation of liquid crystals.

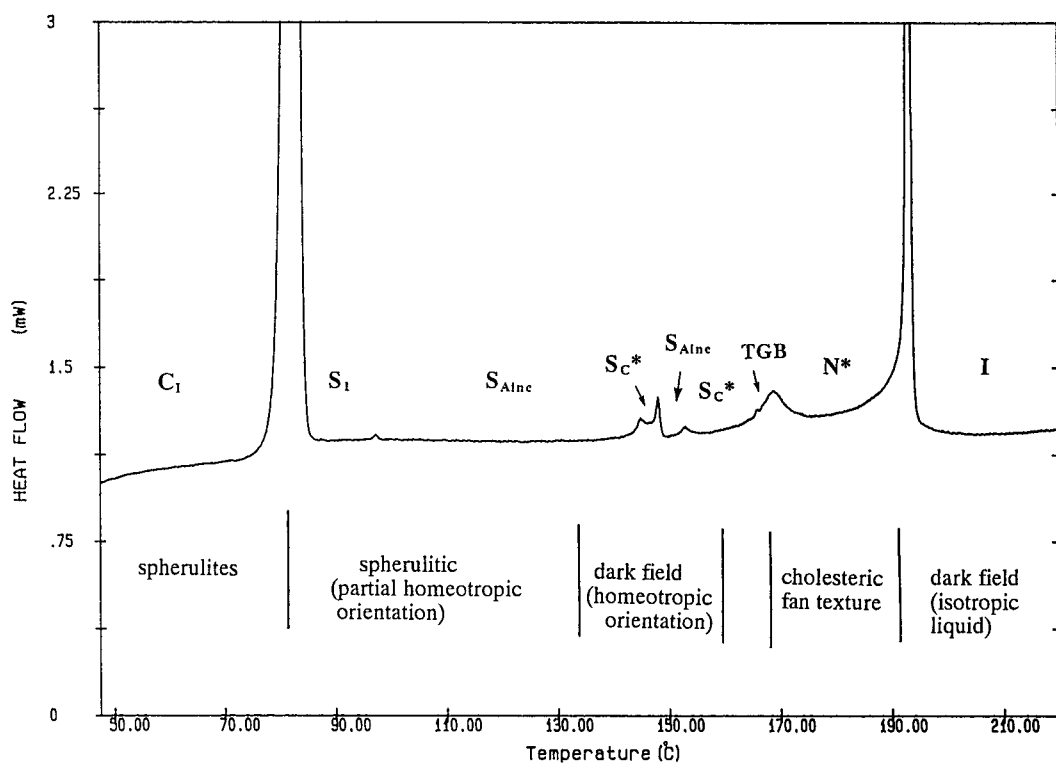


Fig. 1. Typical DSC heating curve added with characteristic texture of the KI5 compound.

A preliminary structural study on the phase transition of the KI5 compound under pressure was performed by using a high-pressure wide-angle X-ray scattering (WAXS) apparatus equipped with a curved position-sensitive proportional counter (PSPC) [29,30]. It is found that a crystal polymorph is formed concurrently with the C_I crystal under pressure above 20–30 MPa, and that the formation of the pressure-induced polymorph (C_{II}) is predominant with increasing pressure above about 100 MPa [15]. The transition behaviour of the dimesogenic liquid crystalline compounds under pressure would be much of interest for the study of thermal properties of the crystal polymorphs and mesophases of the dimesogenic l.c. compounds.

In this study, the effect of pressure on the thermal behaviour of the KI5 and KI5A compounds has been investigated by a high-pressure differential thermal analysis (DTA).

2. Experimental

The synthesis and the characterization of the KI5 and KI5A compounds are described elsewhere [11,12]. The thermal and optical characterizations of both compounds were performed using a Perkin-Elmer DSC 7, DSC IIC apparatus and Olympus polarizing microscope BH-2 equipped with a Mettler FP 82 hot-stage. DSC measurements of the compounds were performed at various scanning rates. High-pressure DTA (HP-DTA) apparatus used in this study is described elsewhere [29,30]. The HP-DTA system was operated at a constant scanning rate of 5°C/min under hydrostatic pressures up to 300 MPa. In this study dimethylsilicone oil of medium-viscosity (100 centistokes) was used as a pressure transmitting medium. Heat of transition under pressure was estimated qualitatively by comparison with the heat of fusion (28.5 J/g) of indium as a reference. The

pressure dependence of the heat of fusion of indium [31] was neglected here because of low pressures adopted in this study. A high-pressure micro hot-stage system [32] developed by us was used with a Leitz polarized optical microscope, Orthoplan, to perform in situ observation of texture of the crystals and mesophases of both compounds under hydrostatic pressure.

3. Results and discussion

3.1. Characterization of the KI5 and KI5A compounds

Fig. 2 shows the polarized optical micrographs of the KI5 compound obtained on cooling. Cooling from the isotropic liquid of the unaligned sample resulted in the formation of an iridescent N^* phase, showing a cholesteric fan texture. Subsequent cooling produced very subtle change to the texture of the S_C^* phase at 160°C. On further cooling, the texture of the S_C^* phase disappeared spontaneously and then the dark field due to the homeotropic orientation remained until the spherulites of the C_1 crystal appeared at about 55°C. These textures are observed reversibly.

The KI5 compound shows an interesting thermal behaviour on cooling from the S_1 or S_{Ainc} phases. Fig. 3 shows the DSC curves of the KI5 compound at various cooling rates of 2, 5 and 20°C/min. The $I-N^*$

rates faster than 10°C/min (Fig. 3(III)) exhibits the typical glass transition behaviour, indicating the substantial suppression of the C_1 crystal growth. The whole system of the supercooled S_1 phase is vitrified completely at low temperatures of 0–10°C. Polarized microscopic observation of the quenched sample exhibited only a dark field with no texture. The sample showed the same WAXS pattern as one of the S_1 phase. Fig. 4 shows the corresponding heating curves of the KI5 compound at 2, 5, 20, and 40°C/min. The heating curve (Fig. 4(I)) at 2°C/min shows the simple melting curve of the C_1 crystal formed, while the heating curve (Fig. 4(III)) at 20°C/min shows clearly a glass transition at about 4°C, then followed by an endothermic peak at about 20°C. After that an exothermic peak appears at about 31°C as the cold crystallization of the C_1 crystals occurs immediately from the S_1 phase. On further heating the DSC curve shows the typical transition pattern, i.e., melting of the C_1 crystal at 82°C, multiple mesomorphic transitions of $S_1-S_{Ainc}-S_C^*-S_{Ainc}-S_C^*-TGB-N^*$ and finally the isotropization at 193°C. The rapid heating curve (Fig. 4(IV)) at 40°C/min shows the glass transition at ~8°C followed by a sharp endothermic peak (~25°C) due to the enthalpy relaxation, and the cold crystallization at 39°C, respectively. The KI5 sample quenched at 100°C/min showed a typical pattern of glass transition behaviour as is shown in Fig. 5. Whole transition scheme of the KI5 compound is summarized in the following.



transition and all the intermediate mesophase transitions are observed with the only exception of crystallization. A broad exothermic peak of crystallization ($S_1 \rightarrow C_1$ transition) is observed at about 50°C on cooling at 2°C/min (Fig. 3(I)), while the cooling curve at 5°C/min (Fig. 3(II)) exhibits a broad peak of crystallization at 39.6°C and a small glass transition at 9.5°C. It is suggested that the S_1 phase is quenched partly into the glassy phase. In this sense, the thermal behaviour of this compound is similar to one of semicrystalline polymers. The DSC curve at cooling

Table 1 compares the thermodynamic quantities accompanied with the glass transition, cold crystallization, melting and isotropization of the KI5 compound at various scanning rates.

In the case of the KI5A compound there are fewer mesomorphic phases between the normal crystal (C_1) and isotropic liquid. Fig. 6 shows the typical DSC curves of the KI5A compound at 5°C/min. The enantiotropic transition process of $C_1-S_{Ainc}-S_C^*-TGB-N^*-I$ clearly observed on the DSC curve. Crystallization of the C_1 crystal is

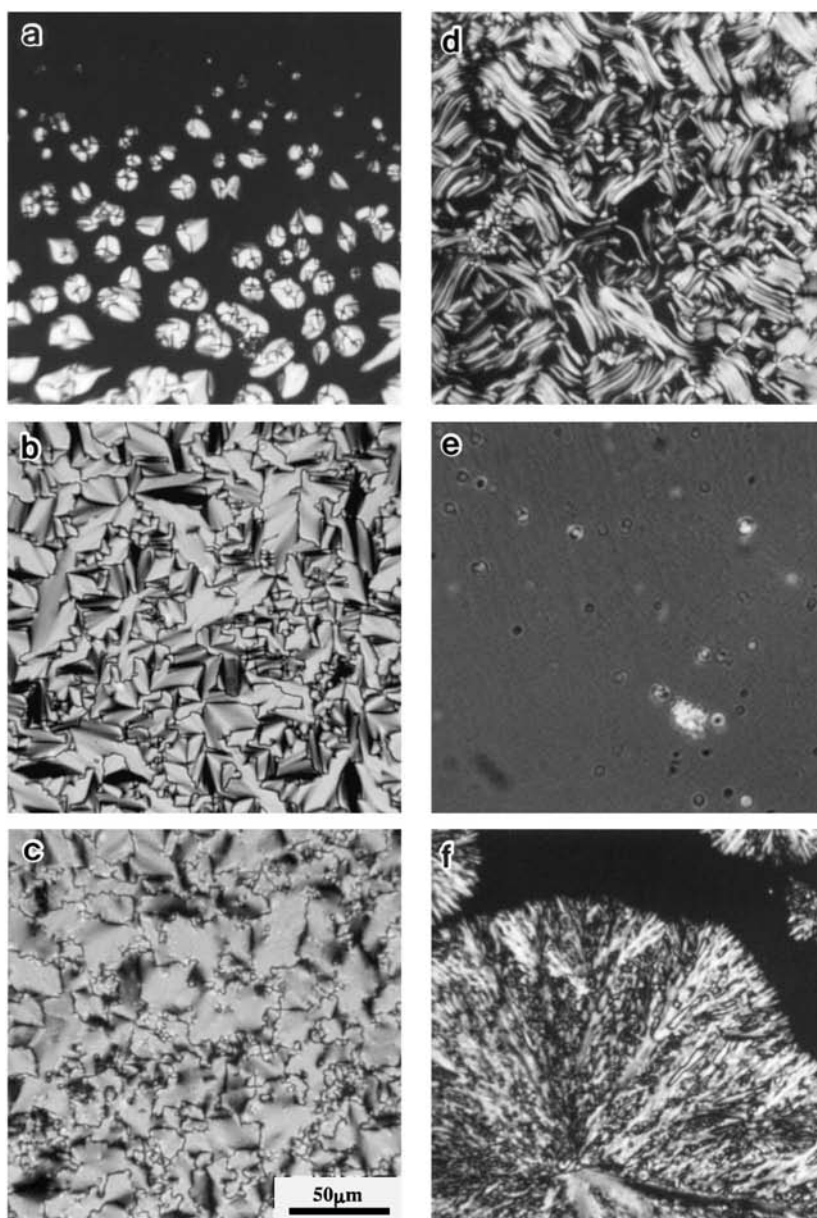


Fig. 2. Polarized micrographs of the KI5 compound on cooling: (a) I-N* transition at 188°C, (b) cholesteric fan texture of the N* phase at 186°C, (c) SC* phase at 160.5°C, (d) SC*-SA_{inc} transition at 159.6°C, (e) homeotropic phase at 60°C, and (f) spherulitic growth of the C₁ crystal at 48°C.

observed even at rapid cooling rates. Table 2 illustrates the representative data of thermodynamic quantities accompanied with the phase transitions at a heating rate of 5°C/min of the KI5 and KI5A compounds.

3.2. High-pressure DTA behaviour of the KI5 compound

Fig. 7 shows the DTA heating curves of the KI5 sample obtained by cooling from the isotropic phase

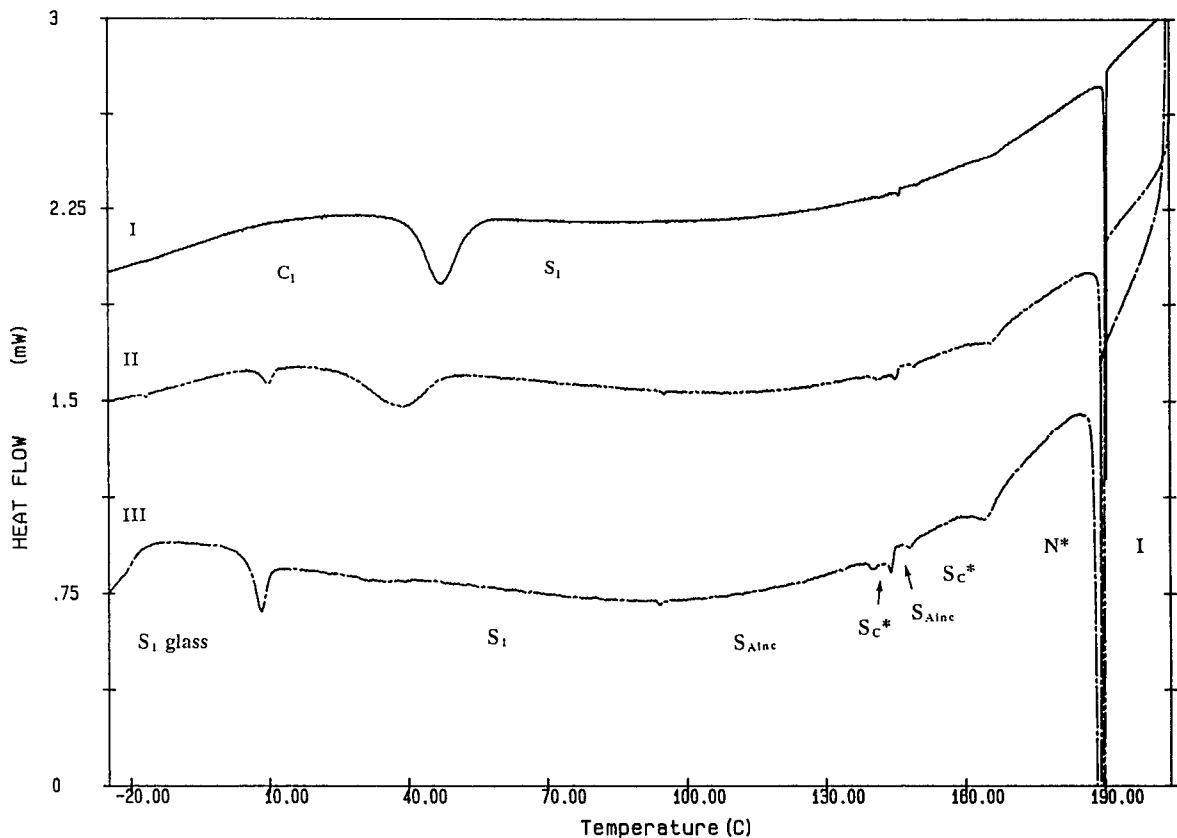


Fig. 3. DSC curves of the KI5 compound cooled at (I) 2°C/min, (II) 5°C/min, and (III) 20°C/min.

under 10, 30 and 120 MPa. One can see a small exothermic peak and a main endothermic peak at lower and intermediate temperatures, respectively. The thermal behaviour at 10 MPa is consistent with the DSC heating curve at 5°C/min in Fig. 4(II), which the two peaks correspond to the cold crystallization and the melting of the C_I crystal, respectively. It is shown that the single peak of melting at 10 MPa is splitted into double peaks at 30 MPa, and then the peak appearing at the higher temperature becomes the main peak at 120 MPa. The thermal behaviour coincides with the WAXS results obtained under pressure [15]; the pressure-induced C_{II} crystal is concurrently formed with the C_I crystal under pressures of 20–100 MPa and the former is predominant at pressures above 20 MPa. Further DTA measurements were performed to study how the C_I crystal is transformed into

the C_{II} crystal on heating. Fig. 8 illustrates the DTA runs showing the double peaks of the C_I and C_{II} crystals at 20 and 30 MPa. The DTA heating curve at 30 MPa shows an exothermic deflection at the middle temperatures between the two melting peaks, which suggests the evidence of exothermic heat due to recrystallization of the molten C_I crystal. When the heating is stopped at a temperature between the melting peaks of the C_I and C_{II} crystals and then the sample is cooled down to room temperature, the reheating curve shows only a single melting peak of the C_{II} crystal at a high temperature. This means that the C_I to C_{II} crystal transformation occurs irreversibly by annealing of the C_I crystal at moderate temperatures and pressures. The experimental results suggest that the C_I to C_{II} transformation proceeds not by a solid-state transition, but through the melting and

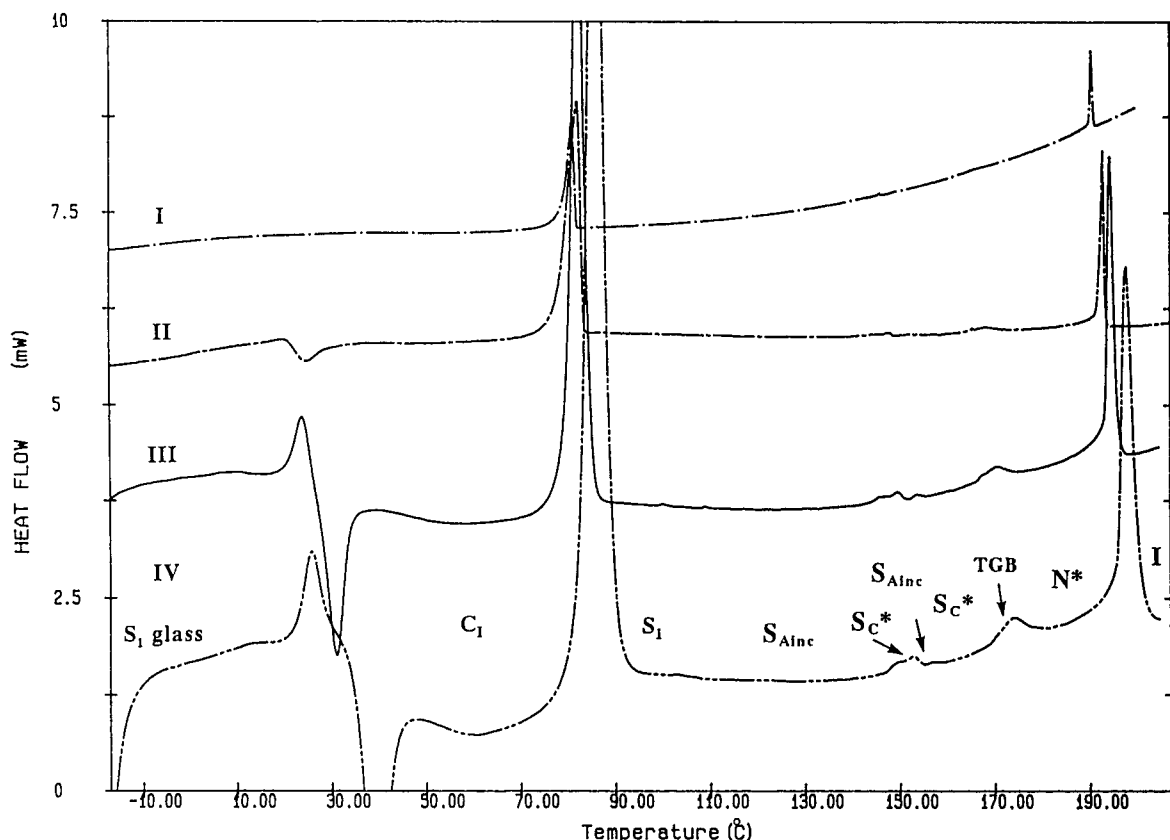


Fig. 4. DSC curves of KI5 compound heated at (I) 2°C/min, (II) 5°C/min, (III) 20°C/min, and (IV) 40°C/min.

recrystallization process. The C_{II} crystal has a higher melting temperature and it is thermally stable even at atmospheric pressure.

The heats of transition of the KI5 compound are plotted as a function of pressure in Fig. 9. The enthalpy of the C_I – S_1 transition decreases rapidly with increasing pressure and finally this disappears at pressures around 100 MPa, while the enthalpy of the C_{II} – S_1 transition appears at about 20 MPa and this reaches to a roughly constant value at high pressures above 70–80 MPa. Fig. 10 shows the DTA heating runs of the KI5 compound at higher pressures up to 300 MPa. Only the two peaks of the C_{II} – S_1 and N^* – I transitions are observed at all pressures above 100 MPa. Unfortunately the multiple mesomorphic transitions between the S_1 and N^* phases could not be detected any more because the transition enthalpies

are two or three decades smaller than those of melting and isotropization. The sensitivity of the present high-pressure DTA apparatus is too short to detect them clearly. The mesomorphic transitions of the KI5 and KI5A compounds should be analyzed by a high-precision high-pressure DTA or DSC apparatus in future. Fig. 11 displays the typical WAXS patterns of the C_I and C_{II} crystals formed at atmospheric pressure and 100 MPa, respectively. The high-pressure DTA results obtained in this study, implying the concurrent formation of the C_I crystal and pressure-induced C_{II} crystal, agree well with the observations obtained from high-pressure WAXS studies [15].

In situ observation of the formation of the C_{II} crystal under pressure was performed successfully by using the high-pressure micro hot-stage developed in our laboratory [33]. When the KI5 compound was cooled

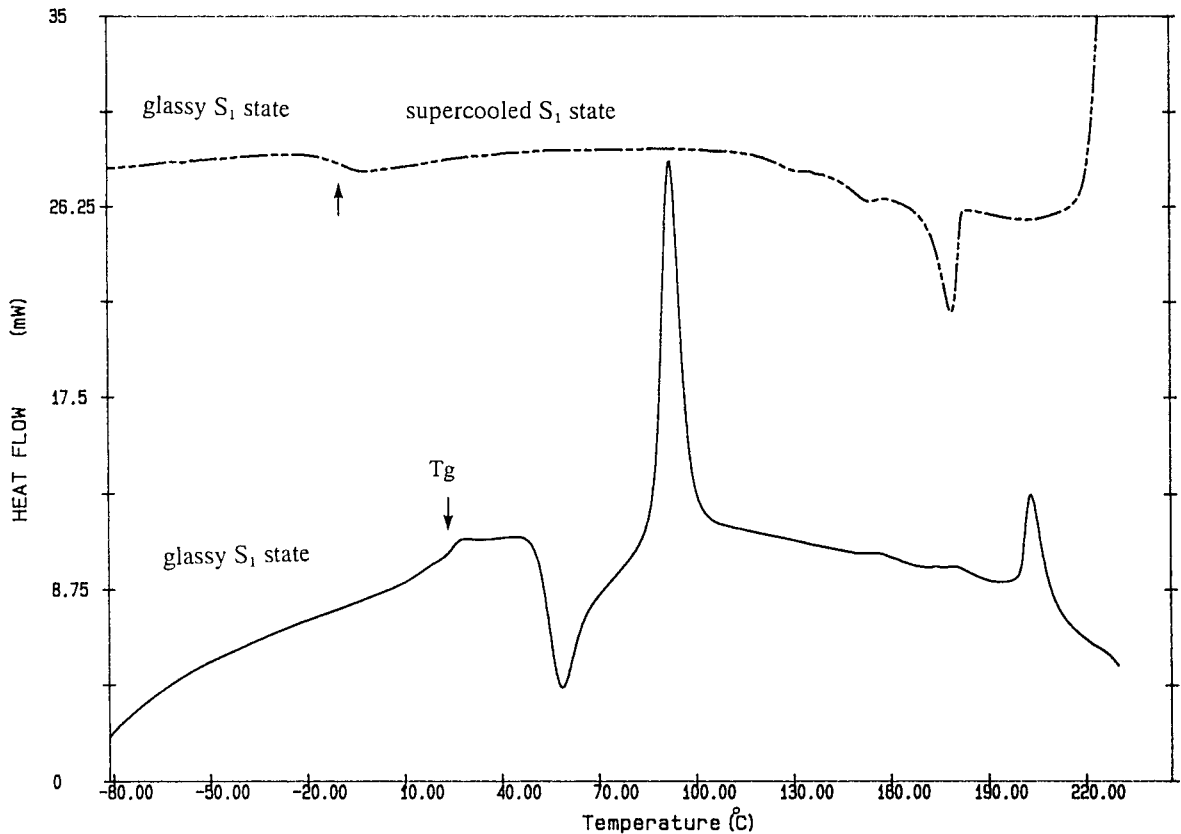


Fig. 5. DSC cooling and heating curves of the KI5 compound at 100°C/min.

from the isotropic liquid at 100 MPa, the C_{II} spherulites having the diameter of 50–100 μm were grown up. The spherulites with similar diameters were observed at 50 and 150 MPa. The C_{II} spherulites are clearly discriminated from the C_I spherulites with diameter of 200–300 μm . The morphological evidence here is in accordance with the results of the high-pressure WAXS apparatus reported earlier by us [15] and the thermal behaviour in this study.

3.3. High-pressure DTA behaviour of the KI5A compound

Fig. 12 shows the DTA heating curves of the KI5A compound observed under pressure of 10, 100, and 160 MPa. Two strong peaks of melting (C_I – S_{Ainc} transition) and isotropization (N^* – I transition) as well as a small peak at intermediate temperatures are observed at lower and higher temperatures, respec-

tively. The subtle peak at intermediate temperatures may correspond to the complex peak of two consecutive S_{C^*} – TGB and TGB – N^* transitions as is shown in Fig. 6. Also in this case the S_{Ainc} – S_{C^*} transition could not be detected due to very small enthalpy of transition. Fig. 13 shows the DTA heating curves of the C_I – S_{Ainc} transition of the KI5A compound at 150, 200, and 300 MPa. Single peak of the C_I – S_{Ainc} transition at low pressures is splitted into double or triple peaks, depending upon the applied pressure above 200 MPa. The triple endothermic peaks at 200 MPa consists of main double peaks and a small peak at a high temperature. The main double peaks are possibly due to similar behaviour to the KI5 compound under pressures above 20 MPa, i.e., the concurrent formation of the C_I crystal and a crystal polymorph (C_{II}). Another small peak at a higher temperature may be regarded as some mesophase (named as S_{hp}) transition. The triple peaks are changed again to single peak

Table 1
Thermodynamic quantities accompanied with the phase transitions of the KI5 compound

Scanning rate (°C/min)	T (°C) ($\Delta H/J\ g^{-1}$)					
	T_g	T_{cc}	T_m (C _I)	T_m (C _{II})	T_{I-N}	T_{N-I}
-2 (cooling)	—	—	47.2 (19.1)	—	190.4 (5.65)	—
+2 (heating)	—	—	—	81.1 (27.6)	—	190.5 (5.50)
-5	—	—	38.6 (5.7)	—	189.7 (5.80)	—
+5	—	24.7 (4.3)	—	82.2 (27.6)	—	192.9 (6.90)
-10	—	—	—	—	188.6 (6.23)	—
+10	—	26.6 (8.8)	—	82.6 (27.2)	—	192.8 (7.16)
-20	—	—	—	—	187.1 (6.09)	—
+20	~4	31.0 (7.9)	—	82.4 (26.1)	—	194.5 (6.66)
-40	~2	—	—	—	184.2 (6.47)	—
+40	~8	39.9 (8.5)	—	86.0 (26.3)	—	197.8 (6.50)
-100	~-10	—	—	—	178.7 (6.75)	—
+100	~17	58.6 (15.5)	—	92.2 (26.2)	—	203.3 (7.05)

^a Multiple mesomorphic transitions are omitted in this table.

Table 2
Thermodynamic quantities accompanied with the phase transitions of the KI5 and KI5A compounds

Sample	T (°C) (ΔH (J g ⁻¹))							Isotropic liquid
	Crystal	Mesophases						
KI5	C _I -S _I	S _I -S _{Ainc}	S _{Ainc} -S _{C*}	S _{C*} -S _{Ainc}	S _{Ainc} -S _{C*}	S _{C*} -TGB	TGB-N*	N*-I
	82.7 (27.6)	97.3 (0.045)	144.0 (0.49)	148.0	153.0 (0.07)	165.2 (0.90)	168.7	192.9 (7.18)
KI5A	C _I -S _{Ainc}	—	S _{Ainc} -S _{C*}	—	—	S _{C*} -TGB	TGB-N*	N*-I
	111.6 (35.8)	—	131.8 (0.24)	—	—	156.4 (1.14)	160.6	192.4 (6.34)

of the C_I-S_{Ainc} transition when pressure is decreased from 200 to 150 MPa. The thermal behaviour is reversible, depending upon the applied pressure. Single peak at 150 MPa and triple peaks at 200 MPa are

reversible. The triple peaks are observed repeatedly on heating at 250 MPa. The first peak of melting of the C_I crystal decreased with increasing pressure, while the second peak of fusion of the C_{II} crystal grew to a main

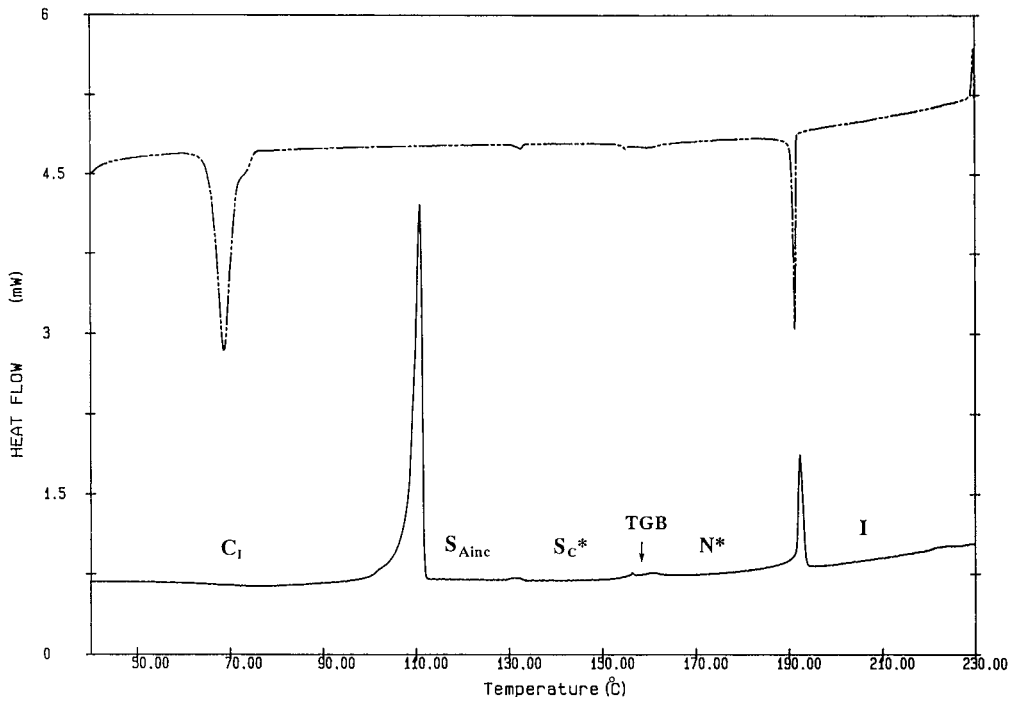


Fig. 6. DSC cooling and heating curves of the KI5A compound at 5°C/min.

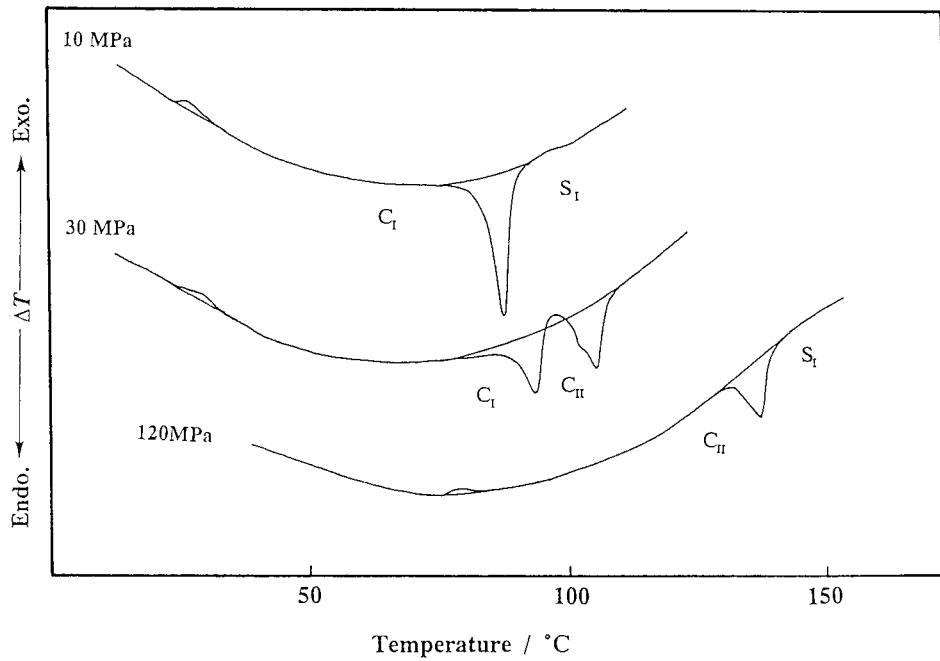


Fig. 7. DTA heating curves of the KI5 compound under pressure. Each sample was cooled from the isotropic phase at indicated pressures, respectively.

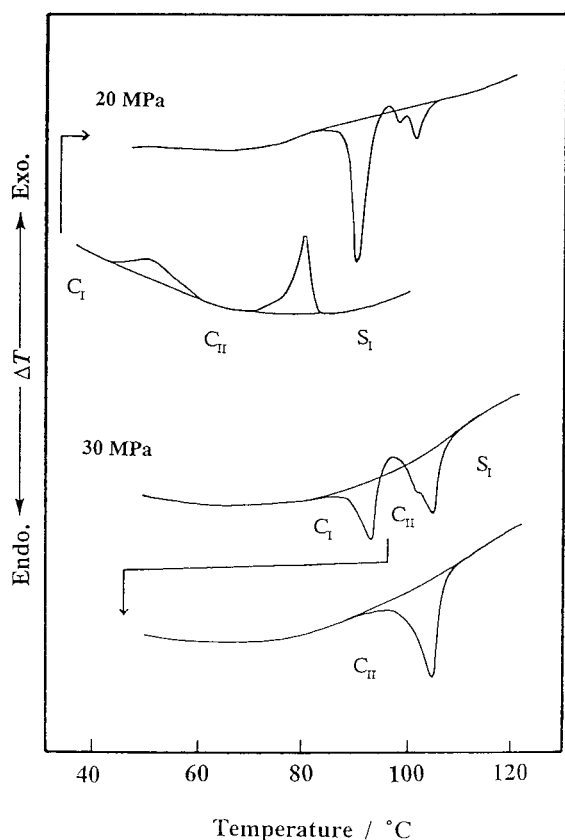


Fig. 8. DTA curves of the KI5 compound at 20 and 30 MPa.

peak. The third peak of the high-pressure mesophase S_{hp} was unchanged under high pressure. Increasing pressure at 300 MPa changed the thermal behaviour to the two peaks that are reduced to the main peak of C_{II} - S_{hp} transition (melting) and a small peak of S_{hp} - S_{Ainc} transition at a high temperature. The transition enthalpies of the C_I - S_{Ainc} , C_{II} - S_{hp} , S_{hp} - S_{Ainc} and N^* -I transitions of the KI5A compound are plotted as a function of pressure in Fig. 14. The enthalpy of C_I - S_{Ainc} transition decreases linearly with increasing pressure up to 180 MPa and then this drops rapidly. On the other hand, the heat of C_{II} - S_{hp} transition rises sharply at pressure above 200 MPa. The enthalpy of N^* -I transition is almost insensitive of pressure. The experimental results in this study indicate that both the C_{II} crystal polymorph and the pressure-induced S_{hp} mesophase appear stably under

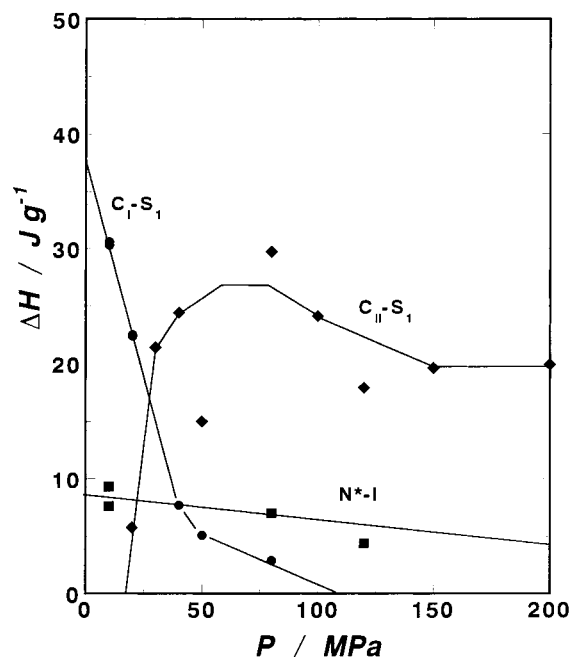


Fig. 9. Pressure dependence of the heats of transition of the C_I - S_I (●), C_{II} - S_I (◆), and the N^* -I (■) transitions.

high pressure above about 200 MPa. The structural analysis and transition mechanism of the unidentified S_{hp} mesophase is now under way by X-ray measurement with high-pressure WAXS apparatus and in-situ observation by polarized optical microscope equipped with a high-pressure micro hot-stage.

The incomplete T vs. P phase diagrams of the KI5 and KI5A compounds are plotted in Figs. 15 and 16, respectively. Although both phase diagrams lack the mesomorphic T vs. P relations, this gives us some interesting information about the concurrent formation of a pressure-induced C_{II} crystal polymorph of the KI5 and KI5A compounds at pressures above about 20 and 180 MPa, respectively, and the additional appearance of a pressure-induced smectic mesophase (S_{hp}) of the KI5A compound at pressures above 200 MPa.

4. Conclusions

The thermal behaviour of two dimesogenic liquid crystal compounds (KI5 and KI5A) has been studied

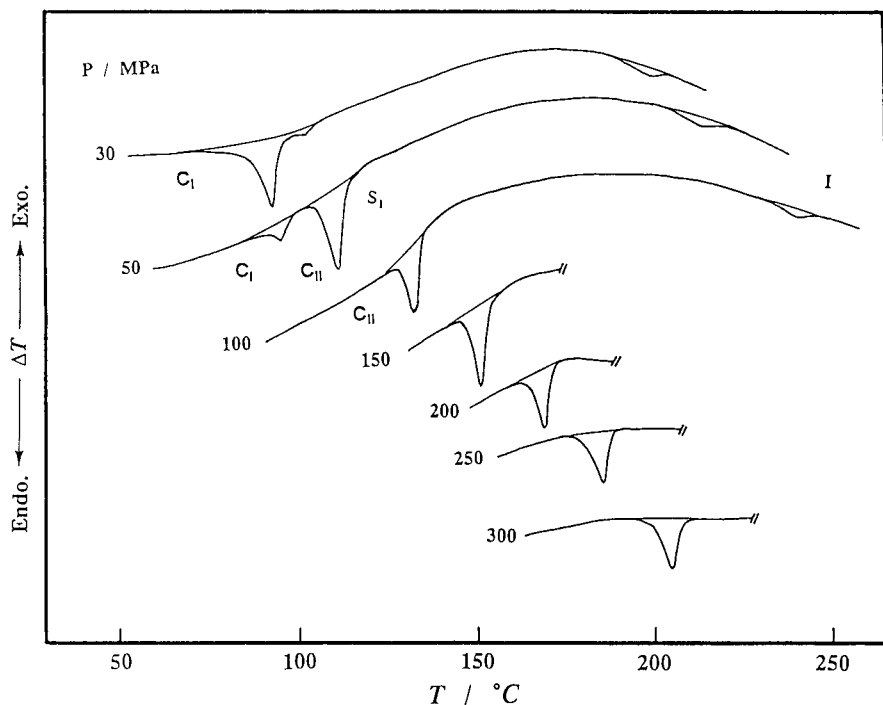


Fig. 10. DTA heating curves of the KI5 compound at indicated pressures.

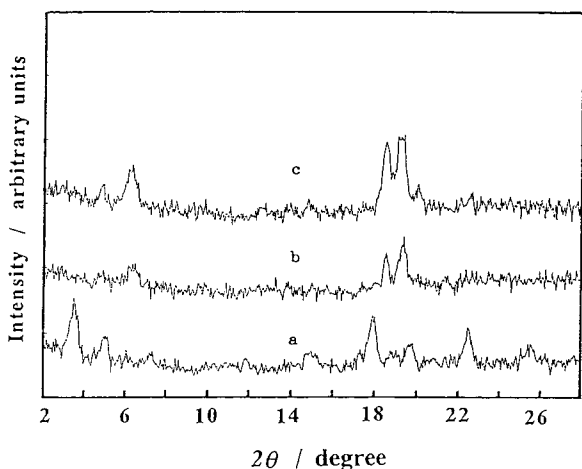


Fig. 11. WAXS patterns of the KI5 compound: (a) C_I crystal formed at atmospheric pressure; (b) C_{II} crystal (formed at 100 MPa) at 26°C and 0.1 MPa; (c) C_{II} crystal at 110°C and 100 MPa.

under hydrostatic pressures up to 300 MPa by using the high-pressure DTA apparatus. We made the in-situ observation of formation of the pressure-induced crystals (C_{II}) of both compounds under hydrostatic pressure.

The spherulites of a new crystal polymorph (C_{II}) of the KI5 compound, different from those of the normal crystal (C_I), is confirmed directly by using polarized optical microscope equipped with a high-pressure micro hot stage. The C_{II} crystals are formed concurrently with the C_I crystals at intermediate pressures between 20 and 100 MPa, and it is predominantly formed at high pressures above 100 MPa. On the other hand, the transition behaviour ($C_I - S_{Ainc} - S_C^* - TGB - N^* - I$) of the KI5A compound is stable in the pressure region between 0.1 and 160 MPa. When hydrostatic pressure between 200 and 300 MPa is applied, however, double or triple peaks are observed reversibly around the $C_I - S_{Ainc}$ transition. The thermal behaviour is due to concurrent formation of the C_I crystal and the C_{II} crystal polymorph, in

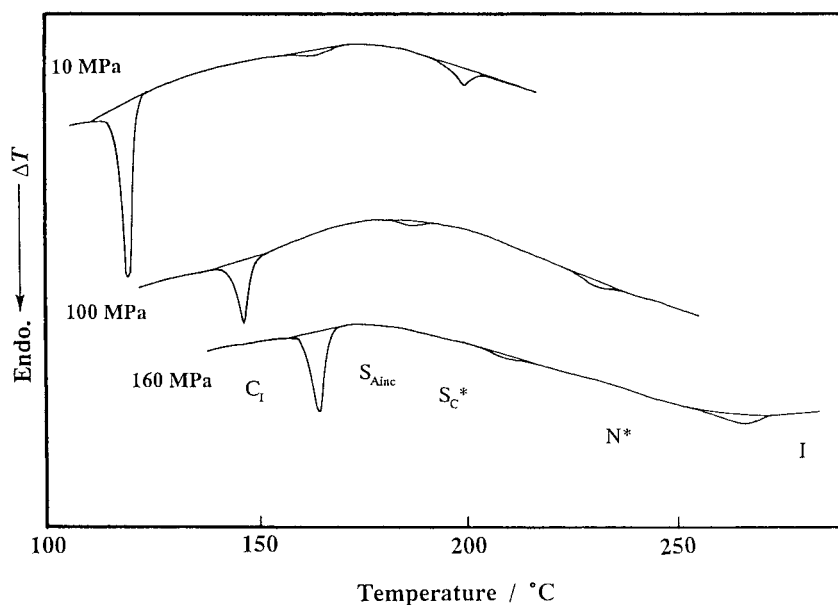


Fig. 12. DTA heating curves of the KI5A compound at 10, 100, and 160 MPa.

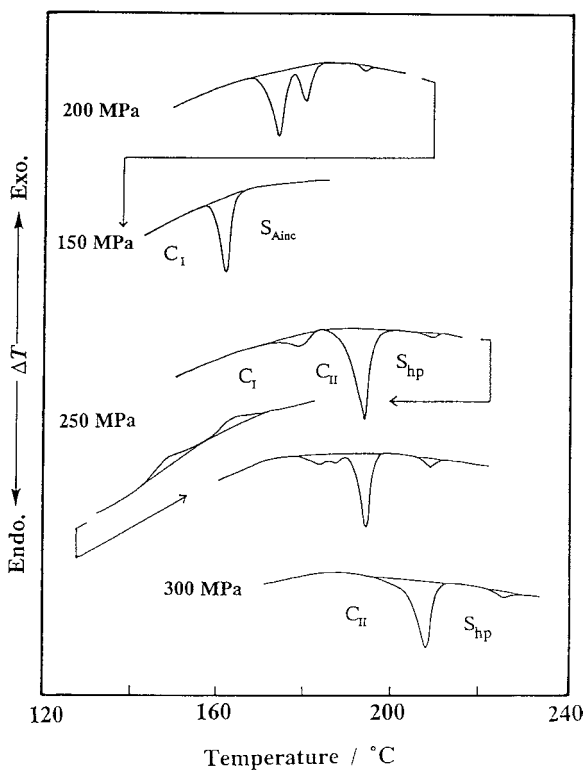


Fig. 13. Transition behaviour of the KI5A compound at 150, 200, 250, and 300 MPa.

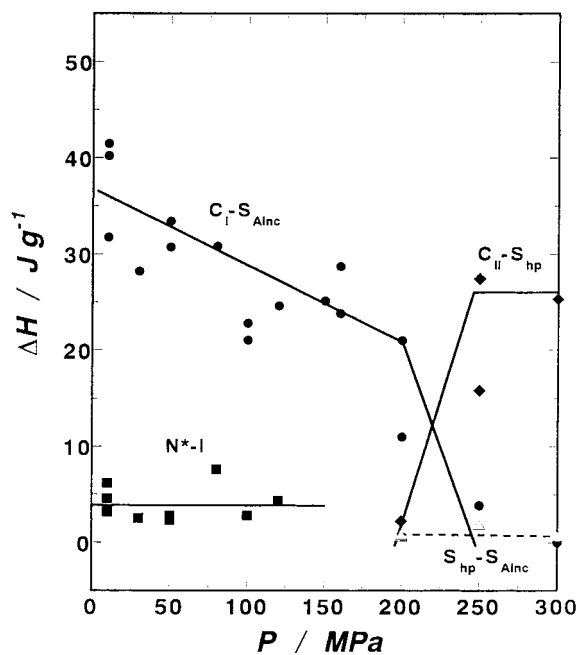


Fig. 14. Pressure dependence of the heats of transition of the C_I - S_{Ainc} (●), C_{II} - S_{hp} (◆), S_{hp} - S_{Ainc} (△), and N^*-I (■) transitions of the KI5A compound.

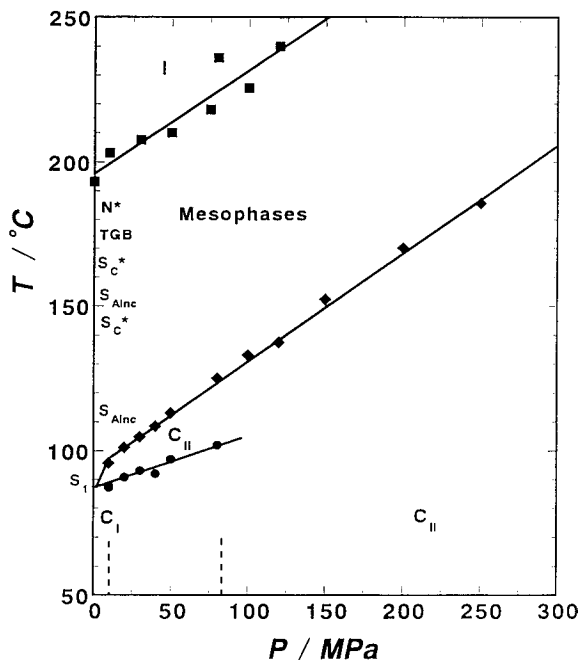


Fig. 15. T vs. P phase diagram of the KI5 compound: The dotted region indicates the region of concurrent formation of the normal crystal C_I and pressure-induced crystal polymorph C_{II} .

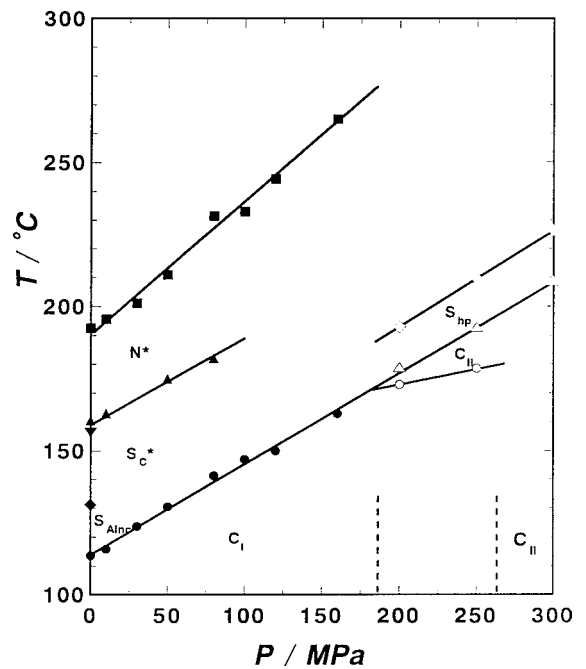


Fig. 16. T vs. P phase diagram of the KI5A compound: C_{II} ; pressure-induced crystal polymorph, S_{hp} ; high-pressure mesophase.

addition to the occurrence of a high-pressure mesophase (S_{hp}).

The incomplete T vs. P phase diagrams of the KI5 and KI5A compounds are constructed. The transition schemes of the KI5 and KI5A compounds are shown below.

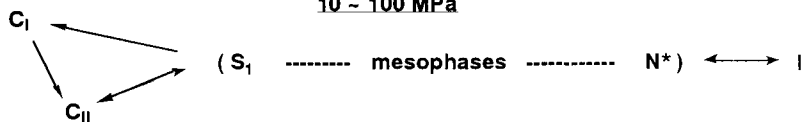
The results of this investigation provide us with several interesting new scientific insights into the phase transition of the dimesogenic liquid crystal compounds under hydrostatic pressure and at the same time, the multiple mesophasic transitions failed to be detected under pressure because of too small transition

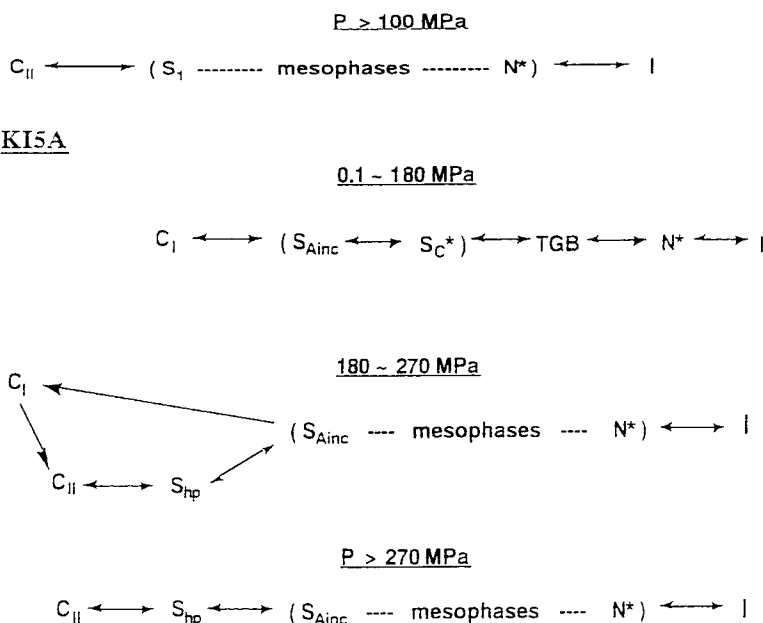
KI5

0.1 ~ 10 MPa



10 ~ 100 MPa





enthalpies. These transitions would be measured by a high precision high-pressure DTA or DSC in future.

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