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HIGH-PRESSURE PHASE TRANSITIONS IN LIQUID CRYSTALS

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Simultaneous measurements of the rate of heat evolution and changes of the mechanical variable of a transformation such as volume or pressure, performed in a p-V-T controlled scanning calorimeter have been applied to investigations of phase transitions in liquid crystals. In the instrument, the phase transitions can be induced by a controlled change of pressure, volume or temperature under isothermal, isobaric or isochoric conditions respectively. The present investigations have ben performed on 4-*n*-penthyl-penthylthiol-4'-decycloxybenzoate which demonstrates in the liquid crystal state a nematic and three smectic phases

Keywords: high-pressure phase transition, liquid crystal

Introduction

Multiplicity and variety of phase transitions in liquid crystals makes them very interesting for investigations by scanning calorimetry, especially when such investigations are performed under various thermodynamic conditions. The known instruments used in such studies use temperature or pressure as inducing variables. Pressure as a variable was used in a pressurised temperature-controlled DSC [1, 2] and in isothermal piezothermal analysis [3]. From measured enthalpies, pressures and temperatures of transformation, the volume change during the transition could be determined with the use of Clapeyron equation [1]. However the error of such determination was estimated to be about 20% [1]. In order to measure directly the energetics of a transition and a change of its mechanical variable, volume or pressure, we have recently presented a p–V–T-controlled scanning calorimeter, which permits to use pressure, volume or temperature as inducing variables in the form of a continuous or stepwise change and to record simultaneously both the rate of heat evolution and the changes (or their rate) of the dependent mechanical variable of the transition performed under directly controlled thermodynamic conditions [4]. In the mentioned paper we have also presented some results of the use of continuous pressure variations in decreasing and increasing modes

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used as inducing variables in an isothermal investigation of 4-*n*-pentyl-phenylthiol-4'-decycloxybenzoate liquid crystal (10S5). It is known from the literature that the 10S5 liquid crystal passes from isotropic liquid phase to the crystalline solid phase through the nematic and three smectic phases and when heating under near-atmospheric pressure the solid phase goes directly to the smetic-A phase [5, 6]. The pressure-controlled investigations confirmed non-symmetric behaviour of the transitions during isothermal compressions and decompressions over the pressure interval from 0.1 to 300 MPa [4]. In the present communication we present recent results of temperature -controlled investigations performed on the same substance under various pressures.

Experimental

The p–V–T-controlled scanning calorimeter has been presented elsewhere [4]. However, some details may be recalled here, especially those related with the pressure control. The hardware of the digital pressure programming system is composed of a piston pump connected to the calorimetric vessel by a stainless steel tubing and driven by a stepping motor and gearbox. The control variable, CV, of the software based on using an 8255 I/O card is composed of two parts, PR, which is a constant proportional to the chosen speed of pressure variations and COR, which is a dynamic correction obtained using the control function, CF, based on the difference between the actual pressure in the system and the value resulting from the set function. The programme starts with the control variable equal to PR, which is sent to the stepping motor via I/O card and a suitable power amplifier. Any change in the internal volume of the system is detected by the correction term of the CV, which is varied in such a manner as to compensate for volume changes and to reach the pressure set function without disturbances. In the case of constant pressure set function the number of motor steps used to keep the pressure constant corresponds directly to the internal volume changes occurred during transformations under study.

Results and discussion

The measurements have been performed on both cooling and heating modes under pressures 80.8 MPa, 134.6 MPa and 174.7 MPa. The heating experiments always resulted with only one peak. On the other hand, the cooling experiments with the rate of 0.8 deg/s resulted with calorimetric thermograms and volume variations which shapes depended on the pressure applied. The coolings always started in the isotropic liquid phase. Results of measurements under pressure of 80.8 MPa over the temperature range from 342.3 K to 326.6 K are presented in Fig. 1. The cooling started at 383.1 K. In Fig. 2 results of similar measurements are presented under pressure of 134.4 MPa over the temperature range 353.3–335.4 K, the cooling started at 403.1 K. The results of measurements under pressure of 174.7 MPa over the temperature range 364.0–337.6 K are given in Fig. 3, the cooling started this time at 413.0 K. Over the temperature regions not shown in the figures no transformations have been observed. The results of the present communication are given as an example of the instrument

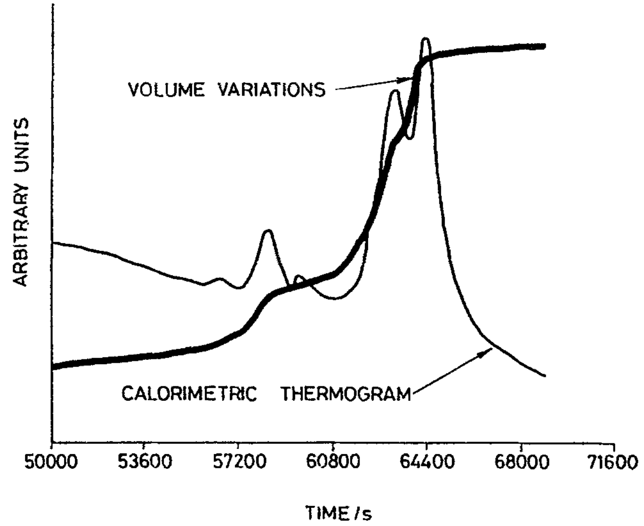

Fig. 1 Heat flow and volume variations in $\overline{10}$S5 liquid crystal under pressure of 80.6 MPa during cooling from 342.3 K to 326.6 K with a rate of 0.8 deg/s

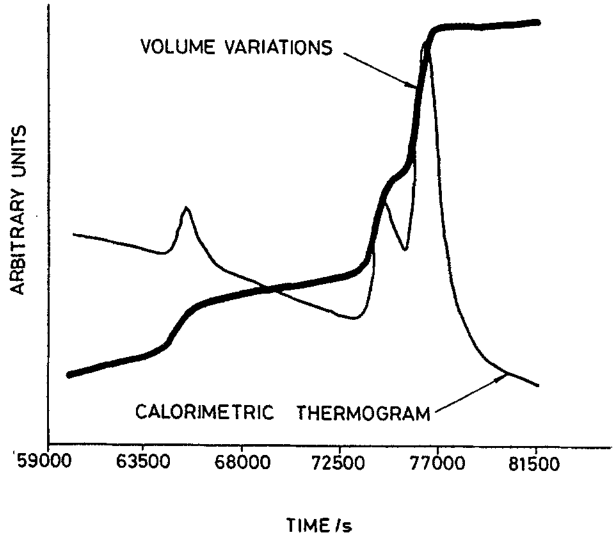

Fig 2 Heat flow and volume variations in $\overline{10}$S5 liquid crystal under pressure of 134.6 MPa during cooling from 353.3 K to 335.4 K with a rate of 0.8 deg/s

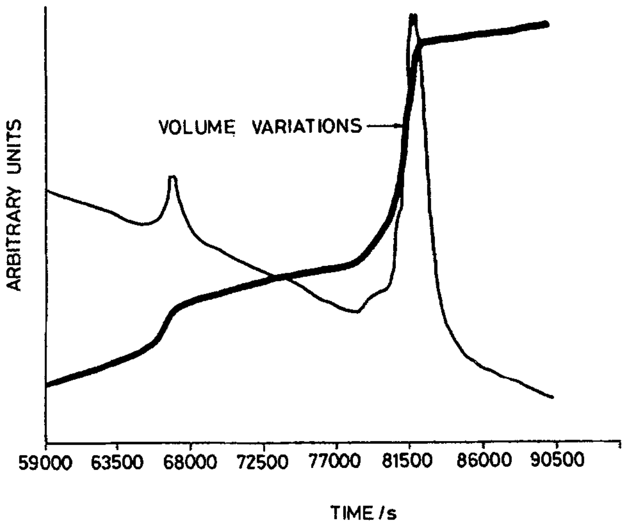

Fig. 3 Heat flow and volume variations in $\overline{10}S5$ liquid crystal under pressure of 174.7 MPa during cooling from 364.0 K to 337.6 K with a rate of 0.8 deg/s

functioning under isobaric conditions in the temperature-controlled mode. Although two independent informations are obtained on the heat flow and the volume change, the description of the system is not complete. Without a structural information it is not possible to say for sure what kind of transformation can be adjusted to a given peak, because it is known that in liquid crystals at high densities re-entrant or supercooled phases can be observed [7]. Thus the final results on the p–T phase diagram of $\overline{10}S5$ liquid crystal will be presented elsewhere.

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Zusammenfassung — In einem p-V-T-kontrollierten Scanning Kalorimeter wurden zur Untersuchung der Phasenumwandlungen in Flüssigkeitskristallen simultane Messungen der Geschwindigkeit der Wärmeentwicklung und der Veränderungen von mechanischen Größen von Umwandlungen, wie z.B. von Volumen oder Druck durchgeführt. In diesem Gerät kann die Phasenumwandlung durch eine kontrollierte Veränderung von Druck, Volumen oder

Temperatur unter isothermen, isobaren oder isochoren Bedingungen ausgelöst werden. Vorliegende Untersuchungen wurden an 4-*n*-Pentyl-phenylthiol-4'-dezyloxybenzoat durchgeführt, welches im Flüssigkristallzustand eine nematische und drei smektische Phasen aufweist.