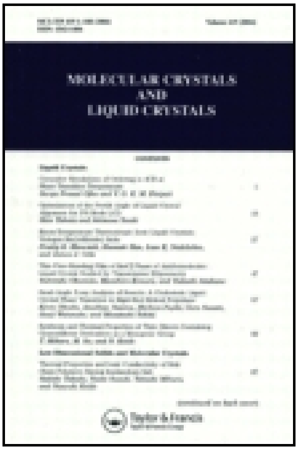

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Sequence of Phase Transitions in Solid Mbba

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SEQUENCE OF PHASE TRANSITIONS IN SOLID MBBA

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ABSTRACT

Combined neutron diffraction and Raman scattering measurements were carried out on a series of different phases of the same MBBA sample. The change in the diffraction patterns and in the optical spectra are used to indicate the transitions between the different phases investigated in the whole temperature range of interest. Besides the isotropic and nematic liquid crystalline phases, 7 different solid structures were found and a schematic phase diagram was constructed to show the thermal procedur for producing these phases.

INTRODUCTION

n-p-Methoxy-benzylidene-p-butyl-aniline (MBBA) is one of the most widely studied nematic liquid crystalline (NLC) compounds. A special feature of this substance is the ability to form different solid state modifications. It has been shown in previous papers [1,2] that a glassy liquid crystal (GLC) phase can be formed by fast cooling. It was also demonstrated that there is no long-range order in this phase, and the transition from GLC to the crystalline phase(s) can be interpreted as a decelerated disorder→order transformation which goes through a few different solid structural modifications. Some of these structures are known in the literature [3,4] however these data contradict each other concerning the number of phases and the heat treatment for producing them.

In order to follow the phase transition procedure under different heating and cooling conditions, we performed a set of experiments where neutron diffraction (ND) and Raman scattering (RS) were combined; in every case the same sample was subjected to measuring by both methods. Here we report on the phase diagram of MBBA as obtained from these experiments in the temperature range where the structural changes were found (80K-320K).

EXPERIMENTAL

Several MBBA samples were used during the measuring period; the samples were always taken from closed ampoules under very clean conditions. The sample was put into an Al container of 50x27x2 mm^3 which was equipped with a quartz window of Ø 8 mm on one of the large planes for the light scattering studies. A low temperature thermostat was used to obtain the correct temperature of the sample with an accuracy of 0.1 K. The sampling part of the specially made thermostat was equipped with an Al-window for the free passage of neutrons in the angular interval of 300^o. Two quartz windows at 45^o served for the light transmission. In this way ND patterns and RS spectra could be recorded simultaneously at any temperature.

Nondeuterated MBBA was used throughout the measurements, although it gives a high incoherent background in neutron scattering patterns. Nevertheless the accuracy of the ND peak positions and width assignement was sufficient to distinguish the structures of different modifications. Using different samples the experimental results could be reproduced.

Neutron diffraction patterns were measured at the 5 MW reactor in the Central Research Institute for Physics, Budapest. Monochromatic neutrons of $\lambda=1.1315$ Å wavelength were obtained from

Zn (2000) single crystal. 30′ collimation was applied in front of as well as behind the sample. To perform detailed studies of the structure of the different modifications was not the aim of this experiment. To distinguish between the different phases, data from the most characteristic Q-range ($Q = \frac{4\pi}{\lambda} \sin \Theta$, Θ - scattering angle) are used where the resolution of the spectrometer was $\Delta Q \sim 0{,}07$ Å^{-1}. The ND patterns are corrected for background and normalized.

Vibration spectra were measured on a RAMANOR HG 2S standard Raman spectrometer (Jobin-Yvon) equipped with an ILA 120 argon-ion laser (Zeiss) at Eötvös Loránd University, Budapest. The 514.5 nm line at ∼200 mW power was used with 3.0 cm^{-1} resolution. Raman spectra were recorded for each phase in the 3-1800 cm^{-1} frequency range, on samples where the structure was controlled by ND. Here we present only the most characteristic parts of the intermolecular, low frequency and intramolecular, high frequency vibration spectra, respectively, in order to demonstrate the change between modifications.

RESULTS AND DISCUSSION

In *Fig. 1* sets of Raman spectra and neutron diffraction patterns are given to compare the different phases. Column a shows a part of high frequency intramolecular vibration modes in the 1120-1220 cm^{-1} interval. The 150-250 cm^{-1} range - denoted by b - covers both external and the most low frequency internal modes. c represents the main ND peaks in the 0.75-2.25 Å^{-1} momentum transfer range. As seen from *Fig. 1* not only low-frequency modes but high frequency ones were significantly changed when phase transitions occure.

The NLC and GLC curves are the same as published earlier [1], but with better statistical accuracy since the neutron intensity was increased by aligning the MBBA molecules by an external magnetic field (the effect of alignment on the structure will be described elswhere: it has no effect on the phase diagram). Phaes labelled by C_1, C_2, C_3 and C_4 were produced by step by step heating from the GLC phase, giving a sequence of irreversible transitions. It means that whenever such a phase is produced (e.g. C_1 from

GLC by heating above ~205 K) it can be stabilized by recooling. This is why these phases could be measured at liquid nitrogen temperatures. To get the next phase (in the above example: C_2) one has to heat again the sample above the transition point (C_1 to C_2 above ~215 K).

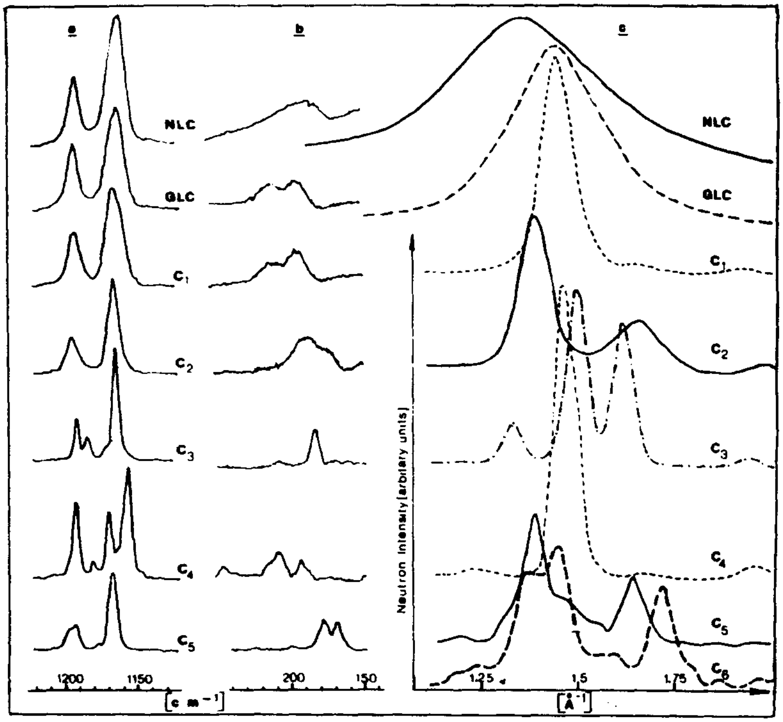

Fig. 1. High (a) *and low frequency* (b) *Raman spectra* (C_6 *is not indicated because of normalization difficulties due to the high temperature measurement); neutron diffraction patterns* (c) *of the MBBA phases.*

Phases C_6 and C_5 can be produced by slow cooling from nematics. The transition between C_6 and C_5 was measured at ~200 K. This transition was found to be reversible, since a control measurment by reheating up to 286 K gave the same picture as observed for C_6. (NLC can be supercooled by a few degrees.)

In Table I, temperatures where a phase was stabilized, the temperature intervals (accuracy not better than ±5 K, since most of the transitions are rather indistinct), and the positions and full widths at half height (FWHH) at the main ND peaks of each phase are given.

Table I

N^0	Phase	T*[K]	T [K]	Q [$Å^{-1}$]	FWHH [$Å^{-1}$]
1	I	-	>318	-	-
2	NLC	-	294-318	1.37 (300 K)	0.378
3	GLC	80	<205	1.47 (80 K)	0.234
4	C_1	207	205-215	1.47	0.093
5	C_2	221	215-245	1.41	0.093
6	C_3	260	245-265	1.50	<0.069
7	C_4	270	265-294	1.47	<0.067
8	C_5	80	<200 (on cooling)	1.45 (286 K)	<0.066
9	C_6	286	>250 (on heating)	1.38	-

If one exanines the ND and RS curves one can see striking differences between the phases: in some cases in the ND patterns, in some others in the RS spectra. For instance Raman spectra of GLC and C_1 are not significantly different, but ND shows clearly that the structure has changed. The case is reversed for C_1 and C_4 where the RS is drastically different for the two phases whereas the ND patterns are similar.

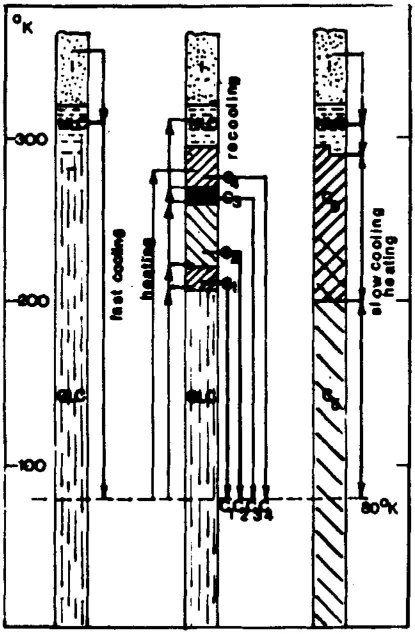

Fig. 2. Thermogram patterns of phase transitions in MBBA.

Figure 2 schematically shows the possible transitions between the different phases. A measuring cycle was always started from the isotropic liquid phase. A waiting time of an hour was used to stabilize the structure. GLC forms from NLC by fast cooling (~1K/s). The C_1-C_4 phases are produced from GLC by heating. Recooling does not affect the further transitions, e.g. C_4 can be formed directly by heating from 80 K to above 265 K or one can make several recoolings in order to measure the intermediate C_1, C_2 and C_3 phases at low temperatures. It is interesting to note that the transformation between C_2 and C_3 as well as that between C_3 and C_4 is continuous; these latter two phases may coexist and the waiting time mentioned above is absolutely necessary to get clean phases.

In the third column of *Fig. 2* the reversible transition $C_5 \leftrightarrow C_6$ and the possibility of supercooling NCL is indicated. A 10 K Raman measurement yields the same spectrum for C_5 as at 80 K, therefore one can suppose that no other phases exist in the intermediate temperature range.

CONCLUSIONS

From the above results one can conclude that the disorder of the centre of mass of the NCL molecules can be frozen in by fast cooling (formation of GLC); the transition to the crystalline structure of, for example, C_3 with long range order, goes through a series of intermediate phases (C_1 and C_2) where the change from phase to phase proceeds by partial reorganization of the molecular order in several steps towards the most stable crystalline structure. This is seen on the one hand directly from the transformation and narrowing of ND peaks and on the other hand from step by step transformation of the vibration spectra. Two cases were found where the width of the ND peaks changed, namely at the transitions between GLC and C_1 furthermore between C_2 and C_3 phases. Therefore C_1 and C_2 can be considered as incompletely ordered phases with a strongly disordered structure. The change of Raman spectra from one phase to another shows the coherence of the vibrational states evolves gradually in the sequence of phase transitions $GLC \rightarrow C_1$, $C_2 \rightarrow C_3$, C_4 consistently with the neutron diffraction observations

Striking differences between high frequency Raman spectra indicate that besides positional rearrangements molecular conformations play an important role in the structural evolution. A detailed analysis of these observations will be given elsewhere.

To sum up, combined ND and RS measurements have allowed us to distinguish seven solid modifications of MBBA that differ from each other in structure and in the spectra of their molecular vibrational states.

REFERENCES

1 V.K. Dolganov, N. Kroó, L. Rosta, E.F. Sheka, *Mol. Cryst. Liq. Cryst.*, 64 (Letters), 115 (1980)

2 A.N. Belushkin, V.K. Dolganov, I. Natkaniec, E.F. Sheka, *Sov. Phys. JETP Letters*, 33, 481 (1981)

3 N. Kirov, M. Fontana, *Mol. Cryst. Liq. Cryst.*, 56 (Letters), 195 (1980)

4 J. Le Brumant, M. Jaffrain, A.T. Nguyen, *J. de Phys.*, 40 C3-193 (1979)