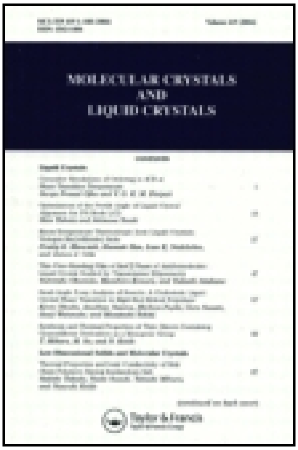

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Fast-Cooled Liquid Crystals

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Fast-Cooled Liquid Crystals†

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Several liquid crystal compounds have the ability to form a glassy solid phase on being quenched. Such materials and the experimental methods for their study are summarized in this paper. Macroscopic and microscopic descriptions of the structures of fast-cooled liquid crystals are given using both published data and our own results. Spectroscopic studies are analysed in order to characterize the intra- and intermolecular motions. The experimental investigations of glassy features of MBBA as a typical nematic liquid crystal are reviewed. The conditions for the production of the glassy state, the solid state polymorphism, molecular short-range and medium-range order, spectra of molecular motions in a wide frequency range are considered. Structural investigations of four samples with different hydrogen/deuterium ratios are described. Effects connected with the liquid crystal origin and the amorphous character of these states are analysed.

INTRODUCTION

Liquid crystals have remained at the centre of interest of solid state physics and chemistry for many years. The appearance of new attractive topics (e.g. discotic systems) proves the fecundity of this research field. The growing number of publications seems to indicate that fast-cooled liquid crystals could well become an interesting branch of oriented molecular systems.

When referring to a fast-cooled liquid crystal, we mean that if a mesophase is cooled sufficiently rapidly below a certain temperature, and amorphous solid state may be produced which retains a structure similar to the starting phase. The possibility of forming such a state has long been known, e.g. in the 50's Broude noticed that complex molecular compounds with aromatic rings easily transform into the

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amorphous state.[1] This occurs for several mesogenic substances and some ten years after Chistyakov and Vainshtein's pioneering work (1963),[2] the existence of the glassy state of liquid crystals was demonstrated for numerous compounds. In the middle of the 70's a more systematic study began.[3-9] A list of the available references, investigated compounds and methods is given in Table I (only thermotropic liquid crystals are considered).

In the literature, fast-cooled liquid crystals have also been described as frozen-in or glassy liquid crystals (GLC), glassy mesophase-smectics, molecular amorphics (from the Russian term). In our opinion it is also reasonable to call this state an oriented molecular glass (OMG).

In this paper we shall review the principal published results on the structure and dynamics of these systems and we shall consider, in more detail, the investigation of *n*-*p*-methoyxbenzylidene-*p*-butylaniline (MBBA) as the most widely studied material in this field. In this way we hope to show that oriented molecular glasses offer an interesting and valuable field of research since they can be dealt with from two aspects:

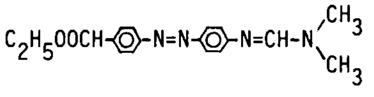
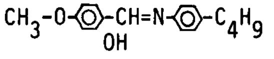
(i) the study of liquid crystal-type properties (at low temperatures!) and/or (ii) the study of features characteristic of amorphous solids. Therefore, the concepts and methods generally used in both cases can be combined and applied to OMG samples.

STRUCTURE OF FAST-COOLED LIQUID CRYSTALS

Several methods have been used to demonstrate such fundamental behaviour of fast-cooled liquid crystals as the non-crystallinity of the structure. Possibly the simplest evidence for an amorphous state, is provided by calorimetric measurements since on reheating a glass → crystal an irreversible phase transition can be observed. In Figure 1 a typical differential scanning calorimeter (DSC) measurement[10] is shown. The MBBA sample was cooled from the nematic liquid crystal (NLC) state at a rate of 80 K/min. The jump in the heat capacity once indicates the onset of freezing. The temperature was then increased and a characteristic glass → crystal transition was observed at T_g = 205 K. Further heating yields solid-solid phase transitions indicating solid state polymorphism, which is present in most cases of materials with glass-forming ability (for details, see Section 4.) The act of fusion—when starting from a glassy state—usually differs from that observed for the melting of a crystal phase which had been previously formed by slow cooling. In the case of MBBA, for ex-

TABLE I

Investigated liquid crystal compounds with glassy state. (DS—dielectric study, DSC—differential scanning calorimetry, DTA—differential thermal analysis, ED—electron diffraction, IISN—inelastic incoherent scattering of neutrons, IR—infrared absorbtion, ND—neutron diffraction, OM—optical microscopy, RS—Raman Scattering, XRD—X-ray diffraction)

Abbr.	Formula	Method	Reference
BAN	H-⌬-N=N-⌬-N=CH-⌬-OCH_3	XRD	2
DBAE	 C_2H_5OOCH-⌬-N=N-⌬-N=CH-$N(CH_3)_2$	ED	15
CBP E_3	R_i-⌬⌬-CN-$(L)_i$ 5 comp.	DS,OM	4, 22
MBBA	CH_3-O-⌬-CH=N-⌬-C_4H_9	see TABLE 2	
OHMBBA	 CH_3-O-⌬(OH)-CH=N-⌬-C_4H_9	DTA,DSC,NMR	3, 20, 25
EBBA	C_2H_5O-⌬-CH=N-⌬-C_4H_9	DSC,DS,IISN, IR,RS	7, 9, 11, 21, 26
HBT	$C_6H_{13}O$-⌬-CH=N-⌬-CH_3	DSC,DTA,XRD	27
CBPA	Cl-⌬-CH=N-⌬-C_5H_{11}	DSC,IR,RS	11
PBPA	C_3H_7O-⌬-CH=N-⌬C_5H_{11}	IR	7
DOBHOP	$C_{10}H_{21}O$-⌬-COO-⌬-OC_6H_{13}	ND,RS	8
5.04	C_5H_{11}-⌬-COO-⌬-OC_4H_9	DSC	28
CHP	Cholesteryl hydrogen phthalate	DTA	29

ample, the transition temperature (to the nematic phase) was found to be a few degrees lower if a glass had been the starting state.

The transition of a nematic liquid crystal to a glass with nematic order upon quenching was confirmed by optical microscopy[4] when a cyanobiphenyl eutectic mixture E3 was investigated. A twisted nematic layer was rapidly solidified by contact with liquid nitrogen and complete extinction was retained, giving positive evidence that a glassy

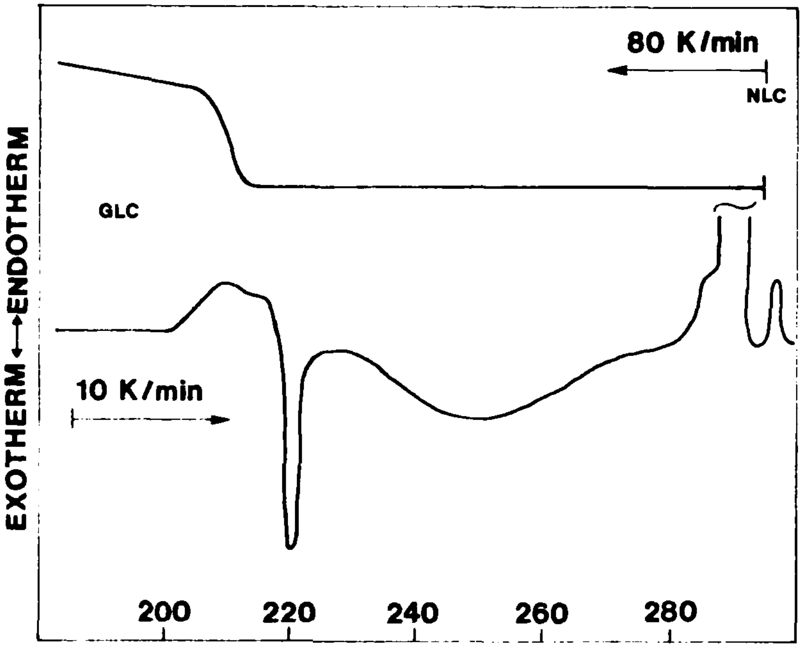


FIGURE 1 DSC curves indicating the fast-cooling and the reheating procedure in MBBA.[10]

rather than a crystalline phase was produced. On warming to room temperature several phase changes could be observed, also demonstrating the series of solid polymorphous modifications.

Besides these bulk methods, considerable efforts have been made to identify the glassy state by studying microscopic properties.

Vibrational spectroscopy was utilized to demonstrate the non-crystallinity of the quenched samples as well as to obtain information about the nature of the orientational ordering. Infrared (IR) absorption,[11] Raman Scattering (RS)[6] and inelastic incoherent scattering of neutrons (ISSN)[9] are able to distinguish between amorphous and crystal phases. The vibration spectra of the different phases were compared in the range of 4–4000 cm^{-1} by these methods. The low frequency part corresponds to intermolecular and soft intramolecular motions, therefore the region about 4–400 cm^{-1} is the most sensitive to structure changes. It will be shown in Section 3, that RS gives the most significant difference between glassy and crystal structures. Typical comparative RS curves are presented in Figure 2[8] measured for DOBHOP.

Light scattering is also able to provide indirect evidence for the

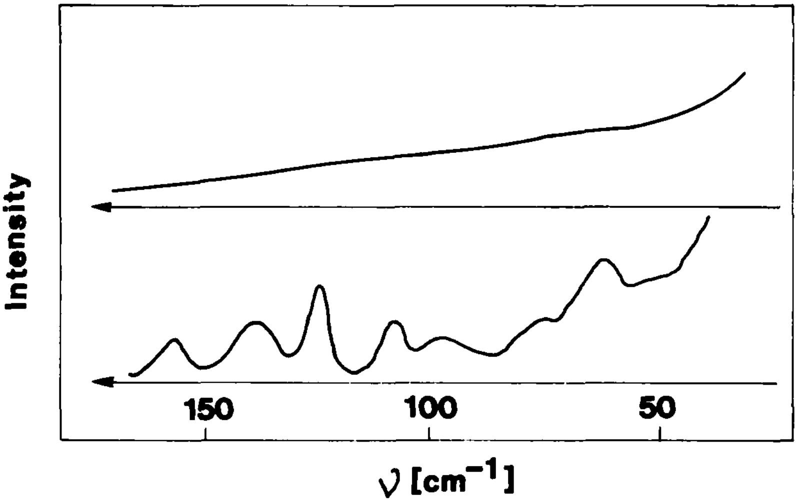


FIGURE 2 Raman spectra of the glassy (upper curve) and the crystalline phases of DOBHOP measured at 80 K.[8]

molecular alignment in the glassy state similar to that in the nematic phase by determining the orientational order parameter

$$S_2 = \frac{1}{2}(3\,\overline{\cos^2\theta} - 1)$$

IR dichroism studies of surface aligned (by rubbing) samples[7] gave very similar values of S_2 for glassy and nematic phases (e.g. 0.45 and 0.46 for MBBA, 0.47 and 0.49 for PBPA, respectively). In contrast, the impurity luminescence method[12] indicated that S_2 is much higher (~0.70) for the glassy phase than in the previous case. Although the contradiction is not understood, these results allowed the authors[7,12] to conclude that the macroscopic alignment and the nematic order remain practically unchanged upon quenching.

The most direct information about the structure can be obtained by diffraction techniques. X-ray[2,5,13] neutron[8,14] and electron[15] diffraction investigations of the glassy phase of liquid crystals have been reported. Figure 3 shows neutron diffraction patterns for MBBA in NLC, glassy (C_0) and in the other solid phases.[16] It is clearly apparent that in the quenched phase (C_0), instead of sharp Bragg reflections, a broad maximum similar to that of the nematic phase is present, indicating that the structure is amorphous. On heating, transitions to more ordered phases can be detected, indicating the solid polymorph-

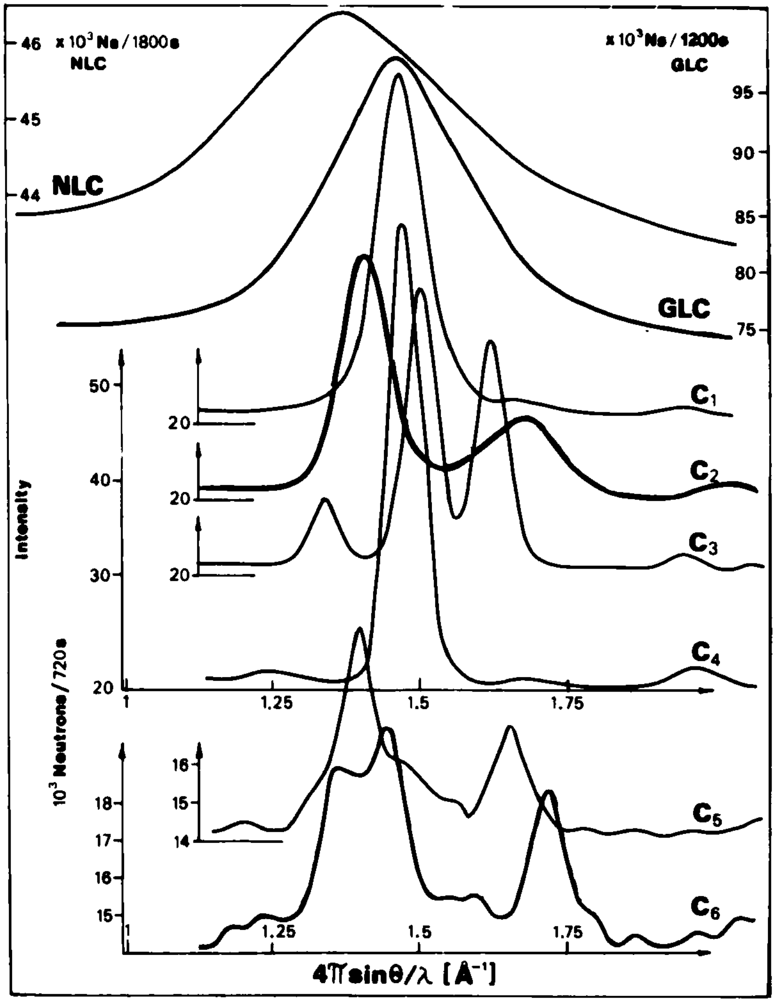


FIGURE 3 Neutron diffraction patterns for the different phases of MBBA.[16]

ism of MBBA. Similar amorphous-type distributions were found for several compounds (see Table 1) indicating the non-crystallinity of the structure, i.e. the absence of positional long range order of molecules.

Magnetic field aligned samples were also studied[13] in a similar manner with the specimen quenched in a magnetic field $\vec{H}$ defining the nematic director $\vec{n}$ parallel to $\vec{H}$. Then the intensity distribution as a function of the rotation angle around $\vec{n}$ was registered at a fixed

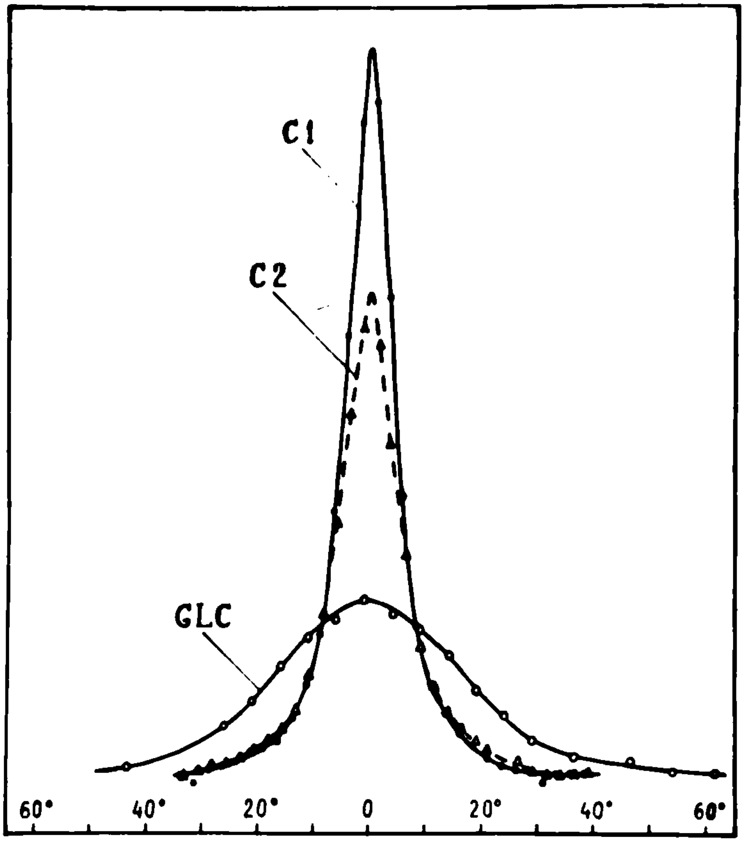


FIGURE 4 Rocking curves for magnetic field aligned sample of MBBA measured by neutron diffraction of the non-crystalline phases.[17]

scattering angle. The corresponding curves are presented in Figure 4 from neutron diffraction measurements on MBBA.[17] It is obvious from the comparison that the degree of orientational ordering defined by the width of the angular distribution is much higher for the glassy state than for the NLC. Therefore a higher S_2 parameter is believed to be reasonable (see above).[2]

A highly relevant means of investigating amorphous structures is to determine the radial distribution function and describe the short and medium range order of molecules. Such studies were made in a very early work[2] by X-ray diffraction and in a recent study by electron diffraction.[15] In the first paper, oriented and non-oriented BAN samples were investigated. The X-ray data were treated by Fourier analysis; the radial distribution function of atoms (scattering from carbon atoms has been considered) has been presented in the non-aligned case:

$$4\pi r^2\rho(r) = 4\pi r^2\rho_0 + \frac{2r^2}{\pi}\int_0^{s_{\max}} s^2 i(s)\,\frac{\sin(sr)}{sr}\,ds$$

(ρ_0 – average atomic density, $i(s) = [I_{\text{exper}}^{\text{norm}}/f_c^2(s)] - 1$, $I_{\text{exper}}^{\text{norm}}$ – normalized experimental intensity, $f_c(s)$ – scattering factor for carbon.) It was emphasized that peaks at $r = 2.4$; 3.8; 4.3; 4.9; 6.2 and 6.9 Å correspond to intramolecular distances. On this basis a planar molecular configuration with coplanar benzene rings has been proposed.

In the case of an oriented sample, a cylindrical distribution function of molecular long axes in the plane perpendicular to the molecular length was calculated: $4\pi rZ_M(r)$. This contained peaks at $r = 3.7$; 5.0 and 6.7 Å, which correspond to intermolecular distances with an arrangement when the molecules are parallel plane to plane, edge to plane and edge to edge, respectively.

In the electron diffraction experiment[15] on DBAE the glassy and the crystal structures were compared. Intermolecular distances obtained from the Fourier transformation of the radial distribution function were compared with the distances corresponding to the nearest reciprocal lattice points and their good coincidence allowed the conclusion to be drawn that in the glassy liquid crystal, the molecular short-range order is very similar to that of the crystal.

DYNAMIC PROPERTIES OF ORIENTED MOLECULAR GLASSES

In this section the molecular motions are considered as a consequence of the freezing of a liquid crystalline state. On the one hand, we compare the properties of liquid crystals with those of the glassy phase; on the other hand new aspects connected with the amorphous structure are discussed.

As briefly mentioned above, vibrational spectroscopy methods; IR, RS and IISN were used in these studies and in addition, NMR and dielectric measurements were reported.

In Figure 2 we illustrate the sensitivity of the Raman scattering to the structure. It is well-known that the spectrum of the intermolecular vibrations changes significantly at crystal-liquid crystal phase transitions, therefore data obtained for the glassy state were used to separate the effect of structural changes on the Raman spectrum from other effects such as anharmonicity or free translational motion of the molecules (these two effects are absent in the glassy state due to the low temperature). The influence of the structure change is striking (Figure 2) but the effect of anharmonicity on the spectrum of Raman active vibrations can also be evaluated when comparing Figure 2, curves a and b.[8]

The reduced density of states function $g(\nu)$ is defined as

$$I(\nu,T) \sim g(\nu)[n(\nu,T) + 1]$$

where $I(\nu,T)$ is the spectrum of Raman-scattered photons and $n(\nu,T)$ represents the population factor which is excluded in this way from the comparison. The resulting curves are shown in Figure 5. It can be seen from the $g(\nu)$ function that the spectrum of the liquid crystal phase is softer than the glassy one. The difference is, however, much smaller than that between the crystalline and glassy states.

A more relevant way to determine the density of vibrational states is the inelastic incoherent scattering of neutrons. Such measurements have been made on MBBA and EBBA. Results of the first technique are shown in Figure 6.[9] One can see that the transition from the fast-cooled MBBA structure to crystalline order does not result in significant changes to the spectrum except at the very low frequency region. Thus the large changes in the vibrational spectra of the different phases measured by optical spectroscopy methods are due to the loss of spatial coherence of vibrations and not to significant changes of the vibrational density of states.

For non-crystalline phases the absence of long-range order and consequently, the absence of translational invariance, leads to the complete loss in the coherence of vibrational states. Invalidity of the selection rules for quasi-momenta results, for the one-phonon Raman

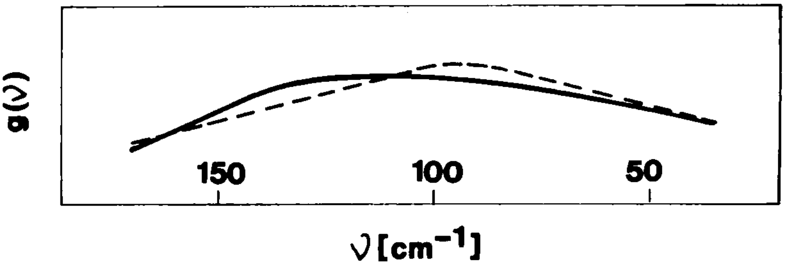


FIGURE 5 Reduced density of states for the smectic A (dashed line) and the glassy phases of DOBHOP[8] derived from Raman scattering measurements.

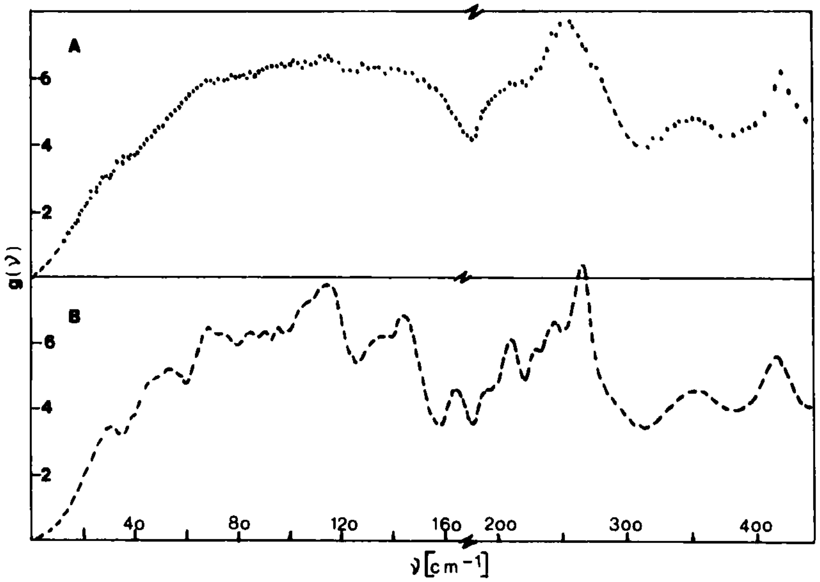


FIGURE 6 Medium- and low-frequency range of the density of states measured on MBBA at 5 K by IISN for the glassy (A) and the C_5 crystalline phases.[9]

scattering, in a structureless continuum of low frequency modes. Consequently, neither an important change in the anharmonicity and translational motion, nor in the density of states is responsible for the drastic change of the spectrum from one phase to another, but it is dominated by the structure. It is valid also for infared absorption measurements; however, very little work has been done in the low frequency range.

Since most of the spectroscopic work relates to the investigation of MBBA we shall return to this question in Section 4. Here we would just mention that IR, RS and calometric measurements[11] on MBBA, EBBA and CBPA provide a useful means of comparing crystalline, glassy and liquid crystal phases in each of them. It was claimed that in the case of the GLC, which is not very different as the liquid crystal phase, the degree of freedom frozen in at T_g will be reduced and the coupling between the molecules becomes stronger. From the calculated enthalpies and activation energies for the phase transition we concluded that molecular conformation changes and internal molecular motions (like end-group rotations) play an important role in the formation of solid polymorphous modifications. NMR measurements on MBBA,[19] for instance, indicate separate relaxations for methyl group reorientations in a normal crystal and the amorphous phases. It was also established that the transition at T_g is associated with a transformation of a metastable material (GLC) above which the molecules can reorient themselves spontaneously to form a more ordered (crystal) structure. NMR results on MBBA and OHMBBA are interpreted[20] so that in the glassy state no molecular tumbling occurs, but the end groups are relatively free to move. The local arrangement as well as the molecular motion in GLC would be very near to that in a crystalline phase.

Dielectric studies in EBBA were reported[21] indicating the glassy state in this chemical. It was also suggested that the end group motion is responsible for the observed dielectric dispersion. Another dielectric experiment on cyanobiphenyl eutectic mixture E_3[22] gave evidence of reorientation of the molecules in the GLC-phase. This low frequency mechanism is explained by the existence of the faults (probably present in large numbers) in the sample. It was assumed that the migration of these imperfections throughout the sample makes the reorientation of molecules possible.

This explanation is supported by the effect of the non-Debye behaviour of the density of states of vibrations at very low frequencies in the amorphous solids and also particularly observed for the glassy state of MBBA and EBBA by IISN[23] and confirmed by also RS.[24] This can be related to the conformational defects of molecules, yielding additional states of motions (see below).

FAST-COOLED MBBA

One of the most widely studied liquid crystal compounds has been MBBA (a molecule is schematically presented in Figure 7). So much attention has been paid to it because of the relative simplicity of the molecule: it has a nematic range conveniently just above room temperature and in particular it is notable for its solid polymorphism as well as its good glass-forming ability. Methods used to investigate the solid phases of MBBA are listed in Table II.

Sample preparation

Even though very different data are to be found in the literature, we are convinced—on the basis of calorimetric measurements at well defined circumstances[10]—that a cooling rate higher than 40 K/min is needed to prepare the glassy state of MBBA. As shown in Figure 1, the sample has to be cooled below 205 K. The easiest way to prepare a GLC sample is to dip it in liquid nitrogen.

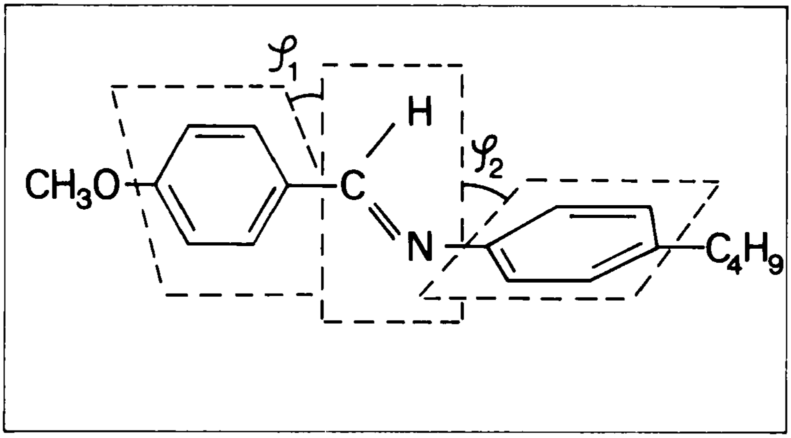


FIGURE 7 Schematic representation of the possible planes formed by the different atomic groups of MBBA.

Polymorphism

The phase diagram of MBBA has been studied between 5 and 350 K and a large number of publications have described the polymorphism of MBBA (see Table II). Recently, combined neutron diffraction (ND) and Raman scattering measurements were reported[16] giving the most complete phase diagram so far (see Figures 3 and 9). Six solid modifications have been identified besides the fast-cooled glassy, nematic and isotropic liquid phases. A schematic phase diagram was constructed to show the thermal procedure for producing these phases (Figure 8). There are some indications[10,30] of the existence of one or two more solid phases in the 280–296 K range, however the conditions for producing them are not clear and these phases are not reproducible.

The results of the ND and RS experiments are supported by DSC measurements[10] and the following conception of polymorphism was developed: Two thermal procedures, the quenching from NLC and then reheating and the equilibrium crystallization, yield two series of polymorphous modifications: $C_0 \rightarrow C_1 \rightarrow C_2 \rightarrow C_3 \rightarrow C_4$ and $C_5 \leftrightarrow C_6$, respectively. This phenomenon was named multimode polymorphism.[10] The sequence of irreversible phase transitions corresponds to different levels of a gradual relaxation of the structure from the amorphous to the crystalline state. The other mode ($C_5 \leftrightarrow C_6$) of solid-solid transition is connected with molecular reorientations due to freezing/melting of some end group motions.

TABLE II

MBBA studies (see abbreviations in TABLE I, PA—positron annihilation)

N°	Method	Type of Study	Reference
1	DS	Polymorphism and Dynamics	31
2	DSC	Polymorphism	10, 19, 20, 26, 37, 38, 39, 40, 42, 43, 46, 47
		Dynamics	20, 31
3	IISN	Dynamics	9, 18, 23
4	IR	Structure	7
		Polymorphism	11, 36, 39, 42, 43
		Dynamics	11, 36
5	ND	Structure and Polymorphism	14, 16, 17, 30, 33
6	NMR	Polymorphis and Dynamics	19
7	PA	Polymorphism	45
8	RS	Polymorphism	6, 11, 12, 14, 16, 17, 24, 26, 34, 35, 43
		Structure and Dynamics	6, 11, 14, 16 17, 24, 34, 35
9	XRD	Strucure and Polymorphism	5, 13, 44

Structure

The structure of solid MBBA has been investigated with respect to the polymorphism and, to our knowledge, no exact determination of the structure (space group or short range order) has been made on any phase. Nevertheless much is known about the relative structure of the different phases and about the molecular arrangements due to the indirect information gained from different experiments (X-ray, ND, RS, IR etc.).

The neutron diffraction patterns of MBBA phases presented in Figure 3 were analysed together with their Raman spectra (Figure 8) measured simultaneously on the same sample.[16] The change of the halfwidth of the main diffraction peaks, the effect of orientational ordering (see Figure 4), and the evolution of the coherence of vibrational states[32] were followed from one phase to another.[17]

It has been deduced from these data that the medium range order of the glassy phase C_0 can be characterized by a coherence length of $L_{coh} \sim 40$ Å. Phases C_1 and C_2 can be considered as structurally

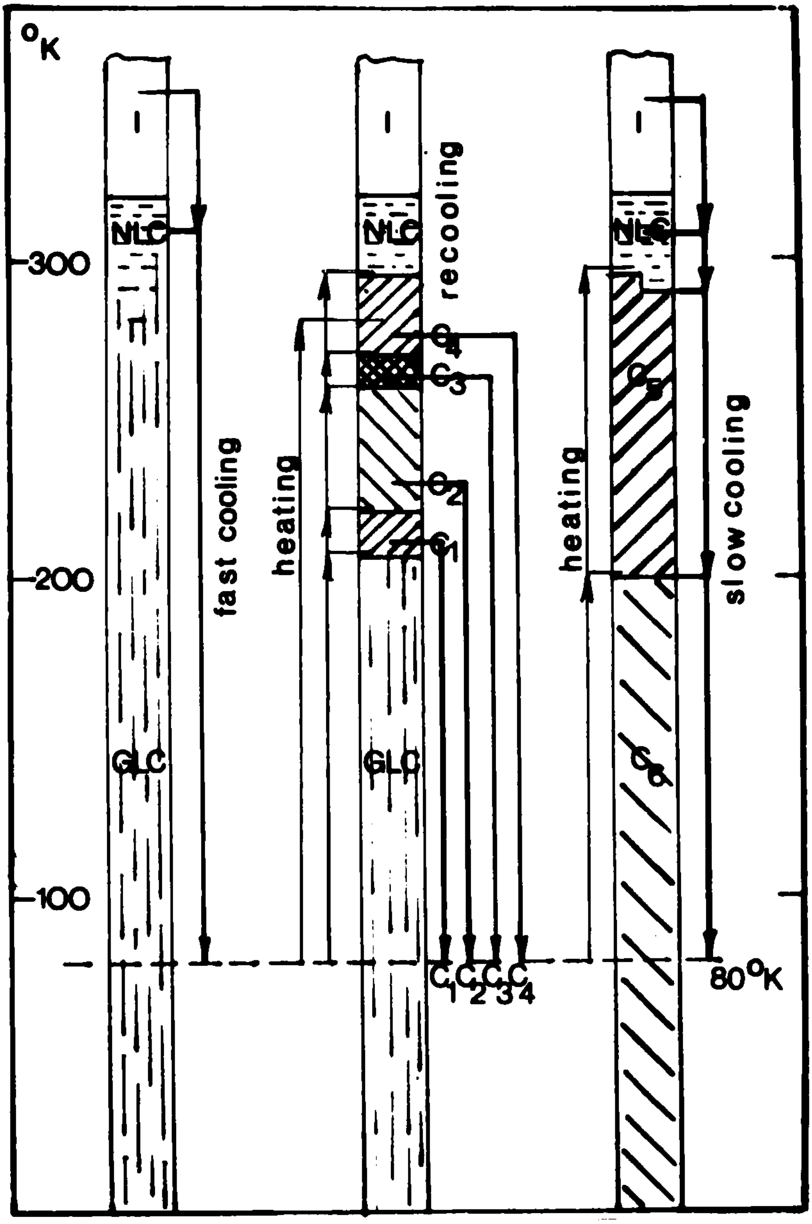


FIGURE 8 Thermogram patterns of heat treatment procedures to produce the different phases of MBBA.[16]

relaxed metastable modifications with $L_{coh} \sim 120$ Å. C_3, C_4 are metastable and C_5, C_6 are stable crystalline phases.

Time-of-flight neutron diffraction measurements[30,33] were made on four MBBA samples with different deuterium/hydrogen ratios

$CH_3—O—C_6H_4—NCH—C_6H_4—C_4H_9$ (D_0)

$CH_3—O—C_6D_4—NCH—C_6D_4—C_4H_9$ (D_8)

$CD_3—O—C_6H_4—NCH—C_6H_4—C_4D_9$ (D_{12})

$CD_3—C—C_6D_4—NCH—C_6D_4—C_4D_9$ (D_{20})

As a preliminary conclusion, it was established that the phase diagram is the same, but the transition temperatures are slightly different for the separate samples. The calculation of the effective scattering lengths of separate molecular groups with different D/H ratios allowed us to estimate qualitatively the molecular arrangement in the glassy state: molecules are lined up nearly parallel with their long axes and the distances between these axes have some distribution around an average value. The end groups have even more random distribution than the molecular cores (benzene rings). The phase transition to the more ordered phases based on reorientational relaxation of molecules is in such a way that the deviation from the mean distance is decreased (the coherence length is increased at the same time) and then the three-dimensional ordering begins to appear only when end groups are relaxed to ordered positions. From these measurements indications of smectic-type ordering have been also derived (see reference 13).

Spectroscopy studies

Three parts of the vibration spectra of MBBA can be analysed separately. The high frequency range ($\nu \geqslant 300\ \mathrm{cm}^{-1}$) corresponds to the intramolecular vibrations. The spectra of all phases in this interval have been observed to be rather similar in the RS, IR and IISN experiments, however significant changes were registered in the 1150–1250 cm^{-1} and 1500–1650 cm^{-1} ranges by RS.[16,33] Additional lines at 1180 cm^{-1} in C_3 and 1180 as well as 1170 cm^{-1} in C_4 with respect to the lower index (non-crystalline) phases should be connected with the deformations of molecules during their reorientation to form the crystal state around the CHN bonds.[34,35] The existence of these lines in the stable C_5 form but the absence of the 1160 cm^{-1} line indicates the difference in the molecular conformation when the crystal is produced by equilibrium crystallization or via the quenching-in of a rather free molecular shape.

Infrared absorption measurements[36,37] suggest the existence of different conformations of the butyl chain and methoxy groups in the glassy state as well as the non-parallel orientation of the benzene rings ($\phi_1 \neq -\phi 2$, Figure 7).

The striking difference between the spectra of modifications (RS and IISN) is observed at medium frequencies $40 \leqslant \nu \leqslant 300\ cm^{-1}$. This range corresponds to intermolecular vibrations and, judging from the calculation of the vibrations of a free MBBA molecule, one can suppose that at least 15 low frequency internal modes fall below 300 cm^{-1}. The mixing of external and internal modes forms the gap-less vibrational spectra of MBBA.[23]

The third region of particular interest is the spectral range $\nu \leqslant 40\ cm^{-1}$.[23,24] From the model of harmonic oscillators it follows that the selection rules for the quasi-momentum $\vec{q} = 0$ in the RS of the glassy state (C_0) do not play a role since the orientational—and the distance correlation lengths are small, consequently all the $\vec{q}$ modes form part of the spectrum. At the $C_0 \rightarrow C_1$ phase transition the correlation length is increased 3–4 times. This gives rise to the long wavelength plane waves of acoustic phonons. The peak at 13 cm^{-1} in the C_1 phase (Figure 9) is connected with this phenomenon. The appearance of new lines in the C_2 phase can be explained as follows: The correlation length is only slightly changed with respect to the preceding phase state but due to molecular reorientations a three dimensional ordering begins with the formation of grains of an elementary cell. Therefore optical modes with $q \sim 0$ provide new Stokes lines in the further modifications correspond to the $q = 0$ modes of crystal phases.

Another feature of this low frequency region is the deviation of the density of vibrational states from the Debye behaviour ($g(\nu) \sim \nu^2$ when $\nu \rightarrow 0$) in the glassy state. Additional scattering was observed in RS[24] as well as ISSN[23] experiments and this may have the same origin. (Such behaviour has also been observed for other types of amorphous materials at low temperature.) This phenomenon can be explained by the defect of short range order, in particular, in the case of long molecules (such as MBBA), the molecules themselves provide certain short range order. Due to the molecular flexibility—after the quenching-in of the rather free molecular shape—quite different molecular configurations, "defects," may occur leading to additional

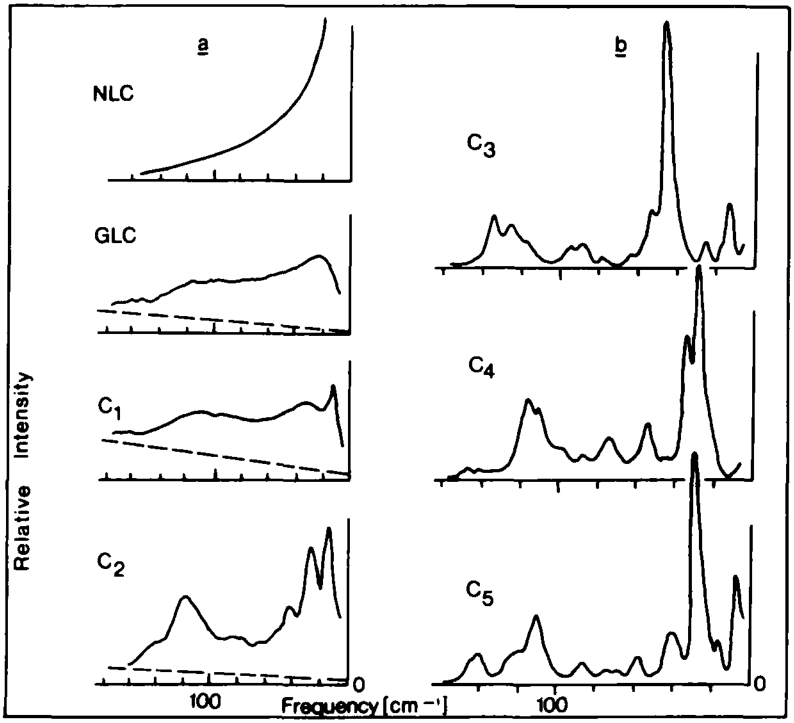


FIGURE 9 Raman spectra of low frequency range of non-crystalline (*a*) and crystalline (*b*) MBBA phases.[32]

collective or diffusive motions[22] (thereby increasing the density of states originating in molecular flexibility). In contrast to this, molecules are more rigid in the crystal phases, so that $g(\nu) \sim \nu^2$ as normal.

SUMMARY

In conclusion, we are aware that several thermotropic liquid crystal compounds can be transformed easily into a glassy solid state. Different experimental methods have been used to investigate the structure and the dynamics of these oriented molecular glasses. It has been shown by comparison of different properties that the OMG should be classified as a state which is intermediate between liquid crystals and real crystals. On the one hand the structure retains the positional disorder of the centre of the mass of molecules as well as the orientational ordering inherited from the liquid crystalline origin; on the other hand the intermolecular short range order is very near to that of the crystalline state.

The procedure of fast-cooling and then the reheating results in a gradual relaxation process when a disorder-order transition takes place. The multimode polymorphism and the non-Debye-type of molecular motion at low frequencies indicate that the molecular flexibility plays an important role in the glass-formation ability of these materials.

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