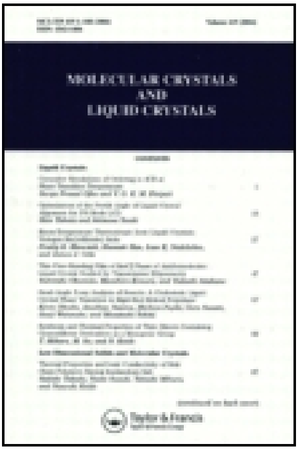

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Raman Evidences for the Existence of Three Solid Modifications in MBBA

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Raman Evidences for the Existence of Three Solid Modifications in MBBA†

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Differences in the Raman spectra occurring at the band assigned to a ring bending vibration at 1163 cm^{-1} for the three solid modifications (one glassy, and two crystalline modifications, a metastable and a stable one) indicate that metastable disorder may not only be due to motions of the end groups of the MBBA molecule, but also due to motions connected with the benzylidene aniline core.

1 INTRODUCTION

The present work reports a study of the solid phase polymorphism in *p*-methoxybenzylidene *p*-*n*-butylaniline (MBBA) based upon observations of changes in the Raman spectra during the transformations between the different polymorphic forms. Earlier Raman and calorimetric studies revealed the existence of three solid modifications in EBBA[1] and the results of the Raman measurements presented here support this conclusion for the case of MBBA.

2 EXPERIMENTAL

Raman spectra were measured in the 100–1 700 cm^{-1} spectral region on a conventional Raman spectrometer which is described in detail elsewhere.[2] The 632.8 nm line of a He-Ne laser was used for excitation. Incident power at the sample was 25 mW. The samples were contained in 0.8 mm capillary tubes whose ends were sealed with an indium plug and epoxy resin. The laser beam

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was focused in the central region of the tube, and 90° scattering from this central region was then observed. The spectral resolution was 6 cm^{-1}.

The samples were heated by a surrounding brass block whose temperature could be varied. MBBA was purified by successive recrystallization in *n*-heptane. No significant laser-induced degradation of the sample has occurred through the temperature cycle.

The Raman spectrum obtained from the nematic phase at room temperature coincides to within 5 cm^{-1} with the spectrum obtained by Vergoten and Fleury.[3]

All measurement procedures concerning solid phase polymorphism started by melting the sample to the nematic phase, after which rapid cooling to liquid nitrogen temperature followed. The sample was then kept at this temperature for a period of 16 h, 4 h, and 0.5–2 h, respectively. Thereupon, the sample was heated to a temperature of 13°C, at which the spectrum was recorded again and again during the transition process.

3 RESULTS

Fast cooling from the nematic phase leads to a glassy modification which after heating to 13°C is stable over 30 min, 15 min, and 6 min, respectively (according to the period of storage at 78°K). It is not much different from the nematic phase in its energetic situation as is evidenced by similar frequencies and intensities of all bands.

The glassy modification finally evolves to a metastable crystalline modification, as is evidenced by the emergence of a splitting of the band assigned to a ring bending vibration at 1163 cm^{-1} (see Ref. 3). It is this frequency where the spectrum is most varied during the transformation from one modification to the other. Figure 1 presents the temporal evolution of this mode in relation to the neighboring line at 1191 cm^{-1}. Note that the integrated intensities of the split and non-split bands are the same.

As has been found by Janik *et al.* by the method of IR spectroscopy,[4] this metastable modification at a temperature of 2°C transforms spontaneously during several hours into a stable crystalline modification, if the sample has been cooled down from the nematic region to a temperature of about 200°K and then kept at this temperature for hours.

Although in our case the transition point is higher (13°C) and consequently the rate at which the metastable form changes into the stable one should be faster, the splitting of the 1163 cm^{-1} band does not change with time at least for several days, i.e., the metastable modification transforms much more slowly into the stable one as compared to Janik's finding. This difference in results may be due to the lower quenching temperature (78°K) in our case, but is more

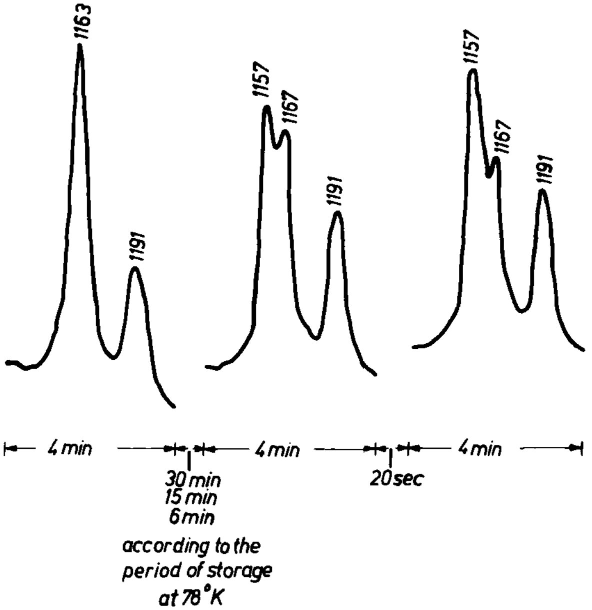

FIGURE 1 Temporal evolution of the band at 1163 cm^{-1}.

likely to be due to the difference in sample thickness for the two experiments. In the infrared work of Janik *et al.* the sample is enclosed between two AgCl windows in form of a thin film a few microns thick, whereas in our Raman experiment it is contained in a capillary tube, in which case only a small fraction of the sample is in contact with the surface. If the surface catalyzes the transformation of the metastable modification into the stable one, that would account for the discrepancy. In the Janik case probably a more heterogeneous nucleation process for the formation of the new modification takes place, whereas in our case a more homogeneous nucleation process occurs: The free energy required to form a critical nucleus in contact with the surface will be lower than that needed to form a nucleus in the interior of the metastable modification. In the same order as the activation energy for nucleation decreases, the nucleation rate will increase, i.e., the rate of transformation of the metastable modification into the stable one will increase too, provided the kinetics of the transformation is effectively governed by the nucleation phenomenon. Surface roughening, which always will be present to an appreciable extent even on a supposedly smooth flat surface, will reduce the free energy of formation of the corresponding critical heterogeneous nucleus still more compared to that needed to form a homogeneous nucleus.

After heating the metastable modification to temperatures above the melting point (22°C), splitting of the 1163 cm^{-1} band disappears and does not appear again at subsequent slow cooling of the nematic melt to a temperature of 13°C, in which case apparently the stable crystalline modification has been reached.

If, however, the metastable modification is heated only to temperatures somewhat below the melting point, splitting of the 1163 cm^{-1} band actually does disappear, but reappear on cooling back to a temperature of 13°C. Thus, heating to temperatures somewhat below the melting point does not destroy the metastable modification but probably only transfer it into some "excited state."

4 DISCUSSION

A model based on a double-well potential for the potential energy of a molecule is proposed for the schematic representation of the glassy and the two crystalline modifications:

In the nematic state there will be excited a large disorder corresponding to a large kinetic energy of the molecule (as indicated schematically by the energy level in Figure 2a), not only due to motions at the ends of the MBBA molecule as suggested by Andrews,[5] but also due to motions connected with the benzylidene aniline core which alone may influence the ring bending vibration at 1163 cm^{-1}.

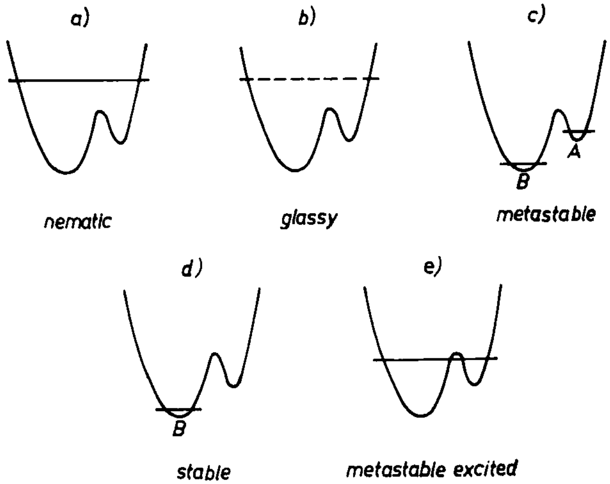

FIGURE 2 Scheme of the observed states in MBBA within a double-well potential for the potential energy of a molecule.

If the nematic liquid is rapidly cooled down, disorder of the molecules will be frozen in. The viscosity now is so large that a molecule has not enough molecular jump freedom to reach a state of minimum potential energy. We obtain a glassy state (as indicated by the broken energy level in Figure 2b).

After heating to 13°C the molecules after some time regain part of their molecular freedom. The molecules now move towards the potential wells at A and B (see Figure 2c). However, at the relatively low temperature of 13°C in question the kinetic energy will not be sufficient to overcome the potential barrier. Consequently, the system will move in a state, in which a molecule will reside with some probability on either side of the potential barrier. This is the metastable modification. If we assume that the energy difference of the states at A and B will appear as some splitting of some specific bands in the vibrational spectrum of the molecule, the integrated intensities of the split and non-split bands must be the same, as indeed has been measured (Figure 1).

After heating the metastable modification to temperatures above the melting point (22°C), the molecules obtain a relatively high excitation energy. Both potential wells are now no longer decoupled. Consequently, there will now be only one energy level, i.e. splitting of the bands will disappear (see Figure 2a). At subsequent cooling of the nematic phase from the relatively high temperatures $T \gtrsim 22°C$ the kinetic energy will be sufficient to overcome the potential barrier, i.e. the molecules reach the state B, in which the potential energy attains its absolute minimum. This is the stable modification (see Figure 2d).

If the metastable modification is heated only to temperatures somewhat below the melting point, the molecules actually do obtain again a relatively high excitation energy occupying again only one energy level, i.e. splitting of the bands will disappear (see Figure 2e). But at subsequent cooling from the lower temperatures $T \lesssim 22°C$ now present the molecules fall into the states at A and B, because the kinetic energy no longer will be sufficient to overcome the potential barrier, i.e. splitting of the bands will reappear (see Figure 2c). Accordingly, state (*e*) may correspond to a metastable modification in some "excited state", state (*c*) to a metastable modification in the ground state.

5 COMPARISON WITH CALORIMETRIC MEASUREMENTS

In order to get some more information as to the energetic situations in the various states, let us finally discuss the differential thermal analysis (DTA) curves for MBBA, as measured by Sorai *et al.*[6] and represented in Figure 3.

Run 1 shows a heating curve of the crystalline material up to the nematic phase at a rate of 2.5°K/min. When cooling from the nematic phase (run 2) thereupon was not rapid enough, a partial crystallization from the supercooled nematic liquid occurred around −30°C, as indicated by the exothermic crystallization peak. However, when the nematic phase was quenched at a cooling rate greater than −10°K/min, a glassy nematic state was frozen in, as indicated by the typical glass transition at −70°C (i.e. the step in the DTA curve). On heating the nematic glass at a rate of 2.5°K/min (run 3), a typical glass transition again was observed at $T_g = -72°C$, followed around −50°C by an exothermic crystallization (divitrification) to what we believe to be the metastable crystalline modification, which on further heating transformed into the nematic phase through an endothermic melting process at $T_m \simeq 22°C$.

In Figure 3 for each phase the corresponding energy level diagram has been added.

At slow cooling from the nematic phase (*n*) the stable crystalline modification (*s*) is reached, the decrease in energy of the molecules, after having fallen into the state at B, corresponding to the exothermic crystallization peak at −30°C. Rapid cooling from the nematic phase (*n*) leads to the glassy nematic state (*gn*), which as to its energetic situation is not much different from the nematic phase.

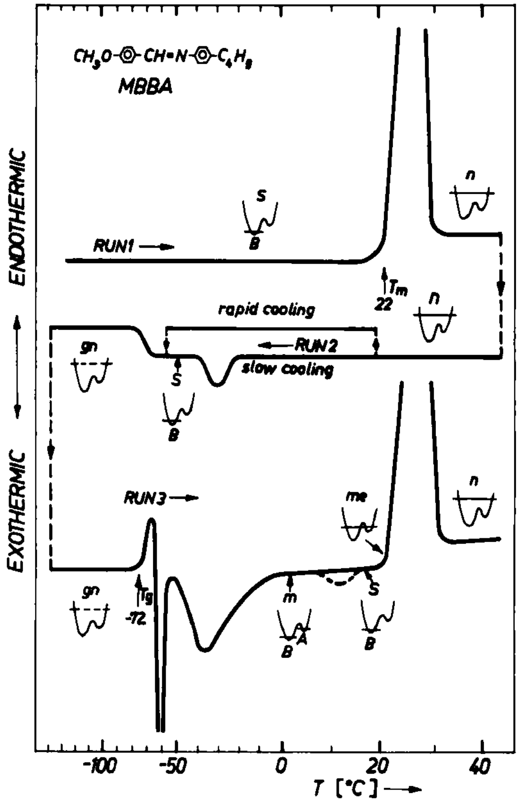

FIGURE 3 DTA curves for MBBA. (According to Ref. 6).

On heating, the glassy modification transforms into the metastable crystalline modification (*m*). The energy stored in the nematic glass partially will be released, the decrease in energy of the molecules, after having fallen with different relaxation times of molecular motions into the states at A and B, corresponding to the two exothermic crystallization peaks observed around −50°C. If the metastable modification thereupon would transform into a stable (*s*) one, an exothermic peak should occur (as indicated by the broken exothermic peak in run 3), which, however, has not been observed: Indeed, as we have seen earlier, the metastable modification transforms during hours and days and certainly not during one DTA trace into the stable one. For the same reason, the double exothermic peak in run 3 around −50°C should not be regarded as one being due to a phase transition from the glassy state to a metastable crystalline modification, followed by a transformation into a stable one.

When the metastable modification (*m*) is heated to temperatures somewhat below the melting point T_m, it transforms into what we have called the metastable excited modification (*me*), the excitation energy, which the molecules obtain, corresponding to the tail of the endothermic melting peak below T_m. When, finally, this metastable excited modification is heated to temperatures above the melting point, it transforms into the nematic phase (*n*), the high excitation energy, which the molecules now obtain, corresponding to the endothermic melting peak completely passed through.

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