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Enthalpy and Entropy of Transitions and Texture of (+)-2-Methylbutyl-*p* ((*p*-methoxy benzylidene) amino)cinnamate

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The results of Differential Scanning Calorimetric and optical studies of (+)-2-methylbutyl-*p* ((*p*-methoxy benzylidene)amino) cinnamate (MB MBAC) are reported. We report an additional solid phase formed on quenching the sample.

INTRODUCTION

(+)-2-methylbutyl-*p*((*p*-methoxy benzylidene)amino) cinnamate (MB MBAC) is the only member of *p*-substituted benzaldehyde series, 2-methyl butyl 4-(*p*-(*n*-alkoxy benzylidene)amino) cinnamates showing cholesteric phase.[1] Liao *et al.*[2] and Bhattacharjee *et al.*[3] have confirmed the existence of two smectic phases by Brillouin scattering and X-ray diffraction studies. The steady flow behaviour has been studied by Friedman and R. S. Porter.[4] In this paper the authors report the results of Differential Scanning Calorimetric (DSC) and optical studies of the above compound.

DSC MEASUREMENTS

The sample was obtained from M/s Eastman Kodak Co., and was used without further purification. The transition thermograms were

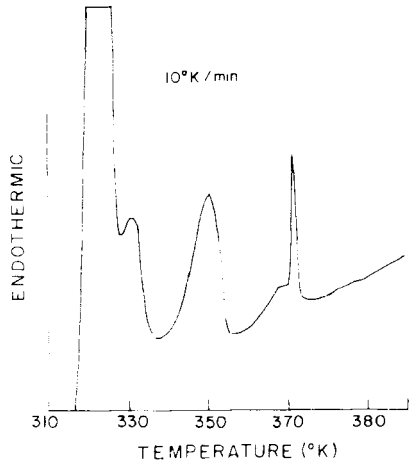

FIGURE 1 The DSC thermogram of (+)-2-methylbutyl(*p*-(*p*-methoxy benzylidene)amino)cinnamate.

recorded on Perkin-Elmer DSC-2 Differential Scanning calorimeter. The transition thermogram is shown in Figure 1. The transition temperatures obtained are in good agreement with those reported earlier. The crystalline solid melts into smectic B phase at 53°C (Figure 2), smectic B to smectic A transition is at 58°C, smectic A to cholesteric transition occurs at 78°C, and cholesteric to isotropic transition occurs at 98.5°C. While cooling the sample from the isotropic phase the peak corresponding to smectic B–crystalline solid

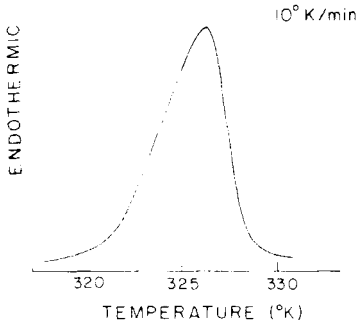

FIGURE 2 The DSC thermogram of crystal to smectic B transition.

TABLE I

Phase change	T_c in °C	H in K cal/mole	S in cal/mole/°K
Crystal–Smectic B	53.0	4.67	14.35
Smectic B–Smectic A	58.0	0.33	1.00
Smectic A–cholesteric	78.0	0.47	1.34
Cholesteric–isotropic	98.5	0.04	0.12

transition was not observed even after cooling up to −5°C. The enthalpy and entropy of transitions are given in Table I.

MICROSCOPIC OBSERVATIONS

A thin sample was taken between a microscope-slide and the coverslip. The textures were observed with a hot stage polarizing microscope with very slow rate of heating. The crystalline solid melts at 53°C.

FIGURE 3 Smectic B phase in a cooled sample. Magnification ×135 at 26°C.

Smectic B phase could not be observed clearly during heating. However, it could be observed in the cooled sample (Figure 3). The transition from spherulitic smectic A to web like cholesteric phase which subsequently changes to planar texture could be observed in wedge shaped sample (Figure 4). The transition to isotropic phase was preceded by blue phase textures. During cooling close to the cholesteric smectic A transition, the helical molecular conformation unwinds as pitch increases rapidly. In thin samples the smectic A phase automatically assumes a homeotropic alignment and appears dark under crossed polars. Smectic B phase continued up to a very low temperature.

FIGURE 4 Transition from spherulitic smectic A to planar cholesteric phase. Smectic A texture changes into web like texture and subsequently changes into planar texture. The flow behaviour can be observed on the lower left of the figure. Magnification × 135.

The flow behaviour of the sample can be observed in Figure 4. On the right, the web like texture of cholesteric is more viscous than the planar texture that appears on the left. The flow along the direction of the gradient can be observed on the lower left of Figure 4. In the flow region the colour of the cholesteric phase turns from bright yellow to bright rose in transparent light. Number of disclination lines could be observed in bright rose region.

RESULTS AND DISCUSSION

The enthalpy and entropy of transition from solid to mesophase is lower compared to the cholesterol derivatives.[5] In fact such a change is observed in many of the non-sterol cholesteric compounds.[6] The enthalpy and entropy of transition for cholesteric–isotropic transition are also very much lower compared to those of sterol cholesteric compounds.[5]

The DSC thermogram of smectic A–cholesteric transition shows a gradual increase starting very much below the actual smectic A cholesteric transition temperature. This has been observed during repeated heating and cooling processes. The microscopic observations also show a gradual change in smectic A texture before the cholesteric phase sets in. At the transition temperature there is a sudden drop showing a first order transition. This thermodynamical and optical behaviour can be explained on the basis of McMillan's theory.[7,8] Firstly, the interactions between central ring structures begins to decrease as the molecules begin to shift from their positions in the Z-direction. This is the density wave transition which is second order. Secondly the change in the angular orientation of the molecules decreases the short range order. The transition in orientational order parameter is first order. The coupling between the density wave order parameter and orientational order parameter turns it into a quasi second order transition[9,10] (which is partly second order followed by partly first order transition). This is clearly shown by the DSC thermogram in Figure 5 (DSC thermogram of a quenched sample) wherein the smectic B–smectic A transition peak on the left is sharper than the smectic A–cholesteric transition peak. It is also evident from the texture photograph of smectic A–cholesteric transition in Figure 6 (a different sample), where we find distortions occurring in smectic A phase just before the transformation into cholesteric phase. We also observe that the transition to the cholesteric phase starts from the

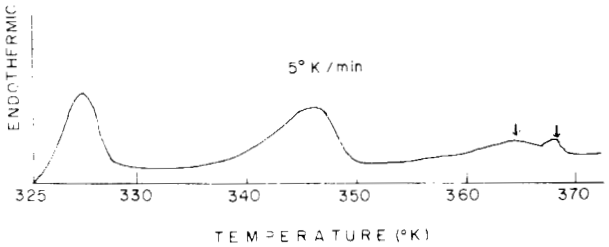

FIGURE 5 DSC thermogram of the sample quenched to 40 °C from its isotropic phase. Arrow marks show the blue phase transitions.

FIGURE 6 Smectic A–Cholesteric transition magnification × 135.

regions where the foci of the focal-conic texture of smectic A phase are concentrated. It may be due to the greater density of dislocations[11] at these points.

CHOLESTERIC-ISOTROPIC TRANSITION

The thermogram of cholesteric-isotropic transition was broadened during slow rate of heating. This is due to the phase transitions that precede the isotropic transition. This intermediate phase viz., Blue phase appears to have several transitions. The textures and thermodynamical properties of this phase have been discussed elsewhere.[12]

QUENCHING EFFECTS

The DSC thermogram during cooling of the sample did not show smectic B–solid transition even after cooling up to $-5\,^{\circ}C$ at a rate of

FIGURE 7 Spherulites formed on quenching the sample to 26 °C from its isotropic phase. Magnification × 135.

5°/min. Other transitions were reversible. The sample was quenched to 40°C from its isotropic phase. Figure 5 shows the thermogram obtained on heating the quenched sample. It is evident from the figure that there is a little shift in the transition temperatures of smectic B–smectic A and smectic A–cholesteric transitions. The cholesteric–isotropic transition is broadened and two broad peaks can be observed. The sample was quenched from isotropic phase to the laboratory temperature (26°C). Figure 6 shows the spherulites formed in solid state in such a sample. When the sample was quenched to 5°C from the isotropic phase solid II phase was formed (Figure 7). The quenched sample was observed under the microscope after nearly 22 days. There was little change in the texture. When the quenched

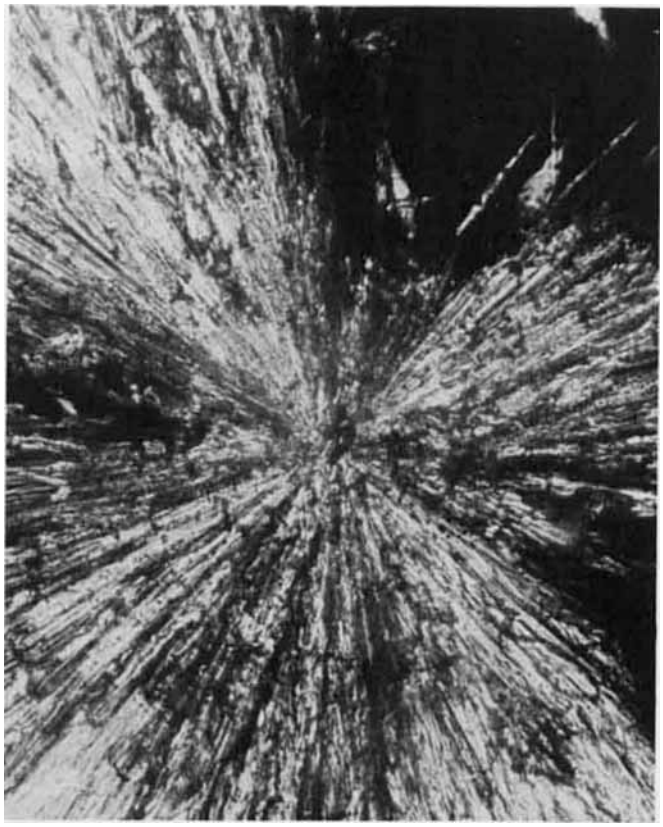

FIGURE 8 Solid II phase formed on quenching the sample to 5°C. Magnification × 300.

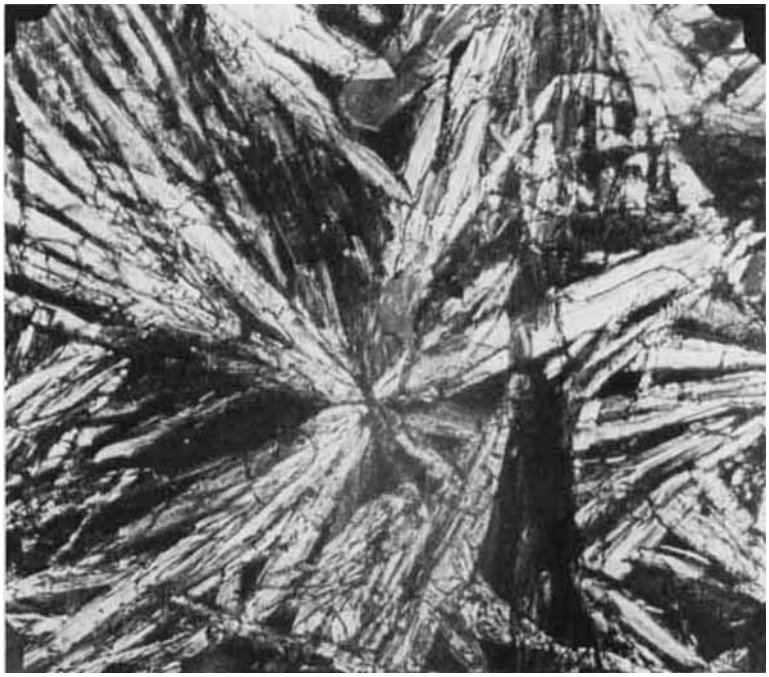

FIGURE 9 Solid I phase formed on heating the quenched sample. Magnification × 300.

sample was heated, it gradually changed to solid I (Figure 8) before melting into smectic B.

CONCLUSIONS

In this paper we have reported the enthalpy and entropy of transitions of MB MBAC, for crystal–smectic B, smectic B–smectic A, smectic A–cholesteric, cholesteric–isotropic transitions. It is found that the enthalpy and entropy of transitions at melting and clearing points are lower than those for sterol cholesteric compounds. Smectic A–cholesteric transition appears to be a weak first order transition. A detailed study of crystal structure analysis and a quantitative study of smectic A–cholesteric transition is envisaged in the near future. The solid II phase occurring on quenching the sample is reported for the first time.

Acknowledgment

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