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In situ observation of the pressure-induced mesophase for 4′-*n*-hexadecyloxy-3′-nitrobiphenyl-4-carboxylic acid

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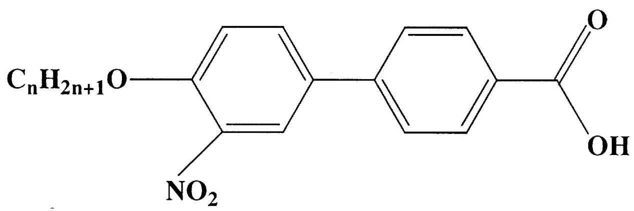
In situ observation of the optical texture, and X-ray patterns of the pressure-induced mesophase seen for 4′-*n*-hexadecyloxy-3′-nitrobiphenyl-4-carboxylic acid (ANBC-16) was performed under hydrostatic pressures up to 100 MPa using a polarizing optical microscope equipped with a high pressure hot stage and a wide angle X-ray diffractometer equipped with a high pressure vessel respectively. It was found that the pressure-induced mesophase (hereafter refered to as 'X') appeared at pressures above 60 MPa, and exhibits a birefringent broken-fan or a sand-like texture that remain unaltered in the SmC phase. The POM-transmitted light intensity curve measured on heating clearly showed the $Cr_4 \rightarrow Cr_1 \rightarrow$ SmC → 'X' → SmA → I transition sequence at 80 MPa. The optical texture and the POM-transmitted light intensity measured during a pressure cycle at 185°C showed a reversible change between the cubic and 'X' phases. The WAXD pattern of the 'X' phase showed a spot-like pattern, suggesting no layered structure for this phase, and also revealed a substantial decrease in the *d*-spacing of the low angle reflection at 80 and 100 MPa, compared with the *d*-spacings of the (0 0 1) reflection of the SmC phase and also the (2 1 1) reflection of the cubic phase. It is concluded from these data that the 'X' phase is a birefringent hexagonal columnar phase.

1. Introduction

The study of thermotropic cubic liquid crystalline phases began as early as 1957, when Gray *et al.* [1] reported the synthesis of 4′-*n*-hexadecyloxy- and 4′-*n*-octadecyloxy-3′-nitrobiphenyl-4-carboxylic acids (ANBC-16 and ANBC-18, respectively). These molecules consist of a nitrobiphenyl-carboxylic acid core and flexible *n*-alkoxy chains:



Demus *et al.* provided evidence for the thermotropic cubic mesophase of ANBC-16 and ANBC-18 from optical microscopic studies [2, 3]. Since then thermotropic cubic phases have attracted much scientific interest because they are optically isotropic. It is now known that ANBC-*n* compounds show cubic phases when *n* ranges from 15 to 26 [4].

Shankar Rao *et al.* reported the interesting *T* vs. *P* phase diagram of ANBC-16 by measuring the intensity of transmitted laser light while cooling the sample [5]. In their phase diagram, the cubic phase disappears at about 40 MPa, while a columnar (Col) phase appears between the smectic C (SmC) and smectic A (SmA) phases at high pressures. One of us also studied, the transitional behaviour of ANBC-16 on heating under pressure using high pressure DTA [6]. The resulting phase diagram indicates the disappearance of the cubic phase at about 65 MPa and the appearance of a new mesophase ('X') at higher pressure. The 'X' phase, in place of the cubic phase, appears between the SmC and SmA phases on heating at high pressures. There is a significant discrepancy between the two phase diagrams; one can see the Cub–Col transition line with a negative slope (dT/dP) in their diagram, while there is no such transition in our diagram. Their triple point at about

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40 MPa and 188°C is for the SmC, Cub and Col phases, while the triple point at 65 MPa and 207.6°C is for the SmC, Cub and SmA phases in our diagram. This discrepancy in triple points seen in the two T vs. P phase diagrams prompted us to observe directly the morphological texture under hydrostatic pressure and to investigate the structure of the 'X' mesophase seen for ANBC-16 under pressure.

In this study we report the experimental results for the 'X' phase seen for ANBC-16 obtained using polarizing optical microscopy (POM) and wide angle X-ray diffraction on isobaric and isothermal processes under hydrostatic pressures up to 100 MPa.

2. Experimental

2.1. *Sample preparation*

ANBC-16 was prepared according to the method described by Gray *et al.* [1]. Samples were recrystallized from ethanol several times and the purity was confirmed by infrared, ^{1}H NMR, and mass spectroscopies, and by elemental analysis.

2.2. *Polarizing optical microscope measurements under pressure*

The texture of ANBC-16 was observed using a Leitz Orthoplan polarizing optical microscope (POM) equipped with either a Mettler FP-82 hot stage or a high pressure hot stage which is described in detail elsewhere [7]. Transmitted light intensity through the POM with crossed Nicols was observed using a Mettler FP-90 photomonitor under atmospheric and hydrostatic pressures. Pressure and temperature were monitored simultaneously during the morphological observation. Two procedures were adopted for texture observation under hydrostatic pressure. Procedure 1 was an isobaric process at 65 MPa and involved cooling and heating processes during which the 'X' phase appeared in place of the cubic phase between the SmC and SmA phases. Procedure 2 was an isothermal process at 185°C, which started from the cubic phase at 5 MPa, leading to the 'X' phase at 65 MPa or higher pressures. Figure 1 illustrates these two routes drawn on the T vs. P phase diagram of ANBC-16, which was prepared on heating.

2.3. *Wide angle X-ray diffraction measurements under pressure*

The high pressure wide angle X-ray diffraction (WAXD) apparatus used in this study is described elsewhere [8]. The high-pressure vessel was set on the wide angle goniometer of a 12 kW rotating anode X-ray generator (Rotaflex RU-200, Rigaku, Co.). The pressure vessel consisted of a beryllium spindle as the sample cell,

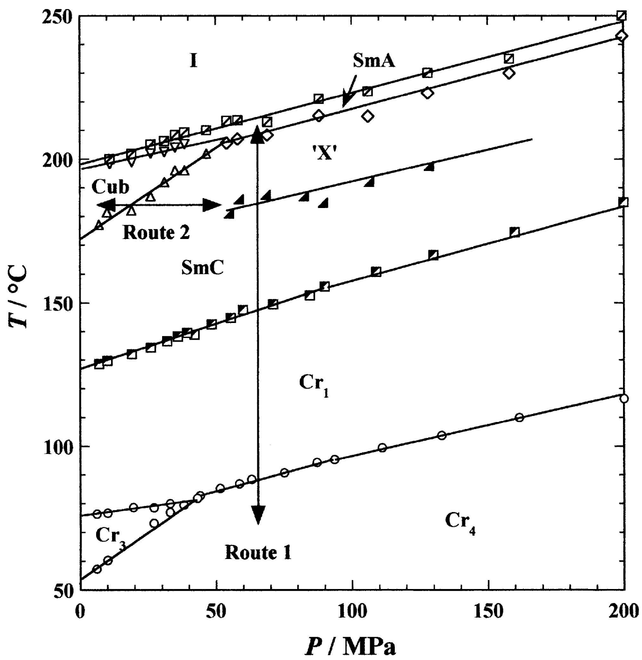

Figure 1. Two procedures for texture observation in the T vs. P phase diagram of ANBC-16: procedure 1, isobaric process at 65 MPa (route 1); procedure 2, isothermal process at 185°C (route 2).

sandwiched between the upper and lower pressure blocks. Dimethylsilicone oil of low viscosity (10 cSt) was used as a pressure medium. The sample was inserted into the vertical hole of the beryllium spindle. The beryllium spindle was mechanically sealed by the upper and lower pressure blocks and then the sample was pressurized hydrostatically at pressures up to 100 MPa. Ni-filtered Cu K_α X-rays were used to irradiate the sample and the X-ray reflections were detected on the equatorial line using a curved PSPC detector (PSPC-30, Rigaku Co). The reflection was taken during a 200–300 s period of time. The WAXD patterns were obtained using an imaging plate detector (BAS-IP 127 mm × 127 mm, Fuji Photo Film Co).

3. Results and discussion

3.1. *Texture observations of ANBC-16 under pressure*

The calorimetric heating scan for ANBC-16 shows three small crystal–crystal transitions at 47.5, 74.5 and 89.4°C, a major Cr–SmC transition at 124.9°C, a small but sharp SmC–Cub transition at 175.1°C, double peaks for the Cub–SmA and SmA–I_1 transitions at 197.9 and 198.8°C, and finally a broad isotropization peak of the I_1–I_2 transition at 203.1°C on heating. All the peaks are thermodynamically first order transitions.

When one views the SmC–Cub transition by POM under crossed polarizers, the black, optically isotropic areas having distinctive square, rectangle, and rhombic shapes are observed and these growing areas eventually coalesce to give a completely optically isotropic field of view in the cubic phase [2–4, 6]. Figure 2 shows the change in POM-transmitted light intensity for ANBC-16 on heating and the subsequent cooling processes under atmospheric pressure. One can easily find the sharp changes associated with the Cr_3–Cr_2, Cr_1–SmC and SmC–Cub transitions on heating, with two smaller changes in the solid region corresponding to the Cr_4–Cr_3 and Cr_2–Cr_1 transitions. On cooling the Cub → SmC and SmC → Cr_1 transitions are accompanied by remarkable changes in the intensity of the transmitted light, due to the birefringence of the SmC phase. After the measurement, ANBC-16 shows the original light intensity at room temperature. The morphological features seen during the Cr–SmC–Cub–SmA–I transition sequence at atmospheric pressure were also observed under hydrostatic pressures up to 50 MPa, except that in the cubic and isotropic liquid phases the field of view became dark brown, not black, under hydrostatic pressure. This is due to the presence of the pressurized silicone oil as the second component under crossed polarizers. Accordingly, low image contrast is inevitable for observation using the high pressure hot stage having thick sapphire windows. Nevertheless, the SmC–Cub transition can be detected clearly under pressure because the dark brown field of view seen for the cubic phase is easy to discriminate from the birefringent textures of the smectic phases. Interestingly the texture change during the SmC → Cub

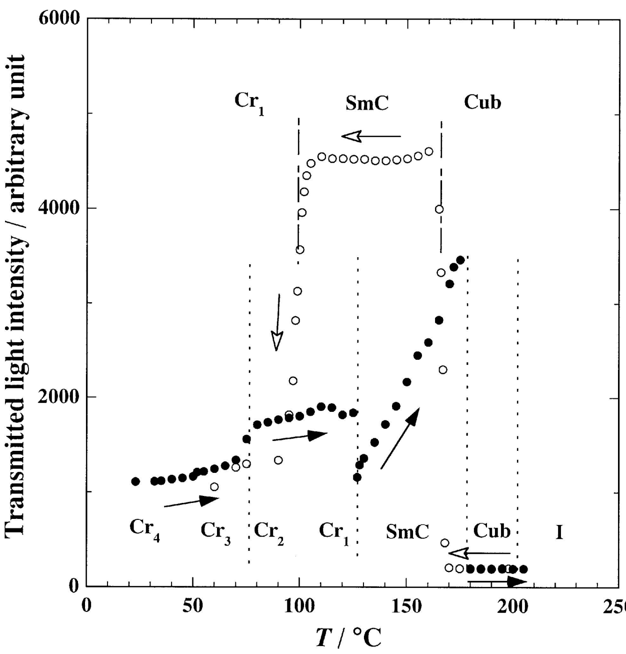

Figure 2. Change in POM-transmitted light intensity of ANBC-16 on heating (●) and cooling (○) under atmospheric pressure.

transition occurred rapidly under hydrostatic pressures, in contrast to the slow change seen at atmospheric pressure.

The stable temperature region of the optically isotropic cubic phase becomes narrower with increasing pressure before disappearing at still higher pressure [6]. The *T* vs. *P* phase diagram shows a new mesophase, denoted here as 'X', appearing in place of the cubic phase under pressures above about 60 MPa. It would be interesting to study the morphological and structural characterization of the 'X' phase under pressure. Figure 3 displays the POM photographs of the texture of ANBC-16 on cooling from the isotropic liquid at 65 MPa. The typical focal-conic texture of the SmA phase was observed at 199°C, figure 3 (*b*), and at 195°C. On further cooling, the uniform focal-conic structure for the SmA phase became broken at 192°C in the 'X' phase, figure 3 (*c*). The 'X' phase showed a plate-like broken-fan texture which was apparently maintained in the SmC phase at 150°C, figure 3 (*d*). The texture for the SmC phase, which is quite similar to that for the 'X' phase, was observed until crystallization occurred at 121°C, figure 3 (*e*). The morphological observation was subsequently performed on heating from 100°C at 65 MPa. The crystal spherulites were observed at temperatures up to *c.* 140°C, as shown in figures 3 (*f*) and 3 (*g*). After the Cr_1–SmC transition, the sand-like texture of the SmC phase, figure 3 (*h*), was observed and persisted to about 185°C, figure 3 (*i*). The sand-like texture was essentially the same at 195°C beyond the SmC–'X' transition at 190°C, but it became finer as shown in figure 3 (*j*), and the brightness changed abruptly. This resulted in an increase in transmitted light intensity during the SmC–'X' transition; this is described later. On further heating to 201°C, the texture was partly focal-conic in nature, characteristic of the SmA phase, figure 3 (*k*). Thus it was determined that the optically isotropic, dark field of view of the cubic phase no longer appears on cooling and heating at 65 MPa.

Figure 4 shows the change in POM-transmitted light intensity for ANBC-16 on heating at 80 MPa. Discontinuous changes in light intensity associated with the Cr_4–Cr_1 and Cr_1–SmC transitions were observed at 90°C and 147°C, respectively. Further increase of temperature saw an abrupt increase in intensity at about 185°C, indicating the existence of a transition, albeit without any substantial change in morphological texture, see figures 3 (*i*) and 3 (*j*). This behaviour corresponds to the SmC–'X' transition. Finally a substantial increase in brightness occurred in the small temperature region of the SmA phase just below the isotropization point. The optical and morphological features for the 'X' phase are clearly different from the cubic phase seen at atmospheric and low pressures: firstly, the texture of the 'X' phase

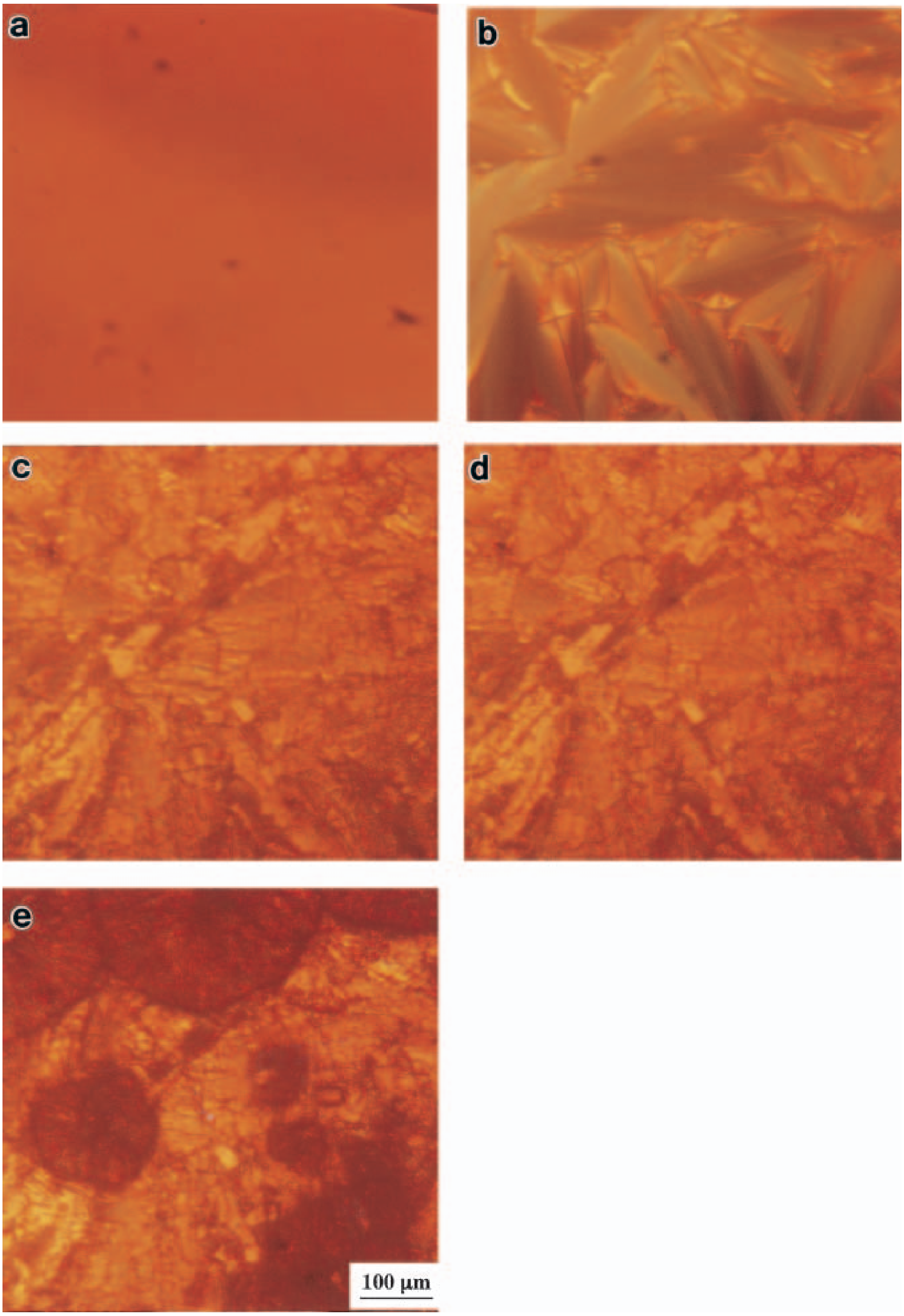

Figure 3. POM photographs of the texture of ANBC-16 on cooling at 65 MPa (route 1 in figure 1): (*a*) dark field of the isotropic liquid at 203°C, (*b*) focal-conic texture of the SmA phase at 199°C, (*c*) broken-fan texture for the 'X' phase at 192°C, (*d*) broken-fan texture for the SmC phase at 150°C, (*e*) crystallization at 121°C. POM observations on heating from 100°C at 65 MPa: (*f*) and (*g*) crystals at 105°C and 140°C, (*h*) and (*i*), sand-like texture for the SmC phase at 150°C and 185°C, (*j*) sand-like texture for the 'X' phase at 195°C, (*k*) texture during the SmA–I_1 transition at 201°C.

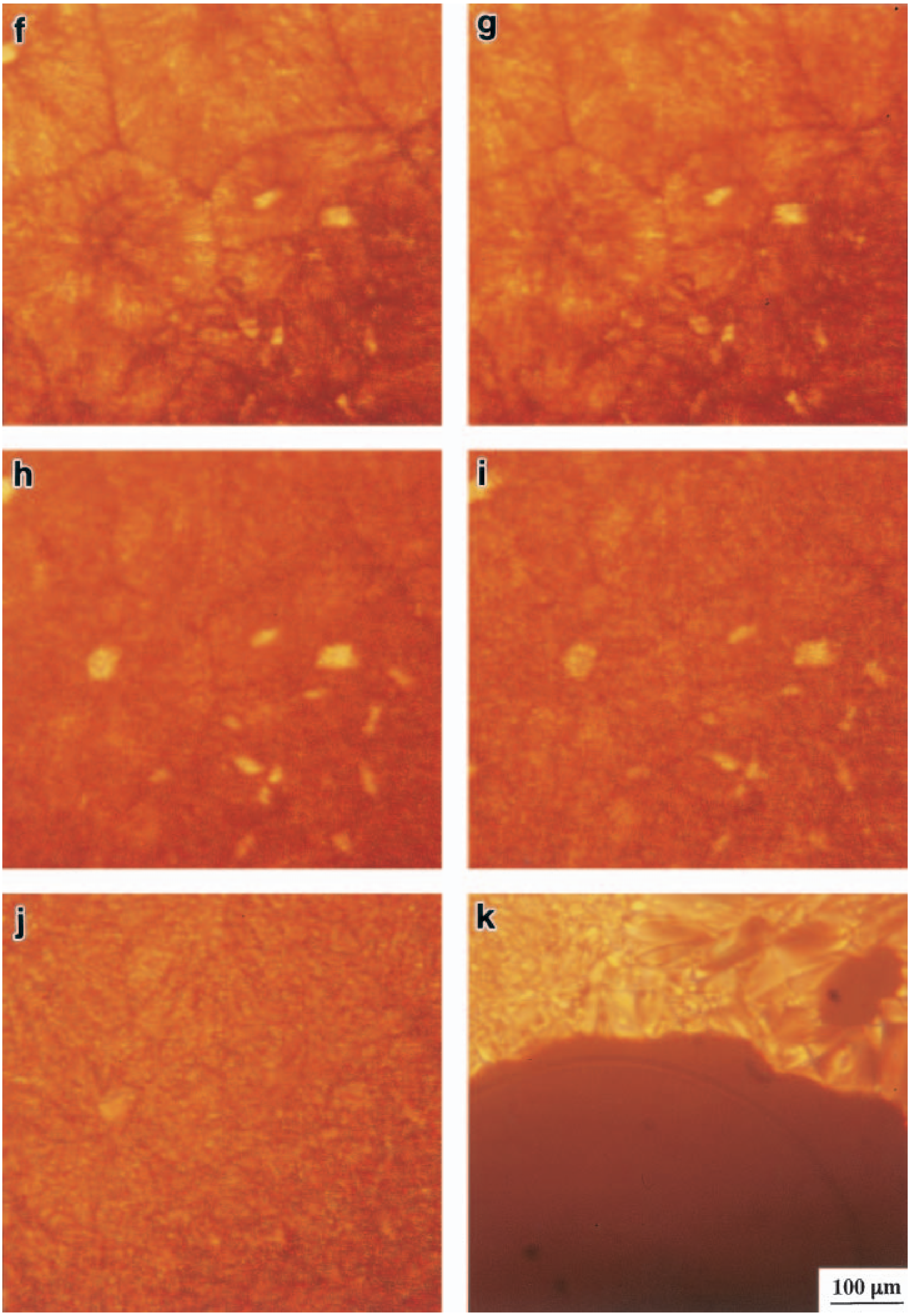

Figure 3. (*continued*).

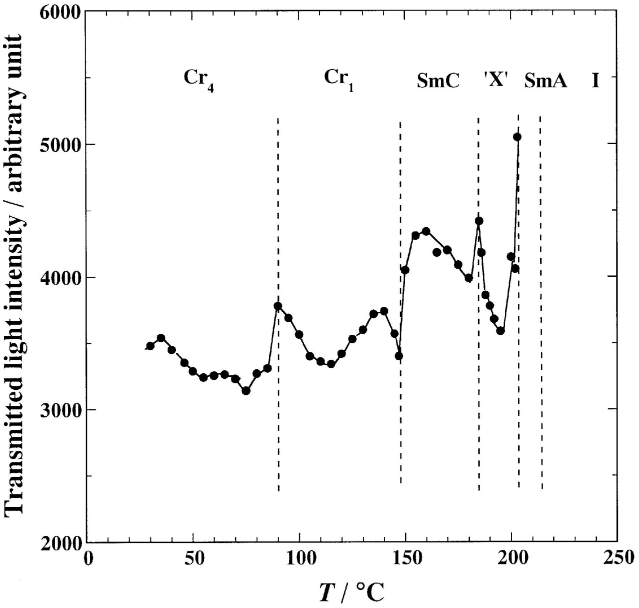

Figure 4. Change in POM-transmitted light intensity for ANBC-16 on heating at 80 MPa.

observed under pressure is birefringent, while the cubic phase shows an optically isotropic, dark field of view. Secondly, the texture for the 'X' phase differs little from that of the SmC phase at high pressures. Thirdly, the POM-transmitted light intensity curve clearly exhibits a remarkable intensity change accompanying the SmC–'X' transition at high pressure. Thus the 'X' phase is an optically anisotropic, birefringent phase with an optical texture similar to that of the SmC phase. The evidence for the 'X' phase obtained using POM is completely consistent with the T vs. P phase diagram reported previously using high pressure DTA [6].

Another POM measurement was performed along the isothermal path denoted route 2 in figure 1. It is interesting to see how the optically isotropic, dark field of view of the cubic phase changes on both increasing and decreasing the pressure. The texture changes seen at 185°C on increasing pressure are shown in figure 5. Figure 5(*a*) is the initial state that was prepared by heating to 185°C at 5 MPa, and the optically isotropic, dark field of view for the cubic phase is seen. The dark field of view persisted for pressures up to 50 MPa, figure 5(*b*). When the pressure was raised to 55 MPa, small bright islands were formed sporadically in the dark field of the cubic phase, figure 5(*c*), indicating the appearance of the 'X' phase. The bright islands grew for 5 min at 55 MPa, figure 5(*d*), and their growth was accelerated at 60 MPa, figure 5(*e*). Finally the bright islands coalesced forming a homogeneous texture with many grain boundaries at 65 MPa figure 5(*f*). The changes were observed in reversed order on decreasing the pressure to 35 MPa, indicating that the morphological changes occur reversibly on changing the pressure. Such morphological phenomena during the Cub–'X' transition are observed also at 180 and 190°C. It is interesting to see that the cubic phase shows irregular shapes during the 'X' → Cub transition at 185°C, in contrast to the regular rectangular, tetragonal, and rhombic domains seen during the SmC–Cub transition at atmospheric pressure. Figure 6 shows the change in POM-transmitted light intensity observed during the Cub–'X' transition at 185°C. It was found that the optical change in POM-transmitted light intensity corresponds well to the change in texture during the Cub–'X' transition in the isothermal process.

3.2. *Structural change of ANBC-16 under pressure*

The X-ray investigation of the cubic phase of ANBC-16 by Diele *et al.* [9] showed two principal features in the diffraction pattern: a diffuse ring at 4.5 Å and a small number of sharp low angle reflections. A more detailed analysis of the X-ray diffraction pattern was performed by Tardieu and Billard [10]. They identified the space group as *Ia*3*d* with the value of the unit cell dimension being $d = 102$ Å. The suggested molecular arrangement is quite analogous to the model for a lyotropic cubic phase proposed by Luzzati and Spegt [11]. The molecules are aggregated in short cylinders and these cylinders are linked to form two interwoven three-dimensional networks with overall cubic symmetry. The Tardieu–Billard model is now widely accepted as the structure of the cubic phase of ANBC-16.

Figure 7 shows three WAXD patterns in the low angle region for ANBC-16, measured (a) at 165°C and 80 MPa in the SmC phase, (*b*) at 201°C and 80 MPa in the 'X' phase and (*c*) at 185°C and atmospheric pressure in the cubic phase. The diffraction pattern of the SmC phase at 80 MPa is similar to that of the same phase at atmospheric pressure, having a low angle ($2\theta \cong 2.0°$) intense arc. On the other hand, the WAXD pattern of the 'X' phase consists of several strong spots and a few weaker ones, and the spot-like pattern is similar to that of the cubic phase, see figure 7(*c*). The spot-like pattern reflects the presence of relatively large domains, suggesting no layered structure for the 'X' phase.

Figure 8 shows the WAXD-PSPC patterns collected on heating at 100 MPa. The (0 0 1) reflection of the SmC phase at $2\theta \cong 2.0°$ was observed at temperatures up to about 191°C. The peak grew gradually with increasing temperature and at the same time shifted slightly to wider angles, suggesting an increase in tilt angle of molecules with respect to the smectic layer normal of the SmC phase. When the SmC–'X' transition occurred at around

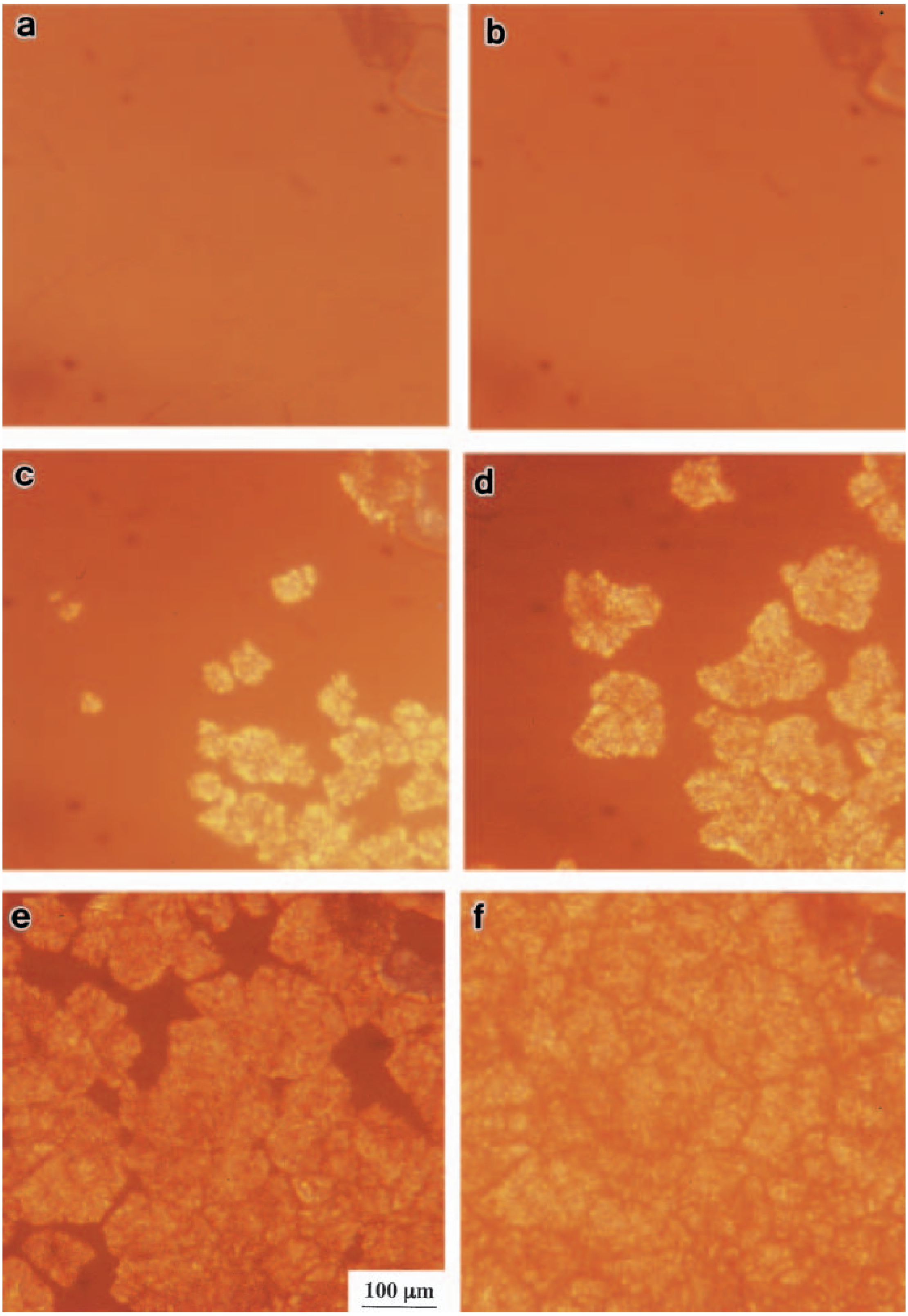

Figure 5. POM photographs of the texture of ANBC-16 at 185°C on increasing the pressure from 5 to 65 MPa along route 2 in figure 1: (*a*) and (*b*) optically isotropic, dark field for the cubic phase at 5 and 50 MPa; (*c*) bright islands for the 'X' phase in the dark field at 55 MPa; (*d*) the same as (*c*), taken after 5 min; (*e*) bright islands coalesce to form a homogeneous texture for the 'X' phase at 60 MPa; (*f*) sand-like texture for the 'X' phase at 65 MPa.

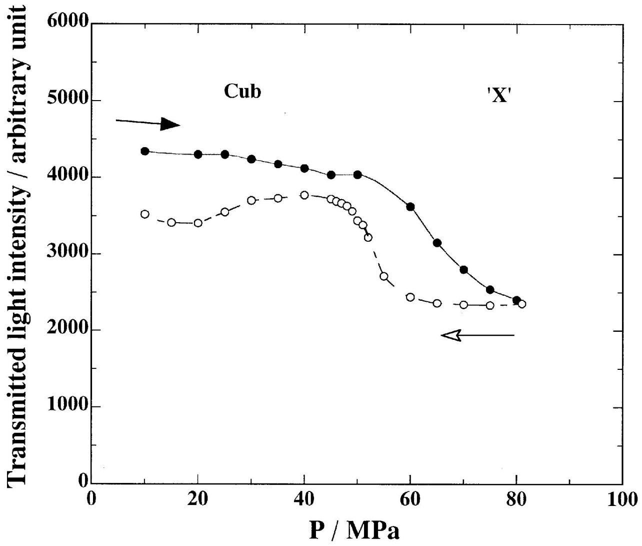

Figure 6. Change in POM-transmitted light intensity for ANBC-16 during the Cub–'X' transition at 185°C.

193°C, the low-angle reflection shifted to wider angles and the peak intensity significantly decreased. The reflection for the 'X' phase was observed at $2\theta \cong 2.14°$ in the temperature region between 193 and 208°C. The value of the *d*-spacing for the low angle reflection at 1 atm and 80 MPa are plotted as a function of temperature in figure 9. Both at 1 atm and 80 MPa, the *d*-spacing of the (0 0 1) reflection for the SmC phase decreased almost linearly with increasing temperature. The (0 0 1) reflection for the SmC phase changed continuously to the (2 1 1) reflection for the cubic phase through the SmC–Cub transition under atmospheric pressure, in agreement with the previous result [12], while the *d*-spacing dropped rapidly from 4.4 to 4.1 nm at the SmC–'X' transition at 80 MPa. The *d*-spacing of about 4.1 nm for the 'X' phase was held in the temperature region between 190 and 203°C. Across the 'X'–SmA transition a large increase in *d*-spacing was seen. Finally the low angle reflection disappeared in the isotropic liquid phase.

In a previous paper [6] we speculated that it is possible that the 'X' phase could be either another cubic modification as seen in ANBC-22 and -26 [13, 14] or a smectic modification different from the SmC and SmA phases. This speculation, however, is not supported by the features of the 'X' phase revealed in this study. Firstly, optical anisotropy is one of the most important features of the 'X' phase. The change in texture between the Cub and 'X' phases during pressure variation at 185°C is an optically isotropic–anisotropic transition. On cooling from the isotropic liquid at 65 MPa, the plate-like texture seen for the 'X' phase was formed by breaking the uniform focal conic texture of the SmA phase and did not change significantly, even in the SmC

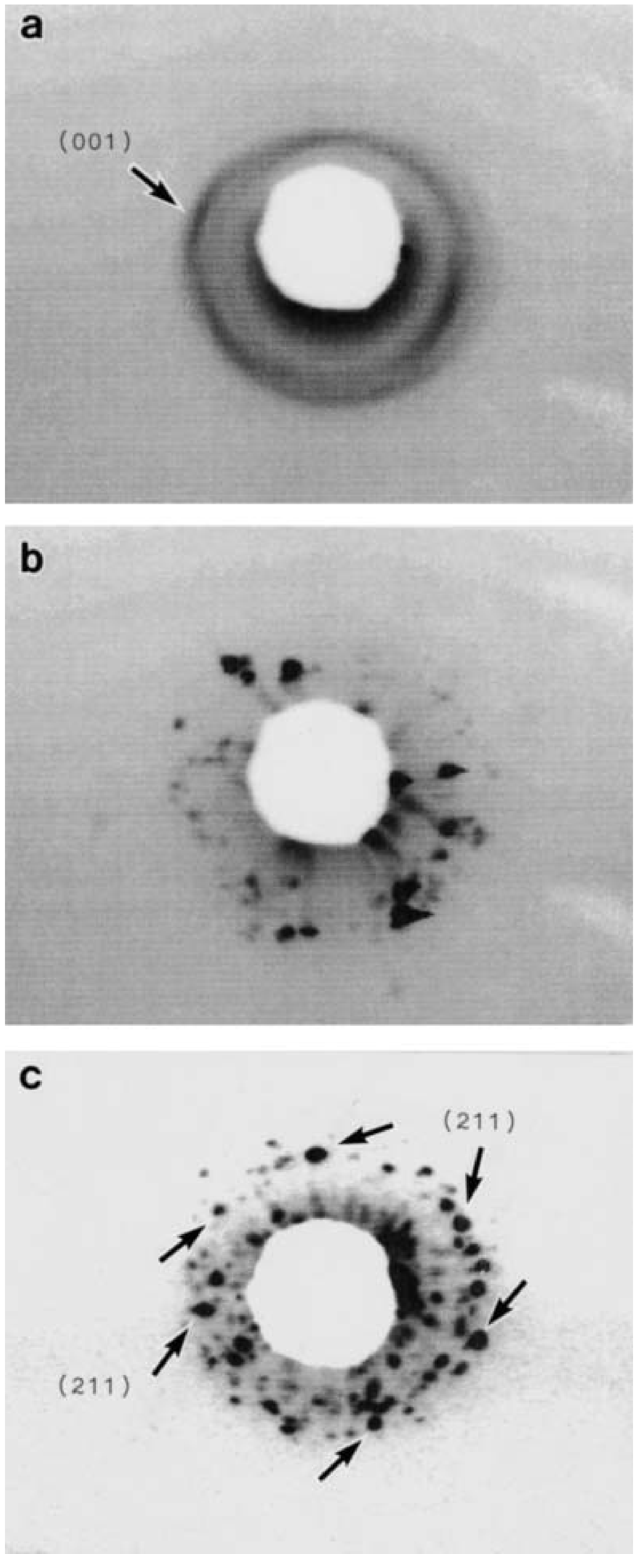

Figure 7. WAXD patterns of ANBC-16 in the low angle region: (*a*) SmC phase at 165°C and 80 MPa; (*b*) 'X' phase at 201°C and 80 MPa; (*c*) cubic phase at 185°C and 1 atm.

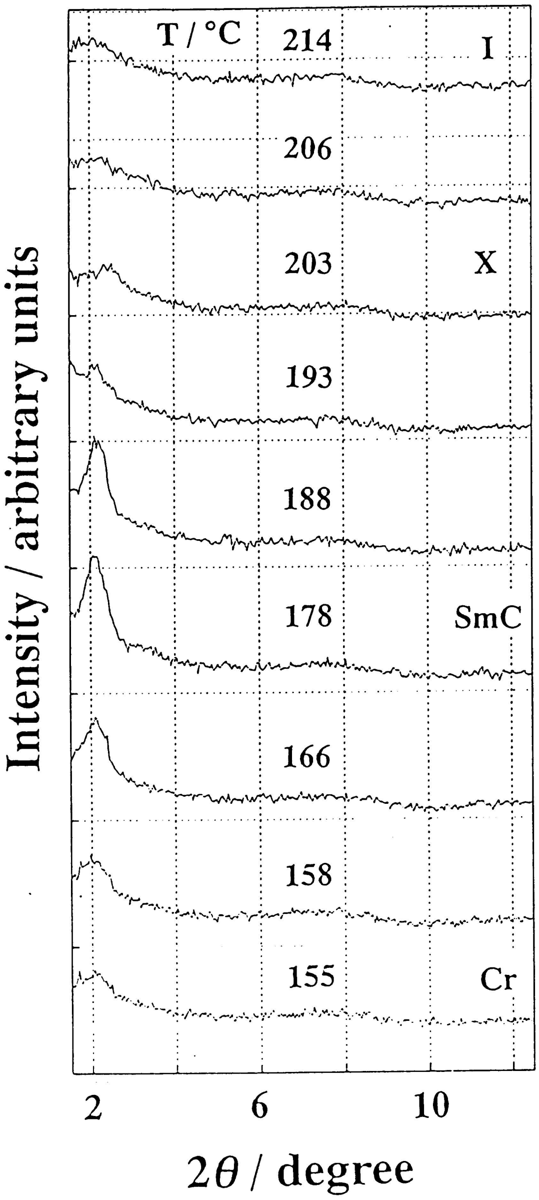

Figure 8. WAXD-PSPC patterns of ANBC-16 measured on heating at 100 MPa.

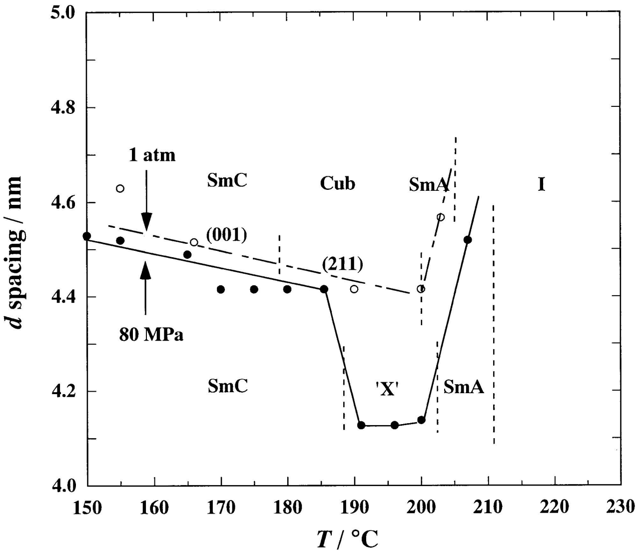

Figure 9. Change in d-spacing for the (0 0 1) reflection of the SmC phase of ANBC-16 on heating at 1 atm (○) and 80 MPa (●).

phase. The texture is apparently different from the rod-like bâtonnets or the mosaic grains seen for the S4 phase reported earlier [2]. Secondly, the WAXD pattern of spot-like reflections for the 'X' phase closely resembles the pattern for the cubic phase, suggesting no layered structure, but the d-spacing of the low-angle reflection is smaller than that of the (2 1 1) reflection for the cubic phase. Thus the 'X' phase has features, intermediate between the SmC and cubic phases from morphological and structural points of view.

Very recently we have re-investigated the transitional behaviour of ANBC-16 on cooling under hydrostatic pressure using high-pressure DTA [15, 16]. It was found that the 'X' phase can be observed reversibly between the SmA and SmC phases under high pressures above 60 MPa, while appearing only on cooling under lower pressures. In the T vs. P phase diagram constructed on cooling [16], the 'X' phase exists in the whole pressure region and it can be seen over a small temperature region between the SmA and cubic phases even at atmospheric pressure. This phase diagram corresponds fairly well with the phase diagram reported by Shankar Rao *et al.* [5]. The intermediate phase between the SmA and cubic phases, appearing in the DSC cooling curve at 5°C min^{-1}, is monotropic as shown in figure 4 in reference [16], and which had been identified in earlier reports as a columnar phase [17, 18]. Accordingly the 'X' phase in this study is consistent with the columnar phase; the 'X' phase is thus probably a hexagonal columnar phase.

To have a complete understanding of the 'X' phase, one should now determine the structure of the 'X' phase of ANBC-16 at high temperature and pressure for a monodomain sample.

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