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Phase Transition and Structure Studies of a Liquid Crystalline Schiff-Base Compound (4O.8)[#]

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Calorimetric and X-ray powder diffraction studies of N-(4-n-butyloxybenzylidene)-4′-n′-octylaniline are presented. Heat capacity measurements have been performed by adiabatic calorimetry in the temperature range from 5 K to 375 K. Three liquid crystalline phases, i.e., nematic, smectic A and smectic B, and an ordered crystal of triclinic structure and two new metastable crystal phases were observed. In addition, the crystalline smectic B phase of different sequence of molecular layers than liquid crystalline smectic B, has been found. Both smectic B phases have been vitrified. For the smectic B phase a hexagonal unit cell has been identified by X-ray diffraction. The diffraction pattern of glass of crystalline smectic B phase is shown.

Keywords Heat capacity; liquid crystal; phase transitions; X-ray diffraction

1. Introduction

Recently, investigations of physical properties of soft matter with various mesophases are in the focus of solid state studies [1]. Mesophases, like liquid crystalline phases, often reveal new features [2]. In this paper, the results obtained for a liquid crystal compound called *N*-(4-*n*-butyloxybenzylidene)-4′-*n*′-octyloaniline (abbreviated as 4O.8 or BBOA) by adiabatic calorimetry and X-ray diffractometry in the wide range of temperature are shown. The substance of chemical formula C_4H_9O-C_6H_4-NCH-C_6H_4-C_8H_{17} belongs to the homologous series of the so-called Schiff basis [3]. The schematic representation of the 4O.8 molecule is shown in Figure 1. The sequence of phases reported in the literature, basing on calorimetric [4,5] and X-ray diffractometric data [6] for heating the 4O.8 samples from the room temperature, is the following: a crystal (Cr), the smectic B phase (SmB), the smectic A phase

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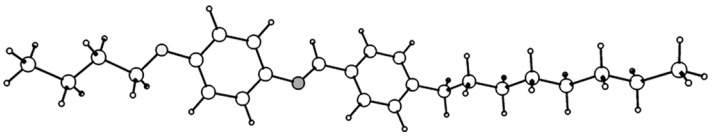

Figure 1. The molecular structure of 4O.8.

(SmA), the nematic phase (N) and the isotropic liquid (I). In addition, the occurrence of a glassy phase of the smectic B phase was found in the Mössbauer experiment [7], with $T_g = 175$ K. In the QENS studies [8], the reorientational motions of the terminal chain and the whole molecule around the molecular axis were detected in the smectic B phase. The purpose of our heat capacity measurements extended down to 5 K was to check the phase polymorphism for 4O.8, especially a formation of glass phase, and to investigate in detail features of phase transitions in various thermal conditions applied to the samples. X-ray diffraction method was used to identify the molecular arrangement in the solid phases and to evaluate temperature dependence of the smectic layer thickness.

2. Experimental

The 4O.8 compound was synthesized in the Millitary University of Technology, Warsaw. It is in the crystalline phase at room temperature. Heat capacity measurements were performed by adiabatic calorimetry method in the wide temperature range from 5 K to 375 K with many experimental runs. The sample was loaded under helium gas atmosphere into a gold-plated vessel of the home-made adiabatic calorimeter, the details of which were described earlier [9]. The mass of the sample was 0.88768 g (2.4283 mmol).

X-ray diffraction patterns were obtained on the X'Pert PRO (PANalytical) diffractometer using graphite monochromatized CuK_α radiation ($\lambda = 1.54$ Å). Scans of diffraction patterns were recorded in the $2\theta = 2^o - 30^o$ range of diffraction angles at each 10 K in the temperature range between 85 K and 355 K. The sample was placed on a copper plate with dimensions $18 \times 9 \times 0.2\,mm^3$.

3. Results and Discussion

3.1. *Thermodynamic Behavior of 4O.8*

In Figure 2, the results of heat capacity measurements, collected in several experimental runs, are presented. Only for the data obtained for the first run, the $C_p(T)$ experimental points (see open squares) are given in the absolute scale, while for other runs they are shifted along the vertical axis for better visualization. Along with $C_p(T)$ changes, evolutions of the drift rate dT/dt were registered and the temperature dependences are presented in Figure 3 in temperatures limited to 200 K–310 K range. The first measurement run has been performed during heating from 4.5 K after cooling a sample from the room temperature, i.e., from the crystal Cr phase. Four endothermic anomalies were detected. The resulting sequence of phases obtained on heating, i.e., Cr −310.5 K – SmB −321.1 K – SmA −335.3 K – N −351.0 K – I, corroborates with the results of previous studies [4–8,10]. In the second run (see open triangles), the measurement has been performed for the sample cooled down to

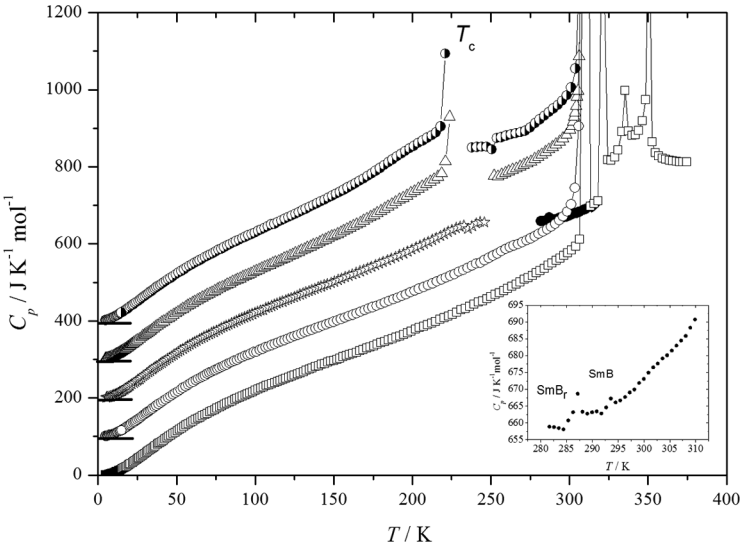

Figure 2. Measured molar heat capacity of 4O.8. Symbols denote the data obtained in different measurement runs, i.e., □ - for ordered crystal phase, obtained after the first cooling from room temperature, and for smectic B, smectic A, nematic and isotropic liquid; 4 and Δ - for experimental points obtained after fast cooling of SmB and I, respectively. Data obtained after annealing the sample at 225 K for 4 h - Ψ and at 250 K for 12 h - . Data for the sample cooled to 280 K shown by, are presented also in the insert showing SmB – SmB_r transition. Only the data shown by □ are presented in the absolute scales. Data of other runs are shifted along the vertical axis for better visualization. T_c means temperature of a spontaneous crystallization.

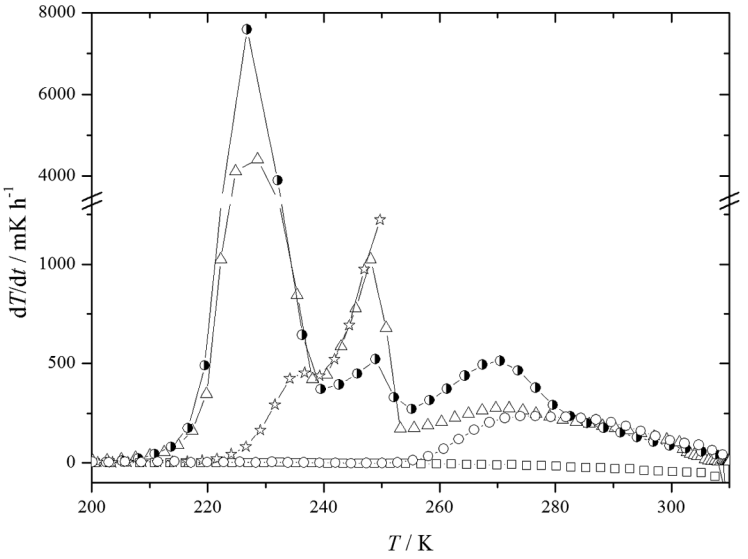

Figure 3. The spontaneous drift rate dT/dt vs. T for 4O.8 in the temperature range of three anomalies of spontaneous stabilization at 225 K, 250 K and 270 K. Experimental symbols as in Figure 2.

liquid helium temperature from the isotropic liquid phase. It was found that the heat capacity data of the two series were different, indicating that either a metastable phase or a glassy phase appeared at low temperatures. In fact, three exothermic anomalies are clearly shown in dT/dt vs. T dependence with maxima near 225 K, 250 K and 270 K (open triangles in Fig. 3). Moreover, we saw a tiny exothermic anomaly around 140 K (not shown in Fig. 3), suggesting that a glass transition exists. Next, the measurements were performed around the anomalies at about 350 K, 335 K, 320 K and 310 K in order to study supercooling effects. However, no traces of supercooling of the smectic A, nematic and isotropic phases were found. Only supercooling of the SmB phase has been evidenced - see filled circles in Figure 2 in the temperature range from 280 K to 330 K. It is worth to note that at 287.2 K one can see a small anomaly. It seems to be illustration of the so-called 'restacking' transition between two SmB phases of different types of stacking sequences of molecular layers as observed between SmB_r and SmB phases in 5O.6 and 7O.7 [11] of the Schiff basis homologous series. The low temperature SmB_r phase was thus found to be more ordered when compared to the higher temperature SmB phase [11,12]. For 4O.8 recent dielectric measurements showed that in course of this transformation not only the structure but also the dynamics changes [13].

In order to obtain a glass of smectic B_r, the sample was annealed at 318 K for 12 h and then rapidly cooled to 5 K at the rate of $-18\ \mathrm{K\ min^{-1}}$. On heating at 10 K/min rate in average, three exothermic anomalies were found in dT/dt vs. T dependence (see half-filled circles in Fig. 3) at the same temperatures as obtained in the second run (triangles). One can therefore suppose that it is caused by a three-step spontaneous stabilization from a super cooled SmB_r phase obtained after softening of the glass phase. In fact, a tiny exothermic anomaly was detected again, but at a higher temperature (160 K). We assume that the phase obtained by cooling of the I phase is a glass of better ordered SmB_r phase. Hence the $C_p(T)$ values obtained at low temperatures are significantly smaller than those obtained by rapid cooling of SmB (see Fig. 5).

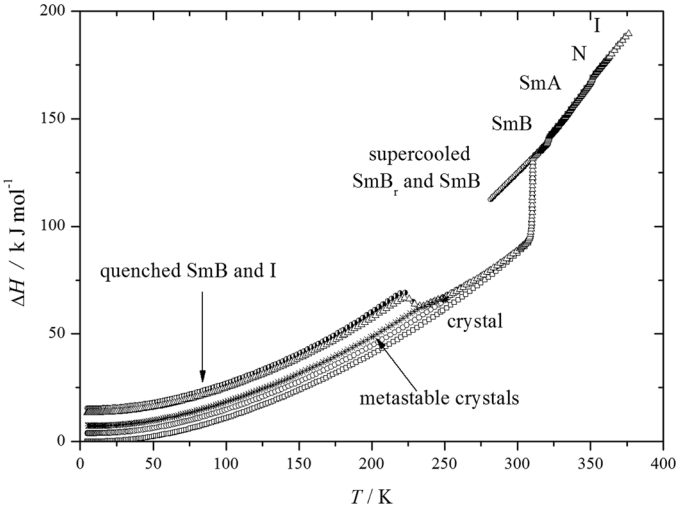

Figure 4. The enthalpy vs. temperature for the various phases of 4O.8. Experimental symbols as in Figure 2.

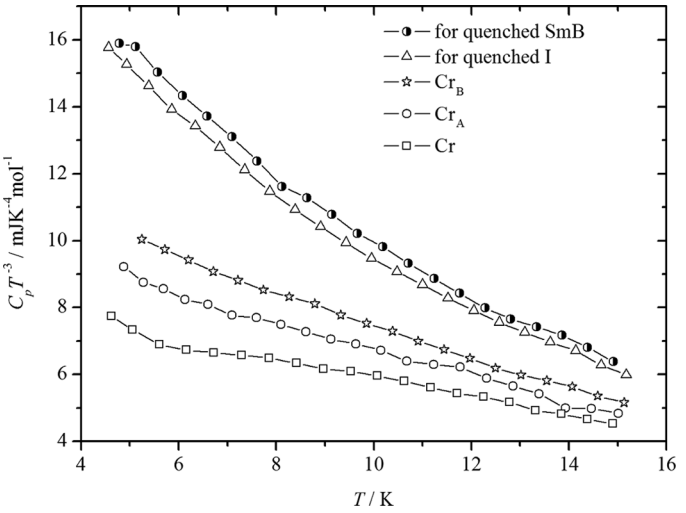

Figure 5. Heat capacity at low temperatures. Experimental symbols as in Figure 2.

To check the reproducibility of the $C_p(T)$ results and to determine a time characteristic of full stabilization, the sample was annealed at 225 K for 4 h and then cooled again down to 5 K (at the rate of -10 K min^{-1}). The heat capacity values measured then on heating (see stars in Fig. 2) were higher than those obtained for a fully ordered crystal Cr observed in the first experimental run. For this new metastable phase (denoted as Cr_B) a spontaneous crystallization was observed at 250 K (see stars in Fig. 2 and Fig. 3). The obtained crystal (denoted as Cr_A) was annealed at 250 K for 12 h and cooled to low temperature. The heat capacity results obtained on heating were slightly higher than those measured for the fully ordered crystal Cr phase. In the vicinity of 270 K transformation to the Cr crystal is visible on heat capacity (very weak anomaly) and on drift curve (see open circles in Fig. 2 and Fig. 3). On further heating the Cr phase transformed to the SmB and a small pretransition effect unobserved earlier was detected. Three distinct exothermic anomalies observed around 225 K, 250 K and 270 K correspond to stabilization processes of meta-stable crystalline phases Cr_B and Cr_A and to the stable phase (Cr), respectively. The last process was found to be extremely slow.

Figure 4 shows the temperature dependence of the enthalpy calculated for various adiabatic runs. At temperatures below 225 K five curves can be distinguished: the highest values are for glass of SmB_r phase (half-filled circles) and the lowest for the ordered crystal Cr (squares). The biggest change in enthalpy for the transition between the crystalline Cr and the SmB phases corresponds to the activation of the rotational degrees of freedom of molecules. Enthalpy change at the SmB - SmA transition is slightly greater than at the SmA - N transition. That means the energy needed to destroy the ordering of the molecules in the layers is larger than to destroy the smectic ordering.

The low-temperature heat capacities measured for the phases obtained in various runs are shown in Figure 5 as a plot of C_p/T^3 versus T. The values for the samples quenched from the SmB phase (with cooling rate -18 K/min) and from the isotropic liquid (I) phase (with cooling rate -14 K min^{-1}) are the highest (half-filled circles and triangles, respectively). They correspond to glassy phases of smectic B

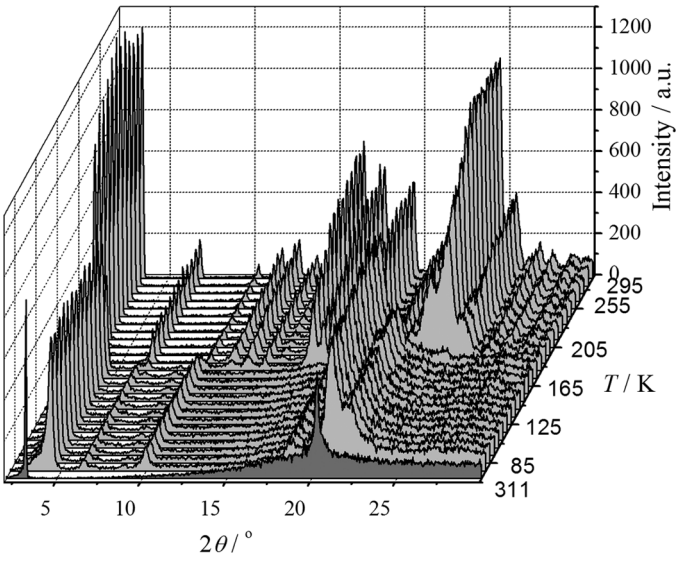

Figure 6. Experimental diffraction patterns measured at 311 K and at each 10 K in the range from 85 K to 305 K.

and smectic B_r phases. One can see that for glass of better ordered smectic B_r phase the C_p/T^3 values are lower. The smallest $C_p(T)/T^3$ values were measured for the ordered phase Cr (squares). Data obtained for two metastable crystals Cr_A (circles) and Cr_B (stars) are slightly higher.

3.2. *Study of Powder X-Ray Patterns*

The structures of phases of 4O.8 were identified in the X-ray experiment. First, a diffraction pattern was recorded at 311 K, i.e., in the smectic phase B phase (see Fig. 6 and the middle panel in Fig. 7). For the SmB phase the hexagonal structure was evaluated with the unit cell parameters a = 5.02 Å and c = 27.56 Å at 311 K. The lattice parameter a is commonly interpreted as a molecular diameter. The obtained value of the a parameter for 4.O8 is typical for compounds with the aromatic cores [14]. Then, the sample was cooled to 85 K at the rate of −10 K/min, in order to form a glass of smectic B_r phase, and the diffraction patterns were recorded on heating every 10 K. Diffraction patterns obtained on heating between 85 K and 185 K differ from those of SmB phase and are believed to correspond to glass of the SmB_r. For phases with well ordered positions of the molecules, like SmB and SmE, glass state is formed because their molecules can rotate like in ODIC phases [13,15,16]. For long molecules of 4O.8 flip-flop motions [13] are possible thanks to the rotational-translational coupling [14]. On approaching a glassy phase a dramatic slowing down of these motions occurs and they are more and more cooperative [17]. At the glass transition the orientational disorder of molecular long axes becomes frozen-in, what result in a slight shift of the (001) peak and smeared shapes of all peaks in the diffractograms below T_g. New diffraction pattern of crystal Cr phase which starts to grow can be observed at 195 K (Fig. 6). For crystal Cr phase the triclinic structure was estimated with a = 26.36 Å, b = 7.95 and c = 5.72 Å for 225 K.

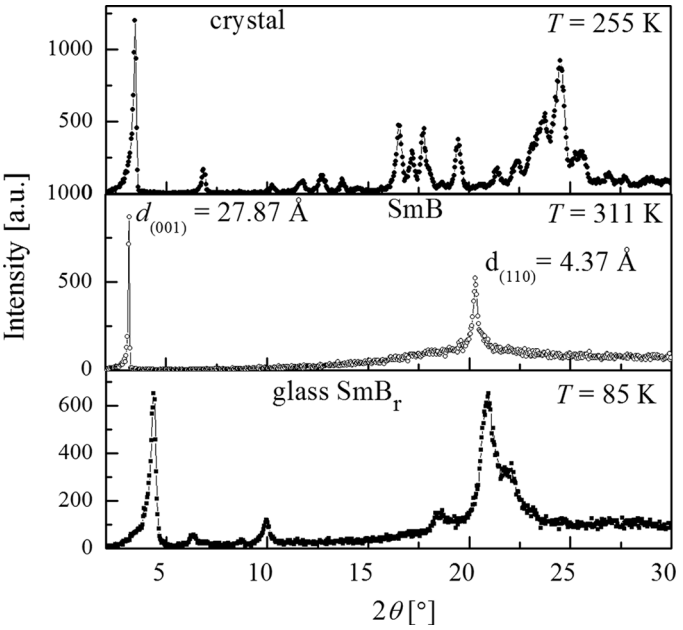

Figure 7. Diffraction patterns for crystal Cr and for SmB and glass of SmB_r phases.

Figure 7 presents the examples of diffraction patterns collected for the crystal Cr, SmB and glass of SmB_r phases. The temperature dependence of the position of the first peak (001), responsible for the layered structure, is nearly continuous. One can see that in the glass of SmB_r the layers are preserved like in smectic B. The layer thickness d was estimated to be equal 27.56 Å for SmB (at 311 K) and only 20.3 Å for a glass of the SmB_r phase (at 85 K). The (110) reflection peak corresponding to a hexagonal arrangement of molecules in the smectic layer is broader at 85 K than at 311 K in the SmB phase. It means that in glass the hexagonal arrangement of molecules within the smectic layer is disturbed due to a vitrification process. The molecular length L calculated for the all-trans configuration of 4O.8 after prior optimization of its structure by the semi-empirical AM1 method [18] is equal 26.02 Å. The diameter of the molecule is equal 5.02 Å. In the SmB phase the layer-thickness to molecular-length ratio was found to be close to 1.06. The corresponding ratio observed for the glass of the smectic B_r decreases to the value 0.78. It means that in the glass phase the molecules are inclined. For the smectic A phase d equals 28.1 Å (at 336 K) and the d/L ratio of 1.08 is slightly larger than in the SmB phase which reflects an increase in the reorientation freedom of molecules within the SmA layers. In the SmA - N transition a decrease of the intensity of first peak observed for smectic phases was found due to disappearance of layered structure. The diffraction pattern in nematic phase was smooth, while for the isotropic phase was completely blurred.

4. Conclusions

Rich polymorphism of 4O.8 was evidenced by the adiabatic calorimetry method applied down to 5 K. Besides the ordered crystal at room temperature and isotropic

liquid phase, three liquid crystalline phases, smectic B, smectic A and nematic, and two metastable crystalline phases were detected on heating. The smectic B phase was easily supercooled and then a transition to the next smectic B_r phase of different type of stacking sequence was observed and identified with a restacking transition. Glasses of both phases, smectic B and the lower temperature smectic B_r, were found to have slightly different heat capacities. The X-ray studies show up a hexagonal arrangement of molecules in the smectic B phase. Diffraction pattern of the glass of SmB_r phase was distinguished. Analysis of diffraction peaks indicated that the layer structure was preserved but long molecular axes become inclined. The hexagonal arrangement of molecules was disturbed due to frozen-in disorder of molecular orientations. Diffraction pattern of SmB_r phase was not distinguished.

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