Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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Version of record first published: 04 Oct 2006.

To cite this article: Yoji Maeda , Yong-Kuk Yun & Jung-Il Jin (1996): Effect of Pressure on Phase Behavior of a Dimesogenic Liquid Crystal Compound, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 280:1, 85-90

To link to this article: http://dx.doi.org/10.1080/10587259608040314

Mol. Cryst. Liq. Cryst., 1996, Vol. 280, pp. 85–90
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EFFECT OF PRESSURE ON PHASE BEHAVIOR OF A DIMESOGENIC LIQUID CRYSTAL COMPOUND

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Abstract Structural phase behavior of a dimesogenic liquid crystalline compound(KI5) was investigated under hydrostatic pressures by wide-angle x-ray scattering apparatus equipped with a high pressure sample vessel. An additional, enantiotropic mesopahse transition is found at all pressures. It is found that applying pressure induces the formation of a crystalline polymorph.

INTRODUCTION

Most of the low molar mass liquid crystals has been composed of two blocks of different chemical nature; in their molecules one single rigid core is covalently bonded to one or two alkyl chains in a rod-like configuration. On this concept of two distinct parts, dimesogenic liquid crystals containing two rigid cores, joined by a central flexible alkylene spacer are of much interest. Hardouin, Achard, Jin, Shin, and Yun[1,2] studied the synthesis and characterization of such liquid crystals containing cholesteryl and other mesogenic units. They reported several interesting results on the phase transition behavior of a dimesogenic liquid crystal, N-[4-(6-cholesteryloxycarbonyl) pentyloxy)-benzylidene]-4-n-butylaniline, called as KI-5, by polarizing optical microscopy, x-ray scattering, and differential scanning calorimetry. The KI-5 compound exhibits many polymorphism including two incommensurate SA(S_A^{inc}) phases as well as cholesteric and helical smectic phases(TGB and S_C^* phases) between the normal crystal C_I and isotropic liquid I. The phase assingment for the KI-5 compound is:

$$C_I \leftrightarrow S_A^{inc} \leftrightarrow S_C^* \leftrightarrow S_A^{inc} \leftrightarrow S_C^* \leftrightarrow TGB \leftrightarrow N^* \leftrightarrow I$$

It is very interesting to study the phase transition behavior of the KI-5 compound under pressures. In this study, the effect of pressure on the phase behavior of the KI-5 compound has been investigated by using a high-pressure wide-angle x-ray scattering apparatus equipped with a curved position-sensitive proportional counter(PSPC) measuring system.

EXPERIMENTAL

The synthesis and the characterization of the KI-5 compound are described elswhere[1,2]. The thermal and optical characterizations of the KI-5 compound were performed using a Perkin Elmer DSC 7 and Olympus polarizing microscope BH-2 equipped with a Mettler FP 82 hot-stage. DSC measurement of the KI-5 compound was performed at a scanning rate of 10°C/min. High-pressure wide-angle x-ray scattering(WAXS) apparatus used in this study is already described elswhere[3,4]. The WAXS system was operated at hydrostatic pressures up to 100 MPa and at temperatures up to 200°C. Dimethyl-silicone oil of low-viscosity(10 centistokes) was used as a pressure transmitting medium. A PSPC counter, having a distance of 200 mm between the sample and itself, is capable of detecting x-ray reflections up to the scattering angle of $2\theta=28°$. The beryllium spindle as sample holder is sandwiched between the upper and lower pressure blocks wound by an electric heater. The sample in the spindle is pressurized hydrostatically at any desired pressure and then x-ray scattering experiments were performed using a Ni-filtered Cu Kα x-rays of an 12 kW rotating anode x-ray generator(Rotaflex RU-200, Rigaku, Ltd.). The resolution of the PSPC probe was less than 200 μm. X-ray diffraction patterns were taken at a counting period of 200 second.

RESULTS and DISCUSSION

The DSC heating curve of the KI-5 compound in Figure 1 shows clearly two strong peaks of the crystal melting at 83°C and isotropization at about 193°C, in addition to the multiple peaks of the mesomorphic transitions between 140°C and 160 °C. In addition to the five enantiotropic transitions already identified[1], a very small transition is found at about 98°C, although the origin for this peak is not clear at present. The transition indicates clearly that an additional smectic phase exists between the normal crystal C_I and the S_A^{inc} phase. Preliminary examination of texture of the KI-5 compound was performed on cooling and heating processes by a polarizing microscope with a Mettler

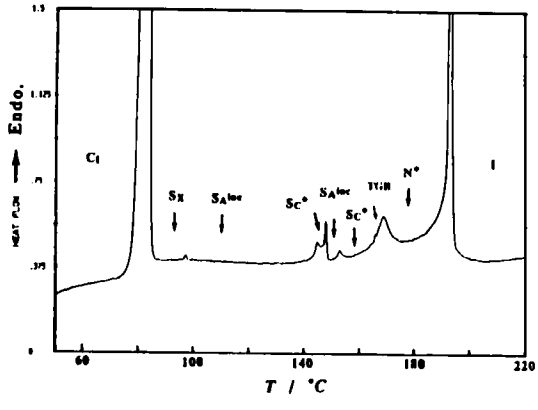

FIGURE 1 DSC heating curve of the KI-5 compound.

FP82 hot stage. Cooling from the isotropic liquid resulted in the formation of an iridescent cholesteric phase, in the form of cholesteric fan texture. Subsequent cooling produced very subtle changes in the texture until 160°C. A homeotropic texture appears spontaneously on further cooling the unaligned sample below 160°C and this texture is kept until the formation of the C_I crystal at about 50°C. The change in texture can be observed reversibly.

X-ray diffraction studies under pressures

We performed the x-ray diffraction experiment of the KI-5 compound at various pressures up to 100 MPa. Figure 2 shows the scattering profiles of the sample on heating at atmospheric pressure. The C_I crystal has several strong crystal reflections over the diffraction angle up to $2\theta=28°$. The x-ray pattern of the C_I crystal changed to the one of an unidentified smectic mesophase (S_X) at 80°C. The S_X phase shows the x-ray pattern having two reflection peaks at lower angles up to $2\theta=5°$. Although a very small enantiotropic transition occurs at about 98°C on the DSC curve, the scattering patterns of the S_X phase at 95°C and the S_A^{inc} phase at 110°C in Figure 2 are slightly different. The profile of the S_A^{inc} phase at temperatures above 110°C shows only a strong reflection peak at $2\theta=2.15°$. The profiles at higher temperatures above 140°C show only a diffuse pattern. Subsequent cooling from 200°C shows the reversible change of the x-ray pattern and the characteristic peak of the S_A^{inc} phase is observed at temperatures as low as 50°C. The typical pattern of the C_I crystal can be seen at room temperature. The d spacings of the diffraction peaks larger than 1.0 nm are plotted against temperature in Figure 3. Applying pressure on

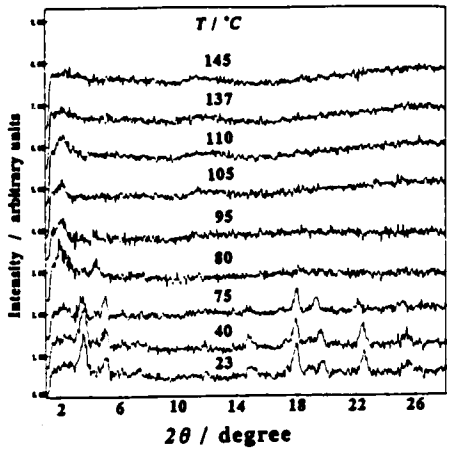

FIGURE 2 WAXS patterns of the KI-5 sample on heating at 0.1 MPa.

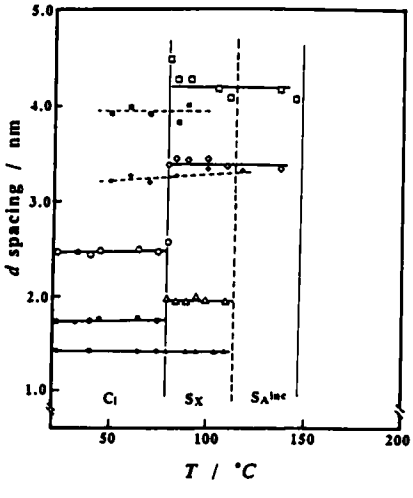

FIGURE 3 Relation of d spacing to T of the KI-5 sample at 0.1 MPa: open and filled symbols are the data on heating and cooling processes, respectively.

the KI-5 compound induces a drastic change in the thermal and structural behavior during the phase transition. The measurements of the x-ray diffraction patterns at 20 and 40 MPa suggest an appearance of a new crystalline phase between the C_I crystal and the S_X phase. The WAXS profile of the KI-5 sample at 100°C and 40 MPa is different from those of the C_I crystal and Sx phase, indicating the formation of a crystal polymorph (C_{II} crystal). On cooling, however, the typical pattern of the C_I crystal is observed at 23°C. Further increasing pressure makes clear the formation of the C_{II} crystal. Figure 4 shows the WAXS patterns of the KI-5 sample on cooling at 80 MPa. The diffraction patterns at relatively low temperatures show an ambigous pattern suggesting a low crystalline solid, but we can see clearly a different crystalline pattern if the applied pressure is released to atmospheric pressure. The WAXS pattern at 30°C and 0.1 MPa shows a profile of crystalline solid with several specific reflections in addition to the typical reflections from the C_I crystal. This suggests strongly the concurrent formation of the C_{II} crystals with the C_I crystal. The double endothermic peaks of the resultant samples in Figure 5 supports the concurrent formation of the C_I and C_{II} crystals. Figure 6 shows the WAXS patterns on subsequent cooling process at 100 MPa. The WAXS patterns on cooling show clearly the structural evidence of the predominant formation of the C_{II} crystal via the S_X phase. Figure 7 shows the temperature dependence of the *d* spacing estimated from the reflection peaks of the KI-5 compound on heating and subsequent cooling at 100 MPa. The relation of *d* spacing to temperature exhibits clearly the specific trend of the characteristic reflections of the C_I, C_{II} crystals, S_X, and S_A^{inc} phases. Both crystals do not have the long periodicity corresponding

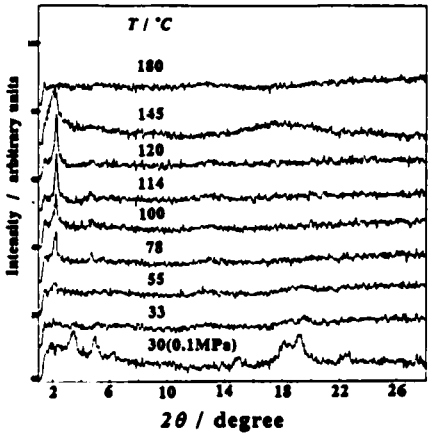

FIGURE 4 WAXS patterns of the KI-5 sample on cooling at 80 MPa.

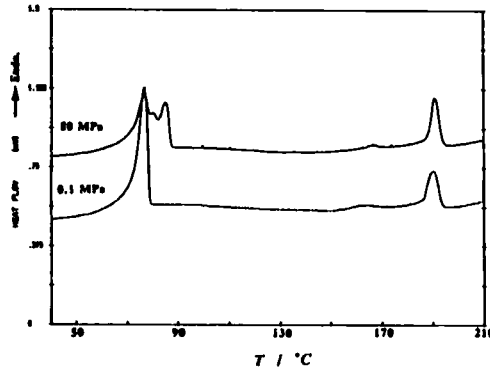

FIGURE 5 DSC heating curves of the samples cooled at 80 MPa and 0.1 MPa.

to the extended chain conformation of the KI-5 molecule. In the S_X phase, two low-angle reflections corresponding to the *d* spacing of about 3.0 and 4.0 nm appear. It is interesting to note that the longest *d* spacing of about 4.0 nm increases gradually with increasing temperature in the Sx phase. The WAXS pattern at 180°C shows the characteristic pattern of the S_A^{inc} phase having a strong reflection at $2\theta=2.1°$ and broad scattering around $2\theta=17°$, while the WAXS pattern at 200°C shows only a diffuse diffraction pattern. On cooling from 200°C, the enantiotropic transition of the mesophases can be observed, except that the C_{II} crystals are formed predominantly at 100 MPa. The C_{II} crystal shows an entirely different pattern from the one of the C_I crystals. From this series of WAXS experiments at various pressures, the phase behavior of the KI-5 compound is summarized as follows. The formation of the C_{II} crystals from the S_X phase is strengthened kinetically with increasing pressure and the C_{II} crystals are formed predominantly at 100 MPa or higher pressures. The S_X mesophase can be discriminated from the C_{II} crystal and also from the S_A^{inc} phase at high pressure because the stable region of the S_X phase is enlarged with increasing pressure. Figure 8 shows the *T vs P* phase diagram of the KI-5 compound obtained by high-pressure WAXS method. It is important to note in Figure 8 that the S_X phase found by the high-pressure WAXS is the same phase as the one observed by DSC at atmospheric pressure. From the experimental facts

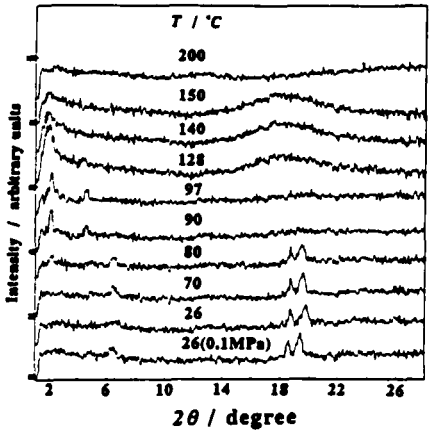

FIGURE 6 WAXS patterns of the KI-5 sample on cooling at 100 MPa.

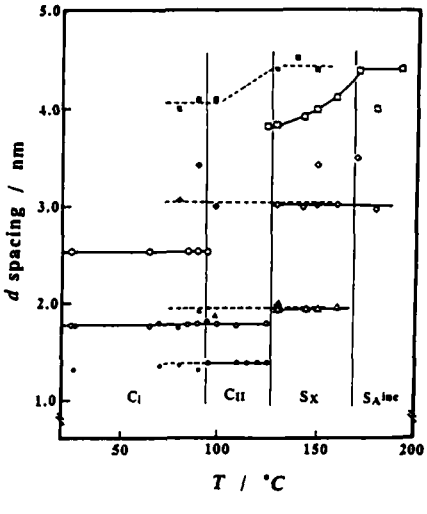

FIGURE 7 Relation of *d* spacing to *T* of the KI-5 sample at 100 MPa: open and filled symbols are the data on heating and cooling processes, respectively.

obtained in this study, the Sx phase might be deduced to be an additional smectic C* phase because the the longest *d* spacing is short of the extended-chain length, 4.6 nm, of the molecular model for the KI-5 compound[1]. A complete description of the Sc* phase would need precise x-ray diffraction studies on aligned samples. In summary, we can modify partly the Hardouin et al's assingment[1] of the phase behavior for the KI-5 compound and propose the formation of a new crystalline polymorph at high pressure :

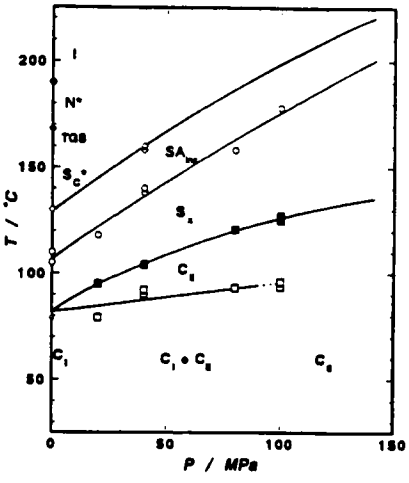

FIGURE 8 *T vs. P* phase diagram of the KI-5 sample.

0.1 MPa

$$C_I \leftrightarrow S_C^* \leftrightarrow S_A^{inc} \leftrightarrow S_C^* \leftrightarrow S_A^{inc} \leftrightarrow S_C^* \leftrightarrow TGB \leftrightarrow N^* \leftrightarrow I$$

P > 100 MPa

$$C_{II} \leftrightarrow S_C^* \leftrightarrow S_A^{inc} \leftrightarrow S_C^* \leftrightarrow \text{possibly the same process} \leftrightarrow N^* \leftrightarrow I$$

Acknowledgement: J.-I. Jin would like to express his thanks to the Ministry of Education, the Republic of Korea, for the support of this research in the fiscal year of 1995(BSRI-95-3406) through the Basic Science Research Institute of Korea University.

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