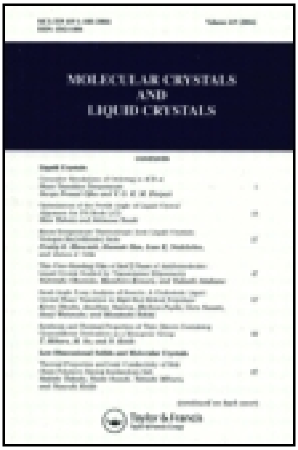

Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

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Version of record first published: 17 Oct 2011.

To cite this article: V. K. Dolganov , N. Kroó , L. Rosta , E. F. Sheka & J. Szabon (1985): Multimode Polymorphism of Solid MBBA, Molecular Crystals and Liquid Crystals, 127:1, 187-194

To link to this article: http://dx.doi.org/10.1080/00268948508080839

Mol. Cryst. Liq. Cryst., 1985, Vol. 127, pp. 187-194
0026-8941/85/1274-0187/$15.00/0

Printed in the United States of America

Multimode Polymorphism of Solid MBBA†

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(*Received July 19, 1984*)

Calorimetric measurements were carried out to investigate the solid state polymorphism of MBBA. Conditions for the production of a glassy liquid crystal phase were studied. The DSC experiments proved the existence of two independent modes of phase transition:[1] (i) a sequence of irreversible transitions based on a molecular relaxation process; (ii) reversible structural transformations involving molecular reorientations. An energy level scheme is proposed to illustrate multimode polymorphism i.e. a phenomenon where at least two phases are stable over the same temperature range.

INTRODUCTION

Considerable interest has been focussed over the past decade on the solid state polymorphism of n-p-methoxybenzylidene-p-butylaniline (MBBA). In recent works[1,2] in addition to the isotropic and nematic liquid crystalline phases, 7 different solid structures have been distinguished by combined neutron and Raman scattering measurements. A glassy state (labelled C_0) can be produced by fast cooling and it can be transformed into the nematic phase through a sequence of irreversible phase transitions from the first to the last of four

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†Presented at the Tenth International Liquid Crystal Conference York, July 15-21, 1984.

different structural modifications (C_1,C_2,C_3 and C_4). Two more phases were found: C_6 produced by slow crystallization from the nematic phase and C_5 produced by further cooling.

It was also established[1,2] that phases C_6,C_5,C_4 and C_3 are crystalline whilst C_0, C_1 and C_2 are amorphous with molecular orientational ordering only. Structural relaxation was found in the transitions from C_0 to C_1 and C_1 to C_2; whilst crystallization occurs between C_2 and C_3. These transition mechanisms were explained by the growth of domains of medium range order. Phase C_0 was classified as an oriented molecular glass (OMG), C_1 and C_2 as relaxed solid mesophases and C_3, C_4 as metastable crystalline phases. C_5 and C_6 are considered to be stable crystals.

Here we report on calorimetric measurements which support the preceding observations on the various phases of MBBA.

EXPERIMENTAL

A Perkin-Elmer DSC-2 differential scanning calorimeter was used to register the thermograms in the 110–350 K temperature range. The 6 mg MBBA sample was placed into a standard Al container, hermetically sealed. The sample was commonly used laboratory pure (not extra purified) material, the isotropic-nematic transition was found at (317 ± 0.5)K. All of the results were found to be perfectly reproducible.

RESULTS

Figure 1 shows thermograms corresponding to fast-cooling and reheating procedures. The observed curves are similar to those published earlier for MBBA[3] and OH MBBA.[4] The step in the cooling curve at ~205 K marks the observed onset of solidification, indicating that the nematic phase is supercooled down to this temperature. The continuous reheating curve includes the solid-solid transition exotherms, and the melting endotherm.

The reheating thermogram was investigated as a function of a) the cooling rate, b) the starting temperature and c) the temperature at which the cooling was stopped over 205 K. At each run—to ensure that all the samples had the same thermal history—the sample was

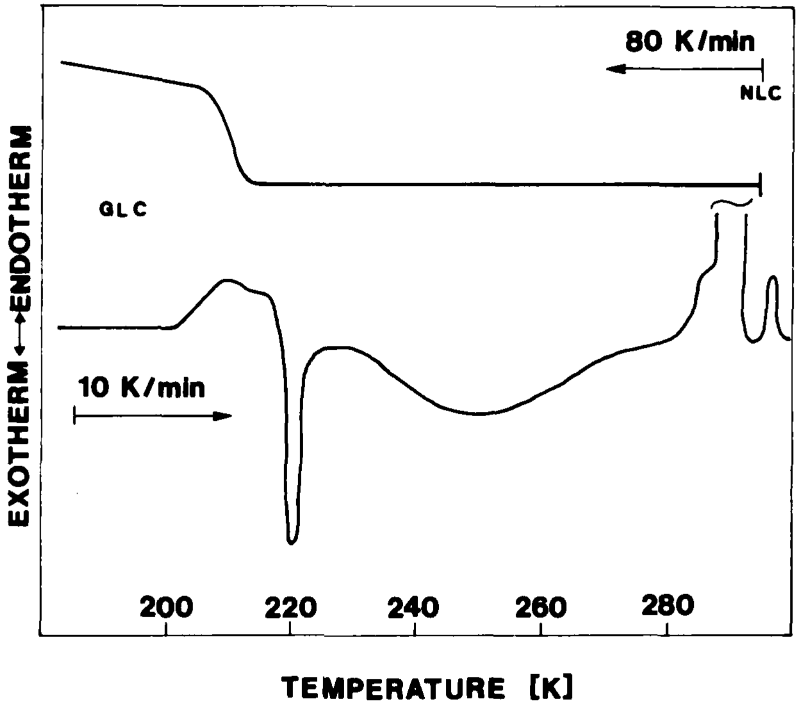

FIGURE 1 DSC curves indicating the fast-cooling and the reheating procedure in MBBA.

kept for 5 min at 330 K in the isotropic liquid state, then it was cooled down to 295 K and kept for 5 min in the nematic phase.

a) It was found that a cooling rate higher than 40 K/min is needed to produce the glassy state. Most of the cooling runs at 20 K/min resulted in crystallization, therefore we conclude that a cooling rate higher than 40 K/min is needed. The circumstances of such an experiment (adiabatic conditions, small quantity of the sample etc) should be considered rather favourable for the production of supercooled material as compared to those required by other types of investigations (e.g. diffraction or light-scattering methods).

b) A few starting temperatures between 295 and 330 K were tried with different cooling rates (up to 160 K/min). No change in the heating curve was observed. At the highest cooling rate (160 K/min) the nematic state is quenched-in from the isotropic liquid. This was confirmed by neutron diffraction measurements.[5]

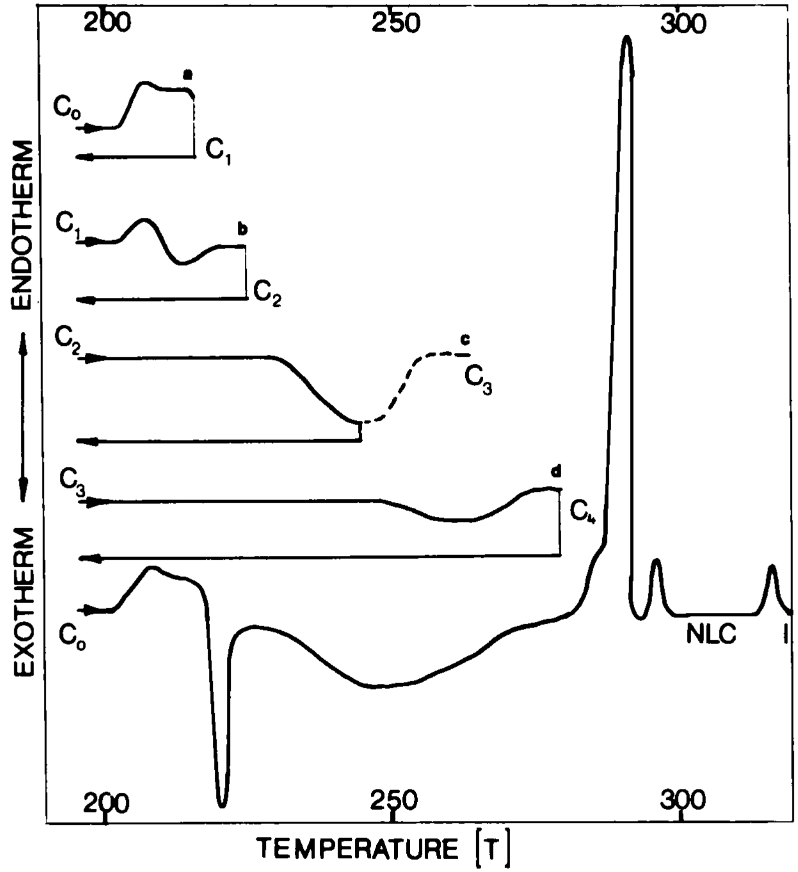

FIGURE 2 DSC thermograms measured after a fast-cooling in order to produce the sequence of irreversible phase transitions. The heating and cooling rate was 10 K/min.

c) When the quench was stopped at a certain temperature over 205 K and kept there or if the sample was further heated, solidification occurred. Supercooling with solidification into the C_0 state occurs only below 205 K.

A detailed analysis of the heating diagram is given in Figure 2. Curves a-d illustrate the separation of the transitions which are integrated in the lowest continuous run. After the sample had been cooled down to 110 K no change was observed on reheating up to ~ 203 K where Tg starts, indicating that the glassy state (C_0) is stable. When heating over the Tg step, up to 207 and immediately cooling below 200 K, no phase change could be observed. Two ways of producing the C_1 phase were examined. Firstly when the heating of C_0 is stopped at 207 K an isothermic transition takes place in 40 minutes. The other way is to raise the temperature at a 10 K/min rate, then, at 219 K, to recool immediately (at the same rate). This case is shown in curve *a* (Figure 2) For both cases the production of C_1 is followed by a transition represented by curve *b*. An isothermal transition at 210 K in 30 min or heating to 220 K (with immediate recooling) yields a complete $C_0 \rightarrow C_2$ transition. Although calorimetry suggests that intermediate stages between the described $C_0 \rightarrow C_1$ and $C_1 \rightarrow C_2$ transition states may occur, no differences in the neutron diffraction pattern which would have indicated these intermediate stages (e.g. different widths of the C_0 phase diffraction peaks) have been detected.

The wide minimum in the continuous heating curve can be divided into two steps. Heating to 248 K and the isothermal transition in 30 min (dashed line in curve *C*) results in a phase which corresponds to C_3. Cooling and reheating confirm that the transformation is irreversible. If the sample had been heated previously over ~248 K the $C_3 \rightarrow C_4$ transition would also have occurred. Heating following procedure *c* yields run *d* with the $C_3 \rightarrow C_4$ transition clearly visible.

Events in the melting region (285–298 K)—as shown by the lowest curve in Figure 2—are rather complicated. For instance, very slow heating may give a maximum and a minimum at 289 K instead of the shoulder on the melting endotherm. The origin of the peak at 295 K is not yet understood. In paper[6] it is suggested that a smectic phase may be present before transformation into NLC. The problem requires further structural investigation.

Two structural modifications can be produced by equilibrium crystallization i.e. the freezing by slow cooling from the nematic phase gives rise to phase C_6. (The nematic liquid has usually been overcooled to ~265 K.) Decreasing the temperature below 205 K produces the $C_6 \rightarrow C_5$ phase transition.This is illustrated in Figure 3. No other phase transitions were detected at lower temperatures.[1] The heating diagram shows that $C_5 \rightarrow C_6$ transition takes place at 215 K.

DISCUSSION

The above calorimetric results are in good agreement with neutron diffraction[1,5] and Ramen scattering[1,7] observations. To illustrate the relationship of the different phase transitions as a function of temperature and structure, a schematic phase diagram analogous to the

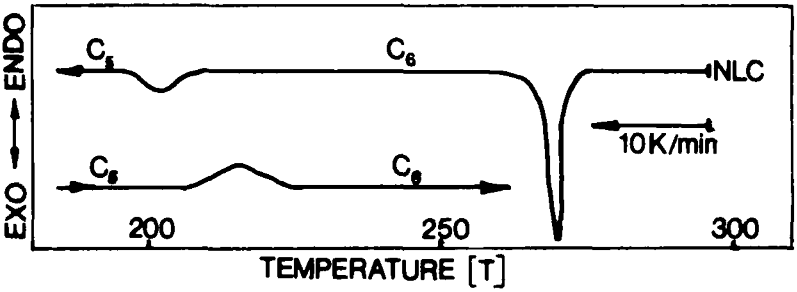

FIGURE 3 DSC runs when the NLC is slowly cooled. The C_5-C_6 phase transition is reversible with ~10 K hysteresis.

one proposed in[6] is presented in Figure 4. The three-dimensional pattern contains the cooling/heating (temperature) pathways corresponding to the free energy minima. The "structural parameter"[6] may be taken as an arbitrarily selected dimension which illustrates the difference in the structure between the phases and embraces short- and medium range orders as well as molecular conformation. The greater the distance along this axis between two phases the greater the difference in the structural parameters.

In Figure 4 one can clearly see the two independent cycles of nematic → solid → nematic transitions:

(i) NLC $\rightarrow C_0 \rightarrow C_1 \rightarrow C_2 \rightarrow C_3 \rightarrow C_4 \rightarrow$ NLC

(ii) NLC $\longleftrightarrow C_6 \longleftrightarrow C_5$ or NLC $\rightarrow C_6 \rightarrow C_5 \rightarrow C_6 \rightarrow$ NLC†

These two modes for producing polymorphic modifications correspond to different structural transition mechanisms.

Mode (i), described as a sequence of irreversible structural transitions, is a result of a gradual relaxation process in which molecular conformation, intermolecular short range order and medium range order change from one phase to another.

The other type of transition (ii) is based on reversible molecular reorientation. The most probable explanation is that since the $C_5 \longleftrightarrow C_6$

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†The second representation expresses more the presence of hysteresis in NLC $\longleftrightarrow$ C_6 and $C_5 \longleftrightarrow C_6$ transitions.

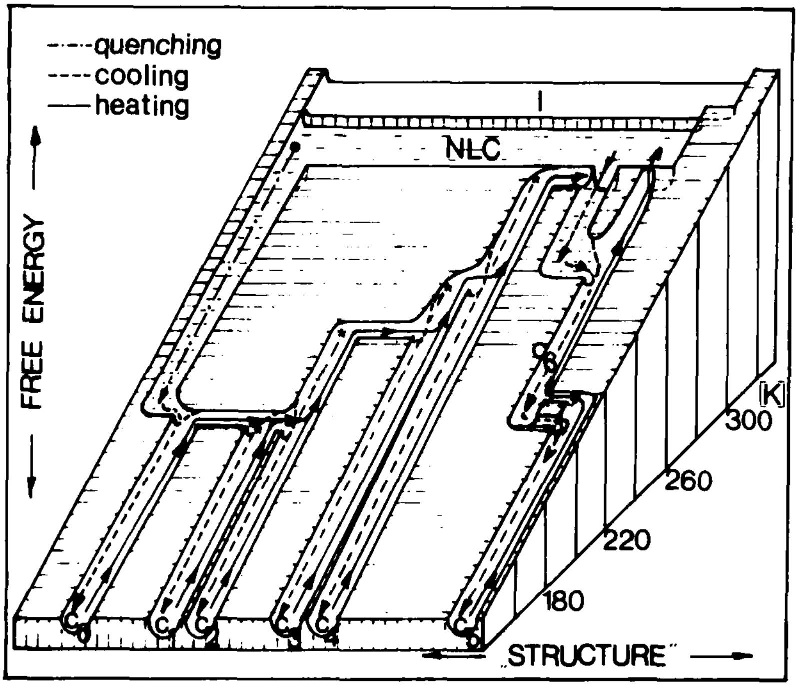

FIGURE 4 Three-dimensional: free energy – temperature – structural parameter diagram of MBBA phase transitions.

transition takes place around 205–215 K, methoxy groups may reorient in this region[8] and this is followed by the reorientation of the molecular cores. This concept is supported by neutron diffraction measurements on MBBA samples with deuterated and non-deuterated benzene rings.[5]

It follows from the existence of two independent polymorphous modification branches ((i) and (ii)) that at any temperature throughout the whole solid MBBA temperature range, at least two phases are possible. The number of modifications possible at various temperatures can be derived from the "free-energy structural parameter" sections of the three-dimensional diagram in Figure 4. Such sections are shown in Figure 5.

The isothermal multiplicity of polymorphous modifications, observed in the case of MBBA, can be termed *multimode polymorphism*.

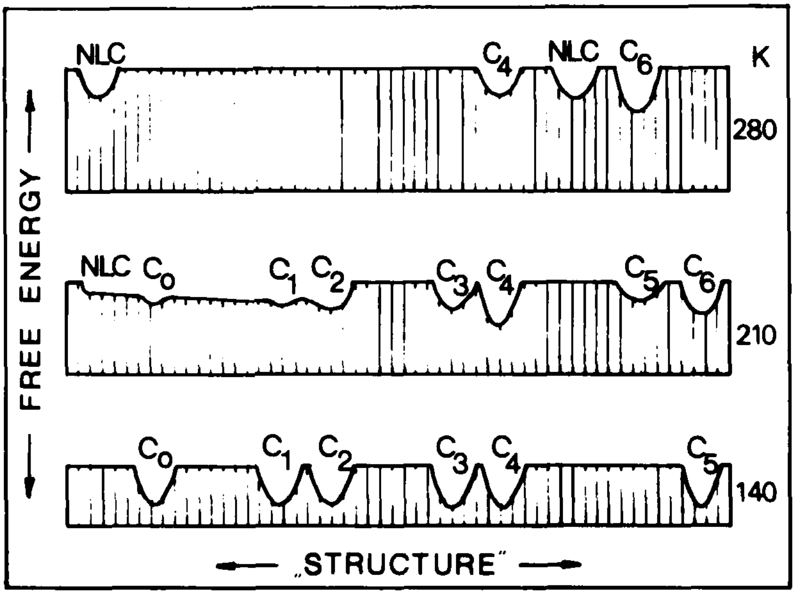

FIGURE 5 Isothermal sections of the three-dimensional free energy-temperature-structure diagram.

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