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Yoji Maeda^a, D. S. Shankar Rao^b, S. Krishna Prasad^b, S. Chandrasekhar^b & Sandeep Kumar^b

^a Nanotechnology Research Institute, National Institute of Industrial Science and Technology, Ibaraki, Tsukuba, 305-8565, Japan

^b Centre for Liquid Crystal Research, Jalahalli, Bangalore, 560 013, India

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PHASE BEHAVIOUR OF THE DISCOTIC MESOGEN 2,3,6,7,10,11-HEXAHEXYL THIOTRIPHENYLENE (HHTT) UNDER PRESSURE

Yoji Maeda*

Nanotechnology Research Institute, National Institute
of Industrial Science and Technology, Tsukuba,
Ibaraki 305-8565, Japan

D. S. Shankar Rao, S. Krishna Prasad, S. Chandrasekhar, and
Sandeep Kumar

Centre for Liquid Crystal Research, Jalahalli,
Bangalore 560 013, India

The phase behaviour of the discotic mesogen 2,3,6,7,10,11-hexahexylthiotriphenylene (HHTT) was investigated under hydrostatic pressures up to 300 MPa using wide-angle X-ray diffraction equipped with a high-pressure vessel. The reversible transitions of HHTT, i.e., crystal (Cr) – helical phase (H) – hexagonal columnar phase (Col_h) – isotropic liquid (I), were observed under pressures up to about 30 MPa. The transition sequence changed significantly depending on the applied pressure. The H phase appeared monotropically in the pressure region between 50 and 180 MPa, indicating the Cr → Col_h → I on heating and I → Col_h → H → Cr transition sequences on cooling. Applying higher pressures altered further the phase behaviour: the enantiotropic Col_h phase changed to monotropic one under high pressures above 180 MPa, indicating the Cr → I on heating and I → Col_h → Cr transition sequences on cooling. The X-ray diffraction pattern of the H phase exhibited a sharp low-angle and a wide-angle reflections corresponding to the intercolumnar and the core-core distances, respectively. This feature is indicative of the three-dimensional ordering present in the H phase. On the other hand, the Col_h phase showed only a low-angle reflection. It was found that the intercolumnar distance in the Col_h phase decreases with increasing temperature at high pressures. This indicates that the negative coefficient of thermal expansion for the column packing in the Col_h phase is held under pressure.

Keywords: HHTT; high-pressure WAXD; *P* vs. *T* phase diagram; helical phase; columnar hexagonal phase; monotropic transitions; triple points

*Corresponding author. E-mail: yoji.maeda@aist.go.jp

INTRODUCTION

Discotic liquid crystals are composed of disk-shaped molecules with rigid central cores and 6–8 flexible hydrocarbon chain tails. They form columnar mesophases which are classified according to the symmetry of the columns and the nature of the intracolumn order. In the commonly observed hexagonal columnar (Dhd or Col_h) phase, the disks stack one on top of another to form columns and the columns in turn organize to a two-dimensional hexagonal lattice. The hexagonal columnar phases consist of triangular arrays of columns with fluid-like intracolumn order. In 1984, a transition between the commonly observed Col_h phase and a phase containing highly ordered columns was observed in 2,3,6,7,10,11-hexahexylthiotriphenylene (HHTT): that is the Dhd–hexagonal ordered one (Dho) [1]. X-ray studies using freely suspended strands revealed that in the Dho phase there is a helicoidal stacking of the triphenylene cores within each column, helical spacing being incommensurate with the intermolecular spacing [2]. In addition, a three-column superlattice develops as a result of the frustration imposed by molecular interdigitation in a triangular symmetry. This helical phase of HHTT is also referred to as the H phase. An unusual feature in the Col_h phase of HHTT is noteworthy: the hexagonal lattice exhibits a negative coefficient of thermal expansion [2]. This is attributed to the stiffening of the hydrocarbon chain tails, which therefore become longer with decreasing temperature and may provide the driving mechanism for the Col_h–H transition by enhanced intercolumn coupling [2].

The novel structure and properties of HHTT have stimulated us to investigate the transitional behaviour of HHTT under elevated pressures, particularly to study the effect of pressure on the phase stability and structure of the H and Col_h phases. The authors reported the thermal behaviour of HHTT and the resultant *T* vs. *P* phase diagrams using high-pressure DTA [3]. In this paper we report the structural behaviour of the discotic mesogen HHTT under hydrostatic pressures up to 300 MPa using a WAXD apparatus equipped with a high-pressure vessel.

EXPERIMENTAL

HHTT was prepared using a modification of previously reported methods [1,4]. Optical characterization of the sample was performed under atmospheric pressure using a Leitz Orthoplan polarizing optical microscope equipped with a Mettler FP82 hot-stage. Thermal characterization was done using a Perkin-Elmer DSC 7 differential scanning calorimeter with a scanning rate of 5°C min⁻¹.

The wide-angle X-ray diffraction (WAXD) apparatus (Rotaflex RU-200, Rigaku Co.) equipped with a high-pressure system used in this study is described elsewhere [5]. The high-pressure vessel set on the wide-angle goniometer consists of a beryllium (Be) spindle as the sample cell and a couple of heater blocks for heating it up. Dimethylsilicone oil of low viscosity (10 cSt) was used as a pressure medium. Sample was inserted into the vertical hole of the Be spindle. The Be spindle was compressed between the upper and lower blocks for mechanical sealing and then the sample was pressurized hydrostatically to a predetermined pressure up to 300 MPa. Ni-filtered Cu K α X-ray was used to irradiate the sample and the X-ray diffractions were detected on the equatorial line using a curved position sensitive proportional counter (PSPC) (PSPC-30, Rigaku Co.). Each diffraction pattern was collected in a period of time for about 200–300 s.

RESULTS AND DISCUSSION

Figure 1 shows the POM photographs of texture of HHTT on cooling from the isotropic liquid at 95°C under atmospheric pressure. In the initial stage of the I \rightarrow Col_h transition, a rocky texture, Figure 1b, appeared at 92.5°C from the dark field, Figure 1a, of the isotropic liquid at 93°C. Then the mosaic texture in (Figure 1c) grew at 90°C, which is the typical texture for the Col_h phase. On further cooling, the texture such as stacks of plates or sheets was seen in the H phase. When the H \rightarrow Cr transition occurred at about 40°C, the plate-like texture began to be covered with the dendritic textures of the crystals, (Figure 1d). The texture at 30°C shows the frozen state of the plate-like mosaic texture covered with the dendritic one, (Figure 1e). Figure 2 shows the typical textures of the H and Col_h phases on the cooling process under atmospheric pressure. The Col_h phase at 90°C, (Figure 2o), shows a mosaic texture in which radial growth was seen in the field. The mosaic texture was broken into several plates during the Col_h–H transition, as shown in Figure 2p. Then the mosaic texture such as many stacks of plates was seen in the H phase at 50°C, (Figure 2q). The morphological textures in HHTT changed clearly, corresponding well to the phase transitions [3]. The DSC curve shows three distinct peaks at 65.0°C (29.3 kJ mol⁻¹), 73.5°C (15.2 kJ mol⁻¹) and 93.2°C (8.9 kJ mol⁻¹) on heating, associated with the Cr–H, H–Col_h and Col_h–I transitions, respectively. The Cr–H–Col_h–I transition is reversible at atmospheric pressure and all of the transitions are first-order.

The authors reported the effect of pressure on the thermal behaviour of HHTT in the pressure region up to 500 MPa, using high pressure DTA measurements [3]. In this study, the structural behaviour of HHTT was investigated using WAXD equipped with a high-pressure sample cell, to

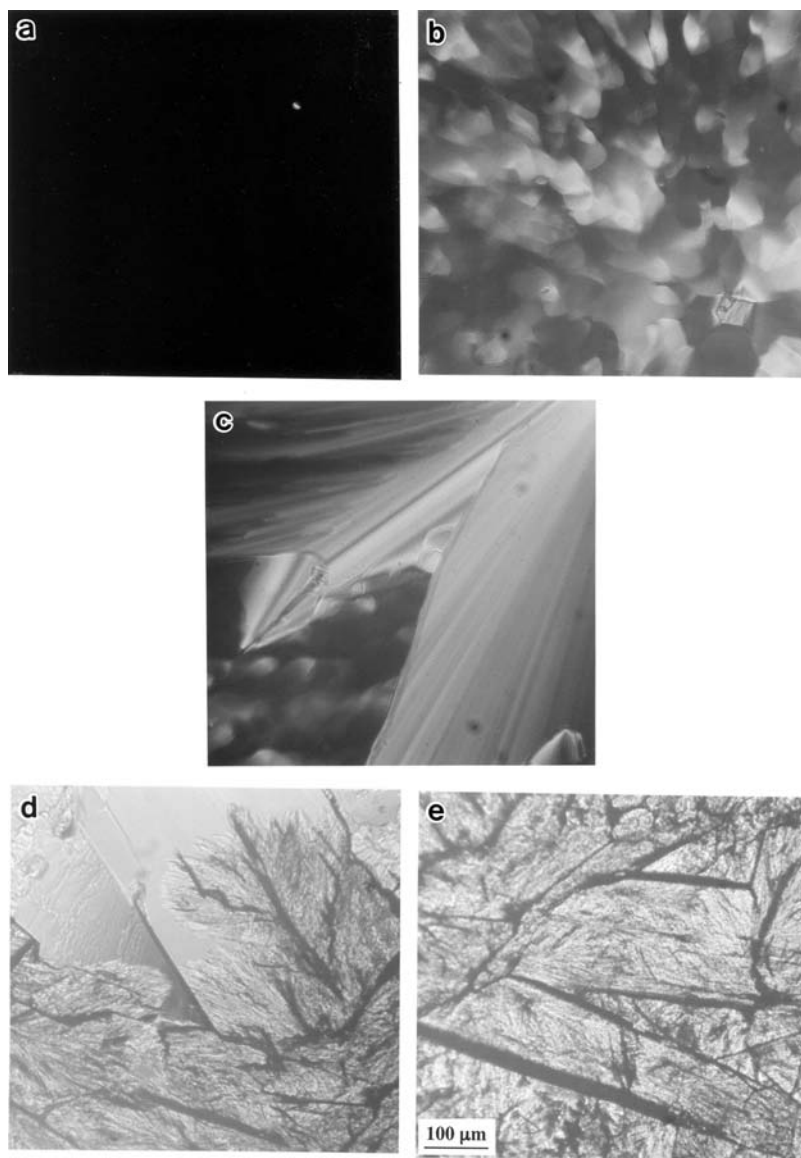


FIGURE 1 Polarizing optical microscopic (POM) photographs of the texture of HHTT observed on cooling from the isotropic liquid at 95°C under atmospheric pressure: (a) black field of isotropic liquid at 93°C, (b) rocky texture observed at 92.5°C, (c) mosaic texture for the Col_h phase at 90°C, (d) the mosaic texture partly covered with the Cr dendritic texture at 40°C, and (e) dendritic texture of the Cr phase at 30°C. (See Color Plates IX, X, XI, XII & XIII).

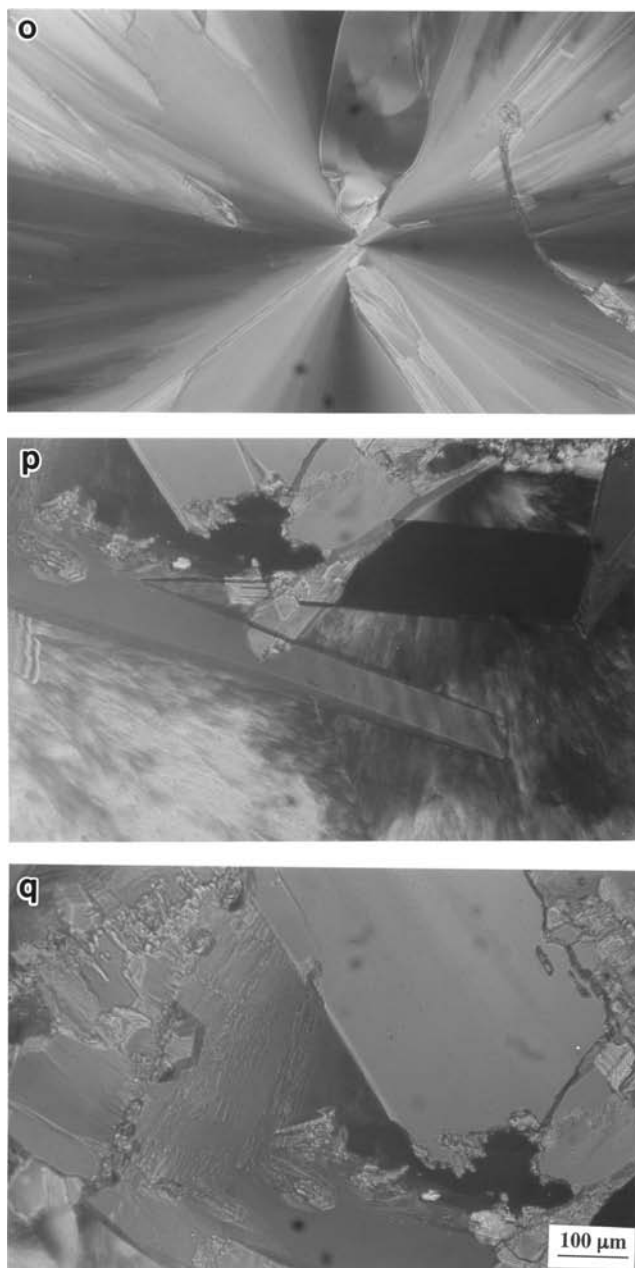


FIGURE 2 POM photographs of the textures of HHTT on cooling: (o) Col_h phase at 90°C, (p) a texture during the Col_h -H transition at 65°C, and (q) the H phase at 50°C. (See Color Plates XIV, XV & XVI).

correlate with the transition behaviour reported already. Figure 3 shows the structural change of the HHTT crystals on heating under atmospheric pressure. The X-ray pattern of the crystals showed a strong reflection at $2\theta = 4.21^\circ$ ($d = 20.95\text{\AA}$) and several weak reflections at wide-angles. On the heating process the X-ray pattern of the crystals was unchanged at temperatures up to about 65°C , above which the diffraction pattern was simplified into a strong low-angle reflection at $2\theta = 4.3^\circ$ and two wide-angle peaks at $2\theta = 19.6^\circ$ ($d = 4.5\text{\AA}$) and 24.4° ($d = 3.6\text{\AA}$) when the $\text{Cr} \rightarrow \text{H}$ transition occurred at about 65°C . The X-ray pattern in the H phase exhibited both the d spacings corresponding to the intercolumnar and the

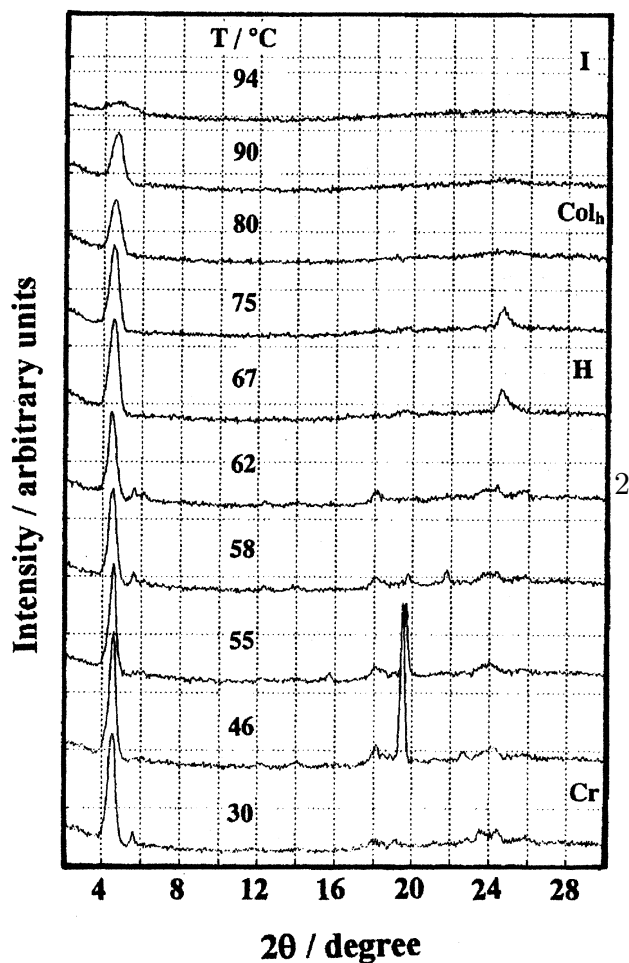


FIGURE 3 X-ray diffraction patterns of HHTT on heating at atmospheric pressure.

core-core distances. The latter feature is indicative of the three-dimensional ordering present in the H phase. The H phase existed in a relatively small temperature region of about 8°C. When the H→Col_h transition occurred at about 74°C, the wide-angle reflections disappeared apparently, while the low-angle reflection still existed. This means the substantially disordered column packing of the Col_h phase in which the order is liquid-like. The peak of the low-angle reflection decreased gradually in intensity. Figure 4 shows the temperature dependence of the d spacing associated with the diffraction peaks of HHTT on heating and cooling processes under atmospheric pressure. It was confirmed that in the Col_h phase the inter-columnar distance decreases reversibly with increasing temperature [2]: the d spacing of 19.7 Å at 70°C changed reversibly to 19.0 Å at 92°C. The

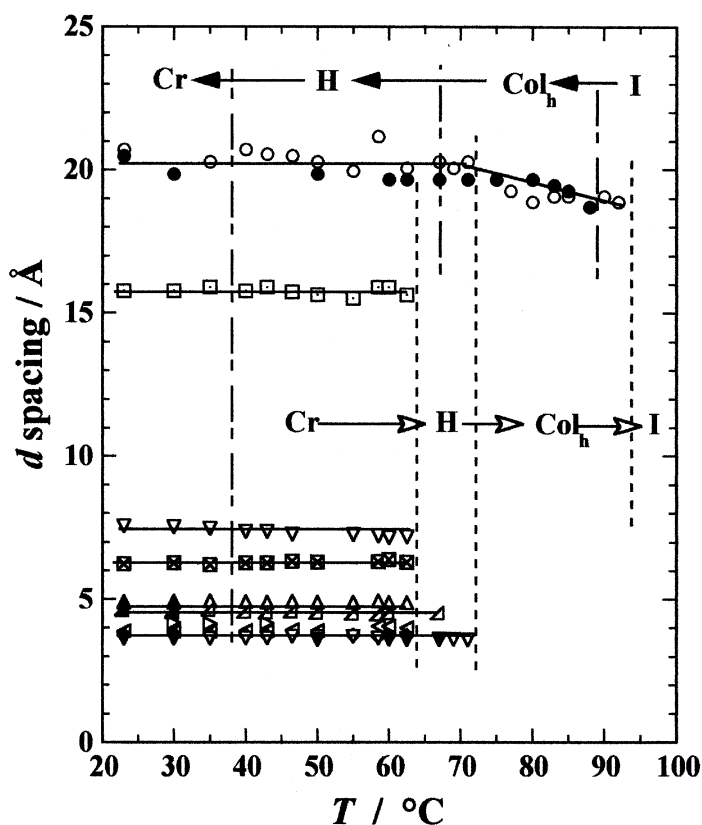


FIGURE 4 Temperature dependence of the d spacing for each reflection peak of HHTT on heating (open symbols) and subsequent cooling (filled symbols) processes at atmospheric pressure.

transitional behaviour of HHTT is corresponding well to the morphological and thermal behaviour under atmospheric pressure. The reversible change in the X-ray diffraction during the Cr-H-Col_h-I transition sequence was confirmed under pressures up to 30 MPa.

The authors reported using a high-pressure DTA that the application of hydrostatic pressure above 32 MPa results in the H and Col_h phases becoming monotropic, depending upon the applied pressure [3]. The H phase was observed as a monotropic phase in the pressure region between 32 and about 180 MPa: the Cr→Col_h→I transition was observed on heating and the I→Col_h→H→Cr transition sequence was recognized on cooling,

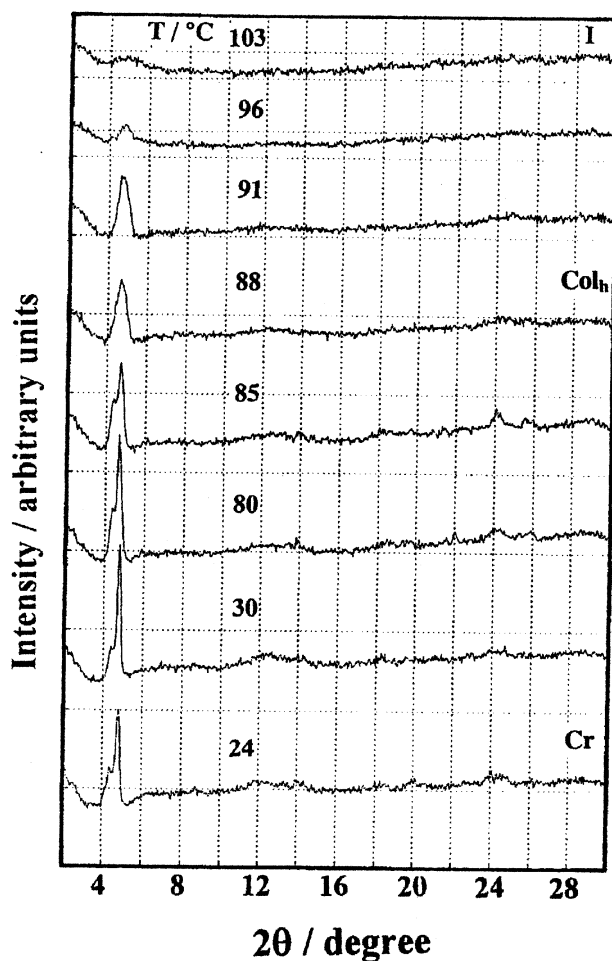


FIGURE 5 X-ray diffraction patterns of HHTT on heating at 75 MPa.

respectively. It is of interest to observe structurally the monotropic transitions such as the metastable H and Col_h phases under pressures, using the high-pressure WAXD technique. Figure 5 shows the temperature dependence of the X-ray diffraction pattern of HHTT on heating at 75 MPa. Here one can see that the hydrostatic compression of the crystals at room temperature often induces the splitting of the low-angle diffraction peak into either doublet or triplet. This may be interpreted as inhomogeneous deformations of the thiohexyl chain tails in the crystalline phase. On the heating process, however, the split low-angle peaks gradually merged into a broad peak in the Col_h phase. Accordingly the intercolumnar distances in the distorted crystals merge to one with a relatively broad distribution around the mean distance. The temperature region of the Col_h phase became narrow

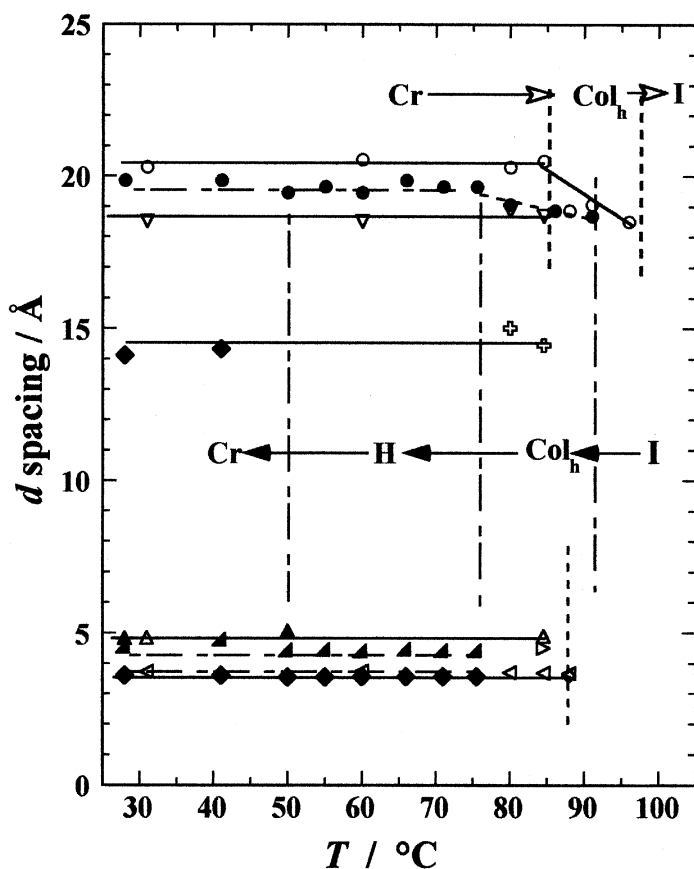


FIGURE 6 Temperature dependence of the d spacing for each reflection of HHTT on heating (open symbols) and cooling (filled symbols) processes at 75 MPa.

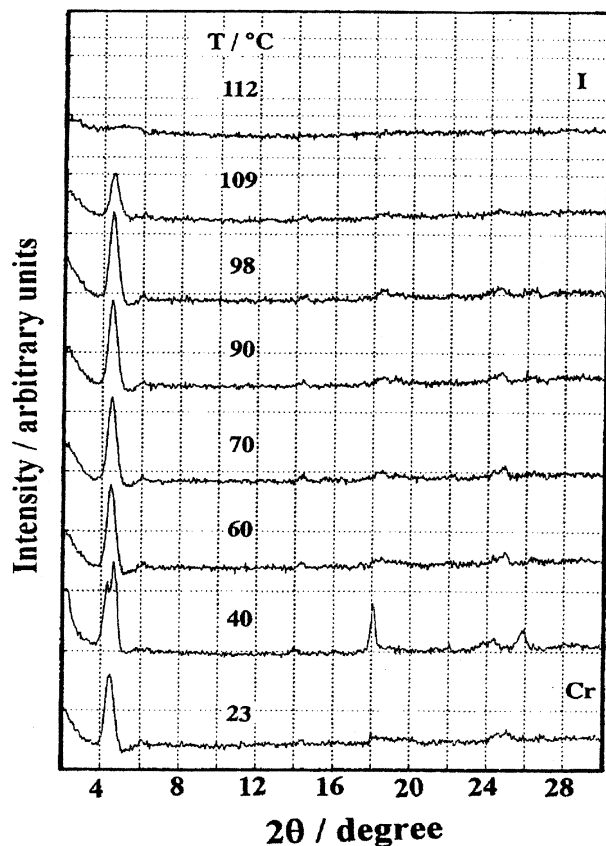


FIGURE 7 X-ray diffraction patterns of HHTT on heating at 200 MPa.

to about 10°C, approximately a half of the temperature region at atmospheric pressure. At the same time the diffraction peak weakened its intensity and disappeared at about 98°C. Figure 6 shows the temperature dependence of the d spacing of the reflections on heating and subsequent cooling processes at 75 MPa. It is clearly seen that the intercolumnar distance in the Col_h phase decreases reversibly with increasing temperature at 75 MPa. The change in X-ray pattern on heating showed the $\text{Cr} \rightarrow \text{Col}_h \rightarrow \text{I}$ transition sequence, while the structural changes on the subsequent cooling were the same as those observed at atmospheric pressure, i.e., the $\text{I} \rightarrow \text{Col}_h \rightarrow \text{H} \rightarrow \text{Cr}$ transition sequence. The lower reflection (d spacing of 18.3 Å) of the split low-angle reflections appeared first in the crystalline phase by applying the pressure. So this reflection reflects the distortion induced in the crystals. In the cooling mode the d spacing of the inter-

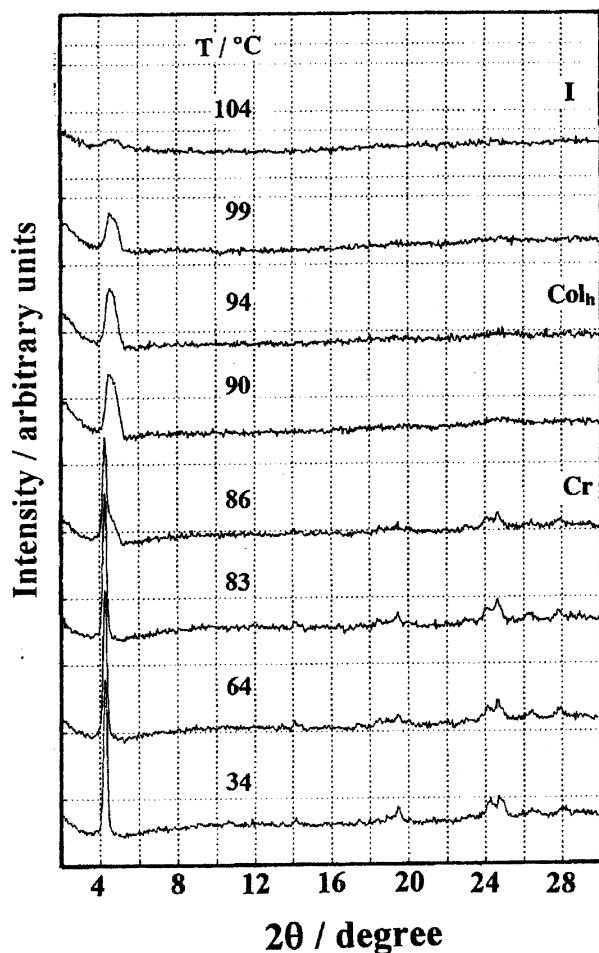


FIGURE 8 X-ray patterns of HHTT on the subsequent cooling process at 200 MPa.

columnar distance in the Col_h phase increased from 18.7 to about 19.9 Å with decreasing temperature. The structural behaviour of HHTT at 100 MPa showed the same transitional behaviour as those observed at 75 MPa. It was confirmed that the H phase appears monotropically between the Col_h and Cr phases on cooling at 75 and 100 MPa and that the Col_h phase shows a negative coefficient of thermal expansion under these pressures. The structural behaviour corresponded well to the thermal behaviour reported in the previous paper [3].

Further increasing pressure above 180 MPa induced more drastic change in the transitional behaviour, as observed using high-pressure DTA. Figures 7

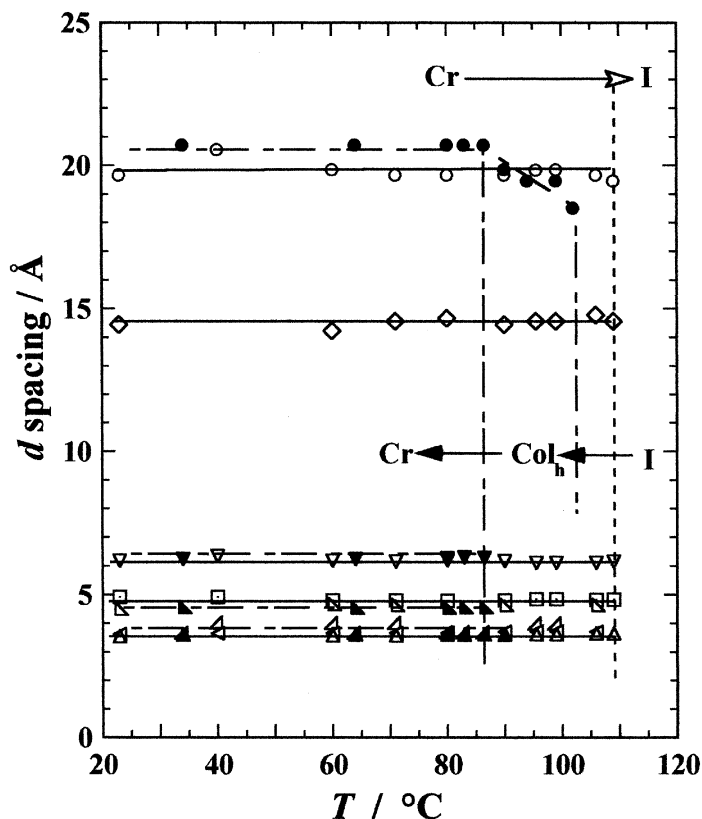


FIGURE 9 Temperature dependence of the d spacing for each reflection of HHTT on heating (open symbols) and cooling (filled symbols) processes at 200 MPa.

and 8 show the temperature dependence of the X-ray patterns of HHTT on heating and subsequent cooling at 200 MPa, respectively. The typical X-ray patterns of the HHTT crystals were observed until the fusion occurred at about 110°C. On the subsequent cooling a broad peak at $2\theta = 4.6^\circ$ appeared in the temperature region between 104 and 91°C, as is shown in Figure 8, indicating the appearance of the Col_h phase with a broad distribution of the intercolumnar distance. When the sample was cooled down to 86°C and lower temperatures, the low-angle peak changed to a sharp one at $2\theta = 4.26^\circ$ ($d = 20.7 \text{ \AA}$) and at the same time several wide-angle reflections appeared clearly, indicating the $\text{Col}_h \rightarrow \text{Cr}$ transformation. It was confirmed structurally that the monotropic Col_h phase can be formed between the isotropic liquid and Cr phase in the cooling mode at 200 MPa: the $\text{Cr} \rightarrow \text{I}$ transition on heating and the $\text{I} \rightarrow \text{Col}_h \rightarrow \text{Cr}$ transition sequence on cooling were observed. Figure 9

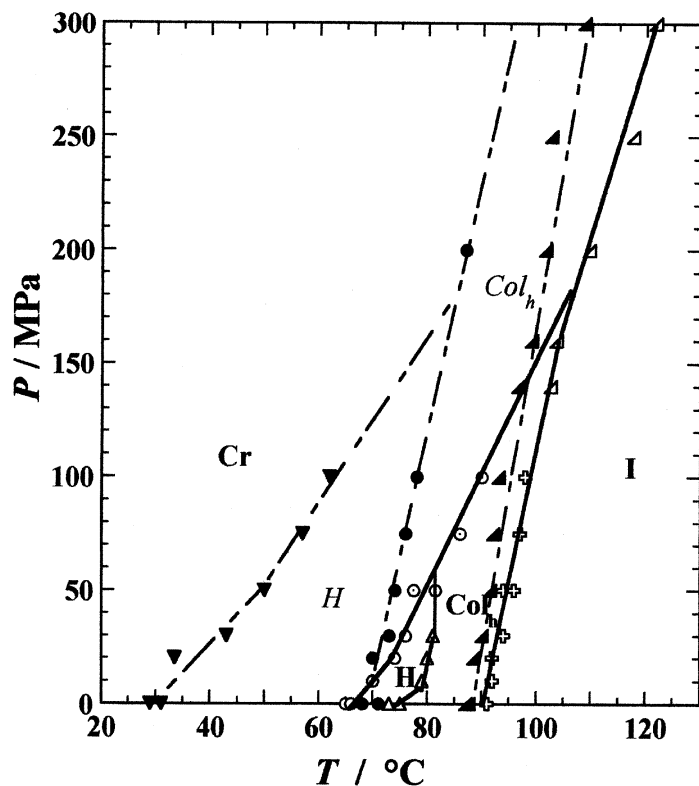


FIGURE 10 P vs. T phase diagrams of HHTT made using the WAXD measurements: solid and broken lines are for the phase diagrams measured on the heating and cooling processes, respectively.

exhibits the temperature dependence of the d spacing for each reflection of HHTT on the heating and subsequent cooling processes at 200 MPa. In the monotropic Col_h phase the intercolumnar distance increased with decreasing temperature, changing from 18.5 Å at 104°C to 20.7 Å at 86°C. This phenomenon exhibits that the negative coefficient of thermal expansion reported by Fontes et al [2] is held even in the monotropic Col_h phase at high pressures. Similar structural behaviour was observed at 250 MPa.

HHTT crystals exist in the two dimensional hexagonal lattice and regularly ordered along the columns. It was found in this study that the low-angle peak in the crystalline phase split into either doublet or triplet by applying pressure up to 300 MPa. The difference in d spacing between the split low-angle peaks reached to be 1–2 Å. This phenomenon suggests the inhomogeneous hexagonal packing of the crystals with different intercolumnar distances

induced by applying hydrostatic pressure. There is a strong possibility that the crystal structure with hexagonally packed columns having the flexible hydrocarbon chain tails can be easily deformed between the intercolumns under strong stresses. This might be the reason for the large shift of the low-angle reflection of the HHTT crystals. But it should be noted that the regularly ordered crystals with an intercolumnar distance recover from the largely deformed crystalline state at high temperatures just below the Cr→I transition point. On the other hand, the H and Col_h phases exist to be stiff and elastic under moderate pressures, depending upon the applied pressure: the H and Col_h phases became monotropic under pressure.

Figure 10 shows the P vs. T phase diagrams of HHTT constructed using the WAXD measurements both on the heating and cooling processes, respectively. The comparison between both the phase diagrams helps us to understand the monotropic features of the H and Col_h phases. The monotropic region of the H phase exists in the intermediate pressure region between about 50 and 180 MPa, while the monotropic region of the Col_h phase is located in the high pressure region above 180 MPa. Of course, the phase diagram made in the heating mode is thermodynamically important because it reveals the stable phases. A relatively good agreement is seen between the WAXD measurements and the precise thermal measurements reported earlier. It was confirmed that there are two triple points; one is estimated as 40 MPa, 77°C for the Cr–H–Col_h triple point and the other is extrapolated as 285 MPa, 118°C for the Cr–Col_h–I triple point [3]. These triple points exhibit the upper limits for the appearance of the stable H and Col_h phases, respectively.

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