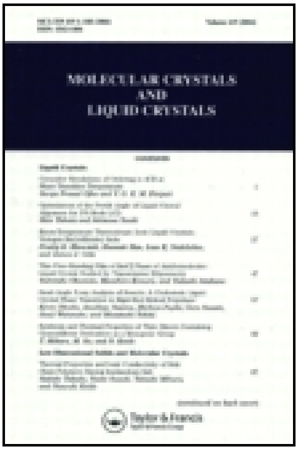

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Phase Transition and Supercooling Studies in MBBA

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Phase Transition and Supercooling Studies in MBBA†

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Phase transition and supercooling studies have been carried out in methoxy-benzylidene p-butylaniline (MBBA) using differential scanning calorimetry (DSC) technique. The measurements were performed over a wide temperature range (180-330K). The supercooling studies indicate that the nematic phase shows significant amount of supercooling, its extent is found to depend on the cooling rate. At cooling rates >4K/min a glass transition is indicated at ~200K. At these cooling rates the nematic phase transforms partially to glassy and supercooled states. It is shown that on heating, the glassy state transforms into a metastable solid whereas the supercooled nematic phase transforms to a stable solid. The transition temperatures obtained agree with the literature reported values.

1. INTRODUCTION

N-(*p*-methoxy benzylidene)-*p*-*n*-butylaniline (MBBA) is one of several liquid crystalline substances with a particularly low melting temperature. It is a well studied liquid crystal forming material. Phase transition studies in MBBA have been carried out using a number of different techniques such as adiabatic calorimetry,[1–3] differential thermal analysis,[4] differential scanning calorimetry,[5] optical microscopy,[6] X-ray diffraction,[7] infrared and Raman spectroscopy[8] and positron annihilation technique.[9,10] The results obtained from these had been conflicting. The major disagreements concern the number of solid phases and their nature. Several interpretations to transition at

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~200K have also been given.[1,3,4] Similarly the formation of metastable solids has also been reported.[1-3] Therefore, to clarify some of these anomalies and to provide a better understanding of the formation of metastable solid, phase transition and supercooling studies in this material have been undertaken. The principle technique employed is the differential scanning calorimetry (DSC). The present paper deals with the results of this investigation.

2. EXPERIMENTAL

DSC measurements were performed on a Perkin-Elmer differential scanning calorimeter model DSC-1B. It has been calibrated by using standard reference materials. These measurements were performed over a wide temperature range of 180-330K and for different heating and cooling rates. Transition temperature were determined from peak positions and the associated changes in enthalpy were estimated from the corresponding peak areas. For carrying out the supercooling studies, the sample was always cooled from the isotropic phase. Cooling rates ranging from 0.5/min to 32K/min were used. In all cases the corresponding cooling curve was recorded. The heating cycles in different cases were always recorded at a fixed rate of 8K/min.

3. RESULTS AND DISCUSSION

Two typical DSC curves for the cooling and heating cycles of the sample cooled at the rates 8K/min and 32K/min are shown in Figures 1 and 2, respectively. The cooling curves recorded for different cooling rates, always indicated a transition from the isotropic to the nematic phase. The supercooling of this transition was found to be small ~2K and more or less independent of the cooling rate. On further cooling the nematic state either underwent crystallization or got partly crystallized and partly supercooled depending upon the cooling rate. The supercooling of the crystallization temperature was found to depend strongly on the cooling rate.

The DSC curve for the heating cycle of a sample prepared by slow cooling (0-5K/min) from the isotropic phase showed two endothermic peaks at temperatures 295K and 314K, respectively. These correspond to the transitions from solid to nematic and nematic to isotropic phases. The observed transition temperatures corresponding to these transitions agree with the literature reported values. In this case no

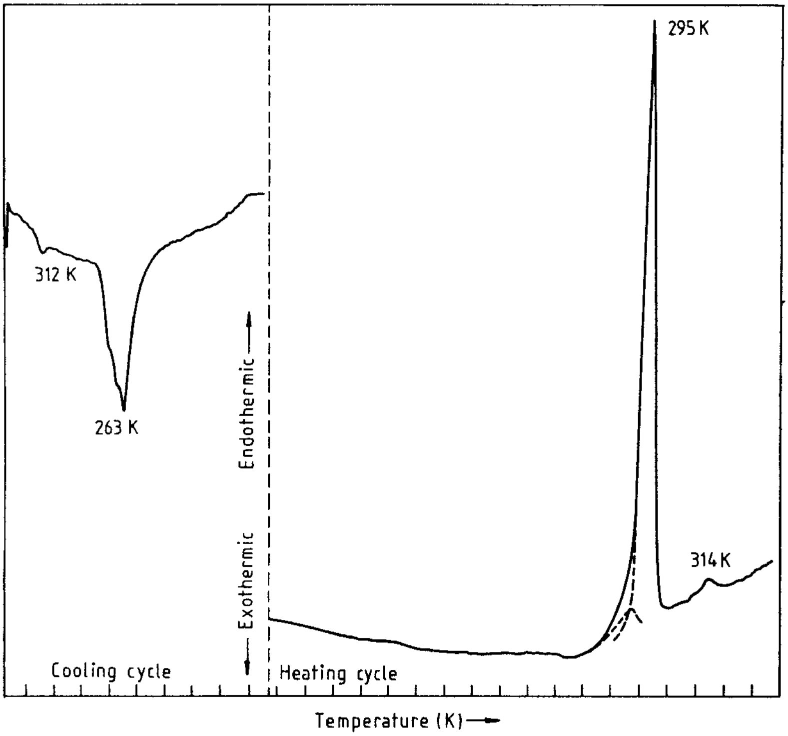


FIGURE 1 DSC curve for the heating cycle of a MBBA sample; cooling rate—8K/min and heating rate—8K/min.

evidence for any transition in the low temperature region was seen. However, the DSC curve for the heating cycle of a sample prepared by rapid cooling (32K/min), shown in Figure 2, is more complex. It shows a transition at ~200K followed by a broad exothermic peak around 230K. The broad exothermic peak is followed by endothermic peaks at 291, 295 and 314K. The transition at 200K, involves only a change in base line and not a peak and further it is followed by a broad recrystallization peak. It is, therefore, a second order transition and probably a glass transition. Furthermore, the absence of such a transition and a recrystallization peak in case of a slow cooled sample also supports this conclusion. Transition at 200K has also been detected by other techniques.[1–4,7,10] However, different interpretations about its nature have been put forward. Some authors consider this to be a glass transition,[2,4,10] while others[1,3,6,11] consider it as an evidence for the formation of a metastable state. The present conclusion

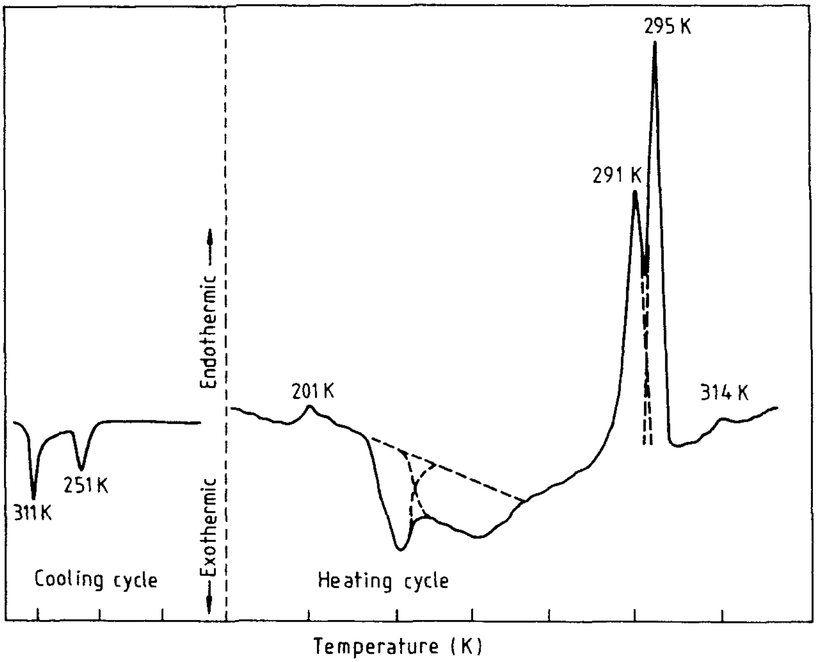


FIGURE 2 DSC curve for the cooling and heating cycles of a MBBA sample; cooling rate 32K/min and heating rate—8K/min.

is in agreement with that of Sorai et al.[4] The positron annihilation studies (PAT) carried out by Jain and Kafle[10] also indicate that this is a glass transition. Typical defreezing of various molecular motions on heating is clearly indicated by these studies.[10] However, it will be shown later that the formation of glassy and metastable states are intimately connected with each other. The two endothermic peaks, shown in Figure 2, at temperatures 291 and 295K are due to solid to nematic transitions of two solids; the first one is due to a metastable solid while the second one is due to a stable solid undergoing a solid nematic transition. Further, evidence supporting this conclusion is provided by the annealing studies carried out at 280K on a sample prepared by rapid cooling (32K/min). It has been observed that with increasing annealing time the area under the peak at 291K decreases while that under that at 295K increases. For long enough annealing times only a single peak is observed at 295K. Thus on annealing, the metastable solid transforms into a stable solid. Formation of a metastable solid has been reported in many liquid crystalline materials. In MBBA calorimetric,[1-3] infrared and far infrared absorption[12] and dielectric measurements[13,16] have indicated the formation of metastable and stable solids. The formation and relative proportions of these modifications depend upon the thermal treatment of the sample. In the present experiment, the broad peak at ~230K (Figure 2) can be decomposed into two components shown by the dotted curves. It is observed that the total area under the broad peak depends on the cooling rate; it decreases with decreasing cooling rates and for cooling rates ≤4K/min no broad peak is observed. Further, the appearance of a broad exothermic peak at ~230K and the endothermic peak at 291K are interrelated. In the absence of a broad peak no endothermic peak at 291K is observed. It is now conjuctured that the broader component of the peak at 230K represents the formation of a metastable solid while the endothermic peak at 291K represents its transformation into the nematic phase. If this be so, the areas under these two peaks must be equal. Similarly, if the crystallization peak during cooling and the narrower component of the peak at 230K are to be attributed to the formation of a stable solid and if the heating rate is fast enough not to permit any transformation of the metastable phase to stable phase, the total area under these two peaks should be equal to the area under the endothermic peak at 295K. These arguments can be better stated with the help of a schematic DSC trace as shown in Figure 3. This diagram represents the cooling and heating cycles of such a material. In this figure the areas under different peaks have been labelled as A_1, A_2 etc. If the above interpretation about the origin of different peaks is valid, then it follows that $A_1 + A_2 = A_5$ and $A_3 = A_4$. The magnitudes of the areas A_i's for different cooling rates but same heating rate (8K/min) are given in Table 1. It is clearly seen that, within experimental errors, for all cooling rates $A_1 + A_2 = A_5$ and $A_3 = A_4$. From this analysis it may be concluded that the glassy solid on recrystallization transforms into a metastable solid. This is perhaps due to the restricted mobility of the molecules at these temperatures. This conclusion is further supported by a low temperature annealing. It is observed that if a supercooled sample is annealed for long enough time at 190K, the fraction of the metastable solid formed increases. By keeping the sample at such temperatures for longer times, a larger fraction of the supercooled nematic phase freezes into a glassy solid which on heating transforms into a metastable solid. However, the fraction of the supercooled nematic phase which does not transform into a glassy solid, on heating recrystallizes into a stable solid. The results of DSC measurements can thus be summarized by the following flow diagrams indicating various phase transitions.

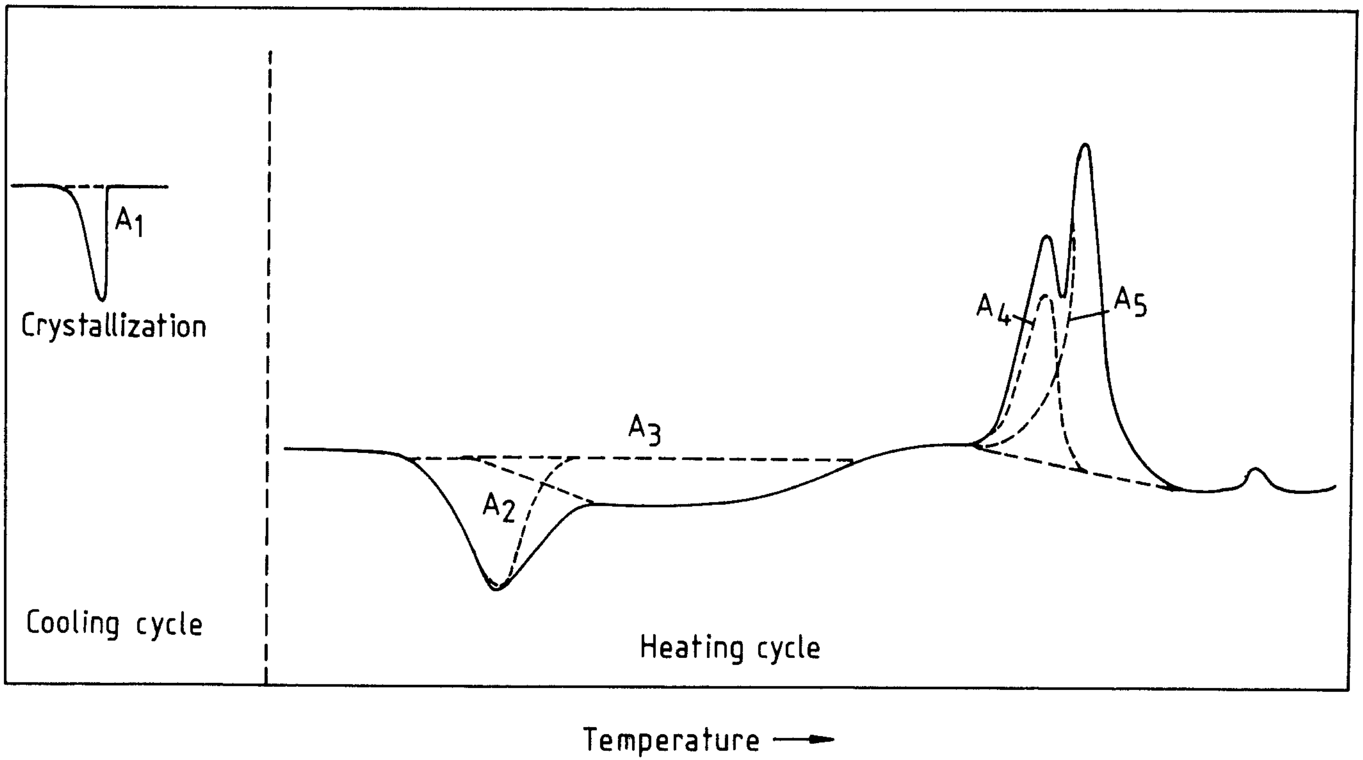
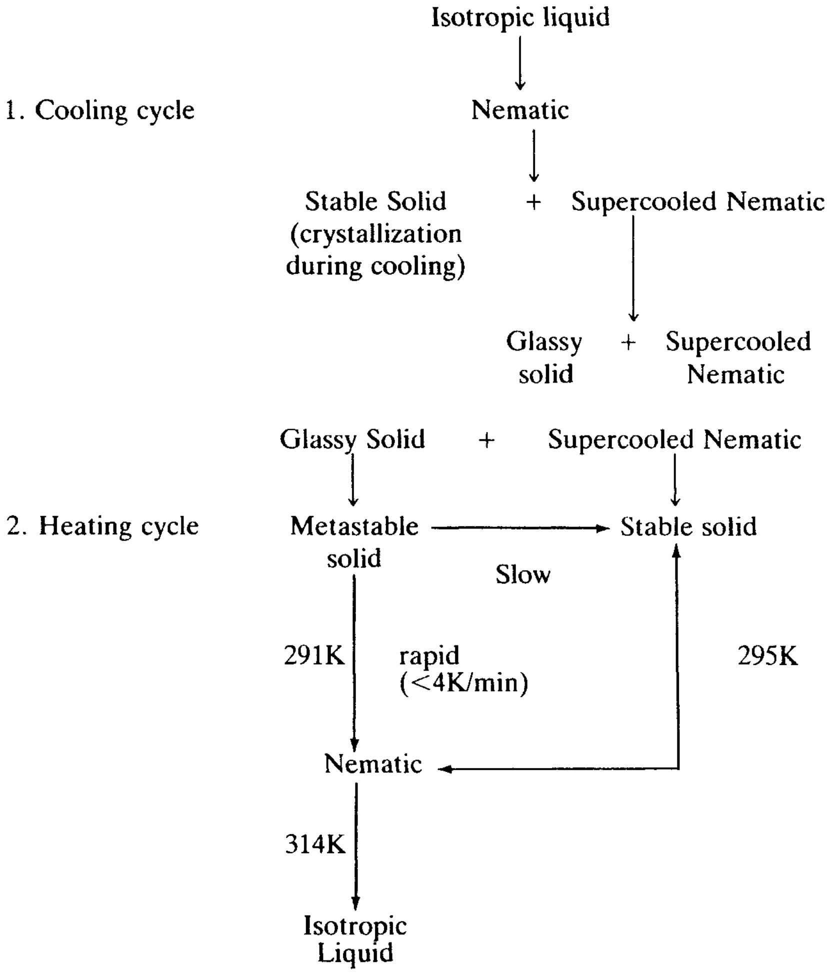


FIGURE 3 A schematic DSC curve for the cooling and heating cycle of a MBBA sample.

TABLE I

Different peak areas as a function of cooling rate

Cooling rate (K/min)	Cooling cycle crystallization peak area A_1	Heating Cycle			
		Exothermic peaks		Endothermic peaks	
		A_2	A_3	A_4	A_5
32	0.14	0.53	0.83	0.86	0.70
16	0.90	0.24	0.50	0.53	1.17
8	0.64	0	0.17	0.14	1.60
4	1.64	0	0	0	1.66



4. CONCLUSIONS

The supercooling studies, carried out by DSC, show that the nematic phase undergoes significant amount of supercooling, its extent depends on the cooling rate. At cooling rates >4K/min it gives evidence for the formation of a glassy state which undergoes glass transition at ~200K. At these cooling rates the nematic phase transforms to glassy and supercooled states. The relative proportion of these is found to depend on the cooling rate. On heating, the glassy phase crystallizes into a metastable solid while the supercooled nematic phase transforms to a stable crystalline solid.

Acknowledgments

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