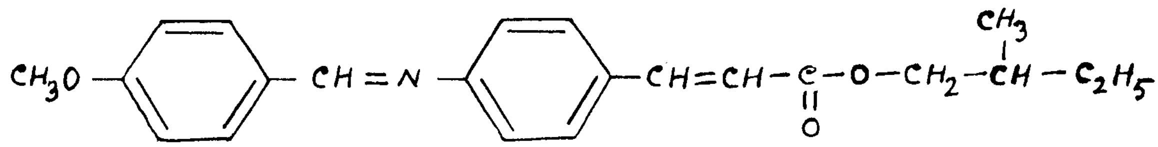
CHAPTER-V

X-RAY DIFFRACTION STUDIES ON (—)-Z-METHYLBUTYL p-(N-(P-METHOXY BENZYLIDENE) AMINO)CINNAMATE (MBAC in short)

5.1 Introduction

The structural formula of (-)-2-methylbutyl p-(N-(P-methoxy benzylidene) amino) cinnamate (MBAC in short) is



Bhattacharjee et al[1] have reported the X-ray diffraction studies of the compound at different temperatures. They measured the apparent molecular length (l) and intermolecular distance (D) throughout the whole mesogenic range. But they were not able to align this compound in magnetic field. Liao et al[2] have studied Brillouin Scattering for this compound. They have attributed a smectic A and smectic B modification to this substance. Gray[3] has given the transition temperatures and Leclercq et al[4] have studied the phase transitions of this compound. Friedman and Porter[5] have given the steady flow viscosity data.

I have studied the magnetically aligned sample of MBAC by X-ray diffraction technique specially in smectic B phase[6]. Orientational order parameters $\langle P_2 \rangle$ and $\langle P_4 \rangle$ have been calculated from X-ray data. Some anomalous behaviour of MBAC was observed, which has been explained as a second order smectic B (polylayer) to smectic B (monolayer) transition in the mesogen.

The compound has the following transition temperatures[1],

$$\text{Solid} \underset{\sim 15^{\circ}C}{\overset{53^{\circ}C}{\rightleftharpoons}} \text{Smectic B} \overset{59^{\circ}C}{\rightleftharpoons} \text{Smectic A} \overset{78^{\circ}C}{\rightleftharpoons} \text{Cholesteric}$$

$$\text{Isotropic} \overset{97^{\circ}C}{\rightleftharpoons}$$

5.2 Experimental methods

The compound was obtained from M/s. Eastman Kodak Company and was dried in vacuum desiccator for two hours. X-ray diffraction photographs were taken in the presence and absence of magnetic field ($\sim$7.0 K.gauss) using Nickel filtered copper K_{α} radiation of wavelength 1.542 Å. For obtaining oriented sample, the sample was first heated to isotropic phase and then cooled down slowly to the desired temperature in presence of magnetic field. I was able to aligh the sample only in the smectic B phase but not in the smectic A phase.

The outer rings of the photographs at different temperatures are so sharp that I could not accurately scan the rings circularly, which is necessary for knowing the angular variation of intensity along the outer circular ring to calculate $\langle P_L \rangle$. So I scanned the film linearly at first and from these readings the values of X-ray intensities along the circular arc were calculated.

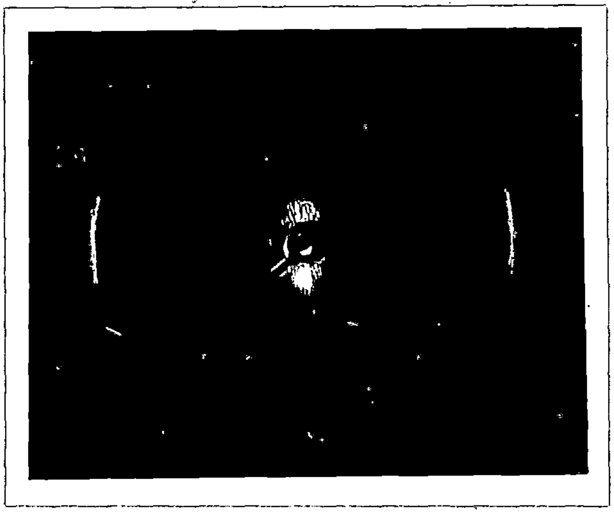


Fig.5.1 X-ray photograph of oriented sample of MBAC at $40^{o}C$.

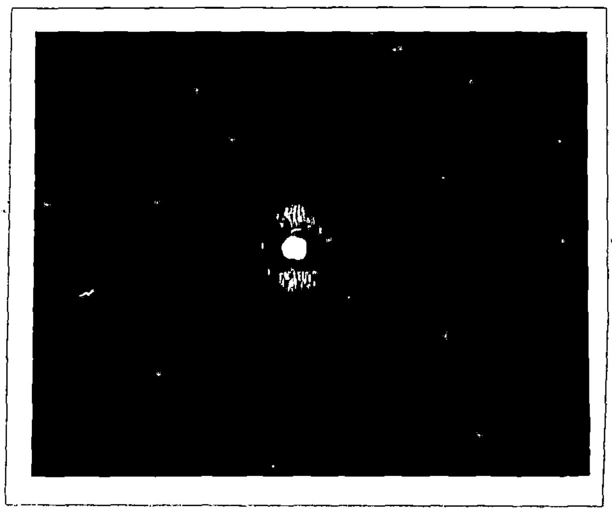


Fig.5.4 X-ray photograph of oriented sample of MBAC at $45^{o}C$.

Fig.5.5 X-ray photograph of oriented sample of MBAC at $50^{o}C$.

5.3 Results and discussions

I did not get the well-known diffraction pattern of smectic B phase (outer ring split into six spots) because the X-ray photographs were taken perpendicular to the direction of magnetic field. On the contrary, I have got sharp outer ring. The figure 5.1 shows the photographs at 40°C. From the angular variation (Table 5.1) of the intensities of the outer rings at different temperatures I calculated $f(\beta)$, the orientational distribution function and the order parameters $\langle P_2 \rangle$ and $\langle P_4 \rangle$ in the smectic B phase of MBAC, following the method described in sections 2.1.1 and 2.1.7. The normalised distribution function $f(\beta)$ at different temperatures is shown in figure 5.2 and tabulated in Table 5.2. Figure 5.3 shows the variation of $\langle P_2 \rangle$ and $\langle P_4 \rangle$ with temperature. The continuous curves are obtained from Maier and Saupe (MS) mean field theory. Tables 5.3 and 5.4 contain the orientational order parameters $\langle P_L \rangle$ and the corresponding coefficients c_L and d_L/k, for angular part of pseudopotential, at different temperatures respectively. Figure 5.3 indicates that the experimental $\langle P_2 \rangle$ and $\langle P_4 \rangle$ values are almost constant, being 0.85 ± 0.03 and 0.60 ± 0.03 respectively. These values are much larger than those calculated from MS theory, showing that the orientational order is much more in smectic B phase than in nematic phase for which MS theory is applicable. This observation is in agreement with the model of herringbone packing of the molecules in the smectic B phase[7], since molecules

Sample : MBAC

Table- 5.1

Experimental intensity I(ψ) at different temperatures after background correction

ψ (degree)	I(ψ) at temperature (°C)						
	20	25	32	40	45	50	55
0	15.00	14.00	14.30	19.00	4.80	18.80	6.00
5	14.05	12.25	12.50	17.05	4.20	14.50	5.40
10	10.05	9.30	9.55	12.01	2.90	8.50	4.25
15	7.10	6.30	6.60	7.05	2.00	5.30	3.15
20	4.11	3.90	4.15	4.90	1.30	3.80	2.10
25	2.35	2.05	2.45	2.80	.80	1.50	1.00
30	1.10	1.00	1.35	1.38	.40	.50	.20
35	.20	.30	.70	.49	0	0	0
40	0	0	0	.05	0	0	0
45	0	0	0	0	0	0	0
50	0	0	0	0	0	0	0
55	0	0	0	0	0	0	0
60	0	0	0	0	0	0	0
65	0	0	0	0	0	0	0
70	0	0	0	0	0	0	0
75	0	0	0	0	0	0	0
80	0	0	0	0	0	0	0
85	0	0	0	0	0	0	0
90	0	0	0	0	0	0	0

Sample : MBAC

Table- 5.2

Normalised distribution function f(β) at different temperatures

β (degree)	f(β) at temperature in ^{o}C						
	20	25	32	40	45	50	55
0	21.97	22.16	22.17	26.36	25.12	31.27	19.39
5	20.21	20.34	20.05	23.45	22.37	27.91	18.08
10	15.69	15.69	14.87	16.47	15.81	19.62	14.67
15	10.25	10.14	9.21	9.20	9.07	10.43	10.42
20	5.65	5.53	5.11	4.46	4.77	3.89	6.51
25	2.72	2.66	2.94	2.48	2.92	1.06	3.52
30	1.27	1.29	1.85	1.75	2.02	.98	1.51
35	.63	.70	1.00	.97	.97	.86	.32
40	.27	.33	.26	.14	-.04	.60	-.18
45	.02	.04	-.12	-.26	-.40	.03	-.18
50	-.11	-.12	-.08	-.10	-.11	-.34	.01
55	-.10	-.11	.06	.15	.22	-.31	.11
60	-.03	-.03	.07	.13	.16	-.06	.05
65	.03	.04	-.02	-.06	-.09	.12	-.05
70	.04	.05	-.06	-.12	-.15	.14	-.06
75	.03	.03	0	0	.01	.07	.01
80	0	0	.04	.08	.10	0	.04
85	-.01	-.01	.01	.02	.02	-.04	.01
90	-.02	-.02	-.02	-.04	-.05	-.05	-.02

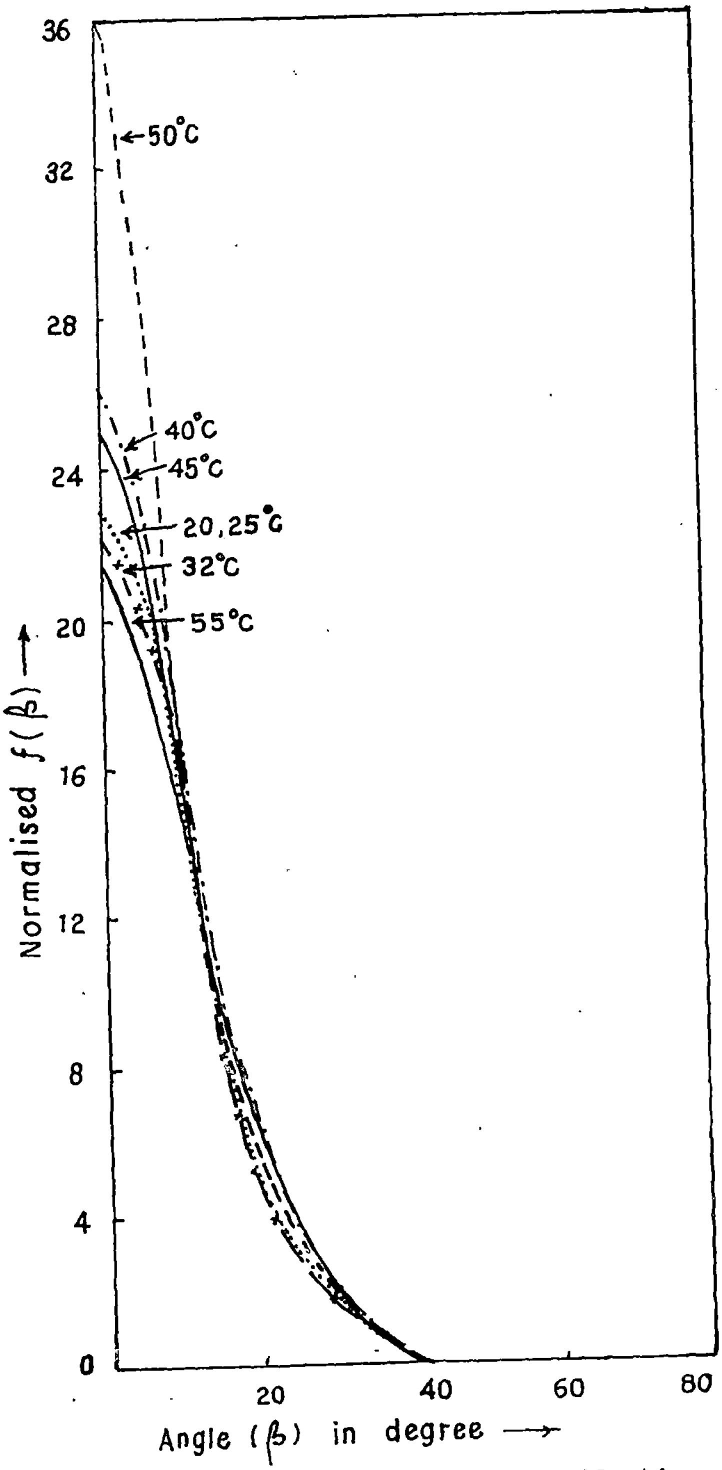


Fig.5.2 Normalised orientational distribution function $f(\beta)$ plotted against the angle β at different temps.

Sample : MBAC

Table- 5.3

Variation of $\langle P_L \rangle$ values with temperature, L = 2 and 4.

Temp. (°C)	$\langle P_2 \rangle_V$	$\langle P_2 \rangle_{expt.}$	$\langle P_2 \rangle_{MF}$	$\langle P_4 \rangle_V$	$\langle P_4 \rangle_{expt.}$	$\langle P_4 \rangle_{MF}$
20	.8655	.8681	.7240	.6199	.6242	.3730
25	.8616	.8659	.7105	.6117	.6202	.3615
32	.8433	.8513	.6960	.5708	.5867	.3425
40	.8504	.8659	.6790	.6000	.6254	.3230
45	.8617	.8625	.6674	.6086	.6050	.3095
50	.8810	.8960	.6534	.6766	.7032	.2949
55	.8754	.8703	.6387	.6450	.6230	.2802

Sample : MBAC

Table- 5.4

c_L and $d_{L/k}$ (L = 2 and 4) at different temperatures

Temp. (°k)	c_0	c_2	c_4	c_6	c_8	c_{10}	d_2/k	d_4/k
293	- 26.85	50.38	- 29.28	9.28	.346	- .746	- 17004	13744
298	- 24.08	45.42	- 26.43	8.62	.289	- .686	- 15631	12699
305	- 25.72	46.00	- 20.90	- .034	5.765	-2.010	- 16481	10865
313	- 56.89	103.55	- 56.52	8.07	8.69	-3.65	- 37431	28287
318	- 7.74	14.96	- 6.72	2.71	.156	- .175	- 5490	3436
323	- 51.33	98.75	- 65.91	23.55	.363	-1.84	- 35598	30274
328	-201.99	397.06	-296.98	137.96	-37.88	4.80	-149645	156355

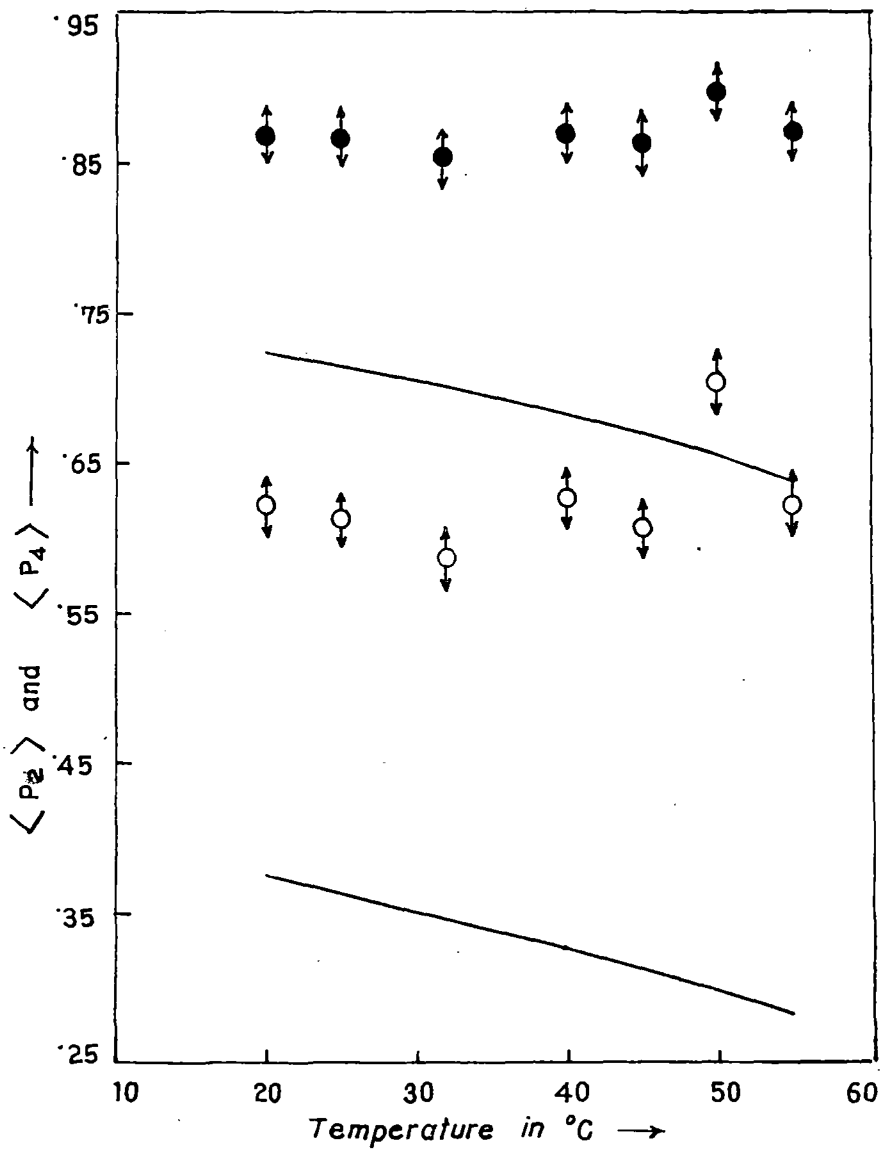


Fig.5.3 Variation of order parameters with temp. of MBAC.

arranged in such a manner will have high degree of ordering. Though the approximation[8] used for calculating $\langle P_L \rangle$ is not valid for $\langle P_2 \rangle \gtrsim 0.8$, I am, however, reporting these orientational order parameter values, since at least qualitatively they show the degree of order of a liquid crystal in smectic B phase for which such values are rare.

The X-ray photographs of MBAC show a definite change between 45^{o}C and 50^{o}C (figures 5.4 and 5.5) implying a phase transition. Heat of transition was not observed either in the DTA of this sample[1] or in the DSC scan of the enantiomer of this sample[9] in this temperature range. Hence the transition must be of second order. When the temperature is equal to or greater than 50^{o}C, two distinct spots are observed in the X-ray diffraction pattern of the smectic phase (Fig. 5.5). But when the temperature is less than 50^{o}C, then, instead of each distinct spot, several smaller spots appear in that region (Figs. 5.1 and 5.4). These spots correspond to smectic layers, as is apparent from the second order spots distinctly seen in the X-ray film. The prints (Figs. 5.1 and 5.4) unfortunately do not clearly show these higher harmonies. To make the point clear I have measured the optical density of the X-ray films in the meridional direction, the result being shown in figure 5.6. The second order X-ray diffraction from the smectic layer is distinctly seen in this figure. So it is possible that a polylayer (either bilayer or trilayer) smectic B to monolayer smectic B second order transition occurs just below 50^{o}C. Such

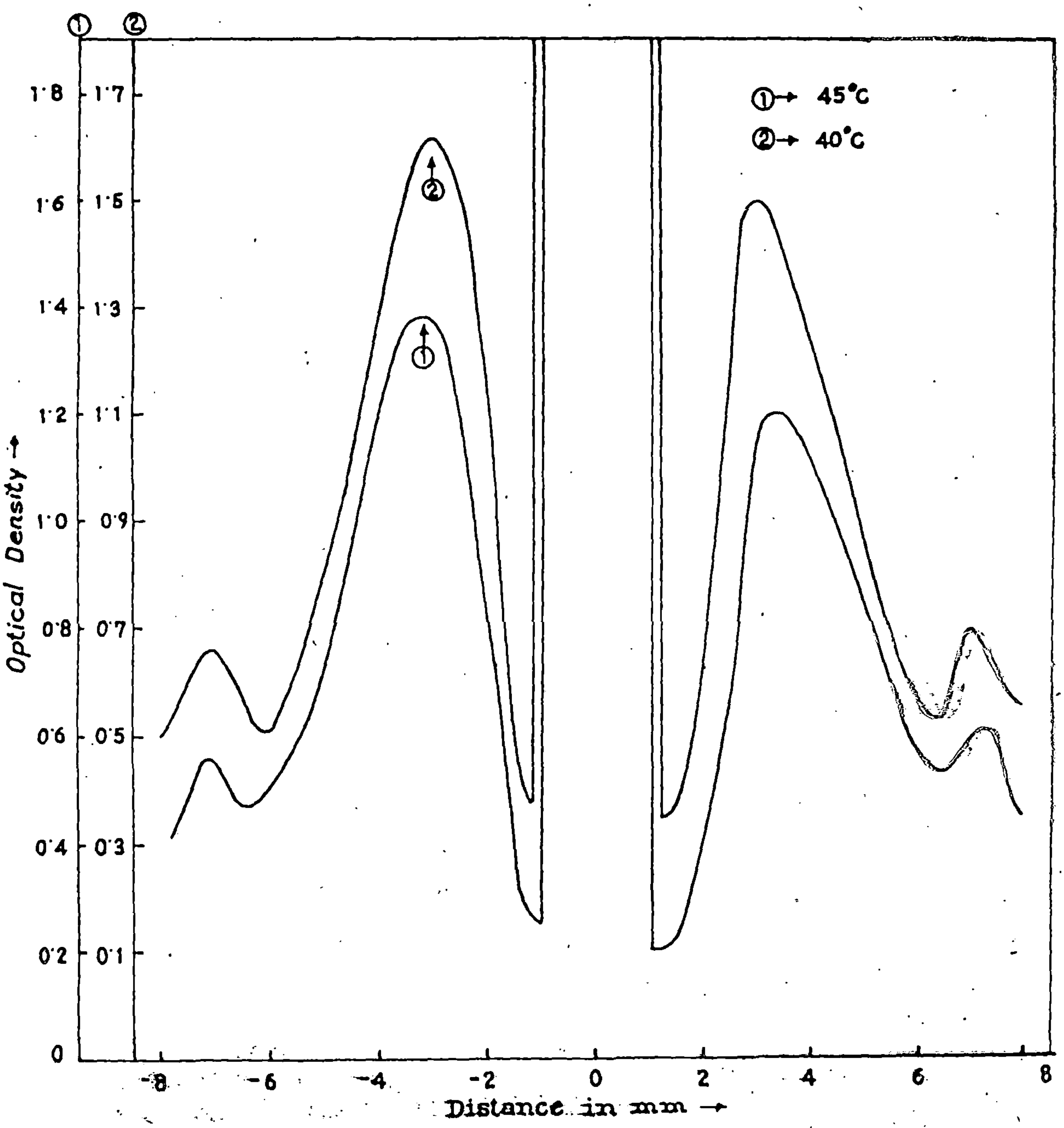


Fig.5.6 Optical density scan in the meridional direction of X-ray patterns of MBAC.

enthalphyless transitions have already been found in the smectic B phase of some other compounds by Gane et al[7]. Leadbetter et al[10] have discussed the possibility of such transition from polylayer to monolayer in smectic B phase. Unfortunately, the resolution of my photographs was not sufficient to identify the polylayer as a trilayer or a bilayer smectic B phase.

Bhattacharjee et al[1] also observed a peculiar trend in the temperature dependance of intermolecular distance in MBAC. They observed that the intermolecular distance is almost temperature independent below 50°C, but it increases with temperature above 50°C. This, in my opinion, is related to the second order phase transition in MBAC.

Also, the order parameters $\langle P_2 \rangle$ and $\langle P_4 \rangle$ at and above 50°C are greater than those below it in the smectic B phase. Since I am unable to say anything about the packing in the smectic B layer from X-ray data, it is not possible to say what causes this anomalous behaviour of orientational order parameters. However, it is strongly indicated from the preceeding observations that this anomalous behaviour is connected with smectic B (polylayer) to smectic B (monolayer) transition.

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