

This article was downloaded by: [Tomsk State University of Control Systems and Radio]

On: 23 February 2013, At: 03:32

Publisher: Taylor & Francis

Informa Ltd Registered in England and Wales Registered Number: 1072954
Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/gmcl16>

Structural and Spectral Studies of Glassy MBBA

V. K. Dolganov^a, N. Kroó^{b a}, L. Rosta^{b a} & E. F. Sheka^a

^a Institute for Solid State Physics, 142432, Chernogolovka, USSR

^b Central Research Institute for Physics, H-1525 Budapest 114, P.O.B. 49, Hungary

Version of record first published: 20 Apr 2011.

To cite this article: V. K. Dolganov, N. Kroó, L. Rosta & E. F. Sheka (1980): Structural and Spectral Studies of Glassy MBBA, *Molecular Crystals and Liquid Crystals*, 64:4, 115-120

To link to this article: <http://dx.doi.org/10.1080/01406568008072007>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.tandfonline.com/page/terms-and-conditions>

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae, and drug doses should be independently verified with primary sources. The publisher shall not be liable

for any loss, actions, claims, proceedings, demand, or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

STRUCTURAL AND SPECTRAL STUDIES OF GLASSY MBBA

V.K. DOLGANOV*, N. KROÓ,
L. ROSTA, E.F. SHEKA*

Central Research Institute for Physics
H-1525 Budapest 114, P.O.B. 49, Hungary

*Institute for Solid State Physics
142432 Chernogolovka, USSR

(Submitted for publication August 29, 1980)

ABSTRACT

Structure measurements were carried out by neutron diffraction on the glassy nematic liquid crystalline and crystalline phases of MBBA. The change of optical spectra of intermolecular vibrations was also followed by Raman scattering around the phase transition from the fast-cooled state to the crystalline one. Parallel investigations of solid state polymorphism were also carried out using both methods.

INTRODUCTION

In the last few years very much interest has centered on the fast-cooled state of liquid crystals (LC) when the nematic phase can be quenched and a glassy solid is formed. Several methods have been used to investigate this glassy state of liquid crystalline materials (GLC).

This interest is based partly on the possibility to be able to perform a continuous transformation from the disordered glassy state having no long range order, to the completely ordered crystalline one. This transformation may be stopped and studied at any intermediate, partly ordered state. On the other hand GLC systems are more suitable subjects for dynamical studies than liquid crystal - since such systems can be cooled to low temperatures where the effect of anharmonicity on "phonon" spectra can be excluded.

The nematic LC compound n-p-methoxy-benzylidene-p-butylaniline (MBBA) has been especially widely studied. X-ray diffraction, adiabatic calorimetry, vibrational spectroscopy [1-3] were used to demonstrate the existence of the GLC phase and to determine its properties. The temperature dependence of the order parameter was also determined [4-5] by optical methods.

In this paper the results of neutron diffraction and Raman scattering measurements are presented for GLC, LC as well as the crystalline phases of MBBA giving some insight into the disorder \rightarrow order phase transition process and solid state polymorphism of this material.

EXPERIMENTAL

The GLC phase was produced by fast cooling from the nematic liquid crystalline phase in a liquid nitrogen cryostat. The cooling rate was measured to be about 50 K/min.

Neutron diffraction patterns were recorded at the 5 MW research reactor in Budapest on the triple axis spectrometer used in elastic scattering geometry. Measurements were obtained at a wavelength $\lambda = 1.32 \text{ \AA}$. A wide momentum transfer range, $0.4 \text{ \AA}^{-1} \leq Q \leq 5 \text{ \AA}^{-1}$, was investigated; however, only a smaller but the most characteristic Q-range is presented here. There was no need for very good resolution to identify structures corresponding to the different phases of MBBA. Rather, since a nondeuterated sample was used giving a high incoherent background the experimental parameters were chosen to get high intensity. The presented diffraction patterns are corrected for background. Gaussian curves were fitted to the observed maxima and are given in the figures.

Vibration spectra of MBBA were measured on a DFS-24 Raman spectrometer equipped with a 50 mW He-Ne laser in the Institute for Solid State Physics, Chernogolovka, USSR.

RESULTS AND DISCUSSION

In FIG. 1 a set of neutron diffraction patterns is given in the most important and characteristic part of the momentum transfer region measured.

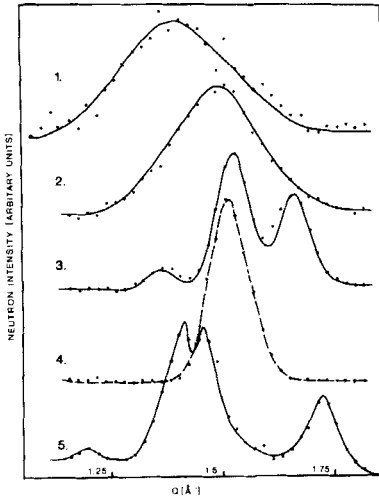


FIGURE 1

Neutron diffraction pattern as a function of $Q = \frac{4\pi}{\lambda} \sin\theta$

(θ - scattering angle) for different phases of MBBA.

1. - Nematics (300 K);
2. - Glassy liquid crystal (77 K);
- 3., 4., 5. - different crystal modifications (77 K).

phases is the same, meaning that their structure should also be very similar. This statement is valid for all the measured Q -regions, not only the given one. The translationally disordered GLC state can be well stabilized below 200 K. If, however, it is warmed up to higher temperatures, transition to the crystalline state occurs. The degree of transition depends on the temperature of the sample (at $T > 200$ K) and the time spent

the characteristic part of the momentum transfer region measured. Curves 1 and 2 correspond to the structures of a non-aligned sample in the nematic liquid crystalline and the glassy phases, respectively. The difference between the two curves is the shift in the peak position namely in the case of GLC towards larger momentum transfers. This corresponds to the decrease of the average molecular distance and the narrowing of the peak in GLC. (This means that the correlation between molecules has increased in GLC compared with the LC phase.) At the same time one can state that the general form of the curves for the GLC and LC

at the particular temperature. This transition is irreversible. Curve 3 in FIG. 1 corresponds to a

crystalline structure after a complete transition produced by heating up to 270 K. On the other hand the transition process can be stabilized at a certain stage by rapidly cooling down the sample. In this way samples can be produced which are partly transformed from the state of translational disorder and orientational order of GLC to the state of complete order of the crystalline phase.

MBBA is known to have different polymorphic crystalline modifications. These structures can be obtained by different heat treatment and distinguished e.g. by their Raman spectra as discussed below or by their neutron diffraction patterns (3, 4 and 5 in FIG. 1). To our knowledge the space groups of these crystalline modifications are not known and no effort was made in the present work either to determine them.

Stokes lines as observed by Raman scattering are presented in FIG. 2 as

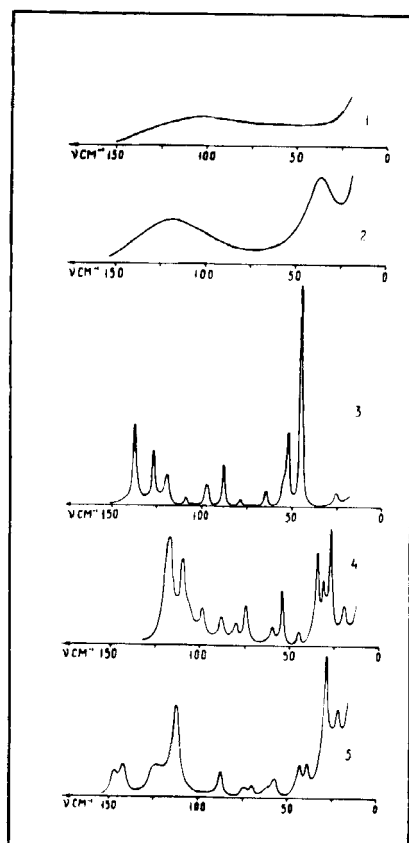


FIGURE 2

Raman spectra of different solid structures of MBBA at 10 K. 1. - Glassy liquid; 2. - partly transformed GLC into crystal; 3., 4., and 5. - different crystal phases.

measured at 10 K. Curve 1 shows the smooth spectrum of the GLC phase. After warming it up the GLC phase transforms to a crystalline one characterized by curve 3. (After transition the sample was cooled down.) Curve 2 was measured when the GLC \rightarrow crystal transition process was stopped in an intermediate state. The partial translational ordering gives rise to a broad line in the 25-50 cm^{-1} frequency range. Its short wavelength edge fits the most characteristic phonon peak of the crystalline phase.

The existence and shape of this peak can be interpreted by the scattering of phonons on crystal defects. It is obvious that the existence of a broad spectral peak in partly disordered samples is connected with the finite, i.e. decreased coherence length of phonon states when the optical transitions into states with $\vec{q} \neq 0$ of the Brillouin zone of the crystal can be resolved [6].

To compare the crystal phase formed from GLC with the other modifications we produced crystalline phases by different heat treatments and measured by Raman scattering; this allows the distinction or identification of phases. The phase represented by curve 4. Phase 3 can be obtained only from the GLC state. Phase 4 forms from 3 but can be produced by other methods too [7]. The stable phase 5 forms from supercooled melt by slow cooling. Raman spectra of phases 4 and 5 are also given in [7] at 80 °K.

Thermal pre-history of our samples for Raman studies was the same as for those used in neutron diffraction. Therefore the 3, 4 and 5 labels both in *FIG. 1* and *FIG. 2* represent the same phases.

CONCLUSIONS

Experiments on many molecular crystals based on neutron inelastic scattering, light spectroscopy etc. have enabled to see intermolecular vibrational modes (phonons) of molecular crystals quite widely studied and understood theoretically as well as experimentally. The microdynamics of liquid crystals is, however,

known at a much lower level. From this point of view the investigations of GLC represent promising way to learn more about the structure and collective excitations of partly disordered systems in general and liquid crystals in particular.

The phase transition $\text{GLC} \rightarrow \text{crystal}$ can be interpreted as a decelerated in time transformation from the LC to the crystalline state. Therefore, the $\text{GLC} \rightarrow \text{crystal}$ phase transition, which can be investigated at different stages, may serve to a certain extent as a model of the $\text{LC} \rightarrow \text{crystal}$ transition (meaning only the change of the structure and not the translational motions of molecules) which is not yet very well understood theoretically although a great deal of effort has been made experimentally.

REFERENCES

- [1] J.E. Lydon, J.O. Kessler, *J. de Phys.*, 36, C1-153 (1957)
- [2] J.A. Janik, J.M. Janik, J. Mayer, E. Sciesinska, J. Sciesinski, J. Twardowski, T. Waluga, W. Witko, *ibid* C1-159
- [3] N. Kirov, F. Cavatorta, M. Fontana, *Mol. Cryst. Liq. Cryst.*, 54, 207 (1979)
- [4] V.K. Dolganov, 2nd Liq. Cryst. Conf., Bulgaria, *Conf. Abstr.*, p.164 (1977)
- [5] N. Kirov, M. Fontana, *Mol. Cryst. Liq. Cryst. Letters*, 56, 195 (1980)
- [6] R. Shiker, R.W. Gammon, *Phys. Rev. Lett.*, 25, 222 (1970)
- [7] J. Le Brumant, M. Joffrain, A.T. Nguyen, *J. de Phys.*, 40, C3-193 (1979)