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In Situ Observation of Texture of a Dimesogenic Liquid Crystal Compound under Hydrostatic Pressure

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In situ observation of microscopic texture of an unaligned sample of a dimesogenic liquid crystal compound, N-[4-(6-cholesteryloxycarbonyl)pentyl-oxy-benzylidene]-4-*n*-butylaniline, called as K15, was performed under hydrostatic pressures up to 250 MPa by a polarized optical microscope equipped with a high-pressure optical hot-stage. The spherulites of the pressure-induced crystal polymorph(C_{II}) of the K15 compound, different from those of the normal crystal (C_I), were confirmed directly at 100 MPa and higher pressures. The C_{II} spherulites were grown up from the dark field (homeotropic orientation) of the supercooled smectic phase under high pressures. This observation coincides with the experimental results by high-pressure X-ray diffraction and thermal analysis already reported. The temperature region of homeotropic orientation including partial homeotropic region decreases from ca. 70°C at 0.1 MPa to ca. 47°C at 100 MPa, and then the homeotropic state persists to higher temperatures of about 40 ± 5°C under higher pressures. The homeotropic region shifts to high temperature with the C_{II}-S_I transition line by applying pressures above 60 MPa, suggesting that homeotropic orientation of the K15 compound occurs immediately after the C_{II}-S_I transition(melting) at high pressure.

Keywords: High-pressure optical hot stage; optical texture; dimesogenic LC compound; pressure-induced crystal polymorph; homeotropic orientation

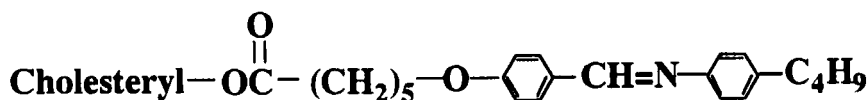
INTRODUCTION

Pressure-induced mesomorphism was found for the first time by Shashidhar, *et al.* [1,2] in 4-methoxybenzoic acid and 4-ethoxybenzoic acid.

*Corresponding author.

High-pressure investigation of the phase behavior of liquid crystals [3–13] helps us to understand the structure-property relationship of crystalline 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.

Dimesogenic liquid crystal compounds containing two different mesogenic cores, joined by a central flexible alkylene spacer show unique phase transitions because of possible formation of a wide variety of mesomorphic phases. Jin, *et al.* [14] first synthesized such a dimesogenic LC compound containing cholesteryl and smectogenic units, i.e., N-[4-(6-cholesteryloxy-carbonyl)pentyloxy-benzylidene]-4-*n*-butylaniline, called as KI5. The chemical structure of the KI5 compound is drawn below.



Hardouin, *et al.* [15,16] reported interesting results on the phase transition of this compound by polarizing optical microscopy, X-ray scattering, and differential scanning calorimetry. The KI5 compound exhibits many polymorphisms including two incommensurate smectic A (S_{Ainc}) phase as well as cholesteric (N^*) and helical smectic phases of twisted grain boundary (TGB) and chiral smectic $C(S_C^*)$ phases between the normal crystal C_1 and isotropic liquid I. We also characterized the KI5 compound by DSC. There are six endothermic peaks of the mesomorphic transitions between the strong peaks of the normal crystal (C_1)-smectic transition (melting) at 82°C and the N^* -I transition (isotropization) at about 190°C [17]. A small enantiotropic transition is found at about 98°C, in addition to the five enantiotropic transitions already characterized by Hardouin, *et al.* This transition is detected only by DSC, while any other evidence for the nature of the mesophase is not available due to its very weak transition. This suggests another smectic mesophase, named as S_1 , between the C_1 crystal and S_{Ainc} phase. So the correct transition scheme of the KI5 compound is drawn as follows:



A structural study on the phase transition of the KI5 compound under pressure was performed by using a high-pressure wide-angle X-ray

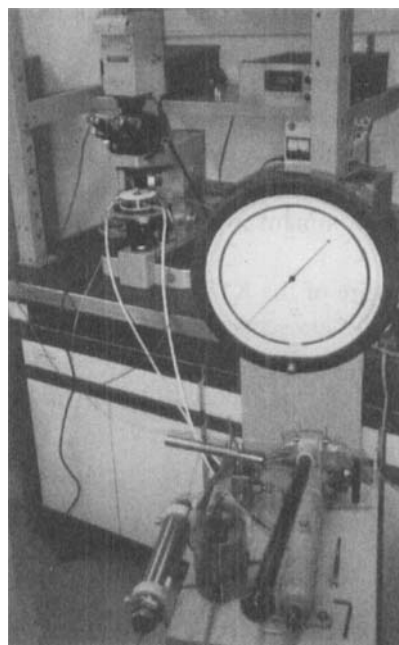
scattering (WAXS) apparatus [18,19] equipped with a curved position-sensitive proportional counter (PSPC). It was found that a crystal polymorph is formed concurrently with the C_I crystal under hydrostatic pressures above 20 MPa, and that the formation of a pressure-induced polymorph (C_{II}) is predominant with increasing pressure above about 100 MPa [17].

In this study, the texture of the KI5 compound has been investigated by using a polarized optical microscope equipped with a new system of high-pressure optical hot-stage. In addition, it would be interesting to study how the homeotropic orientation is influenced by applying pressure.

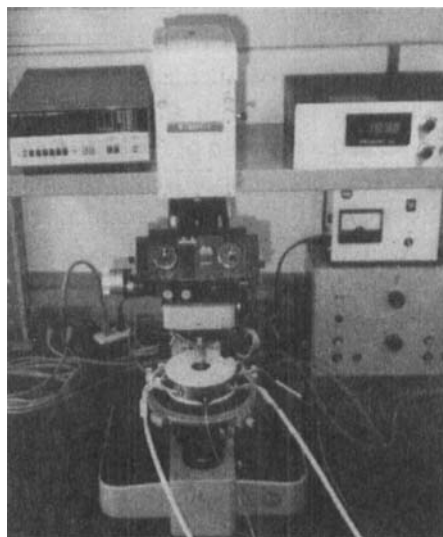
EXPERIMENTAL SECTION

A High-pressure Optical Hot-stage System

Optical characterization of the KI5 compound at atmospheric pressure was performed using a Olympus polarizing microscope BH-2 equipped with a Mettler FP 82 hot-stage. A high-pressure optical hot-stage system [20] developed by one of the authors was used by combining a Leitz polarized optical microscope Orthoplan to perform *in situ* observation of the crystalline and mesomorphic textures of the compound under hydrostatic pressure. A precise description of the high-pressure optical system is described elsewhere. Figures 1a and 1b show a total view of the high-pressure hot stage system and a close-up of the high-pressure optical cell set on the stage of the microscope, respectively. The high-pressure system consists of a manually operated oil-pump, a manganin gauge for pressure measurement, an oil reservoir, and a high-pressure optical hot-stage cell with sapphire windows. The high-pressure optical cell is the same one as that reported before, but the material of conical sleeve and O-ring for sealing of the sapphire windows was changed from phosphor bronze to copper. It was able to hold the sapphire windows for a longer service life until they are cracked. The optical cell is connected to the oil reservoir by a high-pressure capillary tube (0.020 and 1/16 in i.d. and o.d., respectively, Harwood Engineering Co.) of 1.2 m in length. So one can easily handle the optical cell on the stage of the optical microscope. Dimethylsilicone oil of low-viscosity (10 centi-stokes) was used as a pressure transmitting medium. Pressure was measured with a resolution of ± 0.1 MPa by a digital manometer via the manganin gauge. It was calibrated by an accurate broudon gauge (Heise CM, Dresser Industries, Inc.) as a secondary standard. The accuracy of the



(a)



(b)

FIGURE 1 (a) A whole view of a high-pressure optical hot-stage system combined with an optical microscope. (b) A close-up of the high-pressure optical hot-stage cell. (See Color Plate I).

manganin gauge was within ± 1 MPa. A sample film sandwiched between two slide glasses of 5 mm in width and 7 mm in length was held horizontally with a stainless steel holder in the optical cell. The texture of sample can be observed from room temperature to $250 \sim 300^\circ\text{C}$ under hydrostatic pressures up to 300 MPa.

RESULTS AND DISCUSSION

Optical Characterization of the K15 Compound at Atmospheric Pressure

Figure 2 shows the polarized optical micrographs of the unaligned sample of the K15 compound on heating at atmospheric pressure. Characteristic textures of the K15 sample are as follows: (a) spherulites of the normal crystal (C_1) at 20°C , (b) S_{Ainc} phase in a partially homeotropic state at 100°C , (c) totally homeotropic state at 155°C , (d) S_C^* phase at 162°C , (e) N^* phase at 180°C , and (f) N^* -I transition at 188°C . These are corresponded to the transition process of normal crystal (C_1)- 81.1°C - S_1 - 96.2°C - S_{Ainc} - 140.6°C - S_C^* - 146.0°C - S_{Ainc} - 149.2°C - S_C^* - 162.2°C -TGB- 165.0°C - N^* - 190.5°C -I (heating rate: $2^\circ\text{C}/\text{min}$). The C_1 crystals showed a typical spherulitic texture having diameters up to $200 \sim 300 \mu\text{m}$ at room temperature (Fig. 2a). When the sample was heated at temperatures above the C_1 - S_1 transition point, the frame of the spherulites was held even in the S_1 and S_{Ainc} phases. But the fine texture increased disorder with increasing temperature due to its fluidic movement. The texture showed a partial appearance of homeotropism in the S_1 and S_{Ainc} phases (Fig. 2b). Such texture was held at temperatures up to about 135°C just below the S_{Ainc} - S_C^* transition point. Then the texture disappeared completely in the temperature region between 135°C and 159°C , showing a dark field due to the homeotropic orientation (Fig. 2c). On further heating the sample at temperature above 160°C , the sample displayed a beautiful texture characteristic of the chiral smectic C(S_C^*) phase (Fig. 2d) and then an iridescent cholesteric fan texture (Fig. 2e) at high temperatures until the dark field by the isotropic phase appeared (Fig. 2f). In the transformation from the homeotropic region to the S_C^* schlieren phase at about 160°C , a thread-like texture developed spontaneously at the front of the S_C^* phase in a very small temperature region within $1\text{--}2$ degrees. Figure 3 shows the optical micrographs of the thread-like texture of the S_C^* phase at 160 and 161°C under atmospheric pressure. The texture changed reversibly on heating and cooling processes.

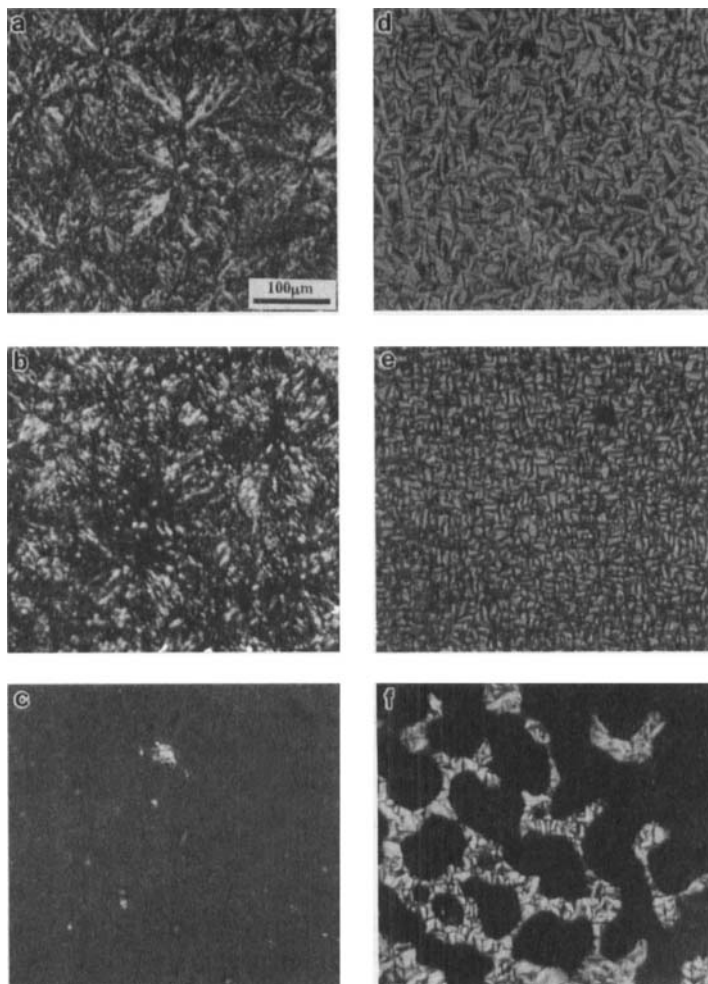


FIGURE 2 Optical micrographs of the KI5 compound on heating at atmospheric pressure: (a) spherulites of C_I crystal at 20°C; (b) S_{Ainc} phase at 100°C; (c) homeotropic texture at 155°C; (d) S_C^* phase at 162°C; (e) cholesteric fan texture at 180°C and (f) isotropization at 188°C. (See Color Plate II).

***In Situ* Observation of a Crystal Polymorph Under Pressure**

The formation of a pressure-induced crystal polymorph (C_{II}) of the KI5 compound is already exhibited by the wide-angle X-ray diffraction (WAXD) and high-pressure DTA analysis under hydrostatic pressure [17]. Figure 4 shows the WAXD patterns of the original sample (C_I crystals) on heating at

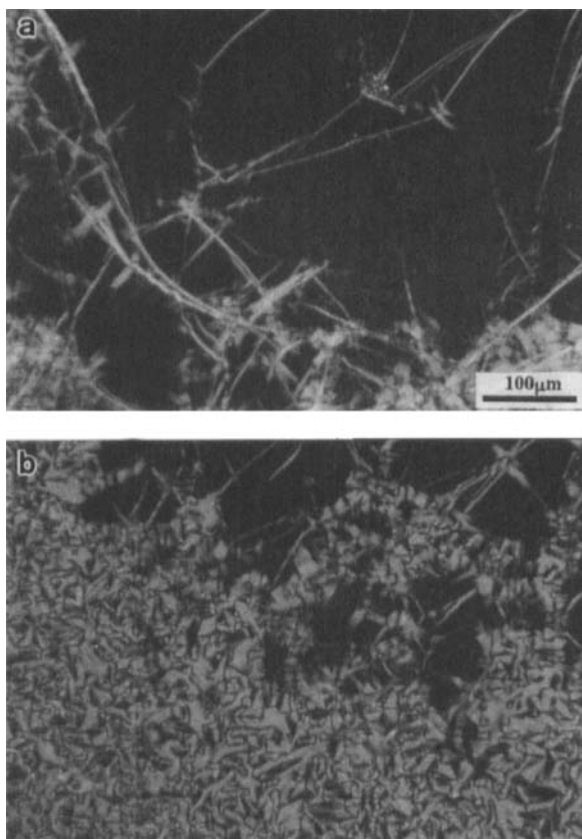


FIGURE 3 Photographs of the thread-like texture in the front of the S_C' phase appearing from the homeotropic region: (a) 160°C and (b) 161°C. (See Color Plate III).

100 MPa. The WAXD pattern of the C_I crystals (4a) clearly changed to one of the C_{II} crystals (4c, 4d) via the C_I - C_{II} crystal transition (4b) at about 95°C. On further heating, the C_{II} crystal was transformed into the S_I phase (4e) at temperatures between 120 and 130°C. The WAXD pattern of the S_I phase at 130°C exhibited two low-angle reflections at $2\theta \sim 2.2^\circ$ and 4.5° , and a broad peak at wide angles ($2\theta \sim 18^\circ$). The S_I phase is a smectic mesophase which is not assigned yet. Since the diffraction patterns of the S_I phase at 130°C and S_{Ainc} phase at 170°C are similar to each other, the structure of the S_I phase probably resembles to one of the S_{Ainc} phase at higher temperatures. The WAXD patterns at 180°C and higher temperatures showed no diffraction peak. Figure 5 shows the WAXD patterns of the K15 compound on the subsequent cooling at 100 MPa. On cooling from the S_{Ainc}

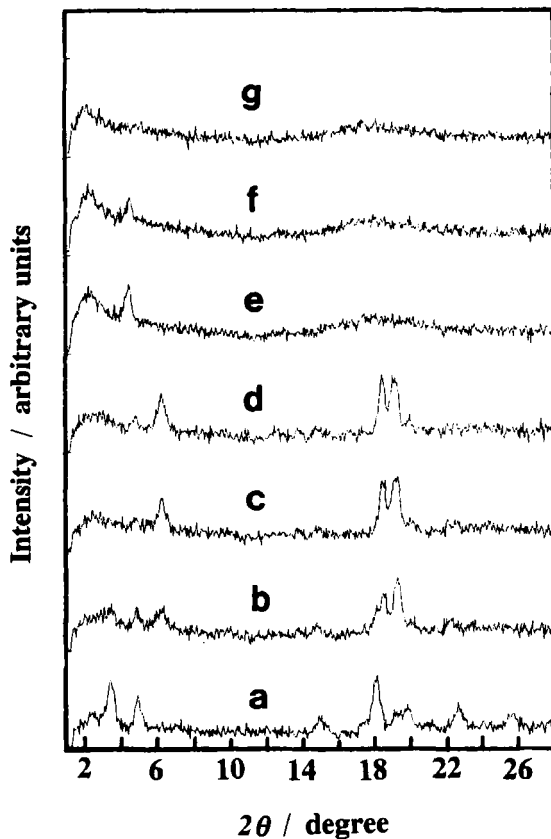


FIGURE 4 WAXD patterns of the original KI5 sample (C_I crystal) on heating at 100 MPa: (a) C_I crystal at 23°C; (b) C_I - C_{II} transition at 95°C; (c) C_{II} crystal at 100°C; (d) C_{II} crystal at 120°C; (e) S_I phase at 130°C; (f) S_{Ainc} phase at 170°C; (g) S_C^* phase at 180°C.

phase (5b, 5c) to the S_I phase (5d, 5e), the two sharp reflections were held at low angles ($2\theta \sim 2.1^\circ$ and 4.6°), while the broad peak of the S_{Ainc} phase at $2\theta \sim 18^\circ$ corresponding to an amorphous halo decreased significantly in the S_I phase. This suggests that the order in the side packing changes at the S_{Ainc} - S_I transition. When the sample was cooled to room temperature, only the WAXD pattern of the C_{II} crystal (5f) was produced at 100 MPa. The resultant C_{II} crystals were stable at room temperature under atmospheric pressure (5g). The resultant C_{II} crystal showed a melting point (C_{II} - S_I transition) higher by about 10°C than that of the C_I crystal [17]. This means that the thermodynamically stable crystal of the KI5 compound is not the C_I crystal, but the C_{II} crystal. The transition behavior corresponds quite well to

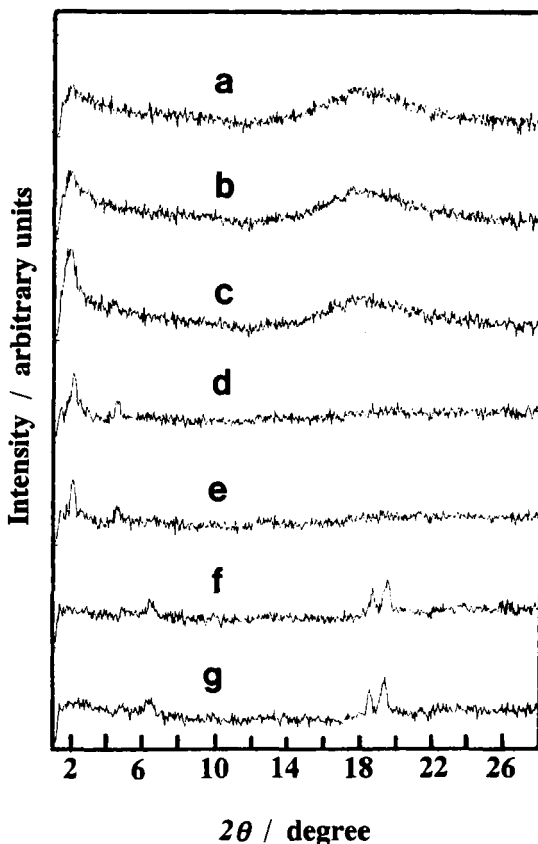


FIGURE 5 WAXD patterns of the KI5 compound on cooling at 100 MPa: (a) smectic phase at 150°C; (b) smectic phase at 140°C; (c) S_{Ainc} phase at 128°C; (d) S_I phase at 97°C; (e) S_I phase at 90°C; (f) C_{II} crystal at 70°C; (g) C_{II} crystal at 26°C and atmospheric pressure.

the data obtained by the high-pressure DTA [21]. Figure 6 shows the DTA heating curves of the C_I crystal of the KI5 compound at various pressures. The C_I crystals as starting material were prepared in the DTA cell by cooling from the melt at 1 MPa. The DTA curves manifest clearly that the single peak (6a) of melting of the C_I crystals at 10 MPa changes to double peak (6b, 6c) of both meltings of the C_I crystals and the pressure-induced crystal polymorph (C_{II} crystal) at 30 and 50 MPa. The peak area of the C_I crystals decreased with increasing pressure, while that of the C_{II} crystals substantially increased. Finally the DTA curves at 120 MPa and higher

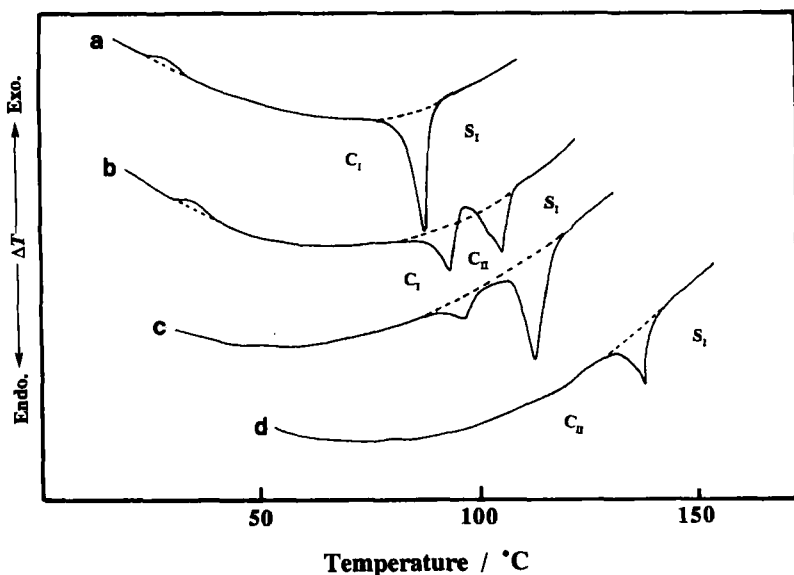


FIGURE 6 DTA melting curves of the KI5 sample (C_I crystal) at various pressures: (a) 10 MPa; (b) 30 MPa; (c) 50 MPa and (d) 120 MPa.

pressures showed only one peak (6d) of melting of the C_{II} crystals. The DTA thermal behavior agrees quite well with the structural result that the C_{II} crystals are predominantly formed at high pressures above 100 MPa.

In situ observation of the KI5 compound was performed to obtain the morphological evidence of the pressure-induced crystal (C_{II}) polymorph. The high-pressure optical hot stage system was used with a Leitz polarized optical microscope Orthoplan. Figure 7 shows optical micrographs of an unaligned sample of the original C_I crystals on heating at 100 MPa. The C_I sample sandwiched between the slide glass and a cover glass was prepared by slow cooling ($\sim 2^\circ\text{C}/\text{min}$) from the isotropic liquid at atmospheric pressure. One can see the crystalline texture of (7a) large spherulites of the C_I crystals with various diameters up to about $300\ \mu\text{m}$. The spherulitic texture was held at temperatures up to 95°C . Then the texture of the C_I spherulites were broken at 96°C and (7b) it became ambiguous at temperatures around the C_I - C_{II} crystal transition. The broken crystalline texture began to be covered gradually by the (7c) partial dark field due to the homeotropic orientation at about 125 – 127°C . The area of the dark field was enlarged with increasing temperature and then the (7d) full homeotropic orientation continued to a high temperature of about 175°C . The (7e) thread-like texture, characteristic of the front of the S_C^* phase against the

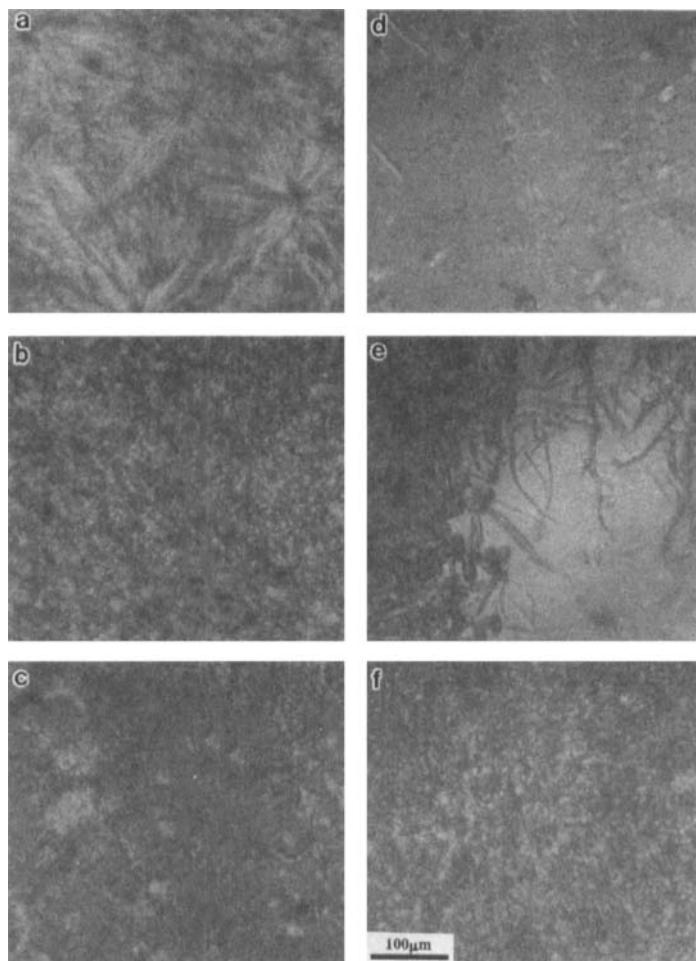


FIGURE 7 Textures of the KI5 compound on heating at 100 MPa: (a) C_1 spherulites at 27°C; (b) crystalline texture (C_{11} crystal) at 120°C; (c) partial dark field at 130°C; (d) dark field (homeotropic orientation) at 174°C; (e) thread-like texture at 176°C and (f) S_C^* phase at 180°C. (See Color Plate IV).

homeotropic state was suddenly observed at 176°C. Afterwards the (7f) smectic texture of the S_C^* phase was observed at 180°C. The S_C^* texture at 100 MPa seems to be finer than that at atmospheric pressure. Figure 8 shows optical micrographs of the KI5 compound on the subsequent cooling at 100 MPa. When the sample was cooled from the S_C^* phase at 185°C, the (8a) dark field due to the homeotropic orientation was observed in a wide temperature region between 174°C and crystallization temperature ($\sim 80^\circ\text{C}$).

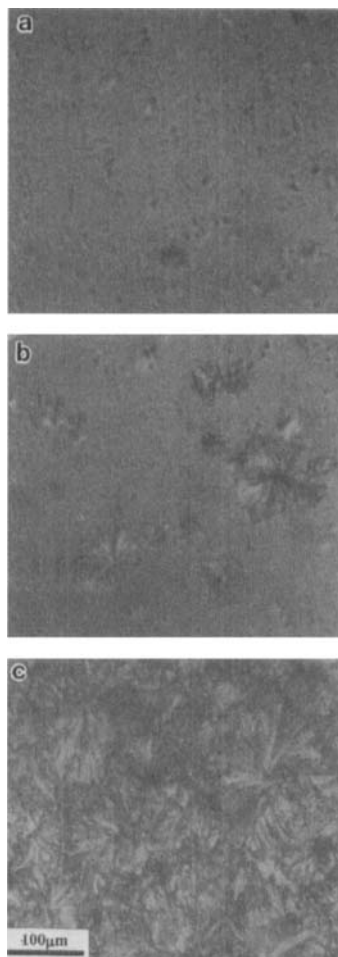


FIGURE 8 Optical micrographs of the KI5 compound on subsequent cooling at 100 MPa: (a) dark field (homeotropic orientation) at 153°C; (b) spherulitic growth of the C_{II} crystals at 74°C and (c) C_{II} spherulites at 35°C. (See Color Plate V).

The (8b) C_{II} spherulites were nucleated sporadically and they were gradually grown in the background of the dark field. Finally the (8c) C_{II} spherulitic texture was observed in the whole field at room temperature. Most of the spherulites showed the size of about 100 to 200 μm in diameter. Here it is noted that the C_{II} spherulites are smaller by 2~3 times than those of the C_I spherulites (max.~300 μm) of the crystals formed at atmospheric pressure. Such morphological differences are corresponded to the experimental results

by the high-pressure WAXD and the high-pressure DTA works reported earlier [17].

Effect of Pressure on the Homeotropic Orientation

The homeotropic orientation of the KI5 compound was observed at all pressures, and the homeotropic temperature region varied with applied pressure. At atmospheric pressure, the partial homeotropic orientation began to appear at about 90°C above the C_I - S_I transition. In the partial homeotropic state, the spherulitic texture of the S_I and S_{Ainc} phases was gradually collapsed by heating at temperatures up to 135°C. Then the dark field due to the full homeotropic orientation continued in a temperature region between 135°C and 159°C. The thread-like texture of the S_C^* phase was observed reversibly at the interface between the dark field (homeotropic orientation) and the S_C^* texture. Since the thread-like texture could be observed at high pressure, it was easy to find the highest temperature of the homeotropic region even under hydrostatic pressure. On the other hand, the partial homeotropic region could not be determined definitely at low pressures below 50 MPa because the C_I - C_{II} crystal transition occurred at pressure above 20 MPa and then the ambiguous texture of the pressure-induced crystal (C_{II}) polymorph was gradually changed into the partial homeotropic texture. Figure 9 shows the pressure dependence of the temperature region of the homeotropic orientation, shown by a stick bar on the T vs P phase diagram, of the KI5 compound. One can see that the C_{II} - S_I transition (melting) line reaches to the stick bar at 50~60 MPa because the transition line rises steeply with pressure, but the dark field due to the homeotropic orientation does not change significantly under pressures up to 50~60 MPa. So the partial homeotropic region is thought to decrease substantially with increasing pressure. Such thermal behavior of the homeotropic orientation changes at higher pressures above 60 MPa. Both the lowest and highest temperatures of the homeotropic orientation shifted linearly to high temperatures along the C_{II} - S_I transition line. The temperature width was estimated at about 70°C (including the partial homeotropic region) at 0.1 MPa, 47°C at 100 MPa, and 35°C at 250 MPa. From the experimental results, it can be stated that the temperature region of the homeotropic orientation including the partial homeotropic region decreases remarkably at low pressures below about 60 MPa, while the temperature region shifts linearly to high temperature because of increasing of the C_{II} - S_I transition point (melting point of the stable crystal) with pressure.

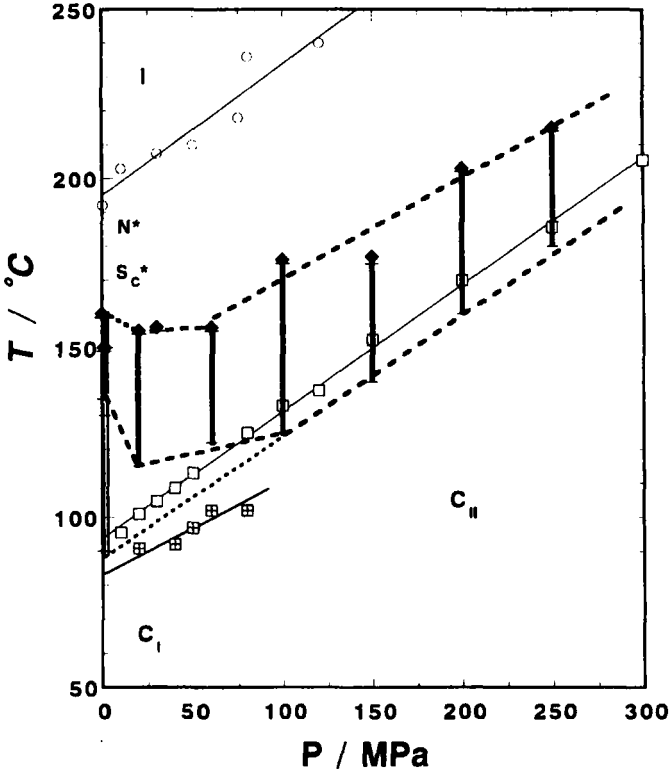


FIGURE 9 Pressure dependence of the temperature region, as shown by solid stick bar, of the homeotropic orientation of the KI5 compound. The double lines at 0.1 MPa indicate the temperature region of partial homeotropic orientation. Filled lozenge shows the temperature of the thread-like texture observed at each pressure. The T vs P phase diagram shows the (\oplus) C_I - C_{II} , (\square) C_{II} - S_I and (o) N^* - I transition lines, respectively.

The homeotropic temperature region of the KI5 compound as well as the transition scheme is shown below.

Atmospheric pressure

C_I - S_I - S_{Ainc} - S_C^* - S_{Ainc} - S_C^* -TGB- N^* - I
90-homeotropic-160

100MPa

C_{II} -(S_I -mesophases)- N^* - I
125-homeotropic-172

200MPa

$C_{II}-(S_1\text{-mesophases})-N^*-I$
160-homeotropic-195

300MPa

$C_{II}-(S_1\text{-mesophases})-N^*-I$
193-homeotropic-220

Such an observation on the temperature dependence of appearance of the homeotropic orientation has never been reported before. The results of the present investigation provide us with several new scientific insights into the structural characteristics of the C_{II} crystal phase and the homeotropic orientation of the K15 compound. First of all, although we do not have an exact structural knowledge for the C_{II} crystal phase, it appears that its structure favors the formation of the homeotropic phase. In other words, a slight structural modification of the C_{II} crystal phase can lead to the spontaneous homeotropic orientation. This conclusion is supported by the fact that the homeotropic texture starts to be observed nearly at the C_{II} - S_1 transition temperature at pressures higher than 50 Mpa as shown in Figure 9. Secondly, the nearly constant temperature range of $30 \sim 40^\circ\text{C}$ for the homeotropic orientation indicates that the counter effects by pressure and temperature in the stabilization of the homeotropic texture are about the same. Of course, any further conclusions on the aspects described above need further studies. For example, we do not yet know whether the formation of a homeotropic texture is more forward under pressure by the S_C^* phase or by the S_{Ainc} phase. Another basic question one can ask is if our present observations can be general phenomena for the LC compounds showing homeotropic textures.

Acknowledgements

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