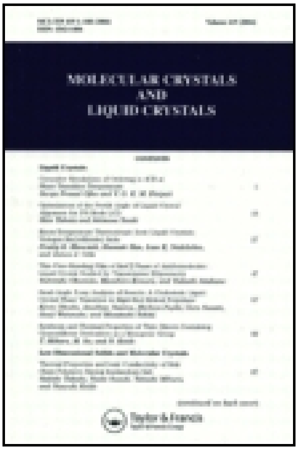

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Phase Behaviour of the Discotic Mesogen 5,10,15,20-Tetrakis(4-N-Dodecylphenyl) Porphyrin under Hydrostatic Pressure

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Phase Behaviour of the Discotic Mesogen 5,10,15,20-Tetrakis(4-N-Dodecylphenyl) Porphyrin under Hydrostatic Pressure

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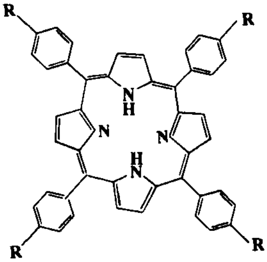
The phase behaviour of the discotic mesogen 5,10,15,20-tetrakis(4-n-dodecylphenyl) porphyrin(C12TPP) was investigated under hydrostatic pressures up to 350 MPa by high-pressure DTA and wide-angle X-ray diffraction measurements. Seven crystal polymorphs are found, depending upon the temperature and pressure. The discotic lamellar(D_L) phase is observed enantiotropically under pressures up to ca. 240 MPa, while the monotropic D_L phase appears on cooling under pressures between 240 and 310 MPa. Further increasing pressure above 310 MPa disappears completely the D_L phase, showing the crystal-isotropic transition.

Keywords: 5,10,15,20-tetrakis(4-n-dodecylphenyl)porphyrin; Monotropic discotic phase; T vs. P phase diagram; triple point

INTRODUCTION

High-pressure investigation of the phase behaviour of liquid crystals helps us to understand the structure-property relationship of crystalline and mesophasic polymorphs. Chandrasekhar, et al[1] found the discotic mesophase of the disk-like molecule, i,e, the benzene-hexa-n-octanoate(BH8). BH8 has the mesophase structure of lamellar order with hexagonal symmetry in two dimensions and liquid-like disorder in the third. They reported the T vs. P phase diagram of BH8 showing the triple point in which the discotic mesophase disappears at pressures above about 140 MPa. Buisine and Soulestin[2] reported the phase behaviour of the (-)2,3,6,7,10,11-hexa-S-(3-methl)-n-nonanoyloxytriphenylene and 2,3,7,8,12,13-hexa-n-decanoyloxytruxene (C_{10}HATX) under pressures up to 600 bars by using a new automated metabolemeter. They reported several discotic-discotic mesophase transitions in C_{10}HATX. Shimizu, et al[3-5] also reported that metal-free 5,10,15,20-tetrakis(4-n-dodecylphenyl)porphyrin,



R: $-(CH_2)_{11}CH_3$

Chemical structure of C12TPP

hereafter abbreviated to C12TPP, exhibits a peculiar discotic lamellar(D_L) phase showing an interesting mesomorphic transition. A photoconductive cell using the pentadecyl homologue, C15TPP, gave a novel bias dependence of the photocurrent which varies with the mesomorphic phase transitions[6]. The authors reported the structural fact on the phase behaviour of the D_L phase of C12TPP in which the D_L phase appears monotropically at high pressures above about 240 MPa, although it appears enantiotropically under low pressures[7].

In this study, the phase behaviour of C12TPP at high pressures up to 350 MPa has been studied in order to understand the nature of phase behaviour of C12TPP by high-pressure differential thermal analysis(DTA) and wide-angle X-ray diffraction(WAXD) measurements.

EXPERIMENTAL

C12TPP was prepared by the usual synthetic approach from tetraphenylporphyrin[8]. The product was purified by column chromatography after oxidation of chlorinated by-product. Further purifications were carried out by the 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 Perkin Elmer differential scanning calorimeter DSC 7 and Olympus polarizing microscope BH-2 equipped with a Mettler FP 82 hot-stage.

The structural change of C12TPP was studied under pressure by using a rotating anode X-ray generator (60 kV and 200 mA; RU-200, Rigaku Co.) equipped with a high-pressure vessel on the goniometer[9]. The high-pressure wide-angle X-ray diffraction (WAXD) system was used at pressures up to 350 MPa in a temperature region between -30°C and 300°C. The sample in a beryllium spindle as sample vessel is pressurized hydrostatically with low viscosity dimethylsilicone oil(10 centiStokes, Toshiba Silicone Co.) and then is irradiated by a beam of Ni-filtered Cu Kα X-rays.

The diffracted X-rays are detected by a position-sensitive proportional counter (PSPC-30, Rigaku Co.) covering diffraction angles of 2θ=28° on the equator.

Thermal behaviour of the C12TPP sample under pressure was studied by a high-pressure DTA apparatus described elswhere[9]. Medium-viscosity dimethylsilicone oil(100 centiStokes) was used as a pressure transmitting medium. The DTA runs were performed at a constant scanning rate of 5°Cmin^{-1} under various pressures. Transition temperature was determined as the temperature at the top of transition peak.

RESULTS AND DISCUSSION

Effect of pressure on transition behaviour of the D_L phase

The DSC cooling and subsequent heating curves show reversibly the low(Cr_2) to high-temperature crystal(Cr_1), Cr_1-D_L, and D_L-I transitions at atmospheric pressure, respectively. The D_L phase is observed in a wide temperature region of about 100°C. The X-ray patterns of the Cr_2 crystal on heating under atmospheric pressure show that the Cr_2-Cr_1 transition occurs at about 38.5°C and that heating the sample at temperatures above 57°C induces a very strong reflection of the D_L phase at 2θ=2.79°(*d*=31.64Å) and several weak reflections at wide angles until the D_L-I transition at 154°C. Based on the C.P.K. molecular model[10], the *d* spacing of the low-angle reflection of the D_L phase indicates the distance between the neighbouring alkylphenyl groups of the C12TPP molecule. The structural change corresponds well to the DSC transition behaviour, showing the reversible Cr_2-Cr_1-D_L-I transition process.

From the DTA cooling and heating curves of the C12TPP sample under pressures up to 300 MPa, the Cr_2-Cr_1-D_L-I transition is maintained under pressures up to about 10 MPa. When higher pressure is applied to the sample, one can see the splitting of the Cr_2-Cr_1 transition peak into two peaks. This exhibits the formation of a new phase(Cr_3) between the Cr_2 and Cr_1 phases, and the temperature region of the Cr_3 phase is enlarged with increasing pressure. The Cr_2-Cr_3 transition is 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. On the other hand, the temperature region of the D_L phase decreases almost linearly with increasing pressure. When pressure is raised above 180 MPa, fourth and fifth crystal polymorphs(Cr_4, Cr_5) are formed at low and high temperatures, respectively. The Cr_5 form is induced at high temperatures about 9°C below the D_L-I transition. The thermal behaviour at 190-200 MPa is described as the Cr_2-Cr_4-Cr_3-Cr_1-(Cr_5)-D_L-I transition scheme. Further increase of pressure generates the ambiguous thermal behaviour of C12TPP: the Cr_3-Cr_1 and Cr_1-Cr_5 transition peaks are too small to be detected, while the Cr_5-D_L transition tends to merge with the D_L-I transition under high pressures at about 220 MPa. The complex thermal behaviour on heating can be analyzed to the occurrence of the two concurrent processes of the Cr_2-Cr_4-Cr_3-Cr_1-D_L-I transition scheme at lower pressure and the Cr_6-Cr_5-(D_L)-I transition scheme at higher pressure. The thermal behaviour is simple at elevated pressures above about 260 MPa: the cooling curve at 300 MPa shows the I-D_L and D_L-Cr_5 transitions at high temperatures and the Cr_5-Cr_6 transition at low temperature, while the subsequent heating shows only two peaks of the Cr_6-Cr_5 and Cr_5-I transitions at low and high temperatures, respectively. The D_L phase is monotropic in the pressure region between 240 and 310 MPa. The WAXD patterns of C12TPP at 300 MPa also shows that the D_L phase appears monotropically at about 150~142°C on cooling. The low-angle reflection of the D_L phase is observed at 2θ~2.7-2.8°(d=31.6-32.7Å) and then several reflections are observed at about 141°C, exhibiting the $D_L \rightarrow Cr_5$ transition. The I-D_L-Cr_5-Cr_6 transition is predominant on cooling at 300 MPa and the subsequent heating shows only the Cr_6-Cr_5 and Cr_5-I transitions at about 45°C and 178°C, respectively.

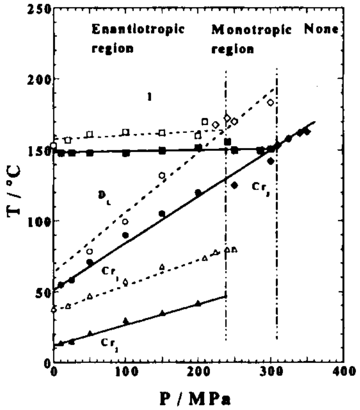
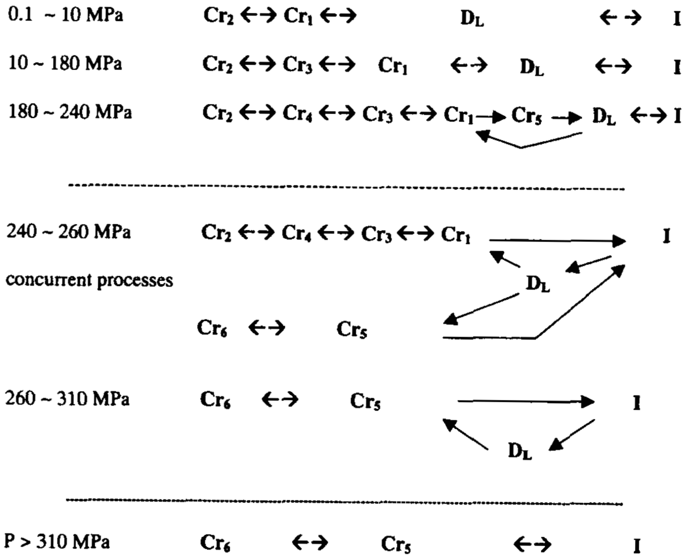


Figure 1. T vs. P phase diagram of the D_L phase of C12TPP on heating(---) and cooling(___).

Figure 1 shows the T vs. P phase diagram of the D_L phase of C12TPP under pressures between 0.1 MPa and 350 MPa. One can divide the phase behaviour of C12TPP into three categories, on the point of the thermal behaviour of the D_L phase. First is the low-pressure region between 0.1 and 240 MPa, in which the D_L phase is observed reversibly. The temperature region of the D_L phase decreases with increasing pressure from about 100 degrees at 0.1 MPa to about 47 degrees at 150 MPa. This occurs because the Cr_1-D_L transition curve with the slope dT/dP of 0.39_2 °C/MPa shifts to higher temperature with increasing pressure, while the D_L-I transition with the slope of 0.06_0 °C/MPa is slightly dependent upon pressure. Second one is the intermediate-pressure region between 240 and 310 MPa, in which the D_L phase is observed as a monotropic transition. One can see a triple point among the D_L, Cr_5 and I phases both on heating and cooling processes. The triple point on heating mode is estimated as 240 MPa and 169°C, while the point on cooling is estimated to be 310 MPa and 152 °C. In fact, the D_L phase was observed on cooling under pressures between 250 and 300 MPa. The existence of a triple point, i.e., disappearance of a discotic phase at high pressure, is first reported by Chandrasekhar, et al[1]. Third category is the high-pressure region above 310 MPa, in which the D_L phase is never observed.

If the crystalline polymorphs also are taken into account for the T vs. P phase diagram, the phase behaviour of C12TPP is divided into six pressure regions.



It is concluded that the D_L phase of C12TPP is unstable at elevated pressures above 310 MPa, via the metastable state in the intermediate-pressure region from the stable state in the low-pressure region including atmospheric pressure.

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