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Crystallization and Melting of Metastable Solid Crystalline Phases of EBBA

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Crystallization and Melting of Metastable Solid Crystalline Phases of EBBA

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The solid crystalline (SC) polymorphism of nematogenic compounds has not been thoroughly investigated. Three SC modifications have been found for the most studied nematogenics, PAA and MBBA.[1,2] Calorimetric data are known[2,3] only for one metastable MBBA phase. Raman spectra[4] of EBBA identifies four SC forms which transform from one form to others only in one direction. Solid crystalline phases are numbered in Figure 1 according to the sequence of monotropic transformations. These transformations are represented as SC I → SC II → SC III → SC IV, where SC IV is a stable form obtained normally by crystallization from alcohol solution.

In a paper by Sorai *et al.*[5] a thorough measurement of the stable form SC IV, has been carried out for the region 14 to 375°K. Attempts to make measurements on the metastable forms have not been successful because before achieving a melting point range between −15°C to +15°C the form transformed to a stable one, producing heat. By the use of Raman spectra we have managed to obtain individual samples of all metastable forms from SC I to SC III which remain unchanged at room temperature for more than a year. In this paper the results of calorimetric measurements of these samples are reported.

The investigation of the melting process of SC forms to the nematic phase (NP) has been done with a differential scanning calorimeter (Model Perkin–Elmer, DSC-2). As a standard for instrument calibration for the temperature and the heat of melting, gallium was used (T_{melt} = 29.78°C, ΔH_{melt} = 19.16 cal/g)[6] which has similar melting characteristics to that of EBBA

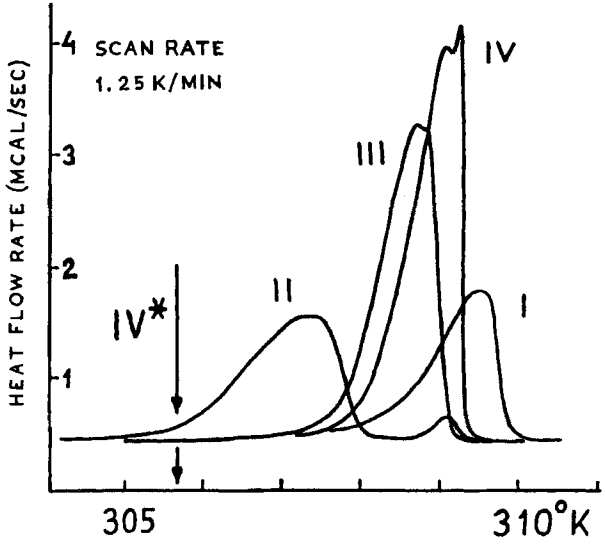

FIGURE 1 Heating thermograms of SC I to SC IV samples of EBBA.

(T^{IV}_{melt} = 32.5°C, ΔH^{IV}_{melt} = 23.0 cal/g).[5] Figure 1 shows typical melting curves of SC I–SC IV using samples with masses of approximately 5 mg. Values of T_{melt} and ΔH_{melt} averaged for no less than five independent measurements are given in Table I. Note the difference between T_{melt} of a stable form measured with an adiabatic calorimeter[5] (corresponding T^{IV}_{melt} marked with vertical line in Figure 1) and that measured with a differential scanning calorimeter. This difference amounts to 2.4° which far exceeds the accuracy of the measurements ±0.2°. Similar values exceeding 2.6° for T_{melt} measured with dynamic methods (heating with a rate of 1 to 2° per minute) have been reported earlier[7] for nematogenic 2,4-OH-MBBA. During the measurement with an adiabatic calorimeter one normally waits

TABLE I

Characteristics of melting of SC forms of EBBA.

SC form	T_{melt}(K)	ΔH_{melt}(cal/mol)
I	308.4	3470 ± 17
II	305.7	4910 ± 28
III	307.7	6160 ± 56
IV	308.1	6630 ± 20
IV[a]	305.68	6470

[a] Data from Reference 5 obtained with adiabatic calorimeter.

for 15 to 35 minutes to establish equilibrium. While heating near the melting point, measurements are carried out on no less than five points in the region of 1°.[2] T_{melt} of EBBA measured with an adiabatic calorimeter compared with T_{melt} of the lowest melting SC II form suggests that at a heating rate ~ 1 deg/hour the transformations in a solid phase in the direction SC IV to SC II take place and then the latter phase is melted.

The difference in the melting heats of the same phases of the same substances reported by different authors exceeds an accuracy of measurement by several tenths. Thus, according to Mayer *et al.*[3] for a stable form MBBA $\Delta H_{stb} = 4310 \pm 20$ and for a metastable one $\Delta H_{mstb} = 3527 \pm 20$ cal/mol, while in Ref. 2 for this case $\Delta H_{stb} = 3909 \pm 5.1$ and $\Delta H_{mstb} = 3142 \pm 2.6$ cal/mol. This fact can be explained by the presence of impurities of the other SC forms in a sample of a given phase. Physical (structural) impurities can be found sometimes by Raman spectra. One can determine quantitatively the phase composition of a sample with the Raman spectrum only in the case when one considers the intensity of any band or group of bands to be the same for all phases. In a general case one can consider a sample to be physically pure if a long storage at a temperature a little less (3–5°) than T_{melt} of the lowest melting modification doesn't cause an appearance of the spectral features of other SC forms.

Normally, metastable forms are obtained by a rapid cooling of a melt[3,8]. Spectral observations have shown that the SC I form of EBBA appearing at a shock cooling (a thin glass tube of diameter ~ 4 mm is put in a water stream at a temperature less than 5°C) transfers after 10 to 20 hours at room temperature (20°C) to the SC IV form or, rarely, to the SC II form. We have found that shock cooling is not necessary to form the SC I modification. Gradual cooling (in air) down to 20 to 22°C may cause crystallization to the SC I form (normally the nematic melt overcools to this temperature). An additional condition is the presence of a metal wire in a melt, for example, thermocouple. The fact of the slow crystallization and of the possibility of stimulation of this process by the presence of particular centers of nucleation of this phase proves that a solid mass of frozen melt consists of crystallized clusters. The solid crystalline SC I phase obtained by this method doesn't differ spectrally from that obtained by shock cooling; however, it doesn't transfer to other SC forms at 20 to 22°C for one year. Obviously at a slow crystallization more large crystallites are formed which have different conditions on boundaries between them, but the same type of molecular packing as for shock cooling. Namely, these stable SC modifications may be heated up to the melting point without transfer to the stable SC IV modification as was reported in Ref. 5.

The melting heat ΔH^{I}_{melt} of the SC I form is almost two-times less than ΔH^{IV}_{melt} (see a Table) while T^{I}_{melt} exceeds T^{IV}_{melt}. Greater thermal stability of

the molecular aggregates with the least condensation energy is in accordance with the fact that a shock cooling causes the formation of a local packing of a SC I type.

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