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The phase behaviour of the discotic mesogen 5,10,15,20-tetrakis(4-*n*-dodecylphenyl)porphyrin (C12TPP) was investigated under hydrostatic pressures up to 300 MPa by high pressure DTA and wide angle X-ray diffraction methods. The typical enantiotropic phase transitions of C12TPP, low- to high-temperature crystal (Cr_2–Cr_1), Cr_1–discotic lamellar phase (D_L), and D_L–isotropic liquid (I) are observed at pressures up to 10 MPa. Application of hydrostatic pressure to the sample generates a pressure-induced crystal polymorph (Cr_3) between the Cr_2 and Cr_1 phases, and the phase transitions Cr_2–Cr_3–Cr_1–D_L–I occur reversibly in the pressure region between 10 and 180 MPa. On heating at higher pressures above 180 MPa, the fourth crystal polymorph (Cr_4) is formed between the Cr_2 and Cr_3 phases at lower temperatures, and at the same time the fifth crystal polymorph (Cr_5) appears abruptly between the Cr_1 and D_L phases at high temperatures. The Cr_2–Cr_4–Cr_3–Cr_1–(Cr_5)–D_L–I transition processes were observed at $180 \sim 200$ MPa. Further increasing the pressure above 270 MPa induces entirely different thermal behaviour: only two peaks for the pressure-induced transition between the sixth and fifth polymorphs (Cr_6–Cr_5) and the Cr_5–I transitions are detected at low and high temperatures on heating, while both the DTA and WAXD experiments on cooling show the formation of the D_L phase as a monotropic phase between the I and Cr_5 phases, indicating the $I \rightarrow D_L \rightarrow Cr_5 \rightarrow Cr_6$ process. The thermal behaviour was ambiguous and complex in the pressure region between 200 and 260 MPa because the peaks for the intermediate crystal transitions were too small to detect with confidence. The two different sequences of the Cr_2–Cr_4–Cr_3–Cr_1–D_L–I and Cr_6–Cr_5–(D_L)–I processes seems to occur competitively. The T vs. P phase diagram of a sample cooled at 300 MPa was studied to determine the triple point of the D_L phase and to investigate the phase stability of the pressure-induced crystal polymorphs. The Cr_6–Cr_5–I transition process was observed on heating at 200 and 300 MPa, while the Cr_6–Cr_5–D_L–I process was detected at lower pressures below 100 MPa. Since the Cr_5–D_L transition temperature changes linearly with a slope $dT/dP \cong 40°C/100$ MPa, while the D_L–I transition temperature changes slightly ($dT/dP \cong 5.5°C/100$ MPa), the D_L phase forms a triangle in the T vs. P diagram. The triple point of the D_L phase was found to be 240.8 MPa and 168.8°C. The Cr_6 polymorph reorganized to the stable Cr_2 form under atmospheric pressure on annealing at room temperature overnight.

1. Introduction

Since the discovery of disk-like mesogens by Chandrasekhar *et al.* [1] in 1977 and by other groups [2, 3] in 1979, the mesomorphism of discogens, including metallomesogens, has been studied because of their intriguing chemical and physico-chemical properties [4]. Especially the photonic properties of metalloporphyrins are interesting for photovoltaic and photoconductive

devices [5]. Their functional properties are profoundly related to morphological aspects of the porphyrin solids, as seen in the case of phthalocyanine photovoltaic cells [6, 7]. Recently, fast hole mobility was reported for a discotic liquid crystal material [8], and the mesomorphism of columnar mesophases is particularly sensitive to the hole mobility [9]. Ohta *et al.* [10] found the discotic lamellar phase in transition metal complexes—bis[1,3-di(*p-n*-alkoxyphenyl)propane-1,3-dionato]-copper(II) with alkyl units ranging from hexyl to

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dodecyl. They deduced that the mesophase is truly a new discotic lamellar phase (D_L) and that the D_L phase has a structure in which the molecules tilt with respect to the layers. Shimizu *et al.* [11–13] also found that metal-free 5,10,15,20-tetrakis(4-*n*-dodecylphenyl)-porphyrin, hereafter abbreviated to C12TPP, exhibits a peculiar D_L phase showing an interesting mesomorphic transition. It was reported that a photoconductive cell using the pentadecyl homologue gives a novel bias dependence of the photocurrent which varies with the mesomorphic phase transitions [14].

High pressure investigation of the phase behaviour of liquid crystals helps us to understand the structure–property relationships for crystal and mesophase polymorphs. Since Shashidhar [15, 16] initiated the study of pressure-induced mesomorphism, many studies on liquid crystals under pressure have been performed up to the present [17–27]. However, only a few studies [1, 28] have been made concerning the effect of pressure on the mesophases of disk-like molecules. Chandrasekhar *et al.* [1] reported the phase diagram for benzene-hexa-*n*-octanoate (BH8) in which a critical point of the discotic mesophase was found at about 1.4 kbar. The discotic mesophase disappears at higher pressures above 1.4 kbar; it has a columnar structure (Col_h) with hexagonal symmetry in two dimensions and liquid-like disorder in the third. Buisine and Soulestin [28] reported the phase behaviour of (-)2,3,6,7,10,11-hexa-*S*-(3-methylnonanoyloxy)triphenylene and 2,3,7,8,12,13-hexa-*n*-decanoyloxytruxene (C10HATX) under pressures up to 600 bar by using a new automated metabolemeter. They reported several discotic–discotic mesophase transitions in C10HATX. Recently the present authors reported an interesting structural fact about the phase behaviour of the discotic lamellar phase (D_L) of C12TPP, the D_L phase appearing monotropically at high pressures above about 250 MPa, although the phase is enantiotropic under hydrostatic pressures below 200 MPa [29].

We have now studied the thermal and structural behaviour of C12TPP under hydrostatic pressure up to 300 MPa by high pressure differential thermal analysis (DTA) and wide angle X-ray diffraction (WAXD) methods. The effects of pressure and the *T* vs. *P* phase diagram have been established in order to understand the nature of the phase behaviour of C12TPP.

2. Experimental

C12TPP was prepared by the usual synthetic approach from tetraphenylporphyrin [30]. The product was purified by column chromatography after oxidation of chlorinated by product. Further purifications were carried out by Soxhlet extraction of impurities with methanol–acetone. Finally, the product was recrystallized from a benzene–acetone (10/90 v/v) mixture. The resultant C12TPP product was characterized by using a Perkin Elmer differential scanning calorimeter DSC 7 and an Olympus polarizing microscope BH-2 equipped with a Mettler FP 82 hot stage.

The structural behaviour of C12TPP was studied under pressure by using a rotating anode X-ray generator (60 kV and 200 mA; Rotaflex RU-200, Rigaku Co.) equipped with a high pressure vessel on the goniometer [31]. The high pressure wide angle X-ray diffraction (WAXD) system was operated at pressures up to 300 MPa in a temperature region between $-30°C$ and 300°C. Pressure was measured within an accuracy of ± 1 MPa by a manganin gauge calibrated against a precision Broudon gauge (Heise, type CM, Dresser-Industries, Inc.) and temperature was measured with a sheathed C-A thermocouple attached to a beryllium spindle. The beryllium spindle was used as sample vessel and also X-ray window. The sample in the hole of the beryllium spindle was pressurized hydrostatically with low viscosity dimethylsilicone oil (10 centiStokes, Toshiba Silicone Co.) and then irradiated by a beam of Ni-filtered Cu K_α X-rays. The diffracted X-rays were detected by a position-sensitive proportional counter (PSPC-30, Rigaku Co.) covering diffraction angles of $2\theta = 28°$ on the equator.

The thermal behaviour of the sample under pressure was studied by a high pressure DTA apparatus described elsewhere [31]. The high pressure DTA system was operated in a temperature region between $-20°C$ and 300°C under hydrostatic pressures up to 300 MPa. Medium viscosity dimethylsilicone oil (100 centiStokes) was used as a pressure transmitting medium. The C12TPP sample was coated with thin epoxy adhesives in the platinum DTA cup in order to fix the sample securely onto the bottom of the cup and also to prohibit temperature depressions by the diluent effect of silicone oil (pressure medium). The DTA runs were performed at a constant scanning rate of $5°C\,min^{-1}$ under various pressures. Transition temperature was measured as the temperature at the top of a transition peak. Heat of transition was estimated qualitatively by comparison with the constant heat of melting $(28.4\,J\,g^{-1})$ of indium under applied pressure.

3. Results and discussion

3.1. *Phase behaviour of C12TPP under atmospheric pressure*

Figure 1 shows the DSC heating curve of the original sample as prepared and the subsequent cooling and heating curves. The original sample as prepared shows two endothermic peaks for the original crystal (Cr_0)–D_L and the D_L–isotropic liquid (I) transitions at 40.8°C and 157.1°C, respectively. The Cr_0 crystal changes reversibly to the D_L phase which remains until the D_L–I transition
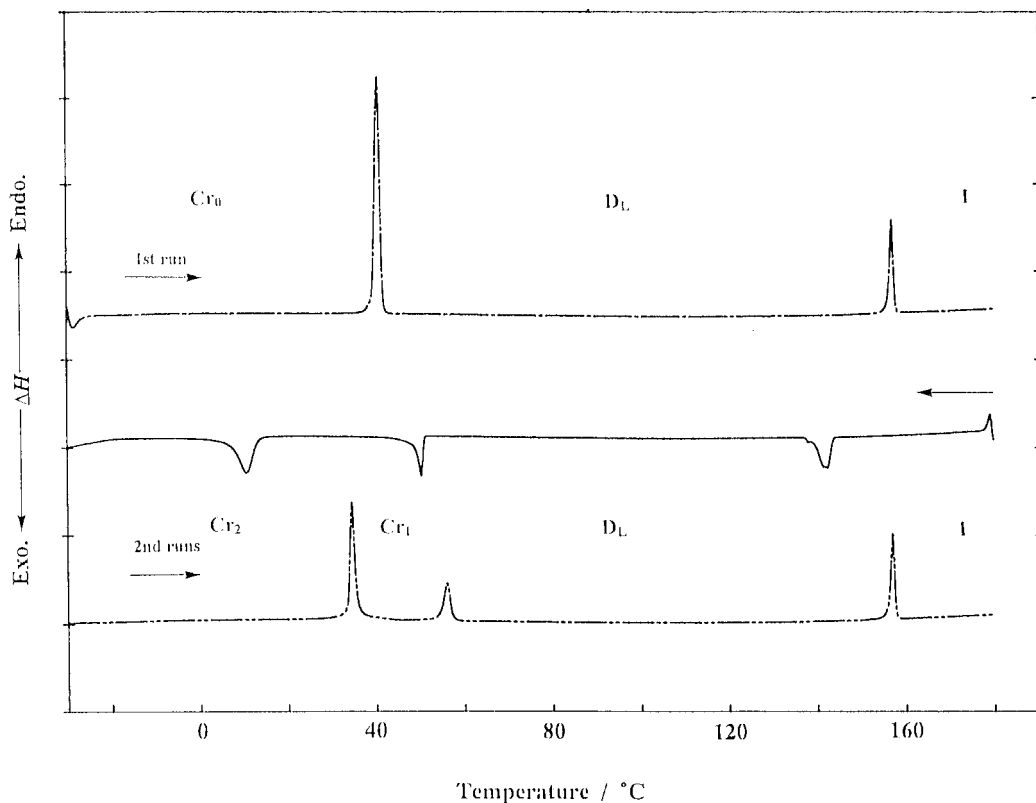

Figure 1. DSC heating curve of C12TPP sample (Cr_0) as prepared, and the subsequent cooling and heating curves. Scanning rate: $10°C min^{-1}$.

occurs. However, this crystal never reappears after the sample is once heated to the isotropic liquid and then cooled down. The subsequent cooling and 2nd heating curves show reversibly the low to high temperature crystal (Cr_2–Cr_1), Cr_1–D_L, and D_L–I transitions at 34.5, 56.0, and 157.0°C, respectively. Therefore the Cr_0 crystal must be thermodynamically metastable. The thermo-dynamic quantities accompanying these transitions are listed in the table.

The transitional structural behaviour of the Cr_2 sample formed under atmospheric pressure was studied by WAXD. Figure 2 shows the temperature dependence of the X-ray patterns of Cr_2 on heating under atmo-spheric pressure. The X-ray pattern of Cr_2 is maintained until the Cr_2–Cr_1 transition occurs at about 38.5°C. The low angle reflection of Cr_2 is observed at $2\theta = 3.21°$ ($d = 27.51$ Å). When the X-ray pattern changes to that of Cr_1, two low angle reflections are found clearly at $2\theta = 2.79°$ ($d = 31.64$ Å) and $3.95°$ ($d = 22.34$ Å). The two low angle reflections of Cr_1 changed in their peak intensities in the temperature region between 38.5°C and 57°C: the latter reflection grew on heating, while the former one decreased. Further heating of the sample induces a very strong reflection of the D_L phase at $2\theta = 2.79°$ ($d = 31.64$ Å) and weak reflections at wide

Table 1. Thermodynamic quantities for the phase transformations of C12TPP.

Sample	Mode	$T/°C$ (ΔH/J g^{-1})	
		Cr_0–D_L	D_L–I
Virgin sample	1st heating	40.8 (64.0)	157.1 (18.9)
	cooling[a]	32.4 (61.9)	

		Cr_2–Cr_1	Cr_1–D_L	D_L–I
Melt-grown sample	2nd heating	34.5 (37.0)	56.0 (13.6)	157.0 (18.0)
	2nd cooling	10.7 (30.0)	50.3 (15.1)	142.2 (17.5)

[a] Sample not heated to the isotropic state.

angles in a wide temperature region between 57 and 154°C. The d spacing of the D_L phase agreed well with the value reported before by Shimizu *et al.* [12]. According to the explanation of Ohta *et al.* [10] based on C.P.K. molecular models, the d spacing of the low
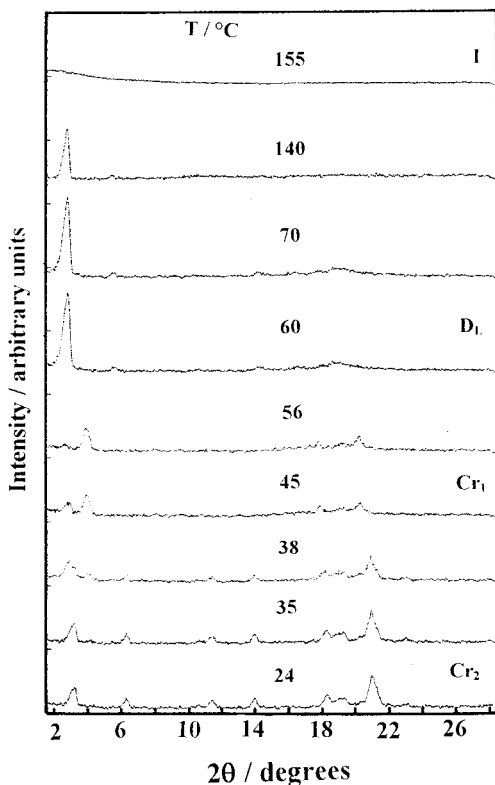
Figure 2. X-ray patterns of C12TPP on heating at atmospheric pressure: Cr_2 crystal at $24 \sim 38°C$, Cr_1 crystal at $40 \sim 56°C$, D_L phase at $60 \sim 155°C$, and isotropic liquid at $160°C$.

angle reflection of C12TPP indicates the distance between the neighbouring alkylphenyl groups. All the reflections, including the low angle reflection, disappear at the D_L–I transition at $154°C$. The change in d spacing of the low angle reflection corresponds well to the DSC transition behaviour, showing the reversible Cr_2–Cr_1–D_L–I transition process at atmospheric pressure.

The transitional behaviour of the Cr_2 crystal prepared at atmospheric pressure was now studied as a function of pressure by high pressure DTA. Figure 3 shows the DTA heating curves for Cr_2 under various pressures up to 300 MPa. The typical transition behaviour of the Cr_2–Cr_1–D_L–I process is observed at 10 MPa. When a hydrostatic pressure of $50 \sim 150$ MPa is applied to the sample, one can see an additional phase between Cr_2 and Cr_1, and the temperature region of the new phase is enlarged with increasing pressure. The new phase is designated as crystal Cr_3. The Cr_2–Cr_3 transition is observed clearly, followed by the Cr_3–Cr_1, Cr_1–D_L and D_L–I transitions on heating under pressures between 20 and 180 MPa. At the same time, the temperature region of the D_L phase is narrowed with increasing pressure because the D_L–I transition temperature is slightly dependent upon pressure. When the pressure is raised above 180 MPa, a fourth crystal polymorph (Cr_4) is formed between Cr_2 and Cr_3, and the double peaks of the Cr_2–Cr_4 and Cr_4–Cr_3 transitions are clearly separated. Furthermore, another new transition is induced at high temperatures just below the D_L–I transition. The new
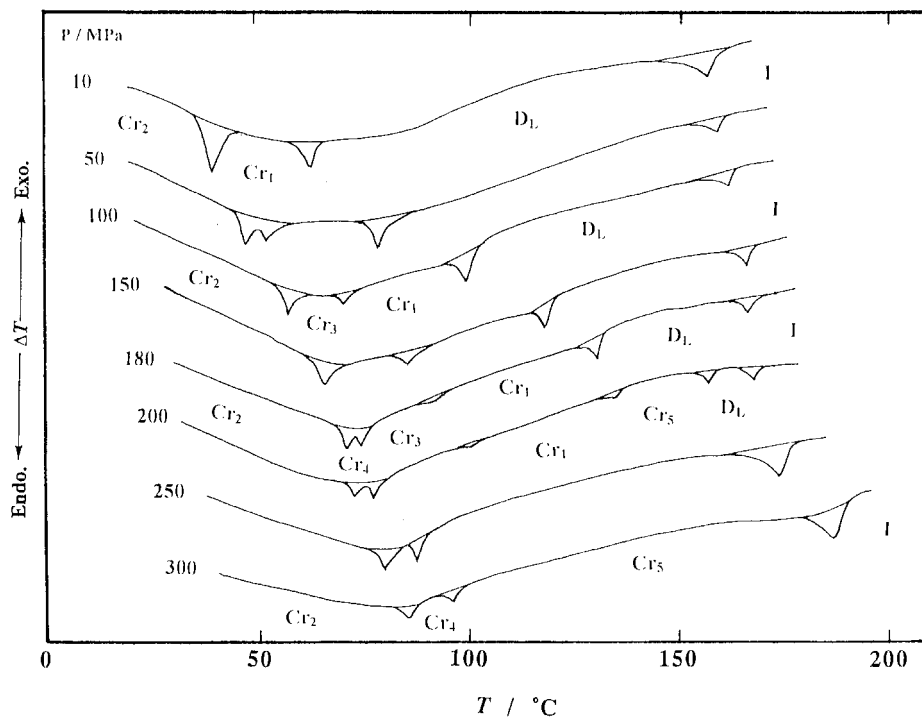

Figure 3. DTA heating curves of the Cr_2 crystal under various pressures. The starting sample of Cr_2 was formed by cooling from the isotropic melt at 1 MPa.
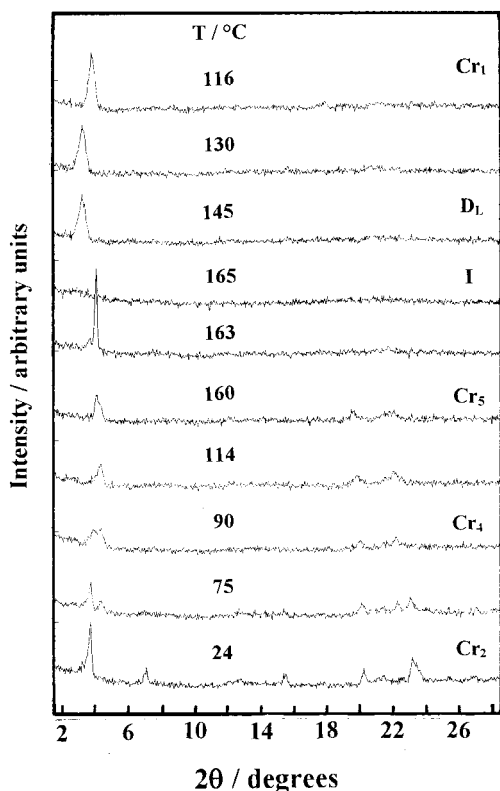
Figure 4. X-ray patterns of the Cr_2 sample on heating and subsequent cooling at 250 MPa: Cr_2 crystal at $24 \sim 70°C$, $Cr_2–Cr_4$ transition at 74°C, $Cr_4 \sim Cr_1$ at $80 \sim 160°C$, Cr_5 crystal at 163°C, isotropic liquid at 165°C and then, on cooling, D_L phase at $148 \sim 130°C$, and Cr_4 crystal at 116°C.

transition relates to the fifth crystal polymorph (Cr_5)–D_L transition in which Cr_5 is formed abruptly during heating at these high pressures. Further increase of pressure generates drastic changes in the thermal behaviour of C12TPP: the $Cr_3–Cr_1$ and $Cr_1–Cr_5$ transition peaks at intermediate temperatures are too small to be detected, while the $Cr_5–D_L$ transition peak tends to merge with the D_L–I peak at pressures above 240 MPa. The DTA heating curves of the Cr_2 sample at 250 and 300 MPa show double peaks for the $Cr_2–Cr_4$ and $Cr_4–Cr_3$ transitions at lower temperatures and a large peak for the Cr_5–I transition at higher temperatures. Therefore Cr_2 is held in a metastable state at high pressures until the $Cr_2–Cr_4$ transition occurs. Figure 4 shows the X-ray patterns of the Cr_2 sample on heating at 250 MPa: the structural changes during the $Cr_2–Cr_4–Cr_1–Cr_5$–I process are seen clearly, but the intermediate transitions such as $Cr_4–Cr_3$ and $Cr_3–Cr_1$ transitions were missed. The D_L phase is monotropic because it does not appear on heating, but appears clearly in a temperature region between 148 and 126°C on subsequent cooling. The X-ray results are generally consistent with the DTA results in figure 3.

3.2. *Effect of pressure on phase behaviour of C12TPP*

Figures 5 and 6 illustrate the DTA cooling and heating curves of C12TPP under various hydrostatic pressures. The $Cr_2–Cr_1–D_L$–I transition behaviour is maintained under pressures up to about 10 MPa. When higher pressure is applied to the sample, crystal polymorph Cr_3 is formed between the Cr_2 and Cr_1 phases and
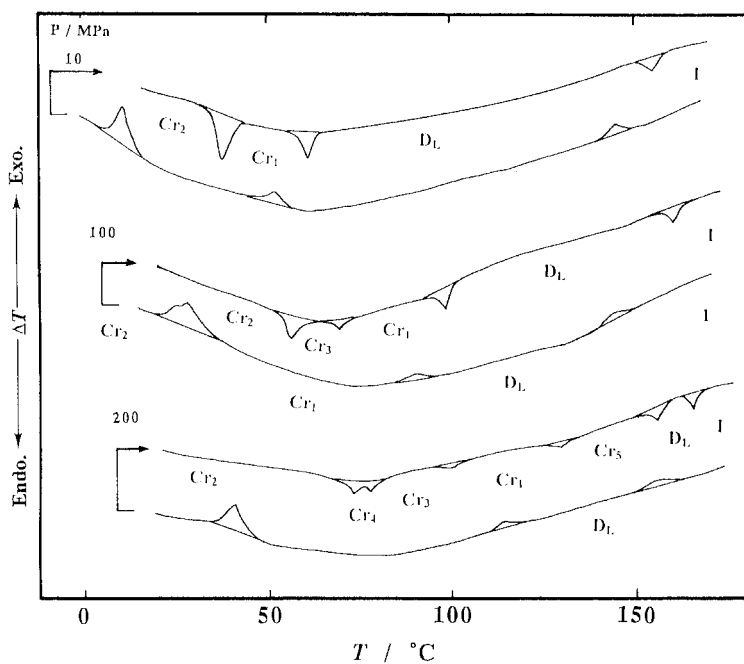

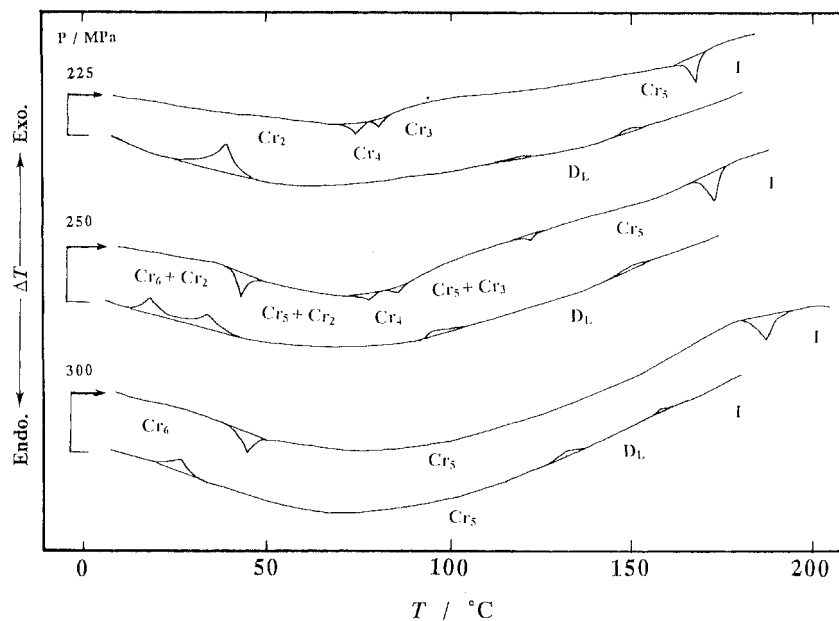Figure 5. DTA cooling and subsequent heating curves of C12TPP at 10, 100, and 200 MPa. Scanning rate: 5°C min⁻¹.

Figure 6. DTA cooling and subsequent heating curves of C12TPP at 225, 250, and 300 MPa. Scanning rate: 5°C min⁻¹.

the Cr_2–Cr_3–Cr_1–D_L–I transition process is observed reversibly in the pressure region $20 \sim 180$ MPa. The X-ray behaviour of the sample on heating at 150 MPa is shown in figure 7. The low angle reflection of Cr_2 at
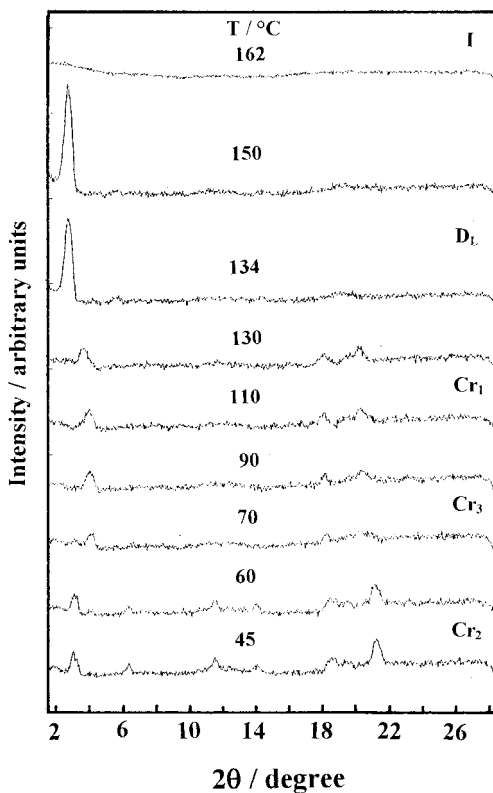

Figure 7. X-ray diffraction patterns of C12TPP on heating at 150 MPa: Cr_2 crystal at $46 \sim 60$°C, Cr_3 crystal at 70°C, Cr_1 crystal at $90 \sim 130$°C, D_L phase at $134 \sim 150$°C, and isotropic liquid at 162°C.

$2\theta = 3.12°$ ($d = 28.34$ Å) is maintained at temperatures up to about 65°C and the double low angle reflections are observed during the Cr_2–Cr_3 transition. The temperature region of the Cr_3 phase is as short as 8–10 degrees. Then the low angle reflection of Cr_3 changes to the low angle reflection of Cr_1 at $2\theta = 4.18°$ ($d = 21.10$ Å). The Cr_1 phase is maintained over a wide temperature range until the Cr_1–D_L transition occurs at about 133°C. The X-ray pattern of the D_L phase shows a very strong reflection at $2\theta = 2.70°$ ($d = 32.73$ Å) and a diffuse peak at wide angles; these remain until the D_L–I transition occurs at about 160°C. The d spacing of the low angle reflection of each phase is plotted as a function of temperature in figure 8. Generally speaking, the transition behaviour can be recognized by the change in d spacing of the low angle reflection of the crystals and D_L phase, except for the intermediate crystal–crystal transitions described later.

When the pressure is raised above about 180 MPa, the thermal behaviour is more complex: the heating curve at 200 MPa shows double peaks for the Cr_2–Cr_4 and Cr_4–Cr_3 transitions, indicating the formation of the fourth crystal polymorph (Cr_4) between the Cr_2 and Cr_3 phases. At the same time, another new peak is induced at a high temperature, about 9° below the D_L–I transition at 190–200 MPa. This exhibits clearly the pressure-induced formation of the fifth crystal polymorph (Cr_5) which is formed under high pressures. Accordingly the transition process at 190–200 MPa is assigned as Cr_2–Cr_4–Cr_3–Cr_1–Cr_5–D_L–I on heating, while the cooling curve shows a different behaviour: the I–D_L and D_L–Cr_1 transition peaks occur, followed by a broad complex peak for the Cr_3–Cr_4–Cr_2 transitions at
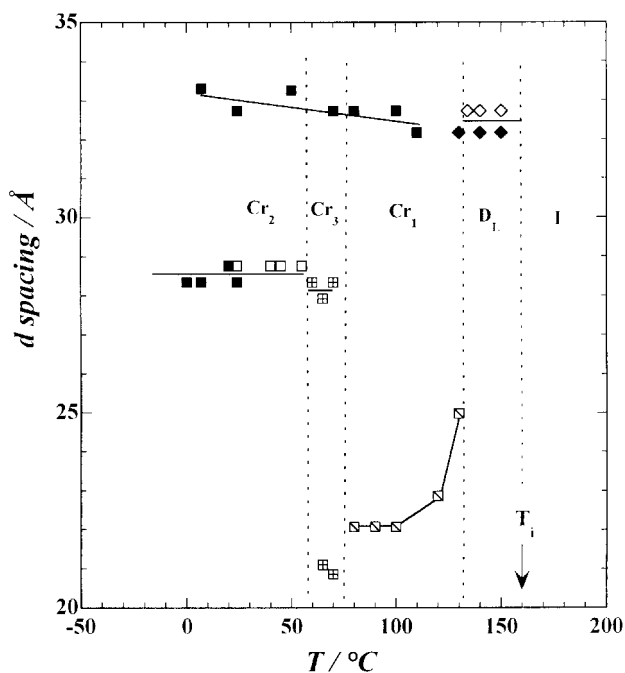
Figure 8. Temperature dependence of the *d* spacings of the low angle reflections in the X-ray patterns at 150 MPa. Open and filled symbols are for the heating and subsequent cooling processes, respectively.

lower temperatures. The temperature dependence of the *d* spacing of the low angle reflection on heating and cooling at 200 MPa is divided into three distinct regions, i.e. the Cr_2 phase at low temperatures, an intermediate temperature region for the Cr_4, Cr_3, Cr_1 and Cr_5 phases which could not be discriminated, and the D_L phase at high temperatures. It could not be explained why the intermediate temperature region shows a constant low angle reflection at about $2\theta = 3.6$–$3.7°$ ($d = 23.4$–24.3 Å), irrespective of the appearance of the Cr_4, Cr_3, Cr_1, and Cr_5 phases. There is one possibility that the structures of the crystal polymorphs might be so close to one another, that structural discrimination by the low angle reflection shows no difference at these pressures. Another strange point is that the low angle reflection with the *d* spacing of 29.2–30.3 Å on cooling, different from the *d* spacing (23.4–24.3 Å) on heating, is observed at 200 MPa. Such strange *d* spacing behaviour on heating and subsequent cooling was also observed at 150 MPa. This phenomenon is different from the reversible structural change at 0.1 MPa. This odd *d* spacing behaviour may be connected with the phenomenon of the two low angle reflections of the Cr_1 phase which vary their intensities with temperature at atmospheric pressure. The intensities of the two low angle reflections may be strongly influenced by either heating or cooling at such high pressures. It is noted that the *d* spacing of the D_L phase is maintained

at about 31–32 Å, irrespective of applied pressure. The structures of these crystal polymorphs is left as research to be carried out in the future.

We often observed the temperature discrepancy between the D_L–I transition points obtained by DTA and WAXD methods because temperature depression of transition points of about 10°C, especially the D_L–I transition, often occurs in the WAXD method by the diluent effect of the silicone oil used as pressure medium. Accordingly the observed transition points are more accurate by the DTA method than by the WAXD method.

The DTA run at 225 MPa in figure 6 shows the Cr_2–Cr_4 and Cr_4–Cr_3 transitions at lower temperatures and the Cr_5–I transition at high temperature on heating, while the I–D_L, D_L–Cr_1 transition peaks and a complex peak for the crystal transitions (Cr_3–Cr_4 and Cr_4–Cr_2) at low temperatures are observed on cooling. The cooling curve at 250 MPa shows the same behaviour as that at 225 MPa, with an additional crystal transition (Cr_5–Cr_6) at a low temperature. The two exothermic peaks at lower temperatures on cooling are probably due to the Cr_3–Cr_4–Cr_2 transitions and the Cr_5–Cr_6 transition (see figure 6). As a result, the Cr_2 and Cr_6 crystals are formed concurrently at these pressures. The subsequent heating run exhibits a complex thermal behaviour which may be interpreted through the occurrence of two concurrent processes of the Cr_2–Cr_4–Cr_3–Cr_1–I transition scheme at low pressures and the Cr_6–Cr_5–I scheme at high pressure.

The I–D_L–Cr_5–Cr_6 transition process is predominant on cooling under high pressures above about 260 MPa and the DTA runs show a very simple curve, quite different from those at 150, 200 and 225 MPa. As shown in figure 6, the DTA heating curve at 300 MPa exhibits only two peaks for the Cr_6–Cr_5 and Cr_5–I transitions at quite low and high temperatures, respectively, while the cooling curve demonstrates further the appearance of the monotropic D_L phase between the I and Cr_5 phases [29]. Figure 9 shows the *in situ* observations of WAXD patterns of C12TPP on cooling from the isotropic liquid at 300 MPa. One can see clearly that the D_L phase appears monotropically in a relatively small temperature region from 150 to 142°C. The *d* spacings of the low angle reflections on cooling and subsequent heating are shown in figure 10. The phase boundaries demarcating the Cr_6, Cr_5, and I phases are recognized clearly, in addition to the existence of the monotropic D_L phase on cooling. The sharp low angle reflection of the D_L phase at $2\theta \sim 2.7$–$2.8°$ ($d = 31.6$–32.7 Å) was observed in the temperature region between 150 and 142°C and then the double low angle reflections appeared at about 141°C, indicating the $D_L \rightarrow Cr_5$ transition. The resultant Cr_5 crystals display a strong low angle reflection at $2\theta = 3.53°$
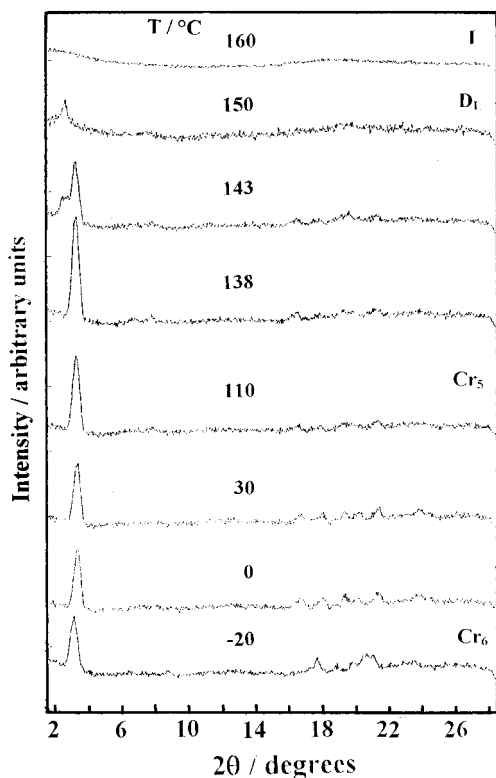
Figure 9. X-ray patterns of C12TPP on cooling from the isotropic liquid at 300 MPa: isotropic liquid at 185 ∼ 160°C, D_L phase at 150 ∼ 143°C, D_L–Cr_5 transition at 143°C, Cr_5 crystal at 138 ∼ – 10°C, and Cr_6 crystal at – 13 ∼ – 20°C.
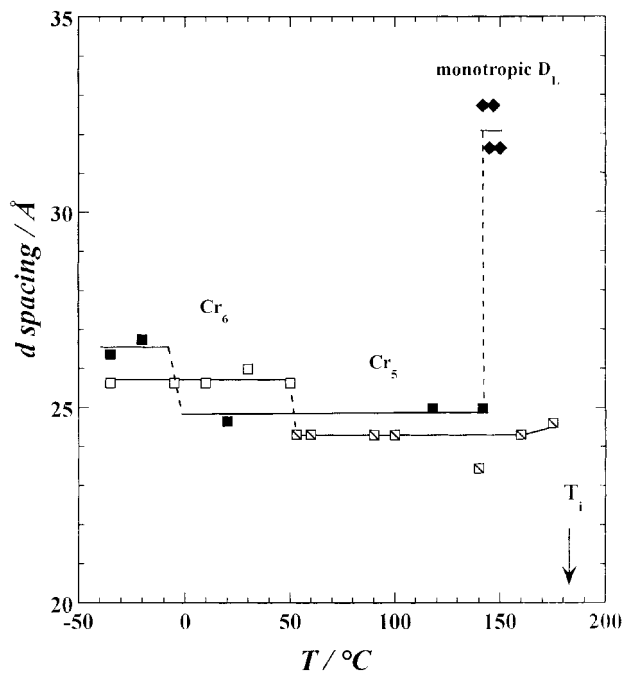

Figure 10. Temperature dependence of the d spacings of the low angle reflections at 300 MPa. Open and filled symbols are for the second heating and cooling processes, respectively.

($d = 24.98$ Å) and several weak reflections at wide angles. Further cooling gives the $Cr_5 \rightarrow Cr_6$ transition at about $0 \sim – 10$°C, with a shift of the low angle reflection from $2\theta = 3.53°$ ($d = 24.98$ Å) to $2\theta = 3.30°$ ($d = 26.74$ Å). Subsequent heating of the resultant Cr_6 sample shows the Cr_6–Cr_5 and Cr_5–I transitions at about 45 and 178°C, respectively, the D_L phase never appearing on heating. Plotting the transition temperatures on cooling versus pressure suggests that the $I \rightarrow D_L$ transition line would cross over the $D_L \rightarrow Cr_5$ transition line at about 320 MPa. Accordingly, the monotropic D_L phase is able to exist in a pressure region between 240 and 320 MPa.

Figure 11 shows the T vs. P relation of C12TPP under pressures between 0.1 and 300 MPa; samples were cooled from the isotropic liquid at each pressure. Figure 11 shows four pressure regions of the Cr_2–Cr_1–D_L–I transition scheme around atmospheric pressure, the Cr_2–Cr_3–Cr_1–D_L–I transition scheme in the low pressure region between 10 and 180 MPa, the pressure region of the concurrent transition schemes at intermediate pressures between 180 and 260 MPa, and the Cr_6–Cr_5–I transition scheme at high pressures above about 260 MPa. The temperature region of the D_L phase in the low pressure region decreases remarkably with increasing
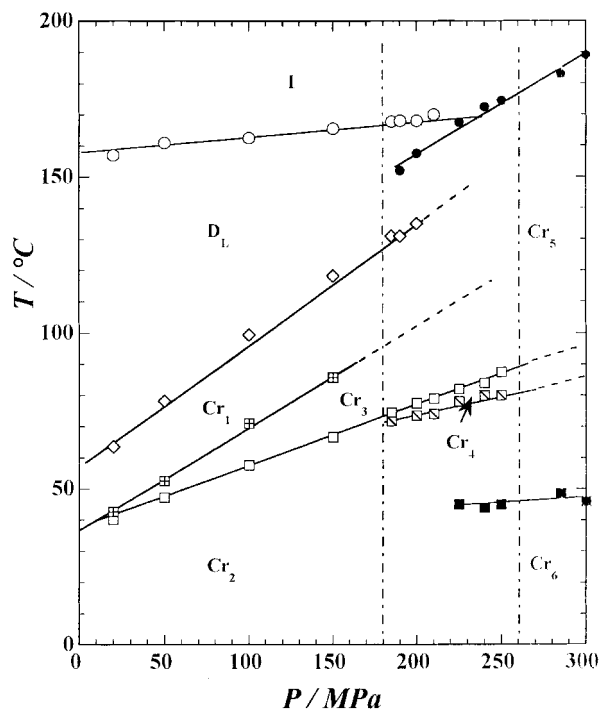

Figure 11. T vs. P relations for C12TPP on heating. Samples were examined on cooling at each pressure in the pressure region between 0.1 and 300 MPa.

pressure, from 110 degrees at 0.1 MPa to about 47 degrees at 150 MPa. This occurs because the Cr_1–D_L transition temperature increases linearly with a slope of $dT/dP \cong 0.392°C/MPa$, while the D_L–I transition temperature is only slightly dependent upon pressure $(dT/dP \cong 0.06°C/MPa)$. Therefore the D_L phase forms a triangle on the T vs. P diagram, in which a triple point can be extrapolated (see below) as the upper limit of the D_L phase. However the hypothetical triple point is never realized because the Cr_5 polymorph is induced suddenly at pressures of $180 \sim 200$ MPa and is located between crystal Cr_1 and the D_L phase. The temperature region of the D_L phase decreases discontinuously from 35 degrees to about 9 degrees at 190 MPa. Further increase of pressure plays a role in the merging of the Cr_5–D_L transition with the D_L–I transition. The temperature of the merged Cr_5–I transition increases to higher temperatures with the slope $dT/dP \cong 0.296°C/MPa$, keeping the same slope as that of the Cr_5–D_L transition line. All the transition lines in figure 11 are well approximated as first order polynormials in pressure as follows.

$0 \sim 10$ MPa
$\quad$ Cr_2–Cr_1 transition: $\qquad T = 36.16 + 0.3352P$
$10 \sim 180$ MPa
$\quad$ Cr_2–Cr_3 transition: $\qquad T = 36.76 + 0.2014P$
$\quad$ Cr_3–Cr_1: $\qquad\qquad\quad T = 36.16 + 0.3352P$
$\quad$ Cr_1–D_L: $\qquad\qquad\quad T = 58.02 + 0.3917P$
$\quad$ D_L–I: $\qquad\qquad\qquad T = 156.70 + 0.0599P$
$180 \sim 260$ MPa
$\quad$ Cr_2–Cr_4 transition: $\qquad T = 43.68 + 0.1485P$
$\quad$ Cr_4–Cr_3: $\qquad\qquad\quad T = 38.98 + 0.1912P$
$\quad$ Cr_5–D_L: $\qquad\qquad\quad T = 100.34 + 0.2962P$
$P > 260$ MPa
$\quad$ Cr_6–Cr_5 transition: $\qquad T = 36.42 + 0.0361P$
$\quad$ Cr_5–I: $\qquad\qquad\qquad T = 100.34 + 0.2962P$

In figure 11, one can expect three triple points for crystals Cr_3 and Cr_4 and the D_L phase. The two triple points for the crystals are extrapolated to 4.5 MPa, 37.6°C and 110.1 MPa, 60.0°C as the lower limits of the Cr_3 and Cr_4 phases, respectively, while a third triple point is extrapolated to 238.5 MPa, 171.0°C as the higher limit of the D_L phase. Disappearance of the liquid crystal properties of a discotic mesogen under pressure was first shown for benzene-hexa-*n*-octanoate (BH8) by Chandrasekhar *et al.* [1]. They reported the disappearance of the mesophase of BH8 at high pressure and gave the phase diagram including the triple point at about 1.4 kbar and 97°C.

The transition enthalpies of the various transitions of C12TPP were estimated qualitatively by comparison with the heat of fusion of indium as standard material. Figure 12 shows the ΔH vs. P relations for the transitions of C12TPP. The enthalpy of the Cr_2–Cr_1 transition has
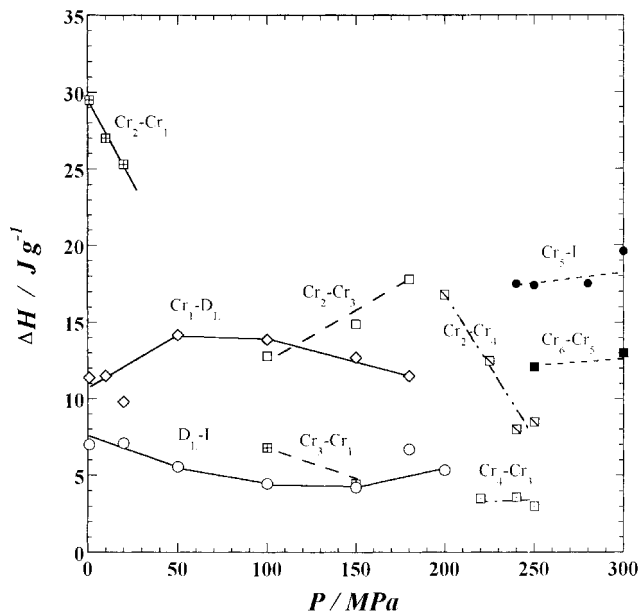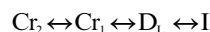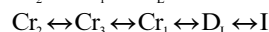

Figure 12. Transition enthalpy vs. pressure relations for the various transitions of C12PP.

a linear decreasing trend with pressure. On the other hand, the enthalpy of the D_L–I transition (about 6 J g^{-1}) is only slightly dependent upon pressure. Here it is noted that the transition enthalpy (~ 18 J g^{-1}) of the Cr_5–I transition is comparable to the sum of the enthalpies of the Cr_1–D_L ($7 \sim 10$ J g^{-1}) and D_L–I ($6 \sim 8$ J g^{-1}) transitions at lower pressures. From the experimental results in this study, the phase behaviour of C12TPP is summarized under five pressure regions.
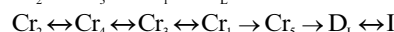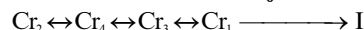
$0.1 \sim 10$ MPa $\qquad$ $Cr_2 \leftrightarrow Cr_1 \leftrightarrow D_L \leftrightarrow I$
$10 \sim 180$ MPa $\qquad$ $Cr_2 \leftrightarrow Cr_3 \leftrightarrow Cr_1 \leftrightarrow D_L \leftrightarrow I$
$180 \sim 240$ MPa $\qquad$ $Cr_2 \leftrightarrow Cr_4 \leftrightarrow Cr_3 \leftrightarrow Cr_1 \rightarrow Cr_5 \rightarrow D_L \leftrightarrow I$

$240 \sim 260$ MPa $\qquad$ $Cr_2 \leftrightarrow Cr_4 \leftrightarrow Cr_3 \leftrightarrow Cr_1 \longrightarrow I$
concurrent processes $\qquad\qquad\qquad\qquad D_L$

$\qquad\qquad\qquad Cr_6 \quad\leftrightarrow\quad Cr_5 \longrightarrow$
$P > 260$ MPa $\qquad$ $Cr_6 \quad\leftrightarrow\quad Cr_5 \longrightarrow I$
$\qquad\qquad\qquad\qquad\qquad\qquad\qquad D_L$

3.3. *Phase behaviour of C12TPP cooled at 300 MPa*

The Cr_6–Cr_5–(D_L)–I transition behaviour which occurs consistently at 300 MPa was studied as a function of pressure, in order to determine the triple point of the D_L phase and at the same time the phase stability of crystals Cr_6 and Cr_5 at lower pressures. Figure 13 shows the DTA heating curves at various pressures for a C12TPP sample which was cooled from the isotropic liquid at 300 MPa. The DTA heating curve at 200 MPa is entirely the same as that at 300 MPa. Since crystal Cr_6 became unstable at low pressures, the DTA curves
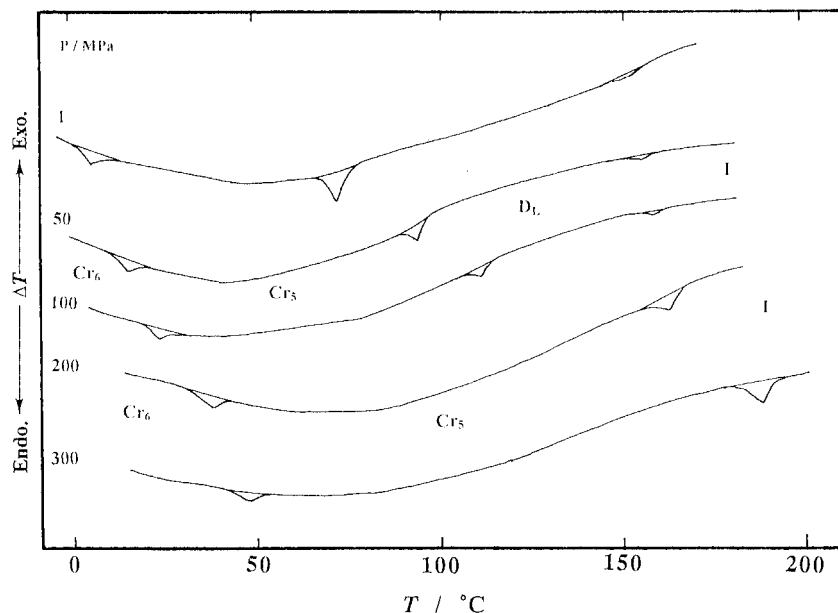
Figure 13. DTA heating curves at various pressures for a C12TPP sample obtained by cooling the isotropic liquid at 300 MPa.

at 0.1 ~ 100 MPa were taken immediately after releasing the pressure from 300 MPa at low temperatures. The heating curves at 100, 50 and 1 MPa show an additional endothermic peak for the Cr_5–D_L transition at an intermediate temperature. Figure 14 illustrates the T vs. P phase diagram of such a sample. The Cr_5–D_L and

Figure 14. T vs. P phase diagram of a C12TPP sample first cooled from the isotropic state at 300 MPa.

D_L–I transition lines are approximated as first order polynomials in pressure, while the Cr_6–Cr_5 transition line is approximated well as a second order polynomial in pressure.

Cr_6–Cr_5 transition: $T = 5.3 + 0.2310P - 3.038 \times 10^{-4} P^2$

Cr_5–D_L: $T = 72.5 + 0.4001P$

D_L–I: $T = 155.5 + 0.0553P$

In this case, the triple point as the upper limit of the D_L phase was estimated clearly to be 240.8 MPa and 168.8°C. Since the phase diagram was obtained for the same sample prepared at 300 MPa, the values are believed to be more reliable than the values of 238.5 MPa and 171.0°C quoted in the previous section. When the Cr_6 sample was left at room temperature overnight at 0.1 MPa, the DTA heating curve showed additional peaks to the normal transition peaks of the Cr_2–Cr_1–D_L–I process. It is concluded that the Cr_6 crystals reorganize slowly to the stable Cr_2 crystal by aging at atmospheric pressure. The phase diagram in figure 14 illustrates only the temporary stability of the Cr_6 and Cr_5 crystals in the low pressure region.

It was found that a supercooled phase was realized when the sample was rapidly cooled ($\sim$ max 50°C min^{-1}) from the isotropic liquid at 300 MPa. Figure 15 shows the subsequent DTA heating curves of the rapidly cooled sample. The heating curve at 300 MPa shows clearly an exothermic peak at 93°C and the isotropization (Cr_5–I transition) peak at 187°C. Here, the exothermic peak is due to a kind of cold crystallization of the supercooled phase to the Cr_5 crystal on subsequent heating. There
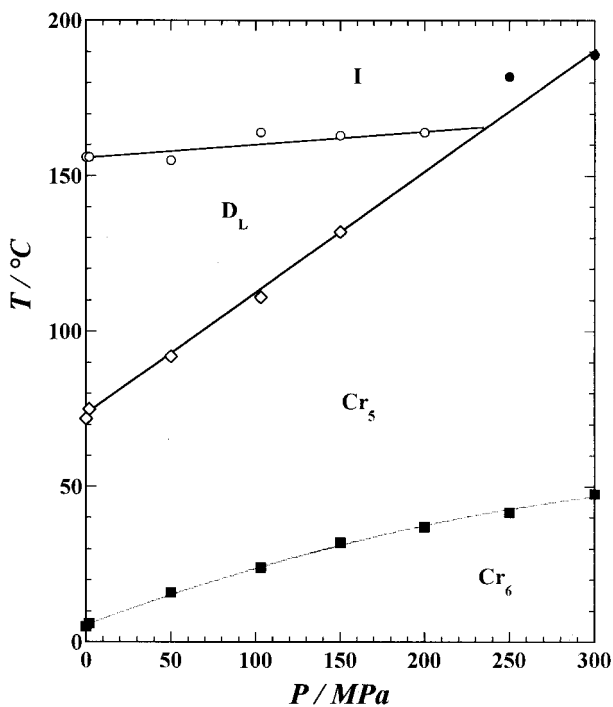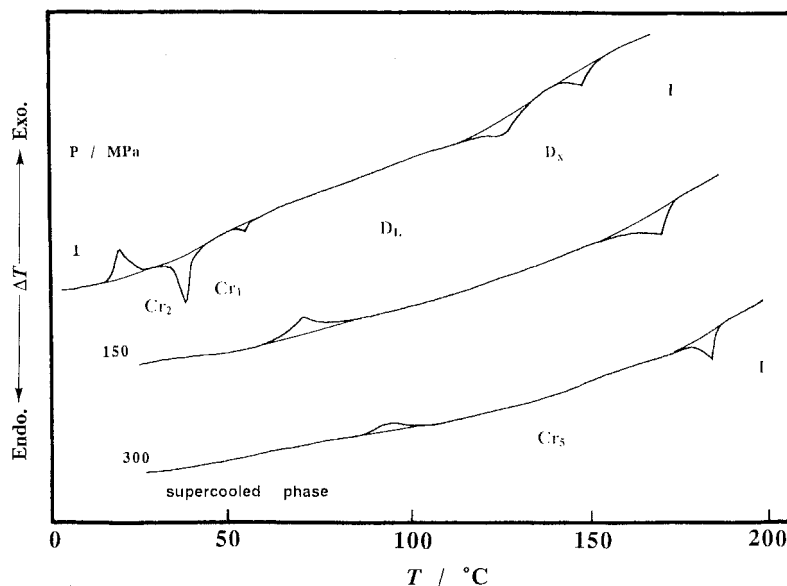
Figure 15. DTA heating curves of a supercooled sample of C12TPP obtained by rapidly cooling of the isotropic liquid at 300 MPa.

are two possibilities for the supercooled phase, i.e. supercooled isotropic liquid (I) and supercooled D_L phase. But in this case the supercooled D_L phase is strongly suggested because the exothermic heat is comparable to that of the D_L–Cr_s transition. A similar heating curve was observed at 150 MPa, with an exothermic peak at 72°C and an endothermic peak at 172°C. After the sample was cooled rapidly at 300 MPa and the pressure then released, the DTA curve at 0.1 MPa showed an exothermic peak for crystallization to Cr_2 at 19°C. Thereafter the normal transition process of Cr_2–38°C–Cr_1–55°C–D_L was observed on heating. On further heating, the sample showed an unusual transition D_L–D_X at about 130°C, just before isotropization at 155°C. The new D_X phase may be another discotic mesophase which must be analysed structurally in the future. Further investigations of the structural behaviour of C12TPP will be made to understand more precisely the phase behaviour and the structures of the crystal polymorphs and discotic mesophases.

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