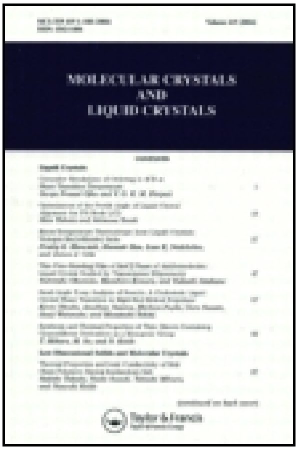

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Ten Phases of MBBA (A New Phase Diagram)

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Ten Phases of MBBA (A New Phase Diagram)

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The solid state polymorphism of MBBA has been studied and its phase diagram completed. Literature data were analysed and, essentially, neutron scattering results were used to describe the phase situation in MBBA. Transitions between the metastable solid modifications—originating from the fast-cooled glassy state—are considered and in particular, the room temperature range was emphasized. As a total, 10 states of MBBA are included in the new phase diagram: 7 solid modifications, a metastable state, the nematic and the isotropic liquid phases.

Keywords: MBBA, fast-cooling, phase diagram, neutron scattering

INTRODUCTION

The nematic liquid crystal compound *p*-methoxy-benzylidene-*p*-*n*-butylaniline (MBBA) can easily be transformed, by fast cooling from room temperature (nematic phase) to liquid N_2 temperature, into a glassy state. During reheating a sequence of polymorphic modifications can be obtained. By slow cooling other solid phases can be produced.

Considerable effort has been devoted to analysing the data on solid state polymorphism of MBBA. Various experimental methods have been applied to study the phase transition and to distinguish between modifications. Calorimetric, dielectric susceptibility, infrared absorption and Raman scattering, neutron and X-ray diffraction, positron annihilation, NMR and neutron inelastic incoherent scattering measurements have been reported on the MBBA solid state. (See, for example the papers cited in Reference 1.)

In order to obtain a reliable description of the phase situation, data from different methods have to be combined. Even simultaneous measurements on the same phase have to be carried out by two different techniques,[2,3] since a given method may not be sensitive enough for a certain phase transition mechanism to clearly register a new modification.

Here we summarize the results of different experiments on the MBBA states and present study of phase transitions by neutron diffraction.

MULTIMODE POLYMORPHISM

Combined neutron diffraction (ND) and Raman scattering (RS) measurements have been reported[3] giving the most complete phase diagram so far. Seven solid modifications have been identified besides the fast-cooled or glassy liquid crystal (GLC), nematic (N) and isotropic (I) liquid state. A schematic phase diagram has been constructed to show the thermal procedure for producing these phases (Figure 1).

The results of the ND and RS experiments were completed by differential scanning calorimetry (DSC) measurements[4] and the following concept of polymorphism is developed. There are two thermal procedures viz. 1. quenching from the nematic state and then reheating; 2. equilibrium crystallization, yielding two series of polymorphous modifications, i.e. $C_0 \rightarrow C_1 \rightarrow C_2 \rightarrow C_3 \rightarrow C_4$ and $C_5 \leftrightarrow C_6$. It means that at any temperature throughout the whole solid MBBA temperature range, at least two phases exist. This isothermal multiplicity of polymorphous modifications has been termed multimode polymorphism.

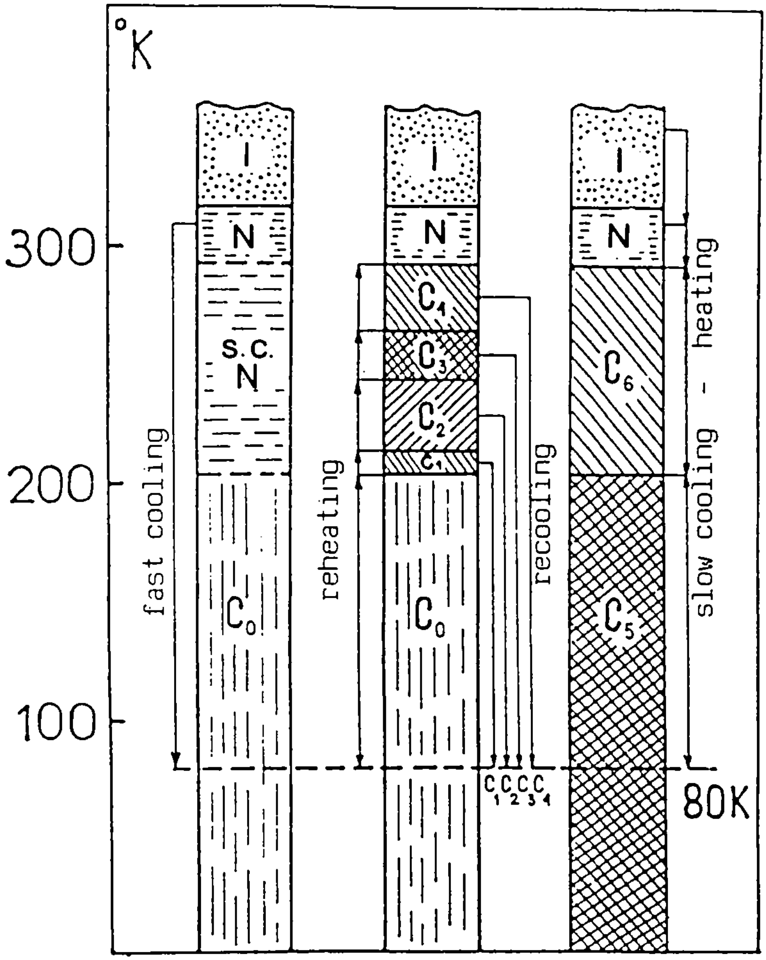

FIGURE 1 Thermogram patterns of heat treatment procedure to produce the different phases of MBBA.

NEUTRON SCATTERING

Notwithstanding that neutron scattering is an expensive and cumbersome method (compared, for example, with X-ray diffraction or DSC), it has been proved to be a very useful tool—besides, its use in structure analysis[5]—for phase transition studies, too. Neutron diffraction patterns clearly show the difference between the phases, as indicated in Figure 2, where curves recorded by the time-of-flight method[6] are represented in the 0.5–3 $Å^{-1}$ momentum transfer range. This was complemented at smaller $Q < 0.8$ $Å^{-1}$ ($Q = 4\pi \sin\theta/\lambda$, θ-scattering, λ-neutron wavelength) values by small-angle-scattering measurements[7] (Figure 3).

Two advantages of the neutron technique were extensively exploited: First, the time-of-flight method (at an intensive pulsed source—the IBR-2 reactor at Dubna) yields the simultaneous recording of the whole diffraction spectra, thus the evolution in time of a new structure was possible during a phase transition. Secondly, samples with different hydrogen/deuterium contents were measured, denoted as follows: D_0—all hydrogen, D_8—benzene rings deuterated, D_{12}—end-groups deuterated, D_{20}—end-groups and benzene rings deuterated. The difference in the neutron coherent scattering length of the H and D atoms provides different diffraction patterns (see Figure 4). In this way the use of four different isotope samples (for the same chemical compound) helps to separate the different phases.

It was established that the phase diagram for the different isotopomers is the same, but the transition temperatures are slightly different for the separate samples as shown in Table I. Some of the temperature limits of transitions are rather indistinct, so the accuracy of the values in the table is not better than 3 degrees. It should be noted that in the series of samples D_0, D_8, D_{12} and D_{20}, temperature ranges for C_1 and C_2 have tendency to decrease, while those of the C_3 and C_4 phases increase (except for D_{20}).

Different external conditions were applied to study the phase transitions. Magnetic fields up to 0.7 Tesla were used to orient the samples: no influence of the orientational magnetic fields was observed on the phase diagram (only the macrostructure of the phases was affected).[6]

Cooling conditions were varied and the essential conclusion is the following (in agreement with statements in[4]): i) quenching either from the I or N phase does not affect the structure of the C_0 phase and the subsequent phase sequence. ii) no influence of the cooling rate was found on the phase diagram, once the glassy state had already been formed.

Reheating results in a variety of phase transitions. Normally the phase sequence $C_0 \rightarrow C_1 \rightarrow C_2 \rightarrow C_3 \rightarrow C_4$ can be recorded with the temperature of transformations as indicated in Table I (the heating rate was varied between 0.2 and 10 K/min.). Spontaneous transitions $C_0 \rightarrow C_3$ were measured (omitting C_1, C_2) in several cases for the different H/D ratio samples (except D_{20}) preferably at 210 ± 2K, however, transitions

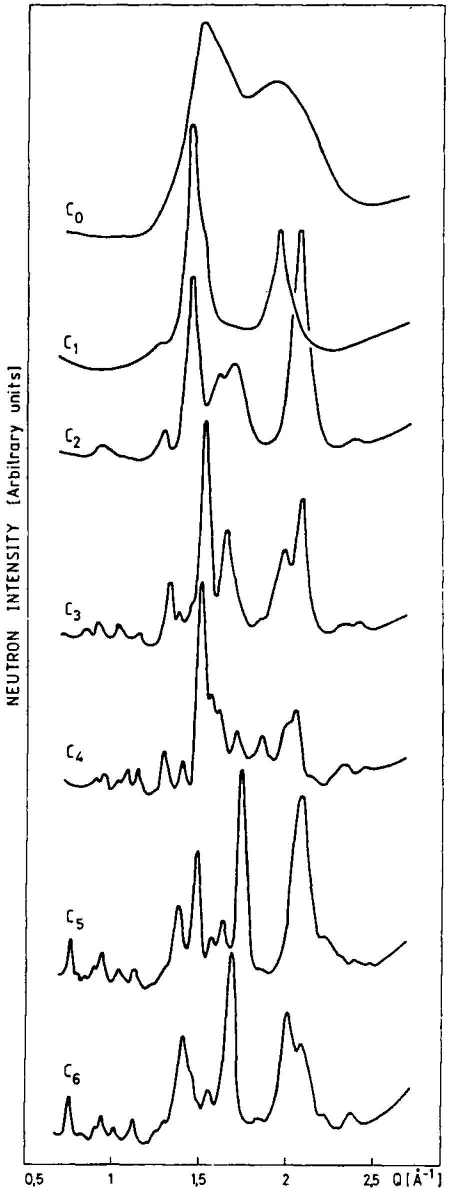

FIGURE 2 Neutron diffraction patterns of different phases of MBBA measured on deuterated sample by time-of-flight diffraction method.

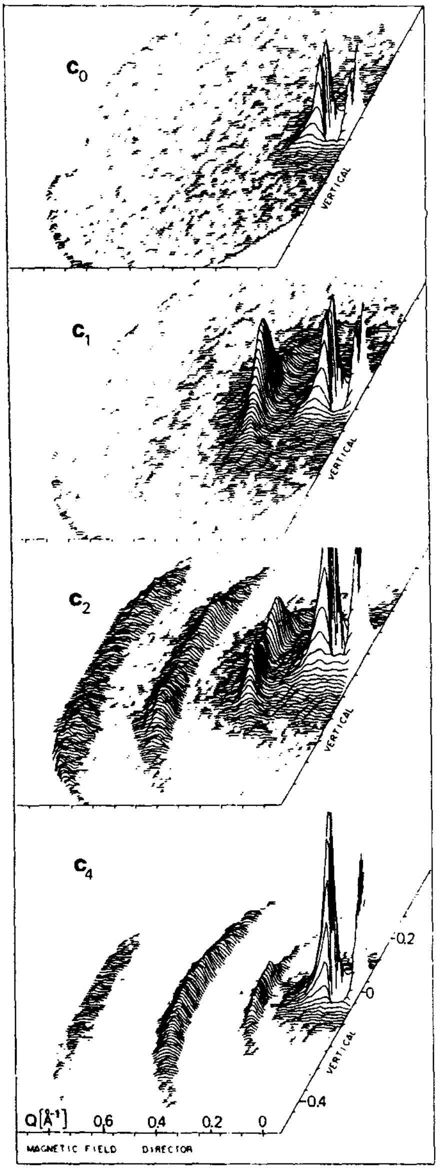

FIGURE 3 Small angle neutron scattering patterns measured with the PAXY instrument at the Orphée reactor in CEN Saclay on a few phases of the D_{20} sample. The scattering intensities are shown over the 128 × 128 cell area of the *XY*-detector in perspective views for the different phases (λ = 3.12 Å wavelength was used and H = 0.7 Tesla magnetic field was applied for the sample orientation).

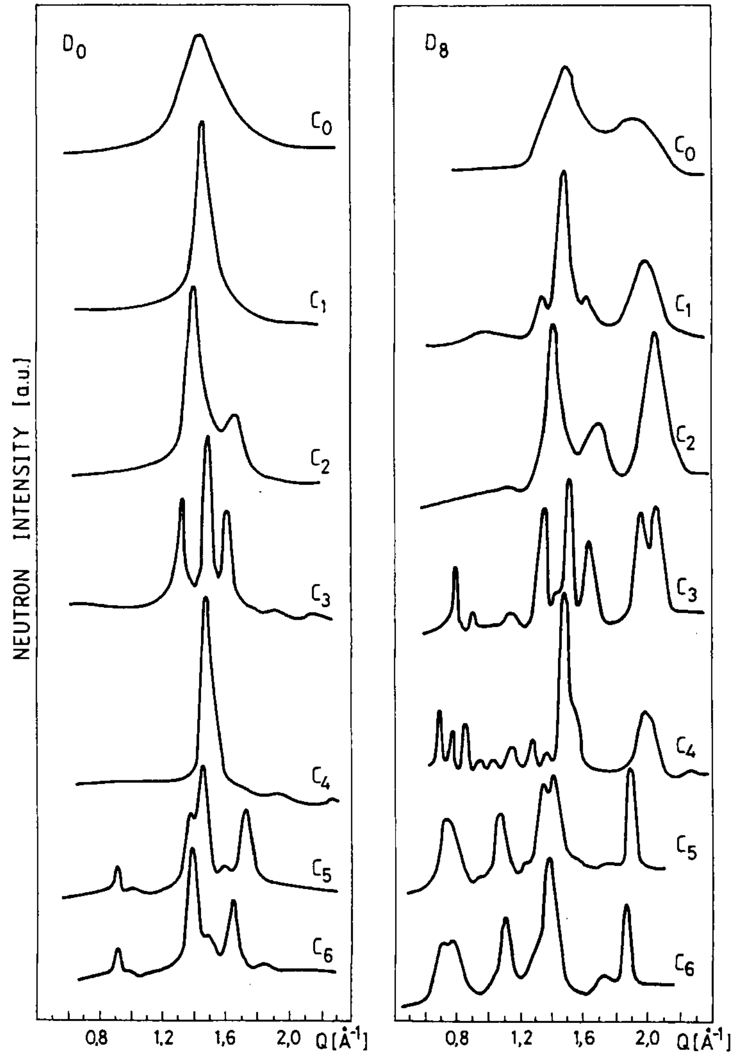

FIGURE 4 Diffraction patterns of different phases for the D_0 and D_8 samples (H = 0, T = 80K, T = 260K for C_6).

were registered at 220 K (D_0) and 226 K (D_8). This is a transformation which takes place very quickly (within 1 min), however, the $C_2 \rightarrow C_3$ transition is a fairly long process, these two phases may even coexist for an order of half an hour at a temperature given in the table for the $C_2 \rightarrow C_3$ transition. In some heating runs traces of C_1 and C_2 phases can be observed when transforming C_0 to C_3 below 220 K. The C_4 phase

TABLE I

Temperature ranges of the MBBA solid phases for the different isotopomers

PHASES	D_0		D_8		D_{12}		D_{20}	
	$T_{min}-T_{max}$	ΔT	$T_{min}-T_{max}$	ΔT	$T_{min}-T_{max}$	ΔT	$T_{min}-T_{max}$	ΔT
C_0	205		207		207		207	
C_1	205 - 215	10	207 - 215	8	207 -215	8	207 - 213	6
C_2	215 - 245	30	215 - 238	23	215 -226	11	213 - 226	13
C_3	245 - 265	20	238 - 255	17	226 -255	39	226 - 258	32
C_4	265 - 294	29	255 - 294	39	255 -294	39	258 - 294	36
C_5	205		205		205		205	
C_6	205 - 294	89	205 - 294	89	205 -294	89	205 - 294	89

is always produced from C_3. An analogous jump from C_0 to C_3 was also observed in the case of DSC and X-ray measurements. Even when varying alternately the quenching and reheating regimes no conditions were obtained enabling one to determine the $C_0 \rightarrow C_1 \rightarrow C_2 \rightarrow C_3 \rightarrow C_4$ or the $C_0 \rightarrow C_3 \rightarrow C_4$ sequence: i.e. exactly the same prehistory of the sample can lead to one or the other series. It is probably because of this latter transition procedure that no more than three metastable modifications have been reported in earlier publications.[8]

ROOM TEMPERATURE REGION

The crystalline modification C_6 can be produced from the nematic state by slow cooling. It was shown[3,4] that this transforms into the phase C_5 which is stable below 205 K. At high temperatures the stability of the C_6 state was studied, and it has been established[9] that at 291 K a very slow transition takes place forming the C_4 structure. The time dependence of the evolution of the $C_6 \rightarrow C_4$ transition was fixed after about 100 hours. This means that the C_6 phase is a met-

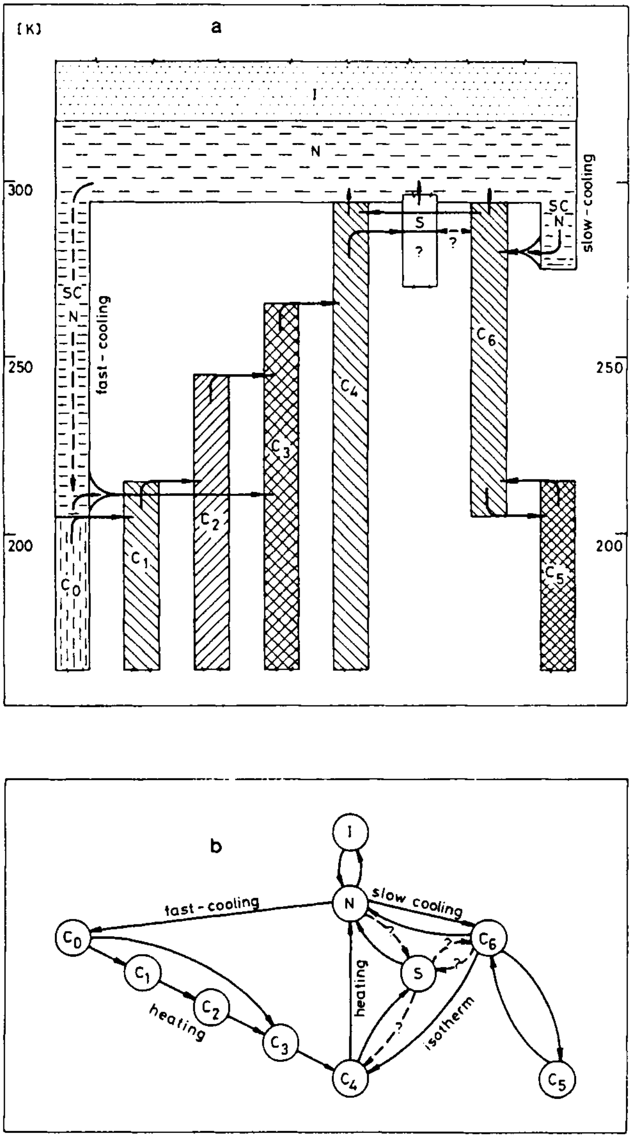

FIGURE 5 Schematic diagram of MBBA phase transitions for the D_0 sample. a—completed version of the thermogram patterns (see Figure 1), b—layout of the transition scheme.

astable modification, which transforms into C_5 (at low temperatures) or into C_4 (at high temperatures). Different methods have indicated that in the temperature range before melting one more phase transition may occur. For example, a slow heating (1.25 K/min) of the C_4 state in the DSC measurement[4] results in an additional transition with an exotherm at ~286 K before melting. The splitting of the 1163 cm^{-1} frequency Raman-line in the measurement of Arendt *et al.*[8] on heating at 286 K is explained by a transition into a phase with an "excited energetic state." Recently, NMR measurements[2] were reported, where the observed transition at 286 K was ascribed to a plastic crystal phase below the nematic state. For a more definite statement on the existence of a phase between C_4 and N (286–295 K) more experiments should be carried out and the nature of this, let us say, S modification should be clarified.

SUMMARY

As a result of phase situation studies, a new phase diagram of MBBA is suggested that contains new transitions with respect to the phase schemes described in Refs. 3,4. Figure 5 shows the scheme of transformations relating to the states of MBBA with different structural and/or dynamic properties: C_0-C_6 solid, S-metastable (unclarified), N-nematic and I-isotropic liquid phases. The final conclusion of this report is that 10 modifications can be indentified at present. Moreover, it is not excluded that new phases and transitions will be able to be observed in the future since there is little doubt that even more careful experiments can be performed, with more sensitive instruments and—what seems to be even more important—with increased patience in waiting for a phase to be stabilized!

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