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Effect of pressure on phase behavior of a thermotropic cubic mesogen

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Abstract

The phase behavior of an optically isotropic, thermotropic cubic mesogen 4-(ethylpentoxy)-anilinebenzylidenen-4′-carboxylic acid was investigated under pressures up to 300 MPa using a high-pressure differential thermal analyzer, a wide-angle X-ray diffractometer (WAXD) and a polarizing optical microscope (POM) equipped with a high-pressure optical cell. The cubic phase was found in the whole pressure region, although its temperature region decreased gradually with increasing pressure. The phase transition sequence, crystal (Cr)–cubic (Cub)–isotropic liquid (I) observed at atmospheric pressure, is held under pressures, while a high-temperature crystal polymorph appears under elevated pressures above about 160 MPa.

Keywords: Thermotropic cubic mesogen; High-pressure DTA; Phase sequence; *T* versus *P* phase diagram; Pressure-induced crystal polymorph

1. Introduction

Study on optically isotropic, thermotropic cubic mesogen started in 1957, when Gray et al. [1] reported the synthesis of 4′-*n*-hexadecyloxy- and 4′-*n*-octadecyloxy-3′-nitrobiphenyl-4-carboxylic acid: referred to as ANBC(16) and ANBC(18), respectively. Since then, a number of thermotropic cubic mesogens have now been reported [2]. The majority of these compounds are carbohydrates and polycatenar compounds including several metalomesogens. The cubic phases for ANBC(16) and ANBC(18) are known to have the structure with *Ia*3*d* space group. The jointed-rod model for the cubic phase with *Ia*3*d* space group, i.e. two interwoven, but unconnected networks of rods linked three by three [3–6], is suggested.

Although many researches into the phase transition behavior of the thermotropic cubic mesogens have been performed, there are only a few studies on the high-pressure investigation of the cubic phases [7–13]. One of the authors (Y.M.) reported the interesting phase behavior of ANBC(16) [8,9], ANBC(20) and ANBC(22) [10], and 1,2-bis(4-*n*-alkyloxybenzoyl)hydrazine (BABH(*n*) with carbon number *n* of methylene groups in the alkoxy chain, $n = 8$, 10–12 [11–13] under hydrostatic pressure. ANBC(*n*)s having the methylene groups of $n = 16$–22 show generally the phase transition sequence of crystal (Cr)–smectic C (SmC)–cubic (Cub)–(SmA for $n = 16$)–isotropic liquid (I), where BABH(*n*)s having the methylene groups of $n = 8$–10 exhibit the Cr–Cub–SmC–I transition sequence. The phase order between the SmC and cubic phases is inversed in the BABH(*n*) system. The *T* versus *P* phase diagrams of ANBC(*n*) system show that the SmC–Cub transition line has positive values for slope (d*T*/d*P*), but the phase diagrams of BABH(8) and BABH(10) exhibit that the Cub–SmC transition lines have negative slopes. The triple point for the Cr, Cub and SmC phases is found at very low pressures in BABH(8) and BABH(10), indicating the upper limit of pressure for the cubic phase formation. Also, in the ANBC(*n*), the cubic phase is destabilized with increasing pressure be-

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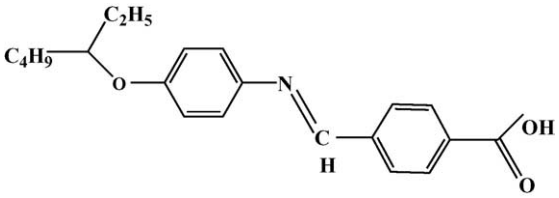
cause the temperature range decreases with increasing pressure.

On the other hand, racemic 4-(ethylpentoxy)-anilinebenzylidene-4′-carboxylic acid, abbreviated as EPABC, shows an optically isotropic cubic phase between the crystalline and isotropic liquid phases. This system exhibits reversibly a simple transition sequence of Cr–Cub–I under atmospheric pressure [14]. The chemical structure of EPABC is shown below.



This molecule has a anilinebenzylidene group as a central core, and ethylpentoxy group as a flexible spacer. Since EPABC molecule has a carboxylic acid group at a molecular end such as ANBC(*n*) system, the molecules form a dimerized structural unit in the crystal and mesophae through hydrogen bonding between the carboxylic acid groups of neighboring molecules. The dimerized molecule has the anilinebenzylidene carboxylic acid dimer as a central core and two ethylpentoxy groups as a flexible spacer. The dimerized molecule here may have a molecular shape of polycatenar compound with a short arm at both ends.

The interesting phase behavior of the cubic phase for ANBC(16) and BABH(8) under pressure prompted us to continue the study on phase behavior of various cubic mesogens under hydrostatic pressure, particularly focused on the effect of pressure on the phase stability of cubic phase. In this paper, we present the experimental results of the effect of pressure on the thermal, morphological and structural behavior of EPABC under hydrostatic pressures up to 300 MPa using a high-pressure DTA, a wide-angle X-ray diffractometer (WAXD) and a polarizing optical microscope (POM) equipped with a high-pressure optical cell.

2. Experimental

2.1. Sample characterization

The EPABC sample used in this study is described in elsewhere [14]. Thermal characterization was performed on a Perkin-Elmer DSC-7 differential scanning calorimeter at a scanning rate of 5 °C min^{-1} under N_2 gas flow. Transition temperature and heat of transition were calibrated using the standard materials (indium and tin). Transition temperatures were determined as the onset of the transition peaks at which the tangential line of the inflection point of the rising part of the peak crosses over the extrapolated baseline. Texture observation was performed using a Leiz Orthoplan polarizing optical microscope (POM) equipped with a Mettler hot stage FP-82.

2.2. DTA measurements under pressure

The high-pressure DTA apparatus used in this study is described elsewhere [15]. The DTA system was operated in a temperature region between room temperature and 250 °C under hydrostatic pressures up to 300 MPa. Dimethylsilicone oil with a medium viscosity (1×10^{-4} m^2/s) was used as the pressurizing medium. The sample weighing about 4 mg was put in the sample cell and coated with epoxy adhesives, to fix the sample at the bottom of the cell and also to prevent direct contact with the silicone oil. New specimen of EPABC was used for each DTA measurement. The DTA runs were performed at a constant heating rate of 5 °C min^{-1} under various pressures. Peak temperatures were adopted as transition temperatures for making the temperature versus pressure phase diagram.

2.3. Morphological and X-ray characterization under pressure

The morphological texture of the sample under hydrostatic pressure was observed using a Leitz Orthoplan POM equipped with a high-pressure optical cell [16]. The texture observation was performed on heating process at 60 and 100 MPa.

The X-ray diffraction patterns of the sample under pressure were obtained using the high-pressure wide-angle X-ray diffraction apparatus [15]. The high-pressure vessel was set on the wide-angle goniometer of a 12 kW rotating anode type of X-ray generator (Rotaflex RU200, Rigaku Co.). The sample was inserted into the vertical hole of the beryllium spindle as the sample cell. The beryllium spindle was mechanically compressed for pressure sealing using upper and lower pressure blocks. Then the sample was pressurized hydrostatically at pressures up to 200 MPa. A Ni-filtered Cu Kα X-ray beam was used to irradiate the sample, and the diffraction patterns were obtained using an imaging plate detector (BAS-IP 127 mm × 127 mm, Fuji Photo Film Co.).

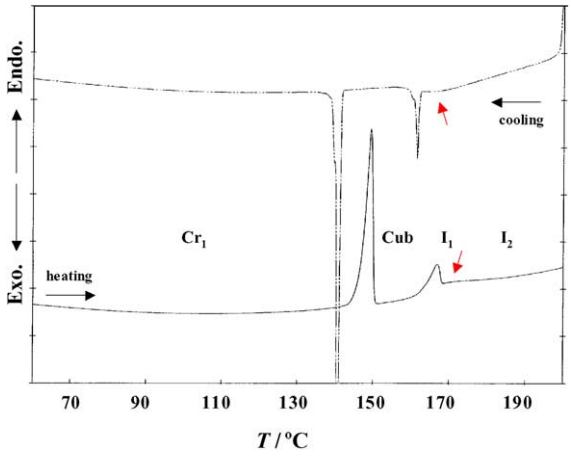


Fig. 1. DSC heating and cooling curves of EPABC. Scanning rate: 5 °C min^{-1}.