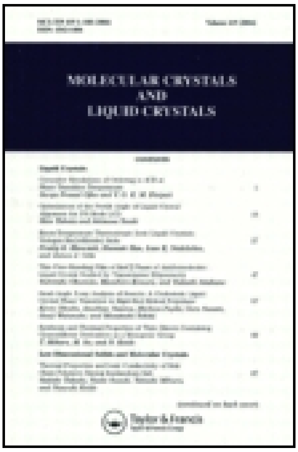

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Polymorphism Studies of Solid N-p-(Ethoxybenzylidene)-p′-Propylaniline

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POLYMORPHISM STUDIES OF SOLID N-p-(ETHOXYBENZYLIDENE)--p'-PROPYLANILINE

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Abstract Ethoxybenzylidene-propylaniline (EBPA) was studied using polarizing microscopy and differential scanning calorimetry (DSC) in the temperarure range 100 K - 380 K with various heating and cooling rates (from 0.1 deg/min to 200 deg//min). The metastable solid crystal phase was discovered. It is formed rapidly on cooling of nematic phase and transforms spontaneously to stable crystal phase. But can be also frozen or separately melted. The rich polymorphism of isomeric to EBPA MBBA compound is also discussed proving the importance of terminal groups in the formation of different polymorphs.

Keywords: liquid crystal polymorphism, polarizing microscopy, DSC, metastable phase

INTRODUCTION.

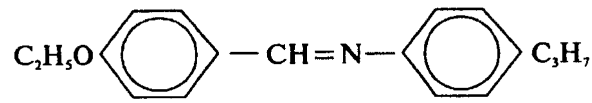
Phase polymorphism is a common phenomenon in the solid state of organic compounds. But it is still very difficult to predict the phase sequence and the appearance of various crystalline forms for the particular compound. Sometimes the new sample has different properties than the sample with some thermal history. There are also examples of "disappearing polymorphs" - the phases which were once undoubtfully discovered, but could not be observed later as being overshadowed by other polymorphic forms[1].

Among the substances with complicated phase diagrams there are benzylidene-anilines. Some of them are mesomorphic, *e.g.* N[p-(methoxybenzylidene)]-p'-butylaniline (MBBA), which was extensively studied in many laboratories[2-4]. For MBBA depending upon thermal treatment of the sample one can observe up to 6 different phases besides isotropic and nematic one.

In order to elucidate the role of terminal groups in polymorphism we have decided to study N[p-(ethoxybenzylidene)]-p'-propylaniline (EBPA) which is isomeric to

MBBA with one methylene group transferred from butyl terminal chain to methoxy group on the other side of benzylideneaniline core.

EBPA



The aim of the studies presented here was to determine the formation of phases as result of different thermal treatment of the sample. Thermodynamic stability of phases was also checked and the influence of the changes of molecular structure on the properties were under investigation by comparing the MBBA and EBPA polymorphism.

EXPERIMENTAL METHODS.

The polarizing microscope Biolar PI (PZO, Warsaw, PL) was used for optical observations. LINKAM Scientific Instruments thermal stage THM600 with temperature controller TMS90 and Hitachi CCD camera with videorecorder was applied for thermal studies and registration of results. The temperature range studied were from 100 K to 380 K with heating /cooling rates from 0.1 deg/min to 100 deg/min. Annealing times up to several hours were applied during measurements.

The DSC (Differential Scanning Calorimetry) experiments were performed using Perkin-Elmer DSC7 with the low temperature cooling device. The temperature range studied were from 100 K to 380 K and heating/cooling rates were 2, 5, 10 deg/min or 200 deg/min. Annealing times up to several hours were also applied.

RESULTS AND DISCUSSION.

The results of the DSC measurements on heating and on cooling are presented on Figures 1 and 2 respectively. On heating one can see two endothermic peaks (Figure 1) which correspond to melting and clearing points. But on cooling there is one more phase transition which is seen on exploded part of Figure 2. The same results were obtained for different heating/cooling rates. The temperatures of phase transitions depend on these rates and the extrapolated value for the clearing temperature is 88.8 ± 0.5 C. (the values extrapolated from cooling and heating are in good agreement). The temperature of clearing point observed in the microscope is slightly higher (but less than 2 degrees) since the thermometer is fixed in silver heating/cooling block and the sample is on this block. There is some heat loss from the sample. For the melting temperature the difference of both methods is less than 1 degree.

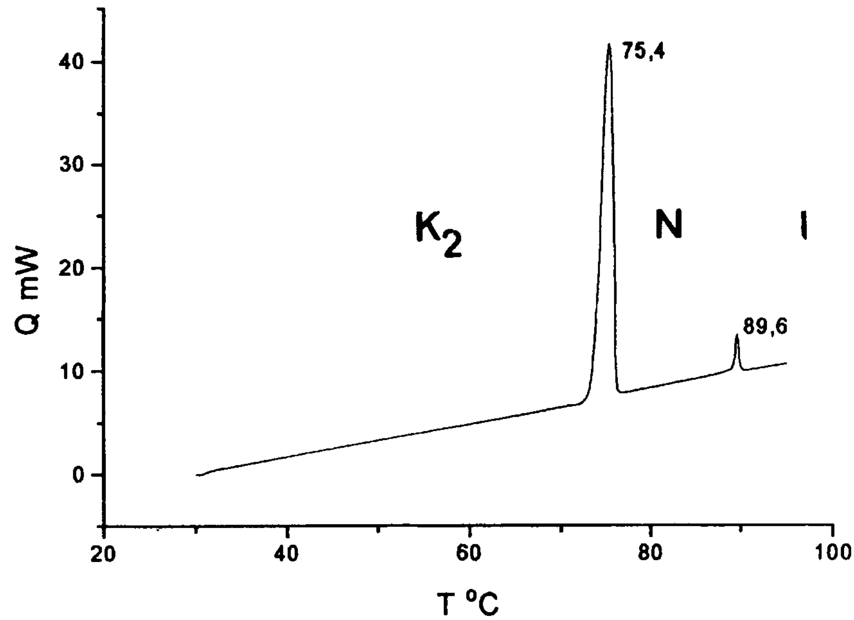


FIGURE 1. DSC results for EBPA on heating (5 deg/min)

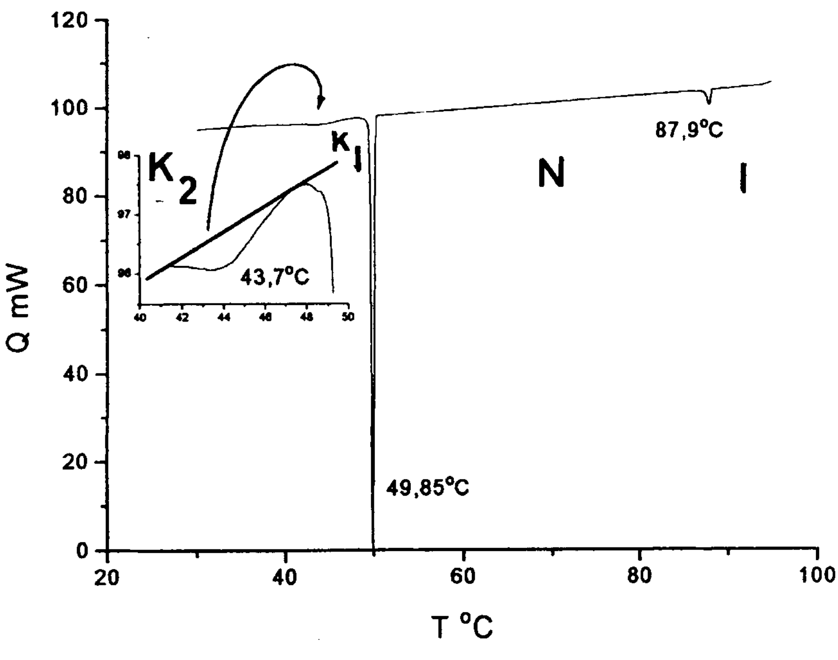
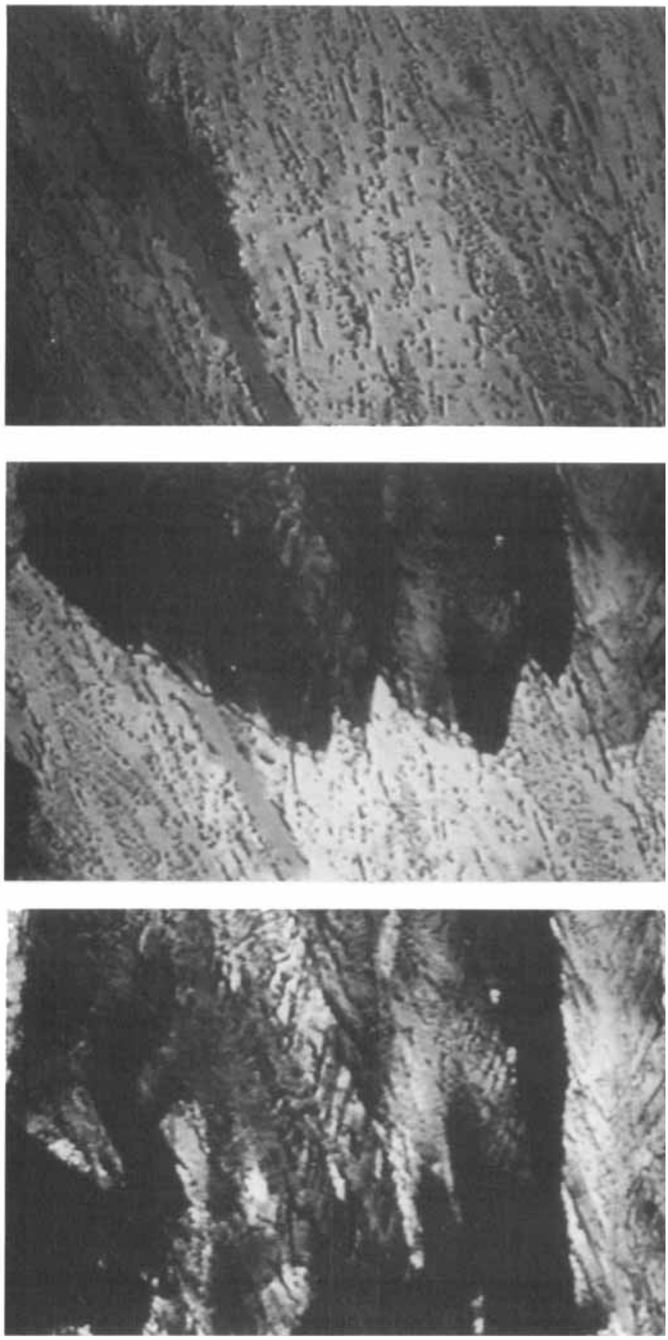


FIGURE 2. DSC results for EBPA on cooling (5 deg/min)



a.

b.

c.

FIGURE 3. Polarizing microscopy results for EBPA :
a. Metastable solid phase K_1
b. Trasition of K_1 to stable K_2
c. Stable crystal phase K_2
(See Color Plate IX).

The formation of solid phase K_1 is a rapid process (*ca.* 0.1 s) whereas its transition to another solid phase K_2 occurs gradually. The shape of K_1 - K_2 interface suggests that this is a ferroelastic phase transition[5]. Some of the results of polarizing microscopy observations are shown in Figure 3, where the part 3a shows the phase K_1, the part 3b presents the K_1- K_2 phase transition and in 3c there is pure phase K_2.

The summary of calorimetric (DSC) and polarizing microscopy results is shown in Figure 4.

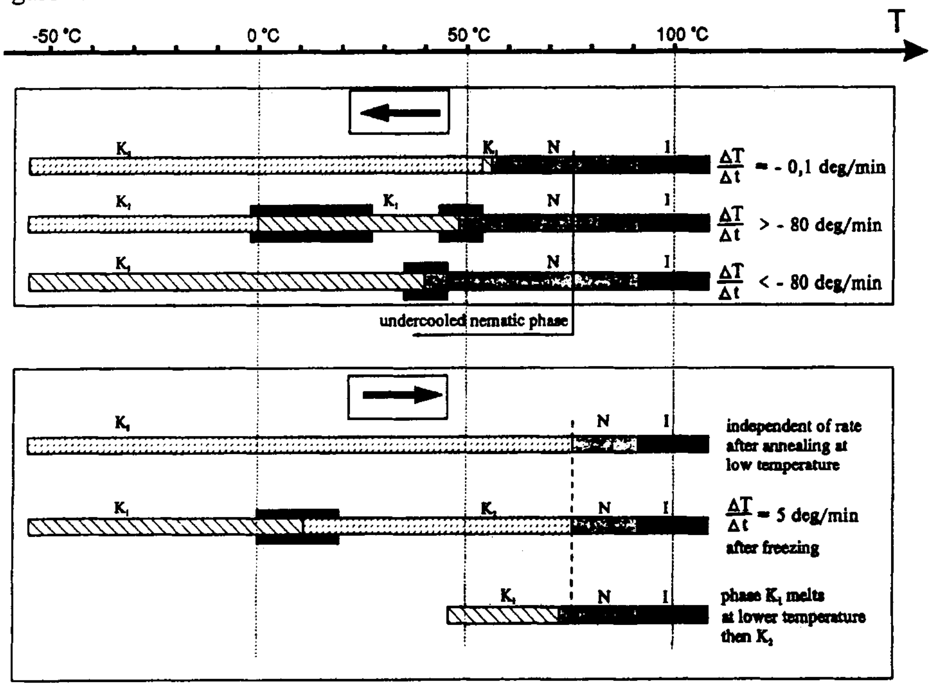


FIGURE 4. Phase transitions of EBPA for different thermal treatment.

From experiments presented here it is obvious that also EBPA exhibits solid phase polymorphism forming on cooling at first rapidly metastable solid phase K_1 which later transforms spontaneously to stable solid phase K_2. Cooling the sample rapidly enough one can freeze phase K_1 to low temperatures. On the other hand heating phase K_1 rapidly one can melt it few degrees below the melting temperature of K_2 phase. This fact together with the irreversibility of K_1 - K_2 transition proves that K_1 is thermodynamically metastable. The sharp DSC peak on cooling at N -K_1 transition and K_1 texture suggest that K_1 is the solid crystal phase.

Normally one cannot obtain directly K_2 phase from nematic phase. But it is possible to form the mixture of K_1 and K_2 by freezing the sample during the K_1 - K_2 transition. Then by heating this mixture rapidly and carefully one can melt only K_1.

Finally by stabilizing temperature below melting of K_2 nematic phase (from the molten K_1 phase) crystallizes directly into K_2 phase.

However we could repeat other studies on glassy MBBA, we were unable to obtain glassy EBPA. Despite many attempts neither starting from isotropic nor nematic phase because always metastable K_1 phase was formed (even very rapid cooling *e.g.* 200 deg/min was leading to phase K_1). This proves the importance of terminal groups in polymorphism, in particular butyl groups. Probably the length of such terminal groups and moderate number of conformers favorizes the formation of glassy state and many crystal phases. Very often homologs with the butyl terminal chains have more polymorphs than other members of the same series[6]. Longer terminal groups must have some sterical hindrance thus the number of polymorphic phases decreases.

CONCLUSIONS

From the studies presented here one can conclude that also EBPA has solid polymorphs however less than isomeric MBBA. EBPA forms two solid modifications K_1 and K_2. Metastable crystal phase K_1 is formed from nematic phase on cooling. Later on it transforms spontaneously to stable K_2 phase. By rapid cooling one can freeze and preserve K_1 phase to low temperatures. In our experiments we were not able to obtain phase K_2 directly from nematic phase. K_1 phase was always formed independently of cooling rate. We could not obtain either glassy EBPA.

The rich polymorphism of MBBA compound, which is isomeric to EBPA must be therefore connected with butyl terminal group since the EBPA has less terminal groups conformers.

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