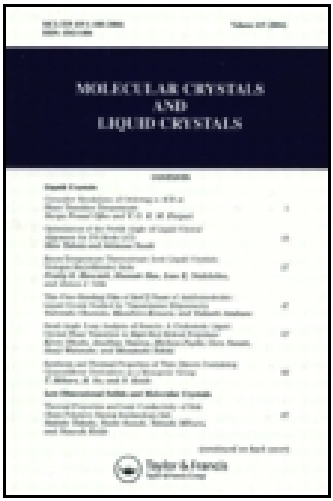

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EXISTENCE OF A THIRD CRYSTALLINE PHASE IN TBBA

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Positron annihilation lineshape (S-parameter) measurements and small angle X-ray scattering (SAXS) using synchrotron X-rays on liquid crystalline terepthal-bis-butylaniline (TBBA) are reported at cryogenic temperatures. The crystalline ↔ crystalline transition at 231 K deviates from the first order nature, as evidenced by the observation of a pronounced hysteresis in the layer spacing and the S-Parameter during the heating and cooling cycles. Presence of a possible third crystalline phase at a still lower temperature of 180 K is identified from X-ray diffraction patterns in corroboration with the slope change in layer spacing and electron density variations reflecting on the lineshape parameter.

Keywords: liquid crystals; positron annihilation; layer spacing

INTRODUCTION

Among the numerous thermotropic mesogens known, terepthal-bis-(4-n-butyl aniline), commonly known as TBBA, occupies a special position by virtue of its polymorphism. It possesses 4 well known mesophases: smectic H (S_H), smectic C (S_C), smectic A (S_A), and the nematic (N) phase, in addition to the isotropic phase. Calorimetric studies have shown that TBBA also adopts monotropically 2 additional smectic phases between the smectic H and the crystalline phase on cooling. Moreover, the monoclinic crystalline phase transforms into a triclinic crystalline phase at cryogenic

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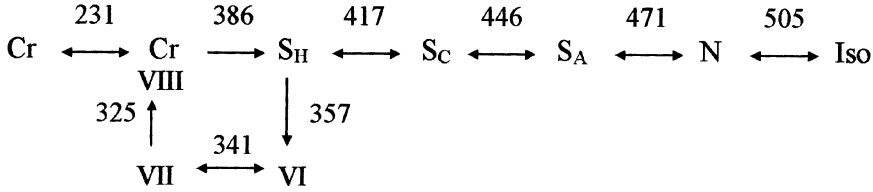


FIGURE 1 Phase transition scheme for TBBA.

temperature [2]. The phase transition scheme for TBBA is shown in Figure 1 with the transition temperatures in Kelvin.

Positron annihilation lifetime spectroscopy (PALS) utilizes positron and its bound state, positronium, as atomic probes for studying electronic structure, phase transitions, and relaxation processes in condensed and liquid media using their lifetimes and the line width/line shape parameters [3] from the annihilation radiation energy distribution spectra. In this context, details of the phase transition behavior in a variety of matrices such as polymers [4], micellar media [5], and superconductors [6] have been successfully undertaken. Amongst the very few studies on liquid crystals [7,8], the sensitivity of this technique in discovering new phases has been highlighted on account of its ability to monitor small changes in the electron densities occurring across a phase transition.

In this article, we report the existence of a new crystalline phase transition at 180 K using low temperature Positron Annihilation Lineshape (PAL) measurements combined with Small angle X-ray scattering (SAXS) studies using the high brilliance and high resolution of a synchroton beam. We also provide evidence for the deviation of the solid-solid transition at 231 K from obeying a first order behavior.

EXPERIMENTAL DETAILS

TBBA was prepared by refluxing 4-n-butylaniline and terepthaldehyde in absolute ethanol for 5–6 h according to the procedure of Taylor et al. [9]. The product after isolation was recrystallized several times from ethanol until the transitions temperatures remained constant. These were determined from changes in the characteristic textures of the mesophases observed under a polarizing microscope (Olympus) fitted with a hot stage. The heat of mesomorphic transition was calculated from the thermographs obtained on a Netzsch DSC-204 calibrated with indium. Details of the Positron Annihilation Lineshape measurements and the SAXS studies have been described earlier [10]. Low temperature X-ray diffraction studies were carried out on a Siemens D500 diffractometer operating at 45 KV power

using Cu-Kα as the incident X-ray beam. The temperature was maintained with an Oxford Continuous Flow Cryostat with an accuracy of ± 0.5 K. The (111) diffracted peak of Silicon NBS 640a was used as an internal standard.

RESULTS AND DISCUSSION

Figure 2 shows the time-resolved evolution of the layer spacing in the small angle region when the sample was cooled down from the solid crystalline phase to 123 K and heated back to room temperature. In order to avoid the exposure of the sample for a long period to the incoming X-ray beam, time slicing during the SAXS measurements was performed. Series of scattering data with high time resolution (5 ms) and angular resolution (5^0) were acquired. This proves beneficial since the signal-to-noise and signal-to-background ratio is increased, thereby assisting in the observation of also the weak scattering reflections. The time resolved data was converted into a 2-D plot (Figures 3(a) and 3(b)) for the variation of the layer spacing and scattered intensity, obtained from the main scattering peak, with temperature. At room temperature TBBA crystallizes in the monoclinic system

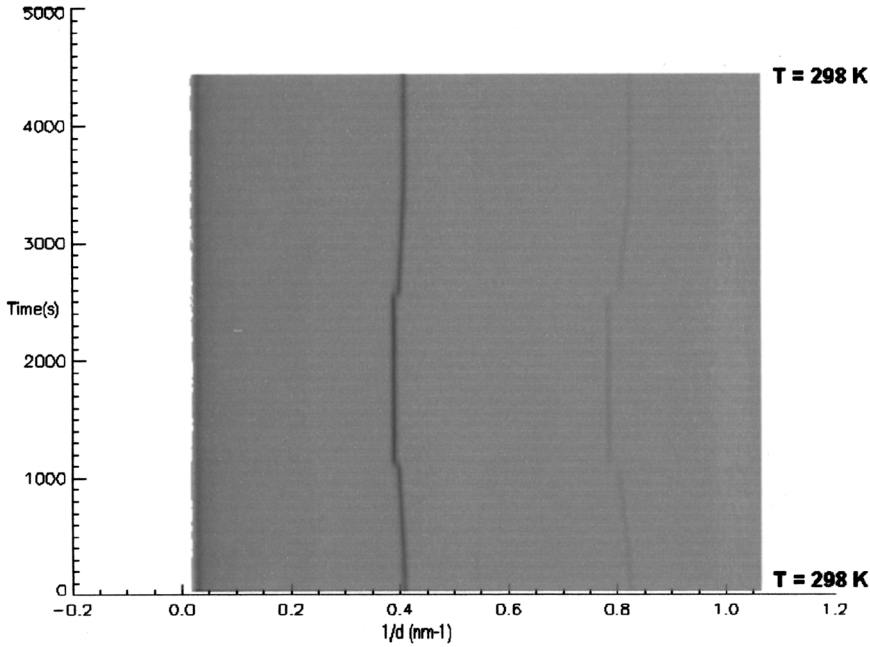
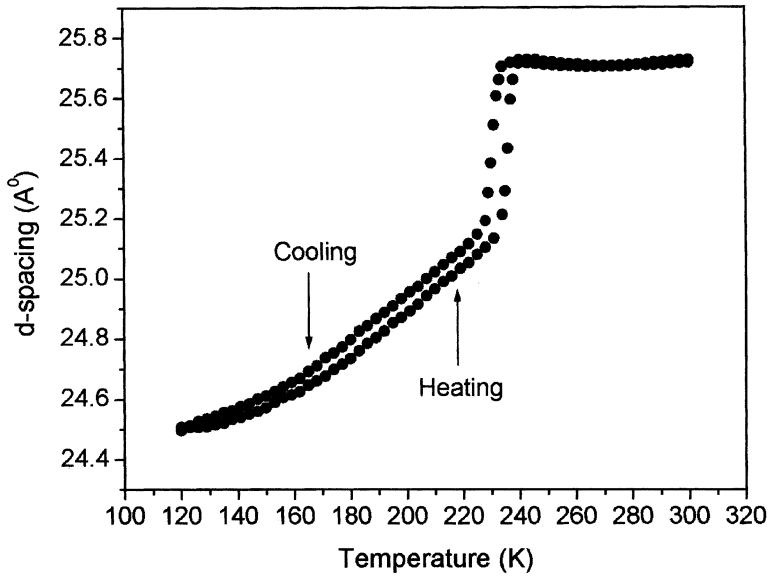
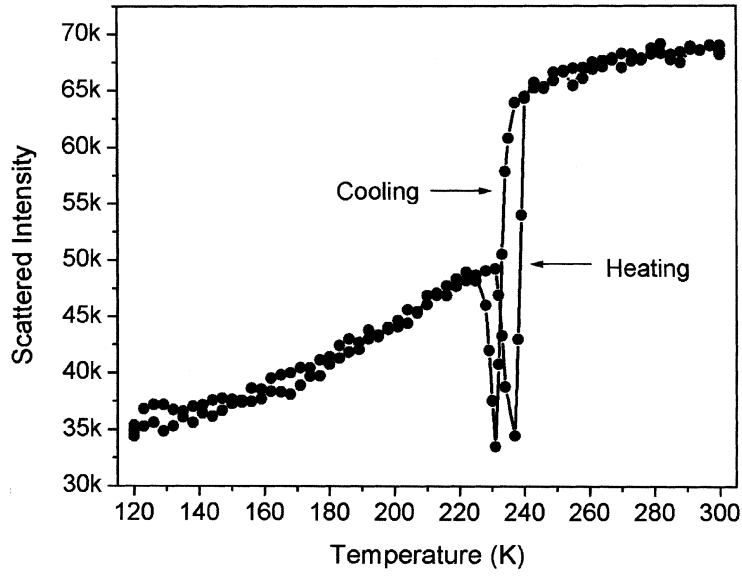


FIGURE 2 Time resolved plot of the variation of layer spacing in the temperature range 298 K–123 K–298 K (cooling and heating) for pristine TBBA. (See COLOR PLATE I)



(a)



(b)

FIGURE 3 (a) Temperature dependence of the layer spacing for the heating and cooling cycles. (b) Temperature dependence of the scattered intensity from the main Bragg peak during the heating and cooling cycle.

and a collective motion of the molecules involves a correlation length of about 7 molecules [10]. This monoclinic structure undergoes a structural change to a triclinic crystalline phase reported by Doucet et al. at 231 K [2] and is also evident in this study from the changes in the layer spacing (Figure 3(a)) and the scattered intensity (Figure 3(b)) near 231 K, both during the cooling and heating cycles. There is a sharp drop at around 231 K, indicating a predominantly first order transition. Also, the transformation shows an evident hysteresis; in Figure 3(a) the transition temperatures we obtain from the cooling and heating cycles are 234 K and 227 K. The hysteresis is also confirmed in the Positron Annihilation Lineshape measurements (Figure 4) where the variation of the lineshape parameter, defined as a ratio of the integrated counts in the central portion of the Doppler shift −0.7 to 0.7 keV to the total counts in the energy range −7 to 7 keV (peak counts corresponding to zero energy), is plotted with temperature. The transition temperatures obtained thus from the cooling and heating cycles differ by ∼7 K. The presence of a pronounced hysteresis in both of the studies then excludes the transition we observe to be a real first-order transition.

An interesting observation can be made from the analysis of Figure 3(a). A significant change in the slope of the layer spacing profile is seen at the

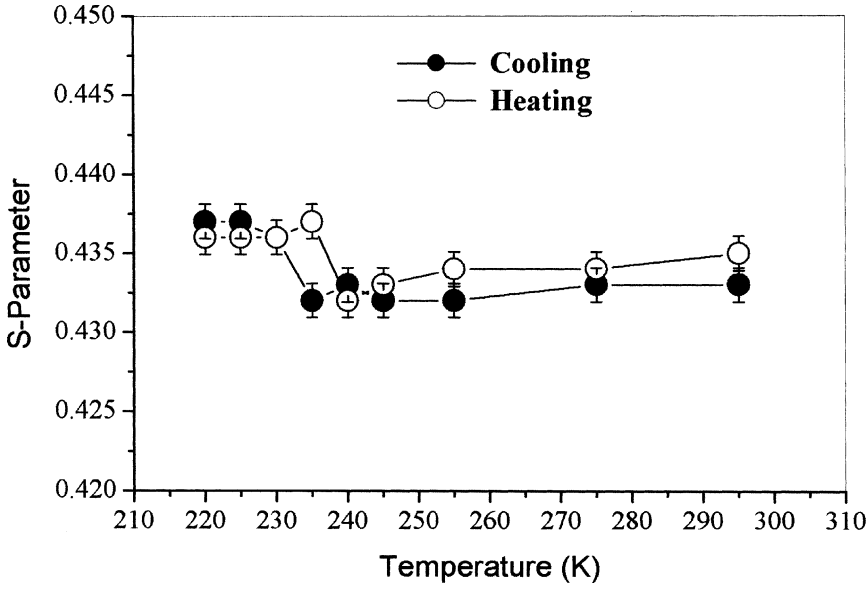


FIGURE 4 Hysteresis phenomenon seen in the temperature dependence of the lineshape parameter (S) for the heating and cooling cycles.

lower end of the temperature scale at around 180 K, associated with both the heating and the cooling profiles. A more accurate picture of the slope change is presented in Figure 5, where the main scattered reflection at different temperatures is plotted as a function of the layer spacing. A change in the peak centroid at 180 K can be easily identified. This finding is further corroborated by a small but significant change in the positron annihilation lineshape parameter at the same temperature (Figure 6). Our previous studies [10] had shown similar changes in the lineshape parameter arising from order parameter fluctuations in the smectic C and H phases of TBBA, which caused electron density fluctuations and were mapped by the S-parameter. However, the changes observed in Figure 6 cannot be assigned to any molecular fluctuations since all molecular motions are effectively reduced at such low temperatures. Under these circumstances, a small structure change occurring in the molecule appears as the only possible reason for the changes in the peak position and the lineshape parameter.

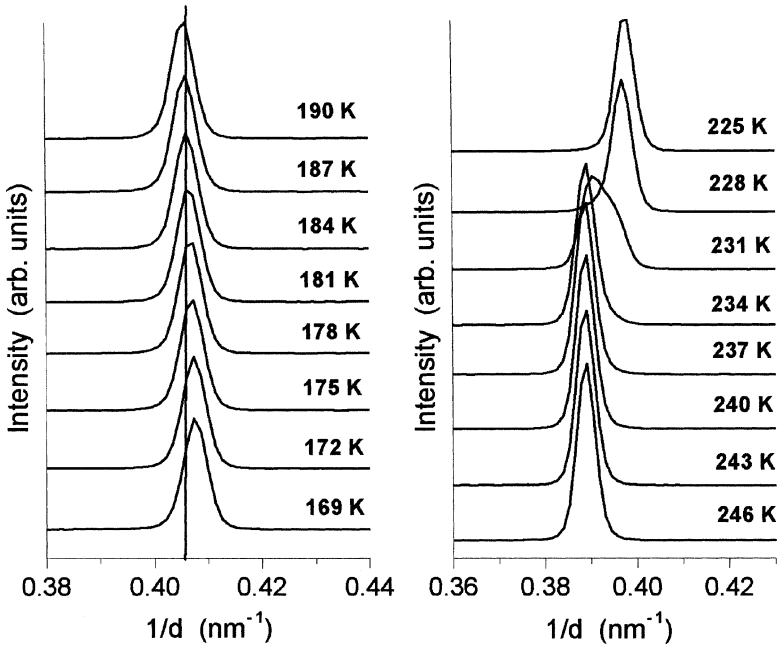


FIGURE 5 Measured X-ray scattered intensity versus layer spacing for the temperature range 190 K to 169 K. A shift in the peak centroid from 180 K onwards is clearly evident. The pronounced shift in the peak position at the 231 K transition is shown for comparison.

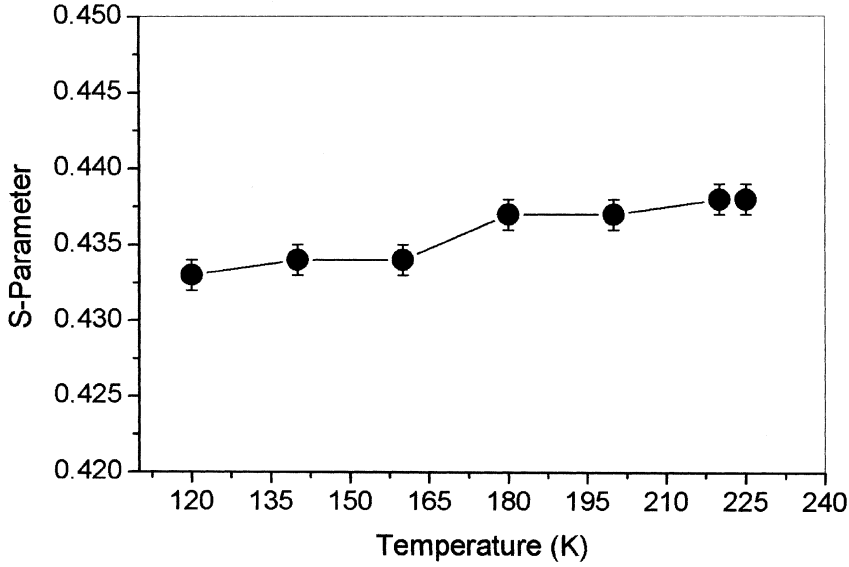


FIGURE 6 S-parameter profile as a function of temperature near 180 K.

In order to examine and confirm this possibility, X-ray diffraction using a cryogenic setup was carried out. Figure 7 shows the variation in the diffraction patterns as a function of decreasing temperature from 290–160 K. The solid-solid phase transition at 231 K is clearly characterized by

1. Appearance of a new diffraction peak at $2\theta = 16.58°$ (marked by *).
2. Complete disappearance of the (312) reflection at $2\theta = 21°$.
3. Decrease in the intensity of the $(11\bar{2})$ reflection and a corresponding increase in the intensity of the shoulder peak adjoining the reflection.
4. Complete reversal of the doublet peak intensity ratio containing the (004) reflection.
5. Increase in the separation of the (204) and the (911) reflection by 0.35° accompanied by a decrease in their intensities.
6. An overall observable centroid shift for all the major peaks.

Similarly, Figure 7 shows evidence of yet another transition occurring at a lower temperature of 180 K. The new reflection observed in the second crystalline phase (existing below 230 K) splits up into a doublet at 180 K and finally splits up completely to form 2 distinct peaks at a lower temperature. The other interesting feature to develop at 180 K is the increase in the intensity ratio of the doublet at $2\theta = 22.74$ and 23.15° from 1:1.2 at 220 K to 1:1.8, and which further increases to 1:3.7 at 160 K. This is also

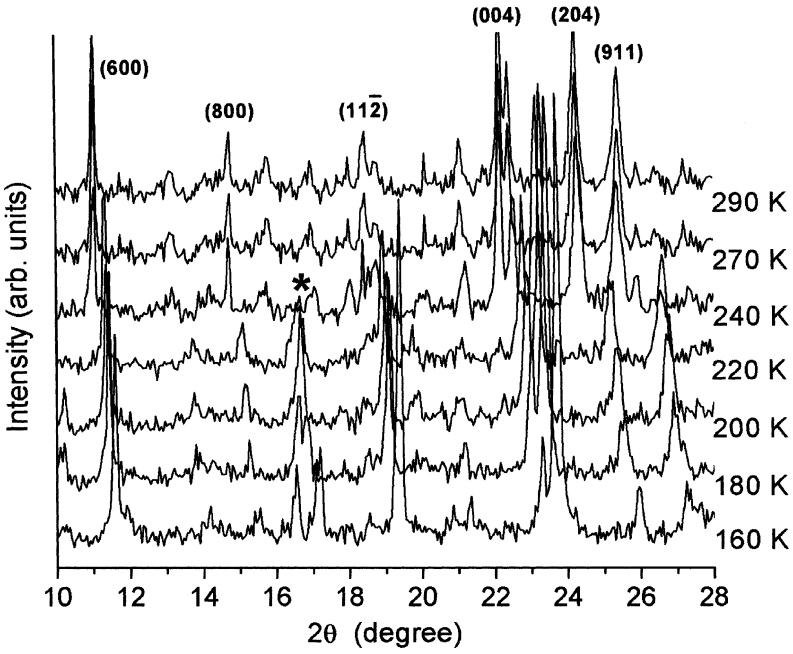


FIGURE 7 X-ray diffraction peaks in TBBA as a function of decreasing temperature.

accompanied by a shift in the peak centroids of all the other peaks and a decrease in the intensity of the (204) and (911) reflections. Thus, a new phase transition at 180 K to a third crystalline phase in TBBA is evident from the diffraction experiments and excellently corroborates the prediction of the Position Annihilation and SAXS measurements.

CONCLUSION

Crystalline polymorphism was studied in TBBA using Positron Annihilation Lineshape measurements along with the high brilliance and high resolution of 8 keV X-rays from a synchrotron radiation source with time slicing. We found that the crystalline phase transformation at 231 K exhibits a pronounced hysteresis behavior leading to a deviation from being an ideal first order transition. Another structural change occurring at a still lower temperature of 180 K, identified through the observed slope change in the layer spacing and change in the lineshape parameter, is further confirmed through appearance of new features in the X-ray diffraction patterns. A complete indexing and characterization of the new phase in under progress.

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