CHAPTER - III

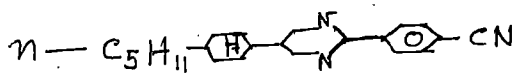
EXPERIMENTAL RESULTS

3.1. X-ray Diffraction and Bi-refringence Studies on PCCPP, PCTP and PBBA.

3.1.1. Introduction:

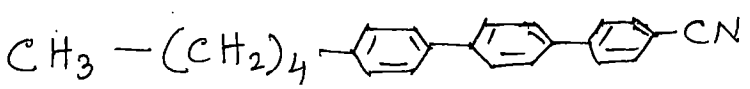
We have determined order parameters from X-ray diffraction studies and also from bi-refringence measurements for some compounds having nematic phase. The names, structural formulae and transition temperatures are given below

I. 5-(4''- n-Pentyl Cyclohexyl)-2-(4'-Cyanophenyl)-Pyrimidine (PCCPP in short).



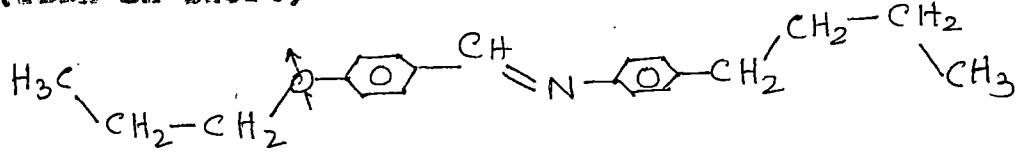
Solid $\underset{68^{\circ}C}{\overset{100.6^{\circ}C}{\rightleftharpoons}}$ Nematic $\overset{234.9^{\circ}C}{\rightleftharpoons}$ Isotropic

II. 4''-n-Pentyl-4-Cyano-p-terphenyl (PCTP in short)



Solid $\overset{129.8^{\circ}C}{\rightleftharpoons}$ Nematic $\overset{238.5^{\circ}C}{\rightleftharpoons}$ Isotropic

III. p-n-Propoxy benzylidene-p-n-butylaniline (PBBA in short)



Solid $\underset{<0^{\circ}C}{\overset{40.5^{\circ}C}{\rightleftharpoons}}$ Nematic $\overset{58.5^{\circ}C}{\rightleftharpoons}$ Isotropic

The samples I and II was supplied by M/s. F.Hoffmann La-Roche & Co. in the purified form and sample III by Prof. M. Wada of Tohoku University, Japan. The sample III (PBBA) has a supercobling well-bellow the room temperature.

3.1.2. Texture Study

A polarizing microscope with magnification 150X equipped with a hot stage has been used to examine the melting behaviour of the liquid cryetals. The transition temperature and supercooling regions found thereof are as stated earlier. Under cross polarising microscope different phases were tried to identify. Nematic thread like textures are obtained in case of sample II and III and thread like textures with inversion line was obtained for the sample I.

3.1.3. X-ray Study:

X-ray diffraction photographs of the samples were taken at different temperature in presence of magnetic field using nickel filtered CuKa radiation of $\lambda = 1.5418$Å. The temperatures were measured and regulated with an accuracy of $\pm$ 0.5°C with the help of a temperature controller (Indotherm 401). The experimental set up, techniques and procedure for analysing X-ray diffraction photographs have already been discussed in the previous chapter. The samples were heated to isotropic state and a magnetic field of about 0.58 Tesla was applied to it. After the magnetic field is stabilised, the sample was allowed to cool slowly to the

desired temperature in the nematic state, and the X-ray photographs were then taken. All the photographs of aligned samples were scanned circularly and linearly with the help of a densitometer (VEB Carl-Zeiss Jena, Microdensitometer Modal - 100). The optical densities were converted to X-ray intensities and orientational order parameters were calculated with the help of computer program developed by us. The photographs of the aligned samples at different temperature distinctly indicate the presence of nematic phase, Fig. 3.1 - 3.3.

Intermolecular distance (D) and Apparent Molecular Length(l):-

The average intermolecular distance (D) and the apparent molecular length (l) have been calculated by using the procedure already stated in Chapt. II. Variation of D and l with temperature is shown in Fig. 3.4 - 3.6. With the help of stereo model unit (Prentice Hall Inc, West Nyack, New York) the possible conformations for the samples were constructed and the molecular lengths (L) in their most extended form were found to be 21 Å, 20.4 Å, and 20.5Å respectively. The average apparent molecular length of the oriented samples as determined from the inner ring of the X-ray diffraction photographs are 26.24 Å, 26.2 Å and 22 Å respectively. Table 3.1 shows the comparison of l and L values. The ratio of l to L are 1.25 and 1.28 for samples PCCPP and PCTP. This may be due to the local strong bi-molecular associations due to high dipole moments. The association is assumed to be an overlapping head to tail

Table 3.1

Compounds	Molecular length from model Kit(L)	Apparent molecular length (average) (l)	l/L
PCCPP	21	26.24	1.25
PCTP	20.4	26.2	1.28
PBBA	20.5	22	1.07

nature having a tendency to local layer formation. Similar results have been found in other nematics[1-3].

Normalised Orientational Distribution Function and Order Parameter $\langle P_2 \rangle$ and $\langle P_4 \rangle$.

For the three samples the normalised orientational distribution function $f(\beta)$ were calculated using the procedure described earlier. The order parameter values $\langle P_2 \rangle$ and $\langle P_4 \rangle$ were also calculated. Table 3.2 - 3.10 show the detail values of the samples for intensity $I(\Psi)$, calculated intensity $I(\Psi)$ and normalised distribution $f(\beta)$ at different temperatures. The Fig. 3.7, 3.8 and 3.9 show the plot of $f(\beta)$ Vs β at different temperatures.

The procedure for calculating $\langle P_2 \rangle$ and $\langle P_4 \rangle$ values have already been described. The $\langle P_2 \rangle$ and $\langle P_4 \rangle$ values of the samples are calculated from the distribution

function with Vainstein approximations and with Leadbetters' approximations. Fig. 3.10 - 3.12 show the variation of $\langle P_2 \rangle$ and $\langle P_4 \rangle$ values with temperature determined by different techniques.

3.1.4. Optical birefringence study:

The procedure for measuring the refractive indices (n_o, n_e) and density have already been described. The refractive indices (n_o, n_e) of the three compounds at different temperature and for different wave lengths atxdifferent are given in Table 3.11 - 3.13 respectively. Fig. 3.13 - 3.15 shows the variation of (n_o, n_e) with temperatures for different wavelengths for the compounds and Fig. 3.16 - 3.18 shows the variation of Δn with the wavelength of the samples I, II and III respectively. The principal polarizabilities (α_o , α_e) fxr from refractive index data were calculated by using both Vuk's formula and Neugebauer's relations. The orientational order parameters $\langle P_2 \rangle$ was calculated by using the relation $\langle P_2 \rangle = \frac{\alpha_e - \alpha_o}{\alpha_{11} - \alpha_\perp}$ Haller's[4] extrapolation procedure is used to get $\alpha_{11} - \alpha_\perp$ Table 3.14 - 3.19 shows the detail results of the three samples.

From bond polarizability values the mean polarizability α and $\alpha_{11} - \alpha_\perp$ was calculated using the values given in the paper by Le Feveres'[5,6] and by Dunmur and Tomes[7]. The results are given in Table 3.20.

Table 3.20

α and ($\alpha_{\parallel} - \alpha_{\perp}$) comparisons of Sample I, II and III

Sample No.	$\alpha \times 10^{24}$ cm^3		($\alpha_{\parallel} - \alpha_{\perp}$) $\times 10^{24}$ cm^3		
	Calculated from bond polarisability	Vuk's/ Neugebauers approach	Calculated from bond polarizability.	Haller's process (Vuk's data)	Haller's process (Neugebauer data)
I	44.56		21.74	27.00	21.32
II	47.21		32.16	40.02	32.80
III	36.88	36.02	18.75	28.00	19.00

3.1.5. Discussion on $\langle P_L \rangle$ values obtained from Different Techniques:

The orientational order parameters of the compounds obtained from X-ray diffraction and bi-refringence methods have been compared with the Maier-Saupe (M$) theoretical values. The samples PCCPP and PCTP are breaking at higher temperatures so appr experimental results at higher temperature i.e. near the transition temperature are not available.

Sample - I (PCCPP)

Fig. 3.19 shows the $\langle P_2 \rangle$ values of the sample. The $\langle P_2 \rangle$ values obtained from X-ray and R.I. data are in well agreement, but both the values are slightly lower than M.S. theoretical values mainly in the higher temperature near the

transition point. This type of results have already been reported[8,9]. The $\langle P_4 \rangle$ values from X-ray data is lower than that of M.S. theoretical values which also obtained by many others also[10-13].

Sample II (PCTP

The comparison of $\langle P_2 \rangle$ values determined by X-ray and R.I. methods with M.S. theoretical values are shown in Fig. 3.10. All the values shows a good agreement. Curiously enough $\langle P_4 \rangle$ values from X-ray data also agreed well with the M.S. values for this sample. Repeatation of the experiments confirm this.

Sample III (PBBA)

The order parameter values of the compound PBBA are compared with that obtained by different workers of our laboratory[14-16] for other Schiff's base compounds namely EBBA, APAPA, BBBA and MBBA. The $\langle P_2 \rangle$ values of PBBA obtained from different methods viz. X-ray. R.I. are in good agreement with M.S. theoretical values like all other Schiff's base compounds as shown in Fig. 3.12. The $\langle P_4 \rangle$ values are significantly lower at all temperature than the theoretical values (Fig. 3.12). Similar discrepancy has already been observed by others[10-13].

For all the three compounds it has been found that the experimental determinations of order parameter both by X-ray and R.I. measurements agree well except near the transition temperatures. But agreement with (M.S.) theoretical values are not the same in all cases. This may be due to the fact that several types of intermolecular forces (such as dipole-dipole, interactions) are not considered in the M.S. theory. We see molecular associations in all the three cases. In PCOPP the ratio of l/b is larger than the other two compounds. It is a cyano compound and dipole-dipole interactions are responsible for molecular associations. But pairs of molecules are not parallel as is evident from Fig. 4.6. Rigid part of one pair has flexibles parts of the other molecular pair as its nearest neighbour The axes of the rigid part and the flexible parts are not parallel (Fig. 4.6). This may cause lowering of the order parameter value.

TABLE 3.2

Sample - I.

Experimental intensity values I(Ψ) at different temperature after background correction.

Degree	378.5	379.5	387.5	396	411.5	418.5	426	440	433	448
0	25.0	10.4	10.75	8.25	51.0	46.00	30.75	18.00	26	34.00
5	22.7	9.75	10.15	7.60	48.5	44.63	29.25	17.25	244.50	32.5
10	19.9	8.25	8.95	6.75	44.25	41.00	27.25	15.63	22.00	30.50
15	16.7	6.8	7.25	5.95	38.25	35.25	23.63	14.00	21.75	28.00
20	11.0	5.45	5.90	4.90	32	28.63	19.75	11.63	16.25	24.75
25	8.2	4.65	4.45	3.80	26.5	22.25	17.38	9.88	13.00	20.75
30	6.2	3.25	3.20	2.75	20.75	16.50	11.88	8.10	10.25	16.75
35	4.6	2.35	2.35	1.95	15.25	12.13	8.38	6.25	7.25	13.00
40	2.9	1.60	1.60	1.25	7.55	8.63	6.25	4.75	4.75	10.25
45	1.6	0.90	0.90	0.70	4.75	6.13	4.38	3.25	3.50	7.75
50	0.6	0.25	0.35	0.35	2.75	4.13	3.00	2.00	2.50	5.00
55	0.2	0.05	0	0.10	0.5	2.63	1.88	1.13	1.75	3.25
60	0	0	0	0	0	1.63	1.30	0.50	1.50	1.50
65	0	0	0	0	0	1.00	0.63	0.25	0.75	0.75
70	0	0	0	0	0	0.63	0.25	0.01	0.50	0.25
75	0	0	0	0	0	0.38	0	0	0.25	0
80	0	0	0	0	0	0.25	0	0	0	0
85	0	0	0	0	0	0.25	0	0	0	0
90	0	0	0	0	0	0	0	0	0	0

TABLE 3.2

Sample - I. Calculated intensity values I(Ψ) at different temperatures.

(Degree)	370.5	379.5	387.5	396	411.5	418.5	426	433	440	448
0	24.609	10.266	10.677	8.029	50.619	46.030	30.559	25.469	17.878	33.376
5	23.345	9.752	10.207	7.736	48.862	44.683	29,712	24.838	17.314	32.818
10	20.012	8.440	8.964	6.953	44.258	40.870	27.364	23.026	15.811	30.923
15	15.725	6.853	7.349	5.901	38.289	35.234	23.989	20.26	13.807	28.021
20	11.633	5.440	5.760	4.796	32.198	28.697	20.102	16.885	11.734	24.455
25	8.408	4.338	4.413	3.762	26.354	22.229	16.104	13.311	9.815	20.611
30	6.087	3.411	3.314	2.824	20.520	16.569	12.288	9.945	8.051	16.826
35	4.357	2.496	2.375	1.978	14.597	12.052	8.909	7.106	6.360	13.322
40	2.916	1.579	1.546	1.249	9.049	8.634	6.180	4.956	4.725	10.194
45	1.677	0.794	0.853	0.683	4.635	6.076	4.194	3.471	3.230	7.456
50	0.728	0.273	0.357	0.309	1.835	4.141	2.854	2.493	1.998	5.11
55	0.157	0.035	0.078	0.108	0.524	2.689	1.943	1.821	1.102	3.183
60	-0.058	-0.011	-0.024	0.026	0.150	1.656	1.258	1.302	0.530	1.714
65	-0.054	0.014	-0.028	0.003	0.135	0.979	0.709	0.866	0.213	0.722
70	0.014	0.035	-0.004	0	0.144	0.575	0.394	0.509	0.062	0.171
75	0.048	0.028	0.010	-0.001	0.086	0.348	0.066	0.243	0.004	-0.038
80	0.030	0.004	0.008	-0.002	-0.007	0.226	-0.028	0.071	-0.009	-0.043
85	-0.009	-0.019	0	-0.002	-0.085	0.165	-0.43	-0.021	-0.008	0.022
90	-0.027	-0.028	-0.005	-0.003	-0.115	0.147	-0.039	-0.050	-0.006	0.056

(58)

TABLE 3.4

Sample II.

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

(Degree)	407.5	415	422.25	429.5	433	440	448	453.5	460.5	467.5	474.5
0	16.60	45.00	20.50	17.0	25.9	30.50	25.08	19.4	16.10	8.6	13.5
5	15.50	43.00	19.40	16.0	24.6	28.35	24.35	18.3	15.20	8.1	12.9
10	13.50	37.50	16.65	14.3	21.8	26.45	22.25	15.7	13.60	7.3	12.1
15	10.8	33.5	13.00	12.2	18.5	22.20	19.08	13.2	12.00	6.3	11.0
20	7.9	25.0	10.20	9.6	15.1	17.65	15.35	10.6	9.60	5.5	9.7
25	5.60	19.0	7.45	7.2	11.5	12.55	11.66	8.2	8.10	4.4	8.2
30	3.80	13.5	5.35	5.3	8.7	9.55	8.53	6.4	6.60	3.5	6.9
35	2.30	9.5	3.85	3.8	6.0	7.00	6.23	4.8	5.30	2.6	5.6
40	1.30	6.25	3.00	2.8	4.0	5.20	4.72	3.8	4.10	2.0	4.5
45	0.80	4.5	2.05	1.9	2.9	3.90	3.75	3.0	3.10	1.5	3.6
50	0.50	2.5	1.40	1.4	2.2	2.90	3.07	2.10	2.10	1.2	2.6
55	0.30	1.75	1.05	1.0	1.5	2.15	2.49	1.4	1.50	0.8	1.8
60	0.20	1.0	0.65	0.7	0.8	1.40	1.95	1.0	0.90	0.6	1.1
65	0.10	1.0	0.35	0.4	1.1	0.90	1.42	0.7	0.50	0.4	0.5
70	0.10	0.5	0.25	0.3	0	0.60	0.96	0.55	0.20	0.2	0.3
75	0	0.25	0.15	0.2	0	0.30	0.55	0.20	0	0	0
80	0	0	0.10	0.1	0	0.10	0.25	0.10	0	0	0
85	0	0	0.05	0	0	0	0.06	0	0	0	0
90	0	0	0	0	0	0	0	0	0	0	0

Table 3.5

Sample II.

Calculated intensity values I(Ψ) at different temperatures

(Degree)	407.5	415	422.5	429.5	433	440	448	453.5	460.5	467.5	474.5
0	16.442	44.645	20.406	16.793	25.618	30.055	25.089	19.173	15.920	8.45	13.326
5	15.652	43.031	19.390	16.167	24.670	29.055	24.362	18.320	15.335	8.167	13.030
10	13.546	38.582	16.714	14.459	22.108	26.236	22.244	16.075	13.787	7.412	12.203
15	10.755	32.305	13.268	12.089	18.612	22.110	19.076	13.187	11.765	6.403	11.001
20	7.950	25.431	9.965	9.55	14.404	17.436	15.351	10.405	9.756	5.351	9.615
25	5.560	18.994	7.328	7.227	11.470	13.016	11.666	8.136	8.024	4.369	8.206
30	3.712	13.598	5.411	5.312	8.520	9.431	8.535	6.396	6.580	3.482	6.875
35	2.355	9.417	4.011	3.837	6.113	6.870	6.225	5.009	5.313	2.692	5.656
40	1.400	6.349	2.923	2.741	4.260	5.254	4.706	3.831	4.145	2.022	4.547
45	0.781	4.185	2.059	1.947	2.924	3.947	3.747	2.834	3.077	1.499	3.530
50	0.433	2.718	1.407	1.38	1.996	2.976	3.076	2.045	2.157	1.115	2.602
55	0.271	1.853	0.951	0.978	1.322	2.132	2.502	1.465	1.421	0.829	1.780
60	0.198	1.153	0.646	0.686	0.786	1.428	1.949	1.046	0.873	0.592	1.097
65	0.148	0.765	0.434	0.466	0.360	0.893	1.418	0.726	0.489	0.384	0.586
70	0.096	0.486	0.277	0.296	0.075	0.522	0.941	0.466	0.240	0.211	0.254
75	0.045	0.269	0.159	0.166	-0.053	0.278	0.545	0.256	0.090	0.086	0.079
80	0.004	0.102	0.074	0.076	-0.061	0.122	0.250	0.100	0.007	0.009	0.012
85	-1.020	-0.006	0.023	0.023	-0.023	0.034	0.069	0.006	-0.034	-0.03	0
90	-0.028	-0.044	0.005	0.006	-0.002	0.005	0.007	-0.026	-0.009	-0.042	0

TABLE 3.6

Mean Intensity Value

Experimental intensity at values I(Ψ) at different temperatures ~~from comperative chart.~~ SAMPLE-III

Degree	296	303	308	313	318	323	328
0	6.32	6.65	5.30	4.92	5.03	4.65	4.10
5	6.01	6.18	5.03	4.57	4.82	4.50	3.94
10	5.49	5.69	4.46	4.15	4.47	4.25	3.67
15	4.70	4.70	3.83	3.64	4.04	3.85	3.34
20	3.83	4.13	3.26	3.18	3.53	3.41	2.97
25	2.99	3.35	2.66	2.71	3.06	2.95	2.61
30	2.28	2.63	2.01	2.19	2.55	2.50	2.20
35	1.73	2.03	1.58	1.81	1.92	2.01	1.84
40	1.30	1.54	1.14	1.41	1.59	1.65	1.52
45	1.00	1.18	0.84	1.13	1.29	1.33	1.42
50	0.78	0.89	0.66	0.87	1.05	1.02	1.05
55	0.61	0.65	0.50	0.62	0.82	0.80	0.86
60	0.50	0.45	0.39	0.47	0.63	0.61	0.69
65	0.38	0.30	0.28	0.32	0.46	0.48	0.51
70	0.26	0.18	0.23	0.21	0.28	0.35	0.39
75	0.18	0.13	0.17	0.13	0.15	0.26	0.22
80	0.11	0.07	0.11	0.10	0.09	0.19	0.18
85	0.05	0.04	0.09	0.03	0.05	0.13	0.11
90	0	0	0.05	0	0.03	0.10	0.04

TABLE 3.7

Mean Intensity value

Calculated intensity I (Ψ) at different temperatures. ~~from compared chart.~~ SAMPLE III

Degree	298	303	308	313	318	323	328
0	6.269	6.529	5.236	4.809	4.972	4.626	4.052
5	6.063	6.292	5.043	4.645	4.849	4.526	3.961
10	5.495	5.665	4.534	4.217	4.515	4.250	3.710
15	4.696	4.845	3.870	3.668	4.051	3.857	3.355
20	3.821	4.022	3.202	3.129	3.536	3.406	2.959
25	22994	3.289	2.599	2.655	3.012	2.942	2.568
30	2.289	2.648	2.063	2.231	2.488	2.486	2.205
35	1.727	2.076	1.580	1.827	2.017	2.050	1.875
40	1.302	1.572	1.161	1.443	1.600	1.650	1.579
45	0.993	1.159	0.838	1.105	1.290	1.304	1.316
50	0.773	0.850	0.622	0.834	1.020	1.022	1.083
55	0.614	0.629	0.468	0.629	0.818	0.800	0.877
60	0.489	0.462	0.397	0.470	0.653	0.624	0.690
65	0.378	0.325	0.315	0.337	0.455	0.478	0.521
70	0.272	0.209	0.234	0.224	0.295	0.354	0.370
75	0.175	0.119	0.161	0.132	0.170	0.252	0.245
80	0.95	0.056	0.106	0.066	0.086	0.175	0.151
85	0.042	0.021	0.073	0.027	0.040	0.129	0.094
~~90x~~ 90	~~0.042~~ 0.023	~~0.021x~~ 0.010	0.063	0.014	0.026	0.113	0.074

(57)

TABLE-3.8

Normalised distribution function $f(\beta)$ at different temperatures. SAMPLE-1

Degree	$f(\beta)$ at temperature in °K									
	370.5	379.5	387.5	396	411.5	418.5	426	433	440	448
0	12.499	11.045	10.625	7.763	9.590	8.160	5.696	9.003	5.54	5.368
5	11.752	10.241	10.045	8.055	8.586	7.834	6.255	7.899	6.046	5.454
10	9.785	8.437	8.535	8.457	6.548	6.977	7.513	5.810	7.132	5.543
15	7.290	6.325	6.641	7.861	4.899	5.847	7.942	4.324	7.431	5.262
20	5.009	4.589	4.889	5.909	4.065	4.672	6.249	3.742	5.649	4.442
25	3.341	3.410	3.542	3.729	3.801	3.578	3.724	3.672	3.385	3.377
30	2.277	2.661	2.595	2.293	3.582	2.622	2.052	3.423	1.972	2.484
35	1.613	2.103	1.905	1.588	2.844	1.837	1.326	2.506	1.423	1.911
40	1.134	1.506	1.321	1.248	1.654	1.239	1.106	1.381	1.361	1.570
45	0.706	0.828	0.780	0.927	0.691	0.816	1.047	0.672	1.427	1.291
50	0.336	0.296	0.351	0.488	0.233	0.531	0.859	0.376	1.169	0.943
55	0.109	0.062	0.112	0.147	0.033	0.339	0.495	0.284	0.576	0.556
60	0	0	0	0.025	0.029	0.208	0.303	0.270	0.733	0.262
65	0	0	0	0.003	0.014	0.120	0.078	0.239	0.043	0.109
70	0	0	0	0	0.008	0.065	0.04	0.140	0.014	0.047
75	0	0	0	0	0.006	0.034	0.034	0.033	0.008	0.038
80	0	0	0	0	0.005	0.019	0	0.013	0	0
85	0	0	0	0	0	0.012	0	0	0	0
90	0	0	0	0	0	0.011	0	0	0	0

TABLE 3.9

ple II.

Normalised distribution function f(β) at different temperatures.

Degree	f (β) at temperature in °K									
	407.5	415	422.5	429.5	433	440	448	453.5	467.5	474.5
0	17.652	12.787	14.989	11.908	8.274	11-511	10.642	12.385	10.443	10.341
5	14.026	10.630	12.362	10.093	8.306	9.770	8.937	10.306	8.686	8.515
10	8.150	6.886	7.754	6.801	8.112	6.609	5.935	6.626	5.614	5.411
15	4.802	4.506	4.763	4.567	7.138	4.466	4.013	4.216	3.665	3.542
20	3.702	3.667	3.527	3.650	5.373	3.589	3.346	8.253	2.990	2.994
25	3.663	3.642	3.188	3.444	3.542	3.391	3.356	3.079	3.070	3.231
30	3.509	3.510	2.930	3.186	2.245	3.125	3.241	2.985	3.851	3.497
35	2.344	2.528	2.182	2.334	1.514	2.279	2.367	2.369	2.777	2.867
40	0.0982	1.258	1.213	1.272	1.126	1.252	1.246	1.418	1.734	1.626
45	0.324	0.522	0.580	0.605	0.866	0.616	0.587	0.733	0.907	0.770
50	0.128	0.253	0.313	0.332	0.610	0.360	0.349	0.425	0.516	0.428
55	0.083	0.180	0.231	0.253	0.358	0.295	0.323	0.332	0.382	0.349
60	0.084	0.175	0.218	0.248	0.177	0.305	0.412	0.326	0.337	0.379
65	0.088	0.162	0.196	0.230	0.083	0.279	0.478	0.298	0.257	0.366
70	0.057	0.094	0.118	0.141	0.043	0.154	0.317	0.180	0.118	0.202
75	0.019	0.029	0.042	0.050	0	0.046	0.101	0.064	0.030	0.054
80	0.004	0.006	0.011	0.013	0	0.010	0.021	0.016	0.005	0.010
85	0	0.002	0.003	0.004	0	0.003	0.005	0.005	0	0
90	0	0	0.002	0.003	0	0.002	0.003	-	0	0

TABLE 3.10

Sample III.

Normalised distribution function f (β) at different temperature

Degree	f (β) values at temp. (^{o}K)						
	298	303	308	313	318	323	326
0	9.327	9.637	8.766	8.318	6.621	5.506	5.504
5	8.272	8.294	7.937	7.212	5.971	5.196	5.113
10	6.177	5.790	6.196	5.126	4.664	4.489	4.260
15	4.523	4.023	4.675	3.630	3.632	3.6784	3.473
20	3.661	3.282	3.747	3.007	3.148	3.279	2.979
25	3.263	3.155	3.215	2.938	3.017	2.928	2.704
30	2.836	3.053	2.725	2.928	2.848	2.573	2.448
35	2.096	2.456	2.065	2.481	2.320	2.103	2.054
40	1.277	1.532	1.350	1.662	1.573	1.568	1.560
45	0.722	0.835	0.816	0.974	0.981	1.108	1.229
50	0.461	0.498	0.519	0.611	0.667	0.795	0.850
55	0.375	0.382	0.383	0.479	0.550	0.609	0.703
60	.369	0.358	0.325	0.444	0.519	0.492	0.616
65	0.350	0.319	0.281	0.393	0.456	0.390	0.509
70	0.250	0.204	0.213	0.259	0.298	0.279	0.332
75	0.122	0.083	0.132	0.114	0.135	0.178	0.198
80	0.048	0.027	0.074	0.040	0.050	0.108	0.102
85	0.021	0.010	0.045	0.016	0.022	0.073	0.059
90	0.015	0.007	0.037	0.011	0.016	0.063	0.048

TABLE 3.11

Refractive indices (n_o, n_e) at different temperatureof sample I

Temp.	6907 Å		5780 Å		5461 Å		4758 Å		Mean
(^oC)	n_o	n_e	n_o	n_e	n_o	n_e	n_o	n_e^b	P_2
90	1.545	1.781	1.551	1.784	1.551	1.796	1.557	1.835	.746
98	1.548	1.780	1.551	1.784	1.554	1.793	1.557	1.832	.743
107	1.550	1.780	1.551	1.784	1.554	1.790	1.557	1.832	.741
115	1.553	1.778	1.554	1.778	1.557	1.790	1.562	1.825	.726
123	1.557	1.775	1.557	1.775	1.562	1.787	1.569	1.825	.71
131	1.560	1.775	1.557	1.775	1.562	1.784	1.569	1.814	.693
139	1.560	1.770	1.559	1.773	1.566	1.780	1.575	1.814	.681
146	1.563	1.770	1.562	1.773	1.569	1.778	1.580	1.808	.663
153	1.565	1.768	1.566	1.769	1.573	1.775	1.580	1.796	.65
160	1.563	1.763	1.569	1.767	1.573	1.774	1.587	1.793	.622
167	1.567	1.763	1.573	1.764	1.578	1.774	1.589	1.793	.614
175	1.569	1.760	1.578	1.762	1.580	1.764	1.599	1.784	.582
181	1.575	1.760	1.578	1.760	1.593	1.760	1.599	1.772	.55
188	1.580	1.750	1.593	1.750	1.605	1.754	1.580	1.758	.501
195	1.580	1.748	1.580	1.748	1.605	1.748	1.605	1.748	.471

TABLE 3.12

Refractive indices (n_o, n_e) at different temperatures of sample II

Temp. in °C	6907 Å		5780 Å		5461 Å		4758 Å	
	n_o	n_e	n_o	n_e	n_o	n_e	n_o	n_e
123	1.461	1.758	1.477	1.776	1.477	1.782	1.495	1.865
135	1.461	1.753	1.477	1.764	1.477	1.776	1.495	1.865
142	1.461	1.747	1.477	1.758	1.477	1.764	1.495	1.859
149	1.465	1.747	1.478	1.759	1.477	1.764	1.495	1.859
153	1.465	1.734	1.480	1.747	1.477	1.758	1.495	1.847
153	1.465	1.728	1.486	1.747	1.477	1.758	1.495	1.847
160	1.465	1.722	1.486	1.74	1.477	1.753	1.495	1.845
167	1.465	1.722	1.486	1.727	1.486	1.743	1.504	1.845
175	1.465	1.722	1.486	1.727	1.489	1.743	1.510	1.842
181	1.474	1.713	1.486	1.725	1.495	1.737	1.516	1.829
188	1.486	1.710	1.492	1.722	1.495	1.731	1.519	1.824
195	1.492	1.701	1.495	1.719	1.498	1.722	1.522	1.820
202	1.495	1.695	1.501	1.713	1.504	1.722	1.528	1.812
216	1.498	1.69	1.504	1.710	1.507	1.719	1.54	1.803
222	1.501	1.683	1.51	1.707	1.513	1.713	1.546	1.797
232	1.54		1.551		1.555		1.599	

Table 3.13

Refractive indices (n_o, n_e) at different temperatures of PBMA

Temp. (°C)	λ = 6907 Å		λ = 5790 Å		λ = 5461 Å		λ = 4358 Å	
	n_o	n_e	n_o	n_e	n_o	n_e	n_o	n_e
27.7	1.538	1.768	1.550	1.779	1.560	1.792	1.588	1.878
32	1.538	1.764	1.550	1.775	1.560	1.788	1.588	1.872
36	1.540	1.758	1.552	1.770	1.562	1.783	1.590	1.866
40	1.542	1.750	1.554	1.765	1.562	1.776	1.592	1.860
44	1.544	1.744	1.558	1.759	1.566	1.769	1.594	1.850
48	1.550	1.736	1.562	1.750	1.570	1.761	1.597	1.839
52	1.555	1.727	1.567	1.740	1.574	1.750	1.602	1.826
56	1.561	1.713	1.573	1.726	1.580	1.735	1.607	1.805
57	1.564	1.707	1.576	1.720	1.582	1.728	1.611	1.795
57.5(Iso)	1.590		1.602		1.612		1.660	
60	1.588		1.600		1.610		1.658	
62	1.586		1.598		1.608		1.656	

Table - 3.14: Density (ρ) Polarizability (α) and Orientational order Parameters P_2 of sample I (Vuks' approach)

Temp °C	Density (ρ) in gm/cm^3	6907 Å			5780 Å			5461 Å			4358 Å			Mean
		α_o	α_e	$\langle P_2 \rangle$	α_o	α_e	$\langle P_2 \rangle$	α_o	α_e	$\langle P_2 \rangle$	α_o	α_e	$\langle P_2 \rangle$	$\langle P_2 \rangle_{AV}$
90	1.098	35.92	56.25	.750	36.28	56.34	.743	36.17	57.27	.754	36.19	60.15	.753	.748
98	1.090	36.39	56.51	.742	36.55	56.75	.748	36.66	57.38	.740	36.48	60.35	.750	.745
107	1.083	36.75	56.83	.740	36.78	57.12	.750	36.92	57.51	.735	36.72	60.74	.750	.743
115	1.073	37.32	57.12	.731	37.42	56.78	.717	37.46	57.97	.732	37.45	60.62	.729	.727
123	1.067	37.82	57.10	.711	37.82	57.10	.714	38.03	57.93	.711	38.12	60.77	.712	.712
131	1.061	37.23	57.38	.705	38.14	56.46	.678	38.27	58.02	.705	38.44	60.24	.655	.693
139	1.053	38.57	57.63	.694	38.57	56.84	.676	38.87	58.03	.684	39.13	60.53	.673	.681
146	1.047	38.99	58.03	.688	38.99	57.09	.670	39.39	57.48	.646	39.74	60.26	.645	.662
153	1.036	39.56	58.12	.681	39.71	67.35	.653	40.03	58.39	.655	40.29	59.92	.617	.651
160	1.028	39.78	58.47	.676	40.25	57.47	.638	40.55	57.12	.592	41.11	59.95	.593	.625
167	1.020	40.37	58.47	.668	40.87	57.57	.618	41.22	57.44	.579	41.56	60.37	.591	.614
175	1.012	40.86	58.63	.656	41.67	56.89	.564	41.68	57.84	.577	42.68	59.83	.539	.584
181	1.022	41.68	59.05	.641	42.21	56.45	.527	43.05	57.74	.524	43.23	59.42	.509	.550
188	0.995	42.27	58.71	.606	42.90	54.77	.440	43.35	58.15	.501	44.15	58.17	.465	.503
195	0.989	42.71	58.67	.589	43.22	54.59	.421	44.55	57.51	.463	44.55	57.51	.407	.470

and are in 10^{-24} cm^3

TABLE 3.15

Density (ρ), Polarizability (α) and Orientational Order Parameters ($\langle P_2 \rangle$) of Sample II

Temp. in °C	Density in gm/cm	6907 Å		5780 Å		5461 Å		4758 Å		Mean
		α_o	α_e	α_o	α_e	α_o	α_e	α_o	α_e	$\langle P_2 \rangle$
123	0.980	36.43	67.12	37.49	68.36	37.43	68.93	37.98	76.21	.755
135	0.976	36.62	66.92	37.77	67.50	37.65	68.64	38.14	76.52	.737
142	0.975	36.72	66.41	37.86	66.99	37.80	67.57	38.24	76.05	.722
149	0.972	37.15	66.50	38.10	66.79	37.92	67.78	38.35	76.27	.712
153	0.971	37.31	65.32	38.36	66.13	38.02	67.27	38.52	75.20	.685
157	0.971	37.37	64.75	38.84	65.96	38.02	67.27	38.52	75.20	.665
160	0.969	37.51	64.31	38.99	65.43	38.15	66.93	38.62	75.17	.653
167	0.966	37.62	64.51	39.29	64.39	39.08	65.92	39.43	75.11	.638
175	0.963	37.74	64.71	39.35	64.68	39.44	66.04	40.05	74.86	.641
181	0.961	38.63	63.72	39.46	64.53	40.05	65.42	40.73	73.58	.615
188	0.958	39.74	63.29	40.09	64.27	40.24	65.05	41.15	73.24	.586
195	0.955	40.44	62.45	40.49	64.10	40.70	64.30	41.55	73.00	.559
202	0.951	40.91	62.05	41.21	63.62	41.35	64.40	42.29	72.34	.539
216	0.944	41.51	61.94	41.79	63.71	41.94	64.50	43.65	71.62	.522
222	0.939	42.05	61.50	42.53	63.59	42.71	64.09	44.42	71.23	.497

α_o, α_e are in 10^{-24} cm^3 and calculated from Vuk's formula.

TABLE 3.16

Density (ρ), Polarisability (α) and Orientational Order Parameter ($\langle P_2 \rangle$) of Sample III (Vuk's approach)

Temp. (°C)	Density (ρ) (gm/cm^3)	λ = 6907 Å			λ = 5780 Å			λ = 5461 Å			λ = 4358 Å		
		α_o	α_e	$\langle P_2 \rangle$	α_o	α_e	$\langle P_2 \rangle$	α_o	α_e	$\langle P_2 \rangle$	α_e	α_o	$\langle P_2 \rangle$
27.7	1.165	29.71	46.26	.6191	30.27	46.73	.6157	30.71	47.36	.6163	31.49	52.30	.6161
32	1.163	29.80	46.08	.6096	30.36	46.55	.6062	30.79	47.19	.6069	31.50	52.00	.6046
36	1.158	30.08	45.85	.5891	30.63	46.38	.5891	31.07	47.02	.5900	31.89	51.79	.5893
40	1.155	30.30	45.36	.5668	30.83	46.10	.5716	31.18	46.65	.5674	32.10	51.45	.5757
44	1.151	30.59	45.12	.5437	31.23	45.82	.5458	31.58	46.31	.5447	32.42	51.00	.5494
48	1.149	31.03	44.55	.5067	31.57	45.23	.5119	31.92	45.79	.5140	32.73	50.29	.5209
52	1.140	31.62	44.21	.4710	32.17	44.82	.4733	32.48	45.34	.4759	33.37	49.72	.4844
56	1.120	32.64	43.94	.4230	33.20	44.57	.4253	33.58	45.03	.4259	34.41	49.10	.4329
57	1.100	33.45	44.27	.4012	34.03	44.91	.4036	34.30	45.33	.4047	35.35	49.24	.4076
58	1.068(Iso)												

α_e and α_o are in units 10^{-24} cm^3

TABLE 3.17

Polarisabilities (α_o , α_e) of sample – I Using Neugebauer's relations

Temp. in ^oC	6907 Å		5780 Å		5461 Å		4758 Å		Mean
	α_o	α_e	α_o	α_e	α_o	α_e	α_o	α_e	P_2
90	37.29	53.52	37.64	53.62	37.61	54.40	37.86	56.81	.746
98	37.75	53.80	37.91	54.01	38.07	54.55	38.14	57.03	.743
107	38.11	54.12	38.16	54.36	38.32	54.71	38.39	57.40	.741
115	38.65	54.44	38.72	54.16	38.86	55.17	39.07	57.39	.726
123	39.12	54.49	39.12	54.48	39.39	53.20	39.71	57.59	.71
131	39.53	54.75	39.38	53.99	39.62	55.32	39.96	57.19	.693
139	39.84	54.83	39.80	54.37	40.18	55.41	40.63	57.53	.681
146	40.26	55.10	40.22	54.64	40.63	55.09	41.19	57.38	.663
153	40.81	55.51	40.90	54.95	41.29	55.07	41.66	57.18	.65
160	41.02	55.63	41.42	55.13	41.68	54.87	42.43	57.31	.622
167	41.60	56.01	42.01	55.29	42.32	55.22	42.89	57.72	.614
175	42.06	56.21	42.70	54.82	42.79	55.63	43.89	57.41	.582
181	42.67	56.68	43.17	54.53	44.06	55.71	44.37	57.15	.55
188	43.39	56.47	43.69	53.19	44.37	56.10	45.13	56.21	.501
195	43.80	56.50	43.98	53.08	45.45	55.71	45.45	55.71	.471

α_o, α_e are in $10^{-24} cm^{-3}$ unit

TABLE 3.18

Polarizability at different temperature of the sample II using Neuguebauer method.

Temp. in °C	6907 Å		5780 Å		5461 Å		4758 Å		Mean
	α_o	α_e	α_o	α_e	α_o	α_e	α_o	α_e	P_2
123	38.29	63.39	39.42	64.51	39.41	64.99	40.51	71.15	.758
135	38.46	63.25	39.61	63.81	39.58	64.77	40.67	71.45	.736
142	38.51	62.83	39.67	63.39	39.65	63.87	40.73	71.05	.720
149	38.93	62.94	39.87	63.24	39.77	64.07	40.86	71.26	.710
153	39.00	61.94	40.08	62.70	39.83	63.65	40.93	70.38	.682
157	39.02	61.46	40.52	62.58	39.83	63.65	40.93	70.39	.663
160	39.11	61.09	40.63	62.15	39.93	63.38	41.01	70.37	.653
167	39.24	61.28	40.79	61.29	40.74	62.58	41.79	70.38	.637
175	39.36	61.47	40.91	61.56	41.09	62.72	42.37	70.22	.641
181	40.14	60.69	41.01	61.45	41.64	62.25	42.92	69.20	.615
188	41.18	60.41	41.59	61.28	41.79	61.96	43.29	68.95	.586
195	41.78	59.76	41.96	61.17	42.17	61.36	43.66	68.78	.557
202	42.21	59.46	42.60	60.83	42.80	61.51	44.30	68.31	.541
216	42.76	59.44	43.15	60.38	43.35	61.67	45.54	67.84	.520
222	43.24	59.13	43.85	60.96	44.05	61.39	46.24	67.60	.495

α_o and α_e are in 10^{-24} cm^{-3} unit.

TABLE 3.19

Polarisability (α) and order parameter ($\langle P_2 \rangle$) for Sample III (PBBA)
(Using Neugebauer's relation)

Temp. (^oC)	λ = 6907 Å			λ = 5780 Å			λ = 5461 Å			λ = 4358 Å		
	α_o	α_e	$\langle P_2 \rangle$	α_o	α_e	$\langle P_2 \rangle$	α_o	α_e	$\langle P_2 \rangle$	α_o	α_e	$\langle P_2 \rangle$
27.7	30.81	44.07	.6143	31.38	44.51	.6146	31.85	45.09	.6181	33.01	49.26	.6128
32.0	30.87	43.87	.6054	31.44	44.37	.6067	31.91	44.94	.6102	33.08	49.03	.6034
36.0	31.12	43.76	.5893	31.69	44.28	.5919	32.16	44.84	.5960	33.34	48.89	.5904
40.0	31.29	43.37	.5657	31.86	44.04	.5761	32.23	44.54	.5803	33.50	48.63	.5766
44.0	31.55	43.21	.5479	32.21	43.86	.5530	32.59	44.30	.5546	33.77	48.29	.5559
48	31.92	42.77	.5135	32.49	43.39	.5208	32.87	43.90	.5252	34.00	47.74	.5288
52.0	32.45	42.55	.4811	33.03	43.13	.4861	33.35	43.59	.4910	34.55	47.36	.4960
56.0	33.38	42.45	.4367	33.96	43.05	.4481	34.30	43.47	.4448	35.47	46.99	.4520
57.0	34.16	42.85	.4200	34.76	43.46	.4250	35.05	43.84	.4280	36.35	47.25	.4300

α_o and α_e are in 10^{-24} cm^{-3} unit.

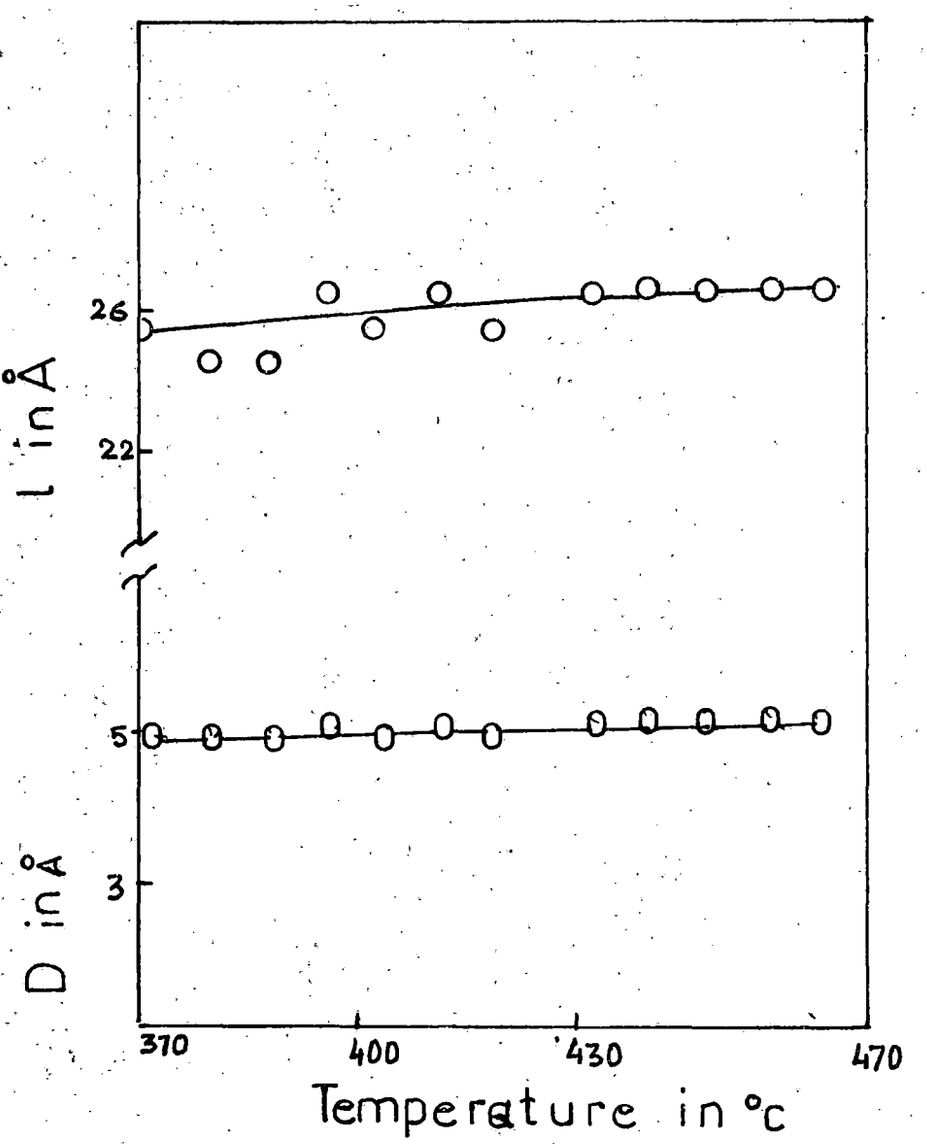


Fig. 3.4

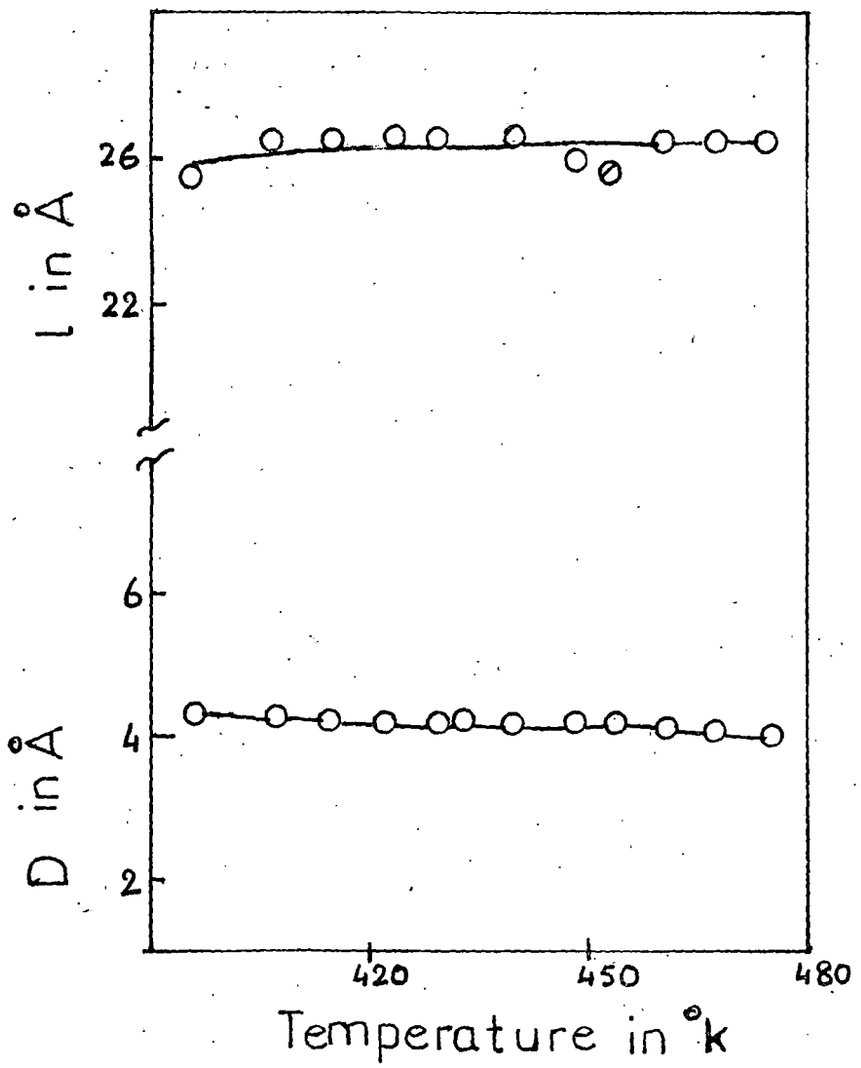


Fig. 3.5

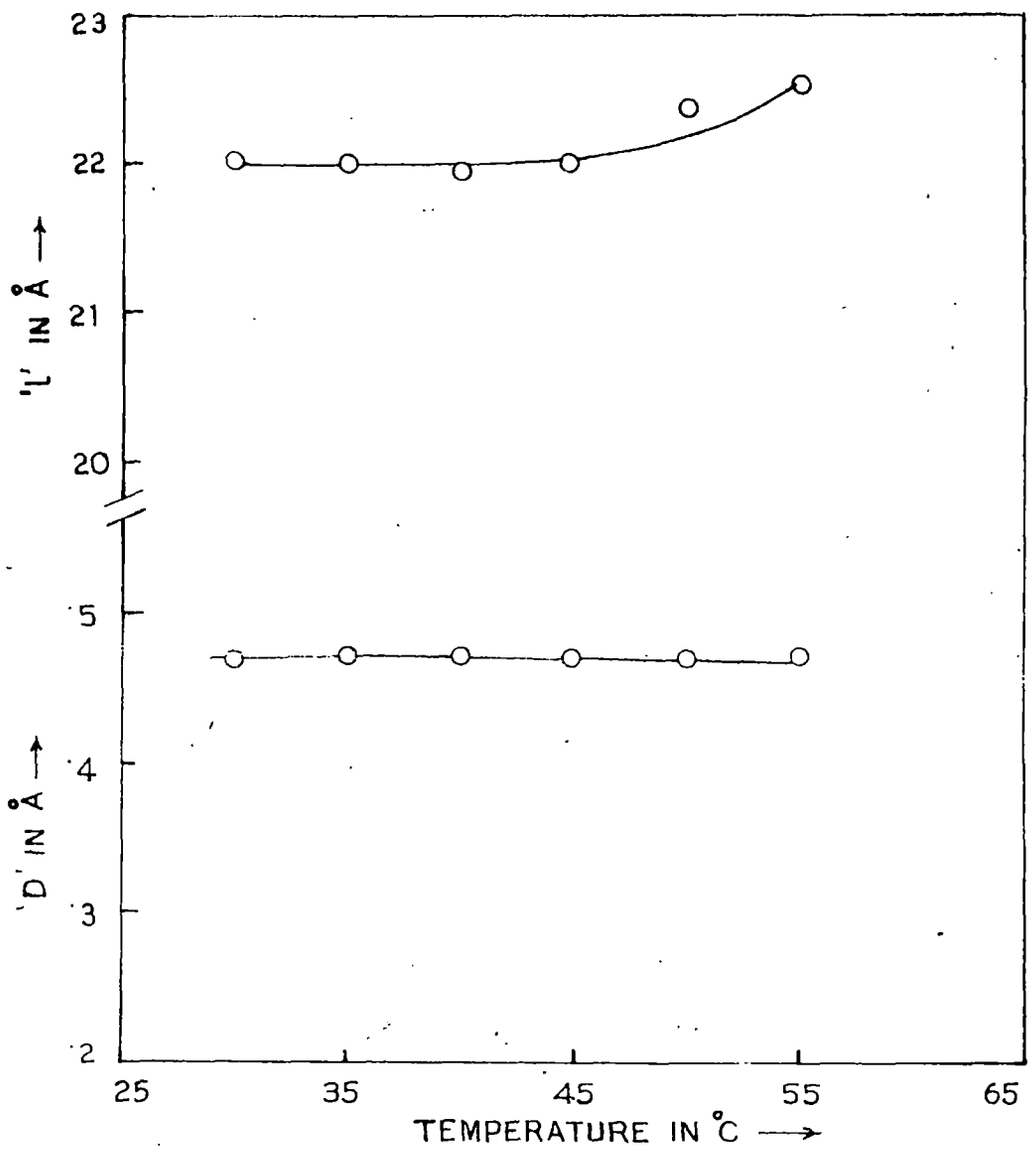


Fig. 3.6

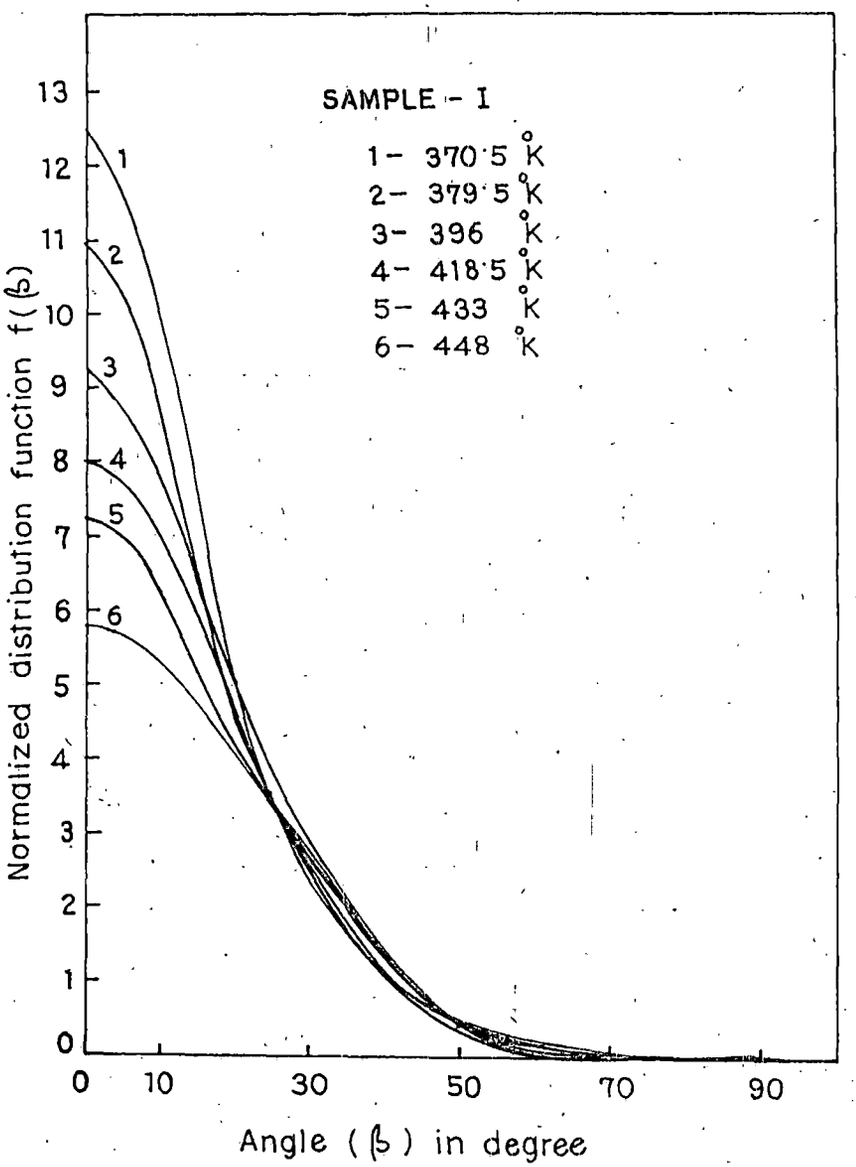

SAMPLE - I
1- 370·5 °K
2- 379·5 °K
3- 396 °K
4- 418·5 °K
5- 433 °K
6- 448 °K
Normalized distribution function f(β)
Angle (β) in degree
0
1
2
3
4
5
6
7
8
9
10
11
12
13
0
10
30
50
70
90

Fig. 3.7

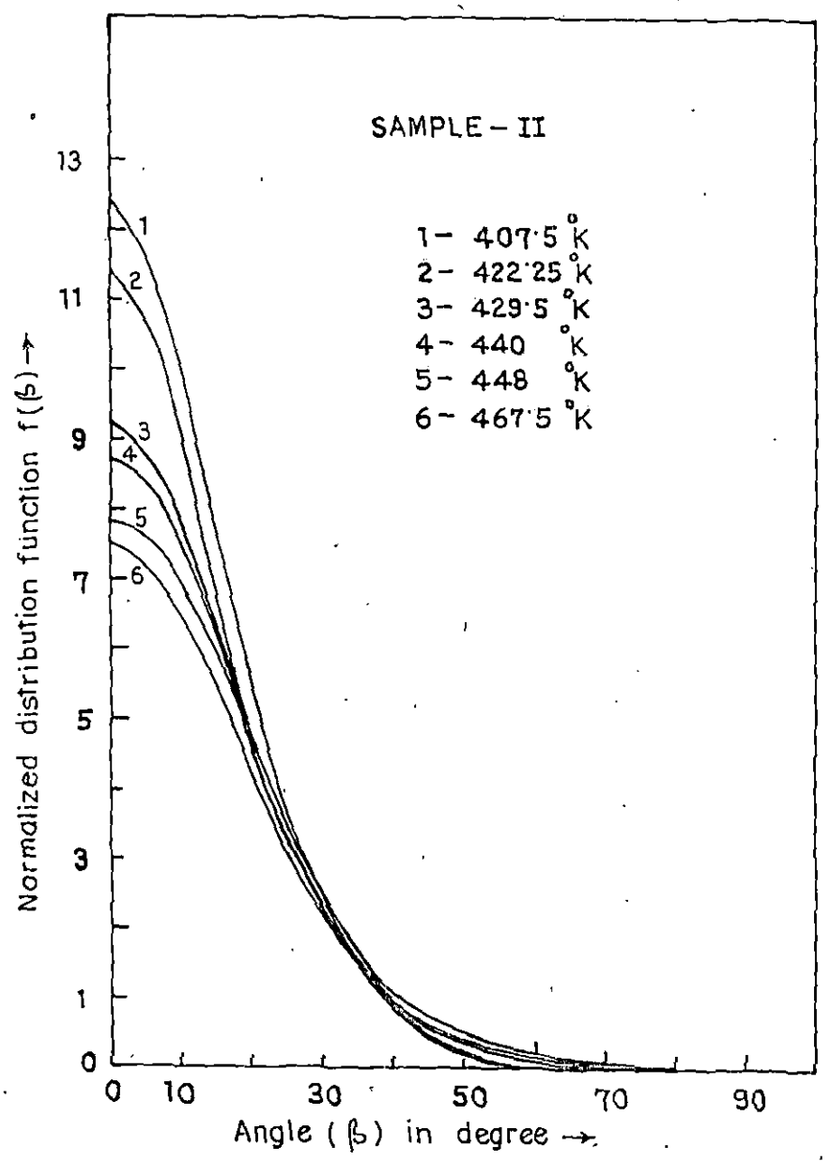

SAMPLE – II
1– 407·5 °K
2– 422·25 °K
3– 429·5 °K
4– 440 °K
5– 448 °K
6– 467·5 °K
Normalized distribution function f(β)→
Angle (β) in degree →
0
1
3
5
7
9
11
13
10
30
50
70
90

Fig. 3.8

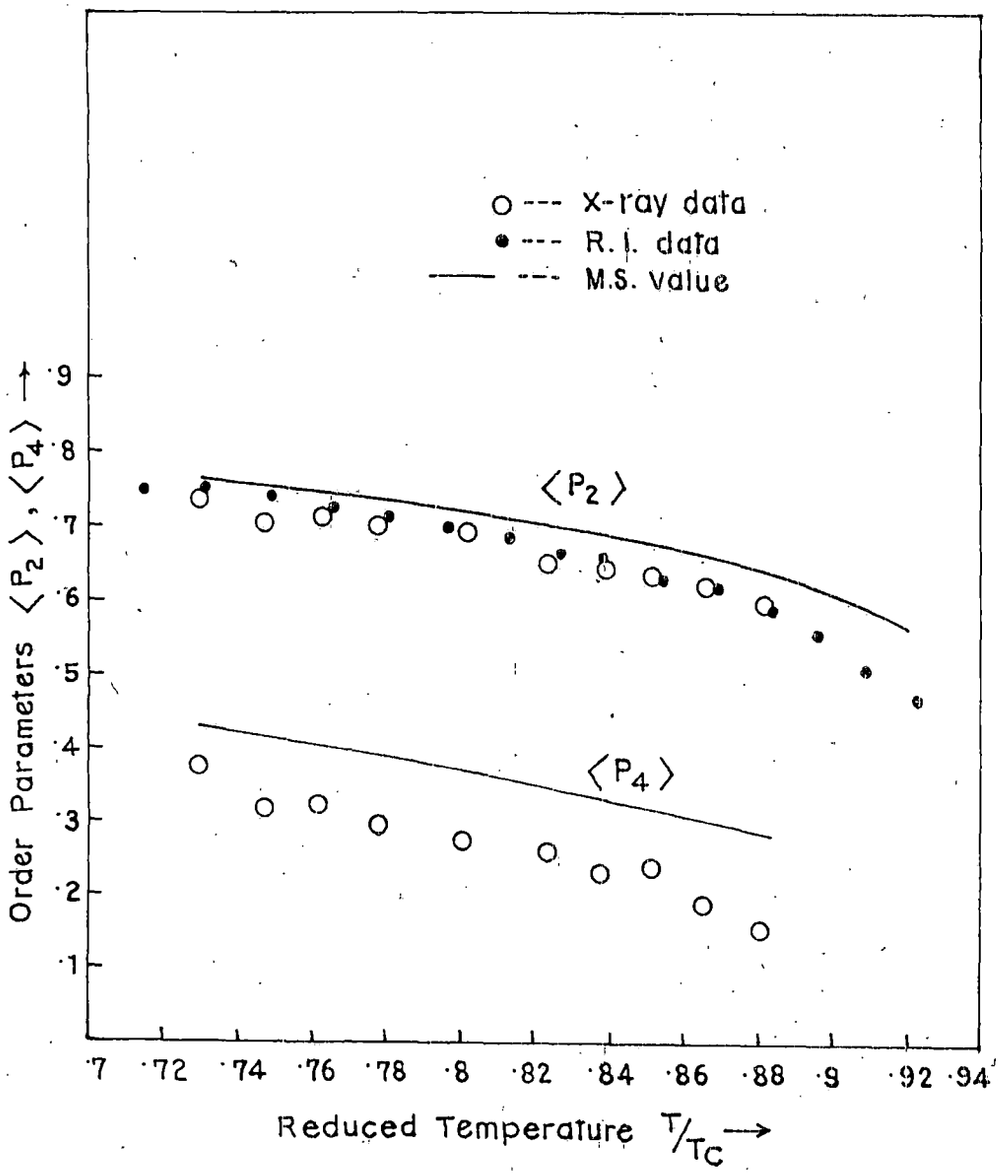

O --- X-ray data
• --- R.I. data
—— --- M.S. value
⟨P2⟩
⟨P4⟩
Order Parameters ⟨P2⟩, ⟨P4⟩ →
·9
·8
·7
·6
·5
·4
·3
·2
·1
·7
·72
·74
·76
·78
·8
·82
·84
·86
·88
·9
·92
·94
Reduced Temperature T/Tc →

Fig. 3.10

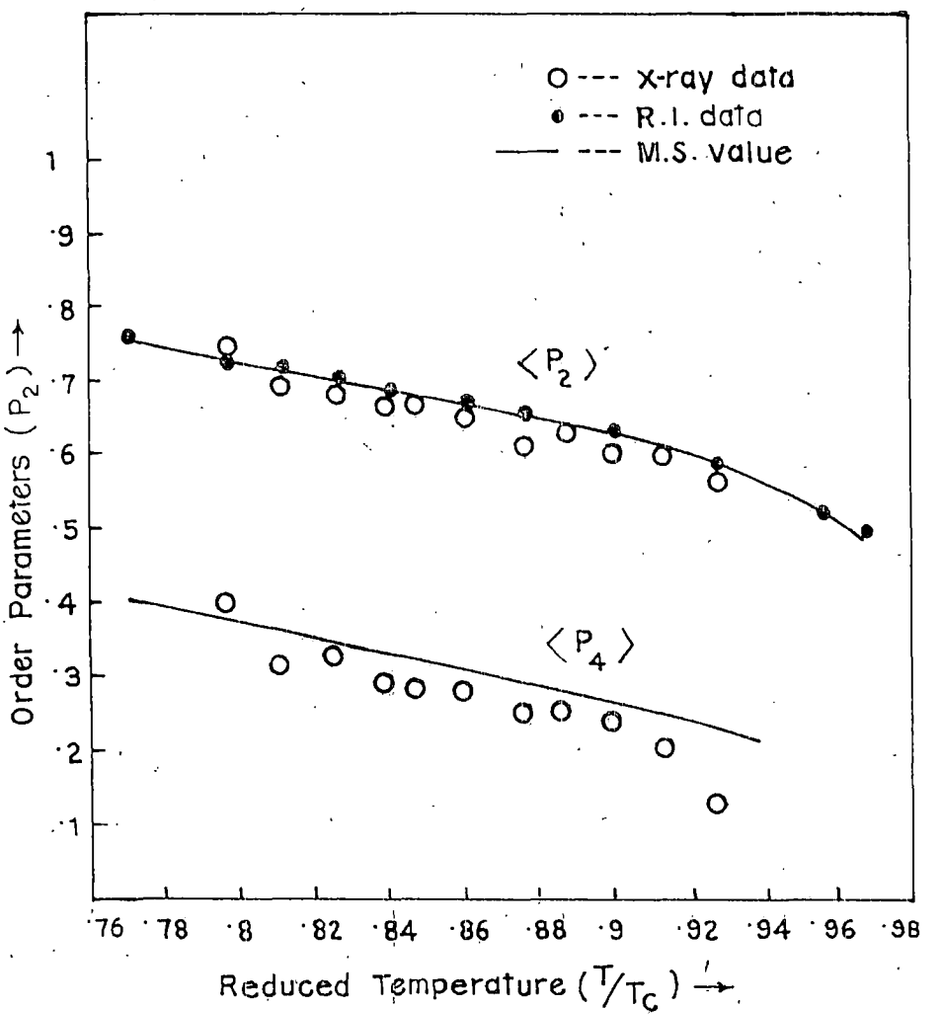

O --- X-ray data
• --- R.I. data
—— --- M.S. value
Order Parameters (P_2) →
1
·9
·8
·7
·6
·5
·4
·3
·2
·1
$\langle P_2 \rangle$
$\langle P_4 \rangle$
·76 ·78 ·8 ·82 ·84 ·86 ·88 ·9 ·92 ·94 ·96 ·98
Reduced Temperature (T/T_C) →

Fig. 3.11

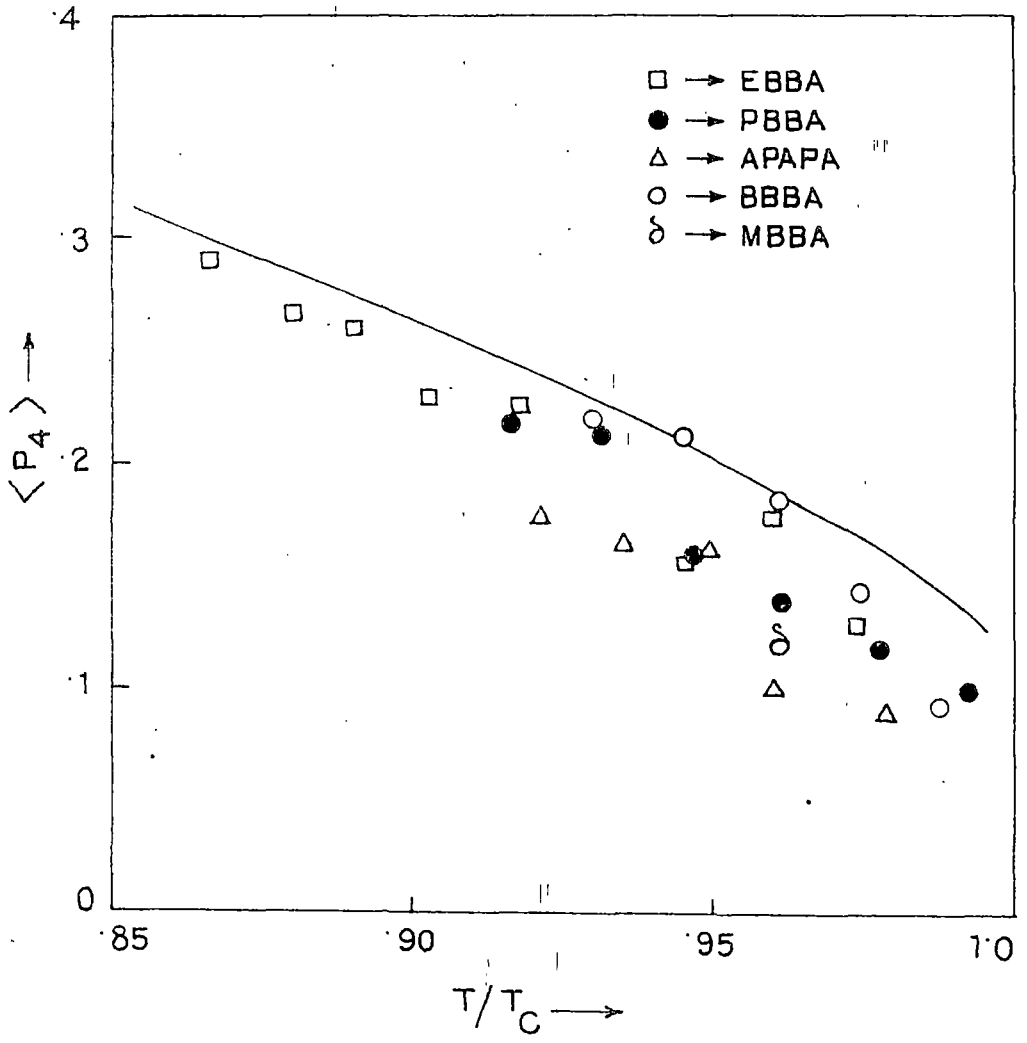


Fig 3.12

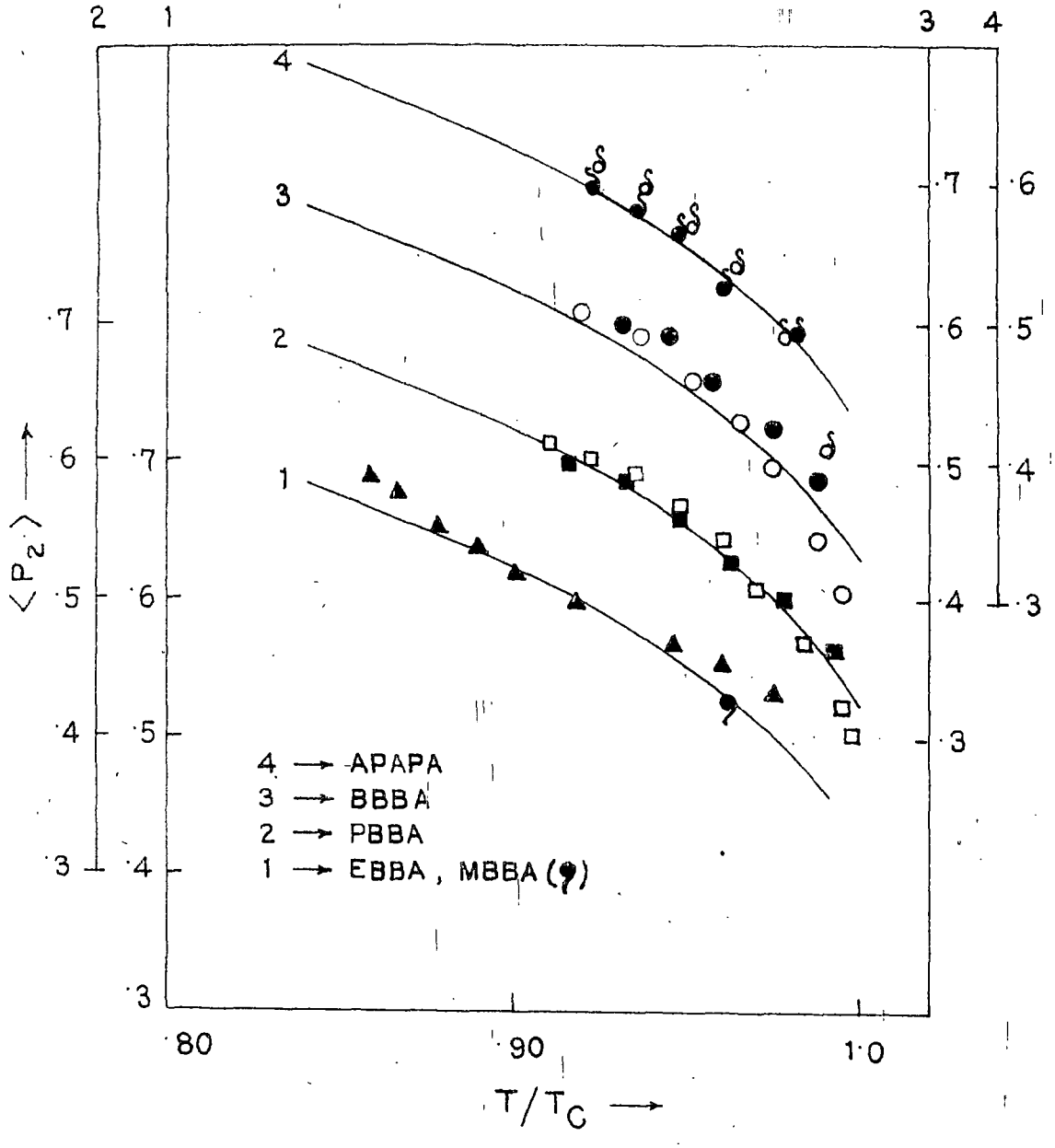

2 1
3 4
4
3
2
1
$\langle P_2 \rangle$
·7
·6
·5
·4
·3
·80
·90
1·0
T/T_C →
4 → APAPA
3 → BBBA
2 → PBBA
1 → EBBA , MBBA (?)

Fig 12a

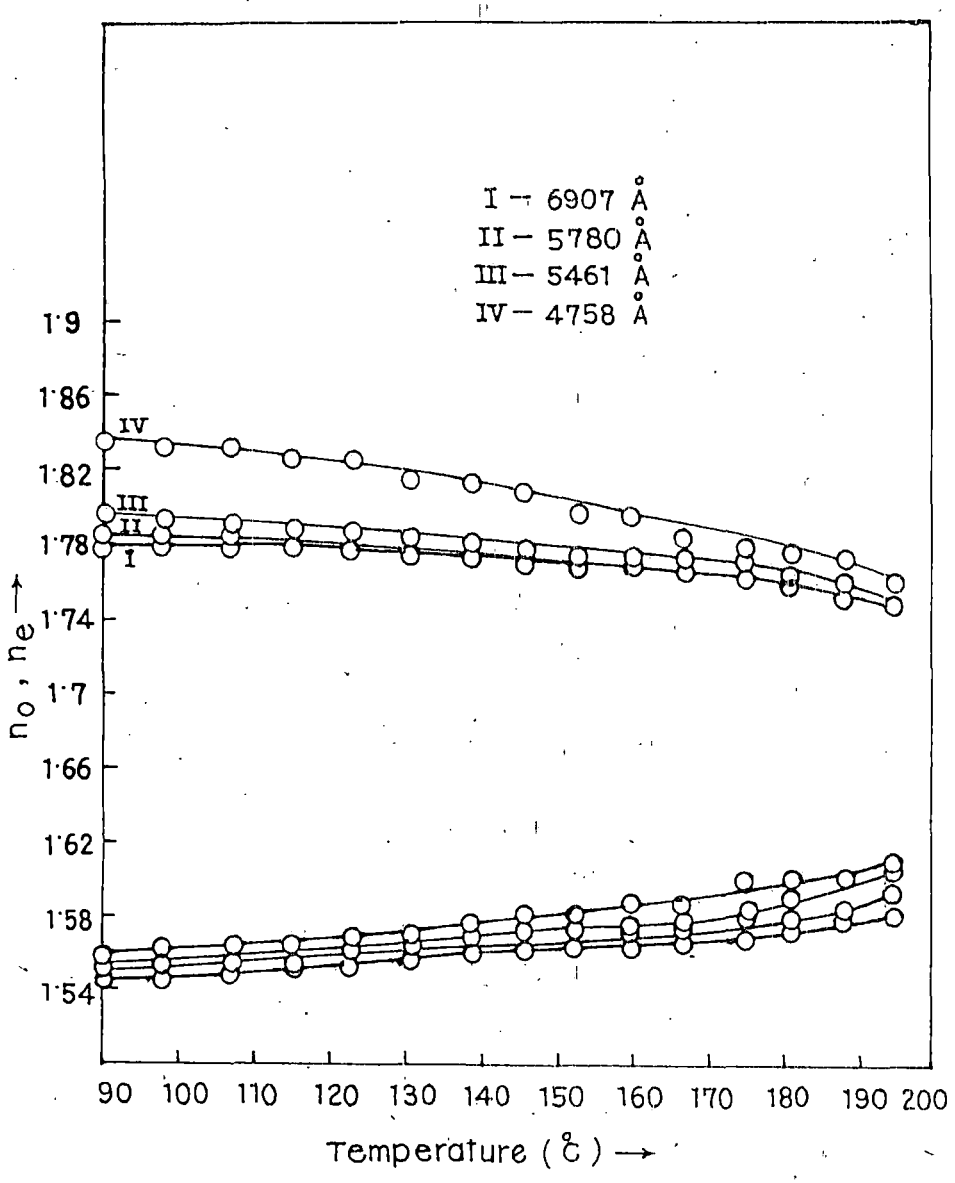

I – 6907 Å
II – 5780 Å
III – 5461 Å
IV – 4758 Å
1·9
1·86
1·82
1·78
1·74
1·7
1·66
1·62
1·58
1·54
IV
III
II
I
n_o , n_e →
90 100 110 120 130 140 150 160 170 180 190 200
Temperature (°C) →

Fig. 3.13

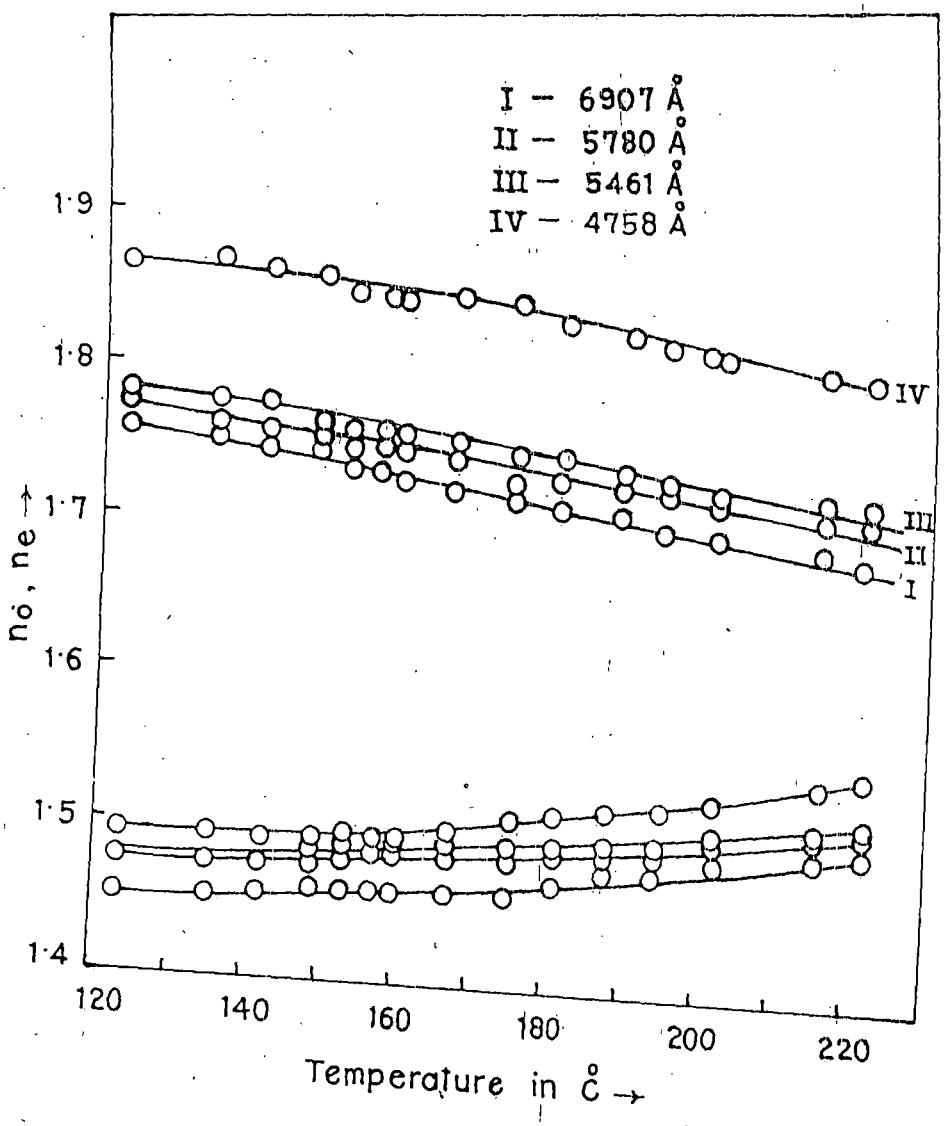

I – 6907 Å
II – 5780 Å
III – 5461 Å
IV – 4758 Å
1·9
1·8
1·7
1·6
1·5
1·4
no, ne
IV
III
II
I
120
140
160
180
200
220
Temperature in °C →

Fig. 3.14

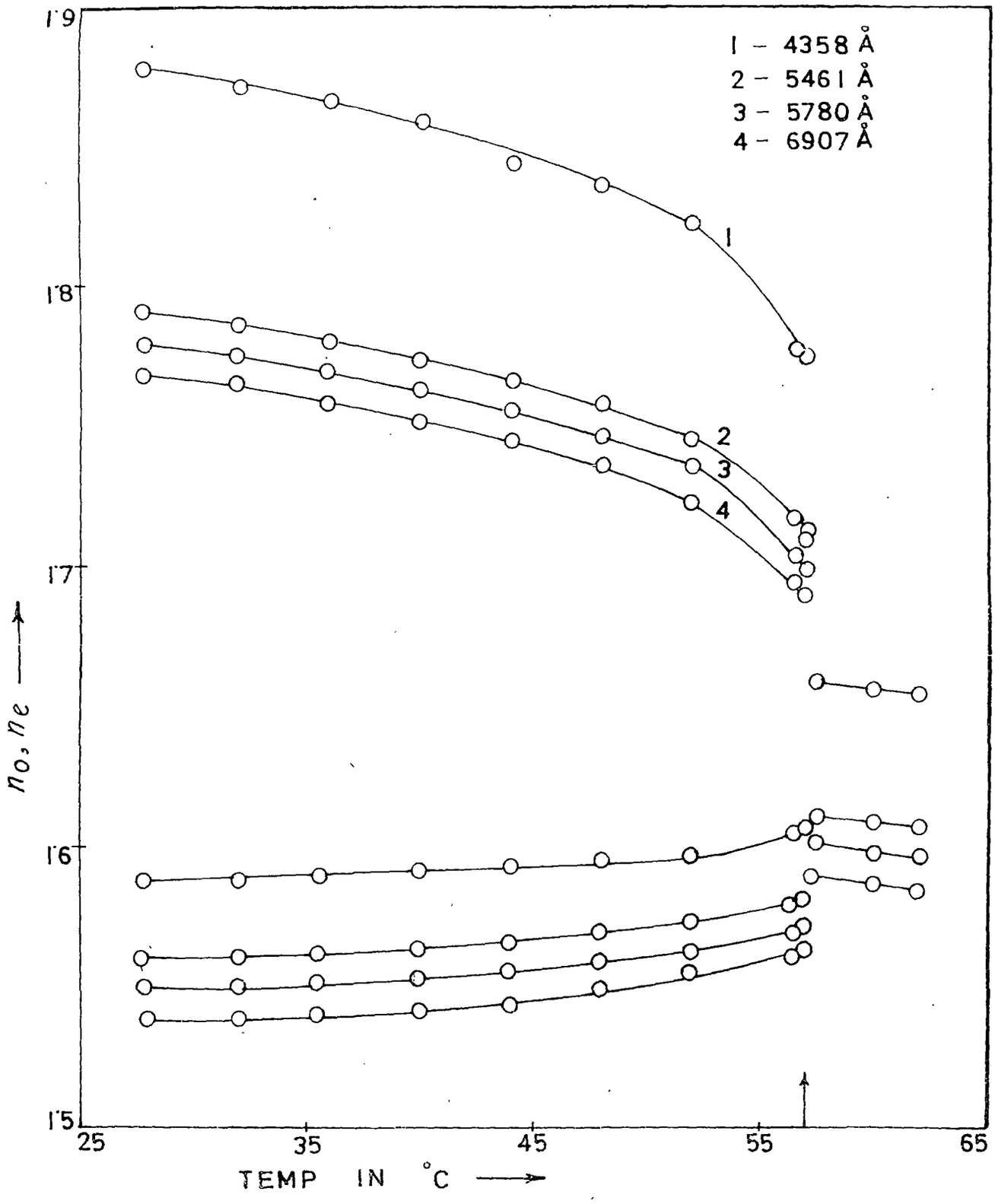

1 – 4358 Å
2 – 5461 Å
3 – 5780 Å
4 – 6907 Å
1
2
3
4
1·9
1·8
1·7
1·6
1·5
25
35
45
55
65
n_o, n_e
TEMP IN °C

Fig 1

Fig. 3.15

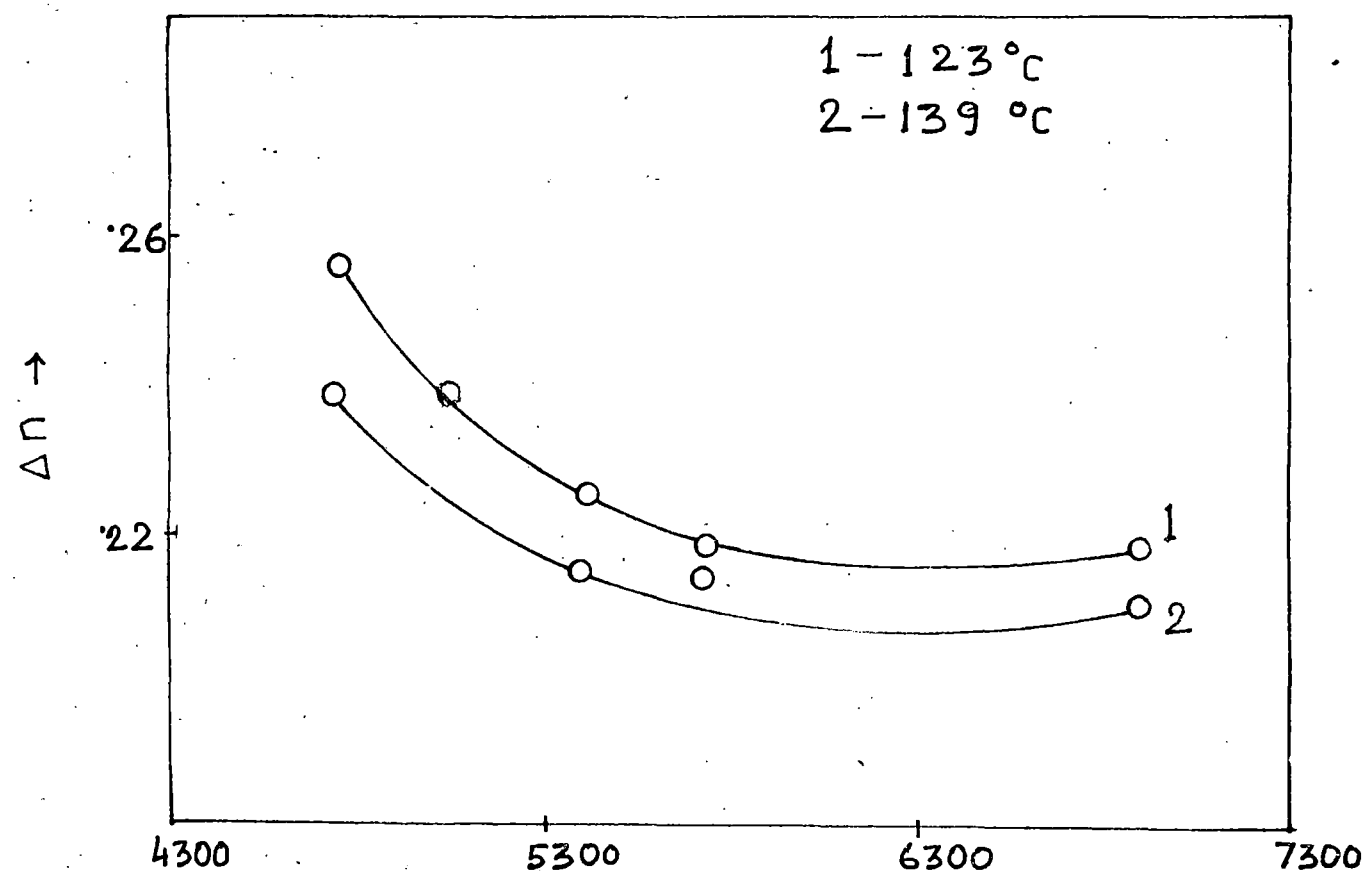


Fig. 3.16

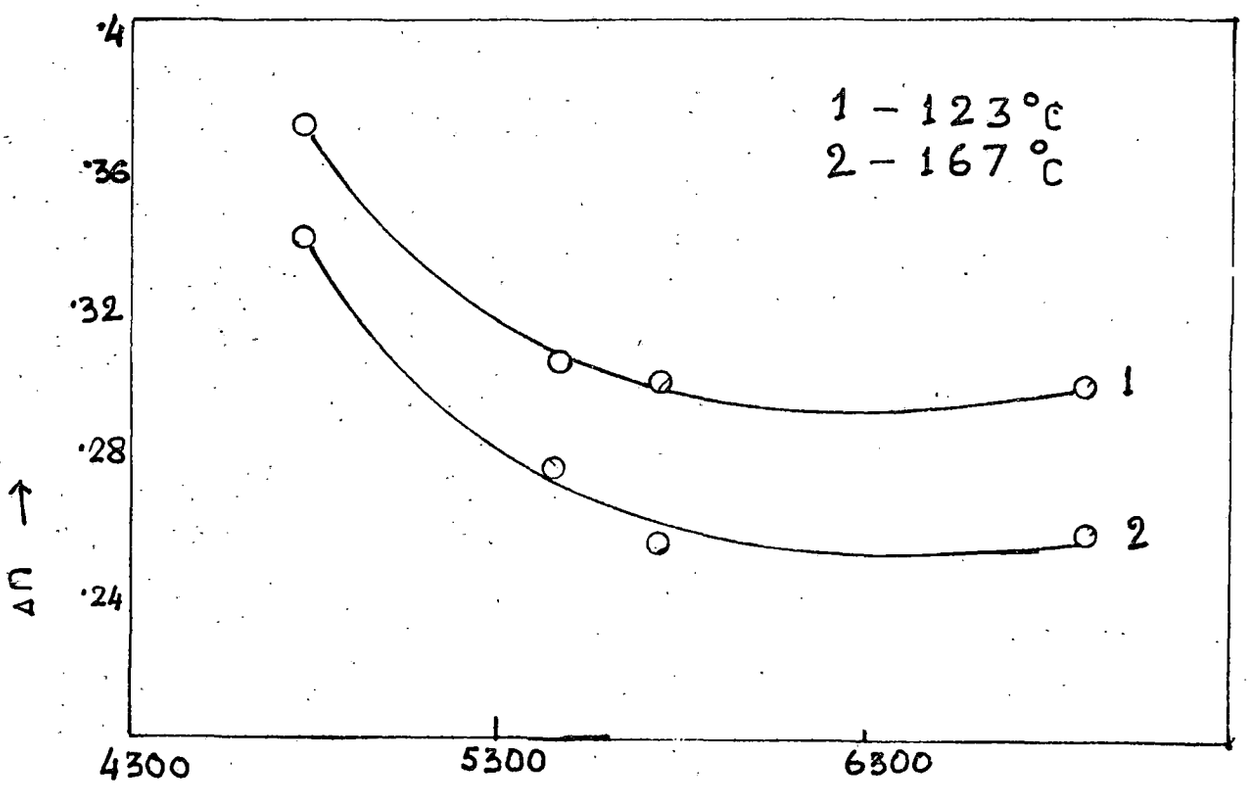


Fig. 3.17. Wavelength λ in Å →

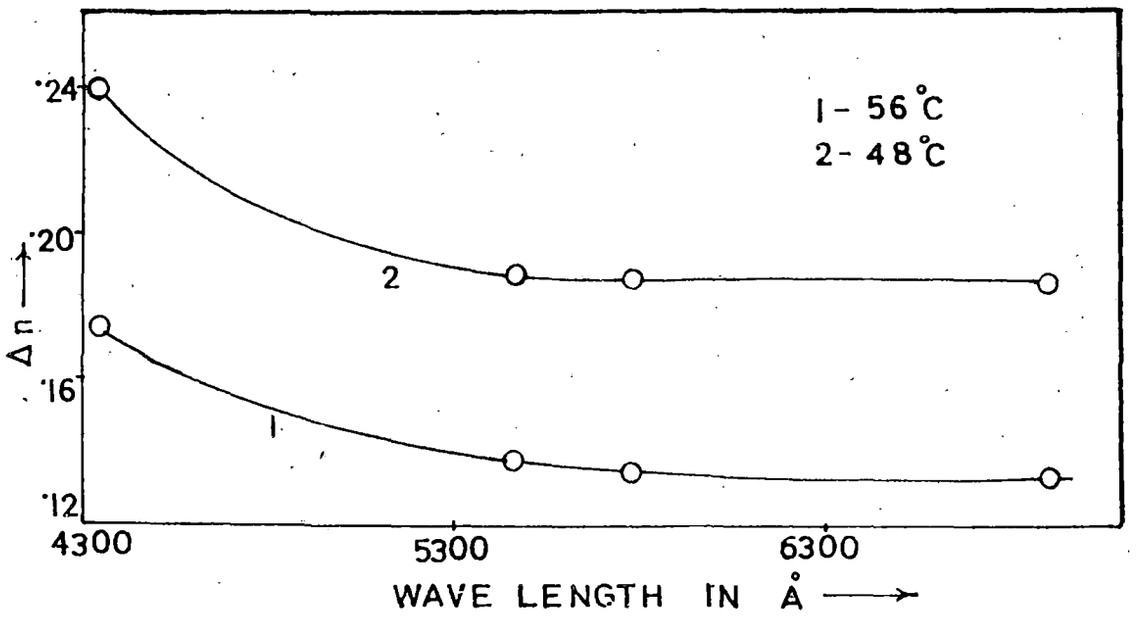
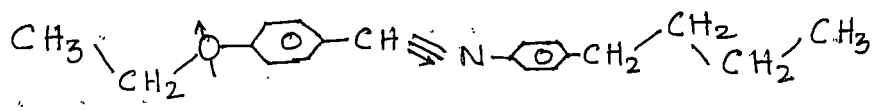


Fig - 3.18

3.2. X-ray Diffraction Studies on P-Ethoxy Benzylidene-p-n-Butylaniline (EBBA).

3.2.1. Introduction:

The structural formula of the sample EBBA is



The X-ray work of the sample have been under taken as a part of the program of the study of the properties of Schiff's base compounds under taken by us. Leadbetter et al[17] have obtained the structure of the sample in meso-phases aligned by magnetic field. But the orientational order parameters have not been determined by them. Order parameter of oriented samples were obtained by NMR, Raman Scattering and IR dichroism measurement by different authors[18-20]. Leadbetter et al[21] have solved the crystal and molecular structure of EBBA. Here we have reported the order parameter values of EBBA from X-ray diffraction data. The apparent molecular length (l) and the average intermolecular spacings (D) have also been calculated and found to be in well agreement with that reported by Leadbetter et al[21].

The sample EBBA supplied to us by Prof.M.Wada of Tohoku University, Japan. The molecular arrangement in nematic phase determined by Wada[22]. The transition temperature according to them is

$$\text{Crystal} \underset{}{\overset{37^{\circ}C}{\rightleftharpoons}} \text{Nematic} \overset{79^{\circ}C}{\rightleftharpoons} \text{Isotropic}$$

The sample found to have a supercooling state, the transition temperature observed by us under polarising microscope and by X-ray photographs is

$$\text{Crystal} \underset{23^{\circ}C}{\overset{37^{\circ}C}{\rightleftharpoons}} \text{Nematic} \overset{79^{\circ}C}{\rightleftharpoons} \text{Isotropic.}$$

The same transition was also reported by Leadbetter et al.

3.2.2. Results and Discussions:-

The detailed of experimental procedures and theoretical backgrounds are discussed earlier. In table 3.21 and 3.22, the intensity values at different temperatures are given.

The normalised distribution function $f(\beta)$ as a function of β at different temperatures as obtained from experimental intensity values are given in Table 2r 3.23, and shown in Fig. 3.19 respectively. We expect as temperature decreases the function to become more packed at $\beta = 0^{\circ}C$. Our curves conforms to this idea. Orientational order parameters $\langle P_2 \rangle$ and $\langle P_4 \rangle$ at different tempe-

ratures are shown in Fig. 3.20. The order parameters are estimated to be accurate within $\pm$ 0.02. The experimental $\langle P_2 \rangle$ values are found to differ slightly from the M.F. theoretical values but within the experimental uncertainity. But lower $\langle P_4 \rangle$ values are obtained near the isotropic region. Such behaviour of $\langle P_4 \rangle$ was found by others also[10-13]. The case of this discrepancy has not been accounted with certainity.

Table 3.21

Sample: EBBA.

Experimental intensity values I (Ψ) at different temperature

Degree	Experimental intensity for temperature ^{o}K							
	302	305	309	313	318	323	333	338
0	83.00	62.00	34.50	30.75	82.50	47.50	66.00	60.50
5	80.00	58.00	33.00	37.48	80.75	46.75	60.25	57.00
10	67.10	50.20	30.25	32.50	74.00	43.58	55.50	52.00
15	54.25	42.10	25.75	27.13	62.50	37.75	47.25	46.75
20	42.50	34.50	21.00	21.30	51.52	31.00	44.25	41.10
25	33.25	25.25	16.50	17.75	42.25	25.25	38.00	35.25
30	26.25	19.50	13.55	13.80	32.0	19.00	31.35	28.50
35	19.40	15.50	9.15	18.28	23.75	14.00	24.75	22.10
40	14.00	10.10	5.60	7.18	19.25	9.50	18.50	16.25
45	10.25	6.50	3.40	4.83	12.90	8.00	13.75	11.00
50	8.15	4.00	2.65	3.38	9.60	5.90	10.00	7.35
55	6.00	2.35	1.90	2.25	7.00	4.25	6.25	5.30
60	4.25	1.15	1.30	1.48	4.35	3.10	4.25	3.60
65	3.10	0.60	0.75	0.88	2.50	2.50	2.50	3.15
70	2.25	0.50	0.40	0.55	1.80	1.90	1.60	2.60
75	1.25	0.10	0.40	0.33	1.10	1.25	0.65	2.15
80	0.85	00	0.25	0.18	0.65	0.65	0.50	1.40
85	0.60	0	0.00	0.05	0.25	0.25	0	0.90
90	0.00	0	.00	0.00	00	00	0	0.65

Table 3.22

Sample: EBBA.

Calculated
~~Experimental~~ intensity I (Ψ) at different temperature

Degree	Calculated intensity for temperature °K							
	302	305	309	313	318	323	333	338
0	83.57	61.21	34.54	38.91	83.00	47.84	64.55	59.66
5	79.04	58.41	33.24	37.16	80.37	46.59	61.81	57.65
10	67.63	51.15	29.88	32.69	73.28	43.07	55.29	52.60
15	54.14	41.98	25.57	27.21	63.53	37.80	46.33	46.53
20	42.41	33.27	21.29	22.12	52.80	31.52	42.81	40.74
25	33.40	26.02	17.03	17.77	42.13	24.96	37.92	35.11
30	26.05	20.02	12.94	13.88	32.18	18.87	32.03	28.94
~~35~~	~~20x02~~	~~12x94~~						
35	19.51	14.79	9.06	10.26	23.70	13.84	24.98	22.32
40	14.07	10.24	5.83	7.14	17.27	10.13	18.28	15.90
45	10.26	6.59	3.63	4.84	12.85	7.59	13.30	10.92
50	7.90	3.99	2.43	3.34	9.66	5.79	9.89	7.52
55	6.14	2.92	1.79	2.30	6.90	4.38	6.99	5.28
60	4.44	1.23	1.32	1.48	4.42	3.23	4.22	3.79
65	2.97	0.62	0.86	0.86	2.59	2.39	2.14	2.92
70	2.02	0.32	0.49	0.51	1.61	1.81	1.24	2.53
75	1.48	0.19	0.27	0.35	1.16	1.30	1.06	2.20
80	0.95	0.096	0.15	0.21	0.73	0.73	0.73	1.61
85	0.37	-0.011	0.07	0.52	0.22	0.21	0.06	0.87
90	0.10	-0.06	0.03	-0.003	-0.02	-0.016	-0.29	0.53

Table 3.23

Sample: EBBA.

Normalised Distribution Function Values f(β) at Different Temperature.

Degree	Distribution function f(β) at temp. ^{o}K							
	302	305	309	313	318	323	333	338
0	11.13	11.17	9.12	9.77	7.74	7.35	7.34	7.19
5	10.35	10.02	8.39	9.02	7.42	7.01	6.82	6.63
10	8.69	7.62	6.84	7.31	6.59	6.16	5.65	5.42
15	6.99	5.52	5.41	5.59	5.54	5.21	4.48	4.34
20	5.33	4.23	4.46	4.30	4.46	4.35	3.84	3.68
25	3.60	3.47	3.78	3.39	3.46	3.53	3.09	3.31
30	2.14	2.82	3.01	2.63	2.57	2.69	2.66	2.94
35	1.25	2.06	2.07	1.92	1.83	1.88	2.19	2.34
40	0.81	1.29	1.21	1.29	1.26	1.21	1.66	1.58
45	0.59	0.73	0.66	0.82	0.87	0.78	1.16	0.95
50	0.43	0.42	0.39	0.52	0.60	0.54	0.77	0.57
55	0.29	0.25	0.27	0.34	0.42	0.41	0.50	0.38
60	0.19	0.15	0.21	0.22	0.29	0.33	0.32	0.28
65	0.14	0.08	0.15	0.14	0.18	0.25	0.19	0.22
70	0.10	0.04	0.08	0.08	0.10	0.17	0.10	0.16
75	0.06	0.01	0.04	0.04	0.05	0.09	0.05	0.11
80	0.03	0.004	0.01	0.02	0.03	0.05	0.02	0.08
85	0.01	0.002	0.007	0.01	0.02	0.03	0.01	0.05
90	0	0	0	0	0	0	0	0.04

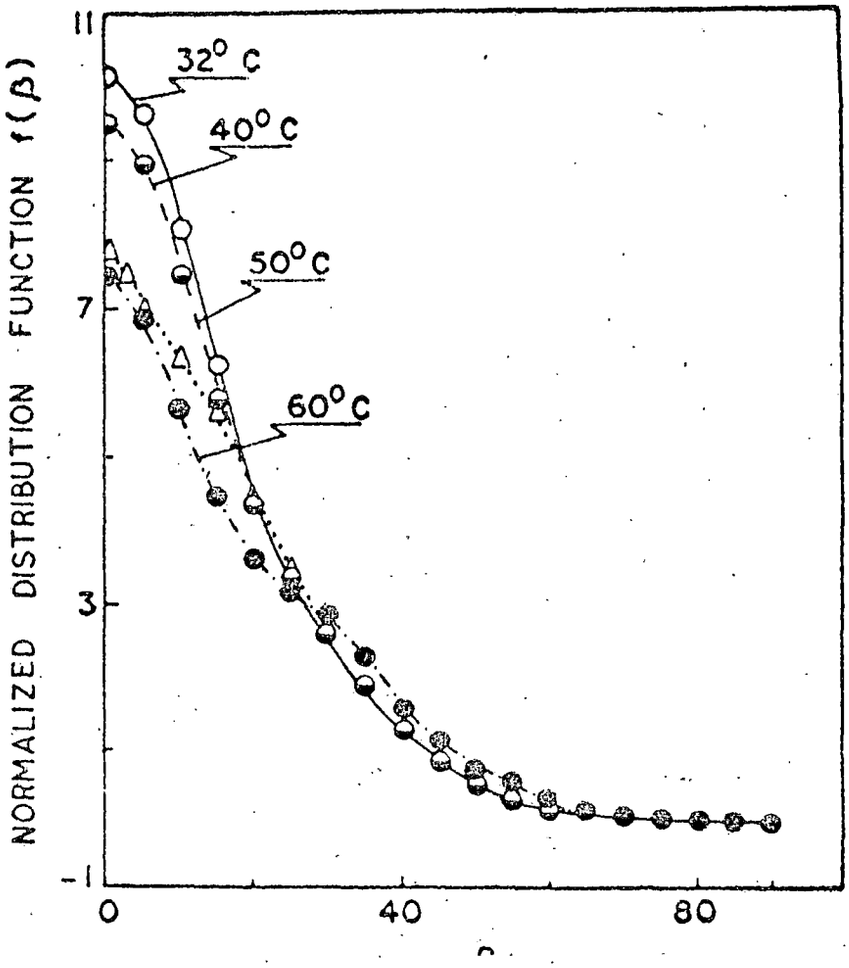

NORMALIZED DISTRIBUTION FUNCTION f(β)
11
7
3
-1
0
40
80
β
32° C
40° C
50° C
60° C

Fig. 3.19

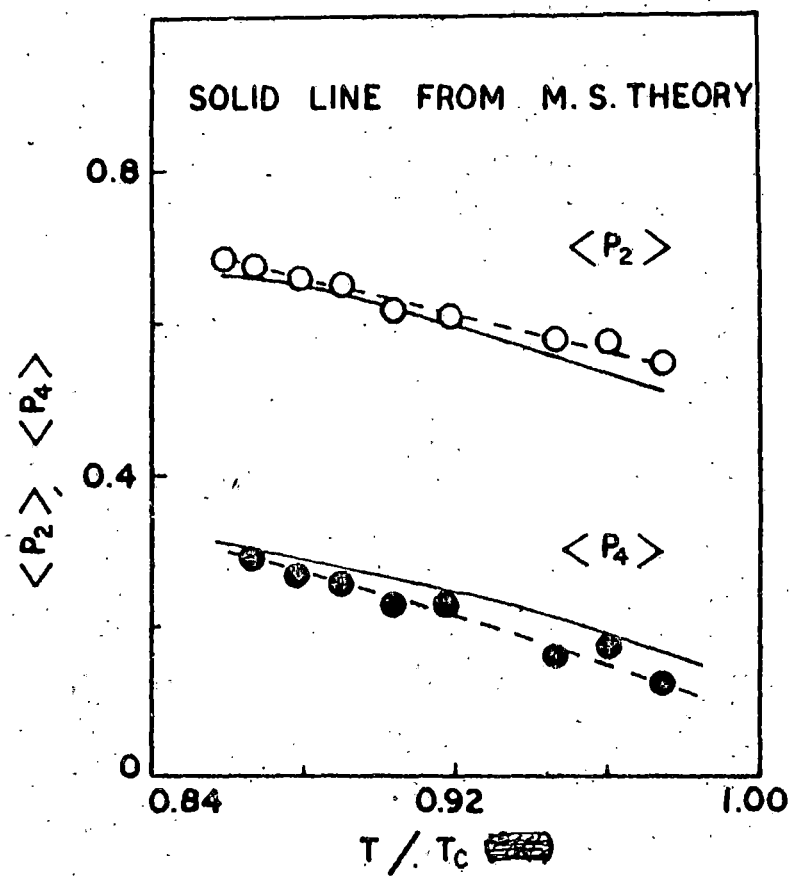
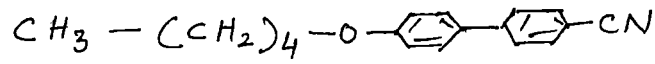

SOLID LINE FROM M. S. THEORY
0.8
0.4
0
$\langle P_2 \rangle$
$\langle P_4 \rangle$
$\langle P_2 \rangle, \langle P_4 \rangle$
0.84
0.92
1.00
T / Tc

Fig- 3.20

3.3. Optical bi-refringence studies on 5OCB and BPCPP

In this section the optical birefringence studies of the following samples are reported.

1. 4'-pentyloxy-4-cyanobiphenyl(5OCB in short)



Solid $\underset{31.5^{\circ}C}{\overset{47.5^{\circ}C}{\rightleftharpoons}}$ Nematic $\rightleftharpoons^{67.5^{\circ}C}$ Isotropic

2. 5-(4-n-Butylphenyl)-2-(4-cyanophenyl)-Pyrimidene (BPCPP in short).

X-ray diffraction studies of the samples 1 and 2 were done in our laboratory by Bhattacharjee et al[23] and B.Jha et al[24] respectively. Orientational order parameters, apparent molecular length average intermolecular distance and the angular part of the mean field potential in the nematic phase of both the sample were studied by them. Crystal structure analysis of the sample 2 with the help of the X-ray diffraction were done by P.Mandal and S.Paul[25] of our laboratory.

The refractive index measurement and the determination of order parameters from bi-refringence study for these compounds are being reported here.

Results and Discussion:-

The experimental details are described earlier. The values of refractive indices (n_o , n_e) at different temperatures and for different wave lengths are given in the Table 3.24, and 3.25 and shown in Fig. 3.25 - 3.26 respectively for the samples. The density, polarizability from Vuk's approach and order parameters calculated are given in the Table 3.26 and 3.27. The results of Neugebaur's approach are given in Table ~~2x~~ 3.28 and 3.29 respectively.

The orientational order parameter $\langle P_2 \rangle$ ~~x~~ was calculated using the relation $\langle P_2 \rangle = (\alpha_e - \alpha_o)/(\alpha_{\parallel} - \alpha_{\perp})$ The values of $(\alpha_{\parallel} - \alpha_{\perp})$ is determined from Haller's extrapolation is described incase of the sample 1 only. The Fig. 3.27 shows the plot of $ln(\alpha_e - \alpha_o)$ Vs. $ln(T_c - T)$ of sample I which is a straight line. The straight line is extrapolated to T = 0°K.

The values of $(\alpha_{\parallel} - \alpha_{\perp}) = \alpha_a$ for Vuk's and Neugebauer's approach are tested by calculating α_a for both the samples by using additive rule of the bond polarizability values available in the literature[5,6,7]. The mean polarizability valuesalso calculated. The table 3.30 shows the α_a and α values of both the sample by different methods. This is clear from the table that the values obtained from Neugebauer's data is very close to that calculated from bond polarizability whereas the α_a values calculated from Vuk's formula is significantly different.

In case of compounds PCCPP, PCTP, PBBA we have found the same results. Discrepancies have also been found in other nematic liquid crystals[26]. Although the Haller's plot is not fully justifiable in all cases and the additive rule of the bond polarizability to estimate the molecular polarizability anisotropy (α_a) may be more realistic, but we have not used the bond polarizability values in any further calculations since the difference between two sets of α_a valuesx one from ~~the~~ bond polarizability and one from Neugebauer's approach, is marginal.

The order parameter values calculated using Vuk's formula and Neugebauer's relations agree well for the compounds in their respective nematic phases. This may be due to the fact that although α_e and α_o vary considerably in the two approaches the variation of $(\alpha_e - \alpha_o)$ with temperature is more or less the same in two cases.

The Fig. 3.28, and 3.29 shows the $\langle P_2 \rangle$ values of the samples obtained from different methods. It is found that the $\langle P_2 \rangle$ values obtained from R.I. data agree well with the M.S. theoretical values expect in the nematic - isotropic transition region. The higher temperature values in case of the sample 2 could not be taken because of experimental limitations. The $\langle P_2 \rangle$ values at the transition region are significantly lower than the theoretical values. Such behaviour near T_c has also been found by others[8,9] $\langle P_2 \rangle$ values from X-ray diffraction techniques are higher than the theoretical values. Different approximations involved in different cases may be the cause of such differences.

In the refractive indices study we rely on surface anchoring only for the formation of monodomain sample as the magnetic field cannot be applied during the measurements hence it is likely that near the nematic isotropic transitions temperature, the samples may not remain ideally monodomain.

Table 3.30

α and $(\alpha_{\parallel} - \alpha_{\perp})$

Sample	$\alpha \times 10^{24}$ cm		$(\alpha_{\parallel} - \alpha_{\perp}) \times 10^{24} cm^3$		
	Calculated from bond polarizability	Vuk's/ Neugebauers approach (Isotropic liquid)	Calculated from bond polarizability	Haller's process (Vuks' data)	Haller's process (Neugebauers' data)
1. 50CB	34.14	34.61	18.42	22.80	18.30
2. DPCPP	43.14		32.09	47.8	33

Table 3.24

Refractive indices (n_o , n_e) at different temperature of sample 5003

Temp °C	6907 Å		5780 Å		5461 Å		4758 Å	
	n_o	n_e	n_o	n_e	n_o	n_e	n_o	n_e
32.5	1.522	1.725	1.533	1.741	1.538	1.752	1.571	1.810
36	1.522	1.720	1.533	1.736	1.538	1.747	1.571	1.805
40	1.522	1.715	1.533	1.731	1.538	1.742	1.571	1.799
44.5	1.522	1.709	1.533	1.725	1.538	1.736	1.571	1.793
48	1.522	1.702	1.533	1.718	1.538	1.729	1.571	1.786
5255	1.525	1.695	1.536	1.711	1.541	1.722	1.575	1.778
57	1.529	1.685	1.540	1.701	1.545	1.712	1.579	1.768
61.5	1.534	1.673	1.545	1.689	1.550	1.700	1.585	1.755
66	1.540	1.658	1.551	1.673	1.556	1.684	1.592	1.738
67	1.545	1.651	1.556	1.666	1.561	1.677	1.599	1.730
70	1.5981		1.593		1.600		1.638	
75	1.580		1.592		1.599		1.637	

Table 3.25

Refractive indices (n) of sample BPCPP at different wavelength (λ)

Temp. in °C	6907 Å		5780 Å		5461 Å		4758 Å	
	n_o	n_e	n_o	n_e	n_o	n_e	n_o	n_e
100	1.483	1.846	1.499	1.862	1.511	1.874	1.546	1.909
110	1.483	1.842	1.499	11858	1.511	1.870	1.546	1.905
120	1.483	1.837	1.499	1.853	1.511	1.865	1.546	1.900
130	1.486	1.831	1.502	1.847	1.514	1.860	1.549	1.895
140	1.490	1.826	1.506	1.842	1.518	1.854	1.553	1.889
150	1.494	1.820	1.510	1.836	1.522	1.848	1.557	1.883
160	1.498	1.814	1.514	1.830	1.526	1.842	1.561	1.877
170	1.502	1.808	1.518	1.824	1.530	1.836	1.565	1.871
180	1.506	1.802	1.522	1.818	1.534	1.830	1.569	1.865
190	1.511	1.796	1.527	1.812	1.539	1.824	1.574	1.859
200	1.516	1.790	1.532	1.806	1.544	1.818	1.579	1.853

TABLE 3.26

Density (ρ), polarizability (α) and orientational order parameter ($\langle P_2 \rangle$) of 5OCB

$\lambda \rightarrow$		6907 Å			5761 Å			5461 Å			4358 Å		
Temp. (°c)	ρ (gm/cm^3)	α_o	α_e	$\langle P_2 \rangle$	α_o	α_e	$\langle P_2 \rangle$	α_o	α_e	$\langle P_2 \rangle$	α_o	α_e	$\langle P_2 \rangle$
32.5	1.067	28.84	45.13	.6325	29.30	45.93	.6325	29.48	46.53	.6321	30.73	49.60	.6310
36	1.0665	28.89	44.83	.6190	29.35	45.63	.6192	29.53	46.23	.6191	30.79	49.28	.6194
40	1.066	28.94	44.53	.6054	29.40	45.34	.6059	29.59	45.87	.6036	30.85	48.92	.6054
44.5	1.0642	29.03	44.22	.5898	29.49	45.03	.5907	29.67	45.63	.5914	30.94	48.69	.5945
48	1.0628	29.11	43.96	.5767	29.57	44.77	.5779	29.75	45.37	.5789	31.02	48.44	.5834
52.5	1.0608	29.42	43.58	.5498	29.88	44.39	.5516	30.06	44.99	.5533	31.40	47.91	.5532
57	1.0573	29.85	43.05	.5124	30.32	43.86	.5150	30.50	44.47	.5177	31.86	47.21	.5140
61.5	1.0523	30.39	42.50	.4699	30.86	43.31	.4734	31.04	43.92	.4772	32.47	46.40	.4657
66	1.0414	31.37	41.78	.4040	31.84	42.60	.4091	32.02	43.21	.4147	33.55	45.57	.4024
67	1.0310	32.01	41.71	.3767	32.48	42.54	.3825	32.67	43.16	.3889	34.33	45.43	.3720

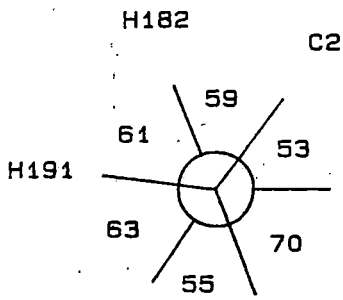
α_o and α_e are in units 10^{-24}cm^3

Table 3.27

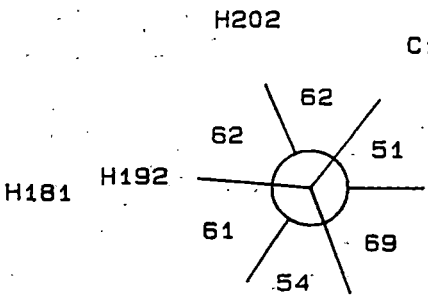
Density (ρ) and orientational order parameters ($\langle P_2 \rangle$) of sample BPCPP(Vuks' approach)

Temp. in ^oC	Density (ρ) in gm/cm.	6907 Å		5780 Å		5461 Å		4753 Å		Mean $\langle P_2 \rangle_{AV}$
		α_o	α_e	α_o	α_e	α_o	α_e	α_o	α_e	
100	.885	36.58	73.45	37.62	74.42	38.38	75.14	40.59	77.20	.768
110	.881	36.81	73.39	37.83	74.39	38.60	75.11	40.80	77.05	.763
120	.877	37.01	73.27	38.05	74.26	38.83	74.99	41.05	77.08	.756
130	.873	37.46	72.95	38.51	73.94	39.28	74.77	41.52	76.87	.741
140	.868	38.03	72.77	39.09	73.77	39.87	74.51	42.12	76.63	.723
150	.863	38.62	72.49	39.69	73.50	40.47	74.25	42.73	76.38	.705
160	.857	39.27	72.30	40.33	73.32	41.13	74.07	43.40	76.22	.689
170	.851	39.92	72.11	40.99	73.13	41.79	73.89	44.08	76.06	.671
180	.846	40.53	71.83	41.61	72.86	42.42	73.63	44.72	75.81	.652
190	.840	41.28	71.60	42.37	72.64	43.14	45.49	45.49	75.62	45x632
200	.833	41.88	69.48	42.18	70.81	42.97	71.57	45.25	73.74	.612

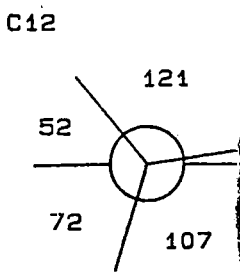
α_o and α_e are in units 10^{-24} cm^3



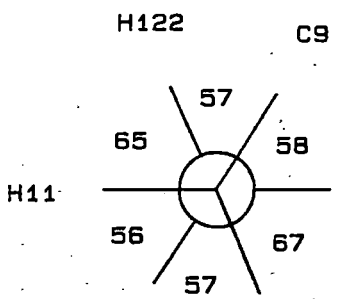
C14 H192
(C19 – C18)



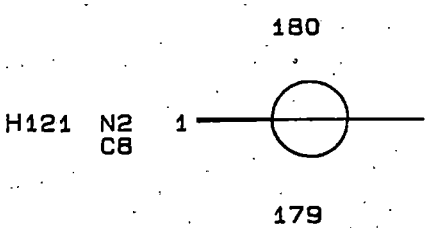
C21 H191
(C19 – C20)



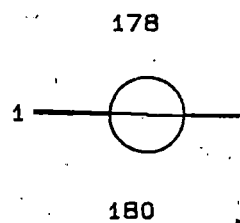
C16
(C11 – C9)



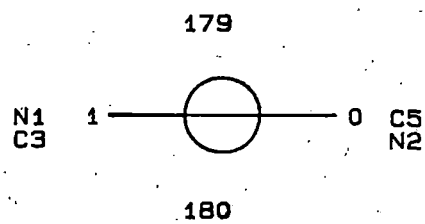
C13 C16
(C11 – C12)

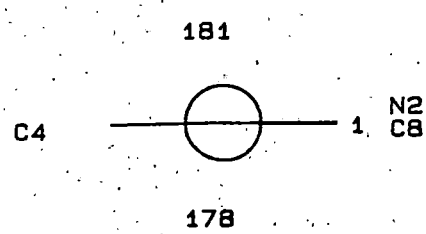


(C9 – C10)



(C9 – C8)





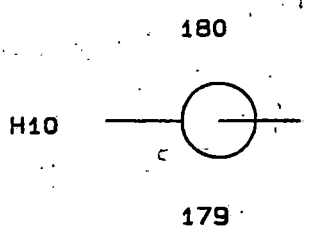


Table 3.29

Polarizability at different temperature from Neugebauer Method of Sample - BPCPP

Temp. in °C	λ → 6907 Å		5780 Å		5461 Å		4758 Å	
	α_o	α_e	α_o	α_e	α_o	α_e	α_o	α_e
100	38.97	68.67	40.06	69.54	40.87	70.18	43.19	72.00
110	39.18	68.66	40.25	69.54	41.06	70.19	43.2	72.0
120	39.34	68.59	40.45	69.47	41.26	70.12	43.61	71.98
130	39.75	68.36	40.86	69.25	41.68	69.99	44.03	71.86
140	40.28	68.27	41.39	69.17	42.21	69.83	44.57	71.73
150	40.82	68.09	41.93	69.01	42.76	69.68	45.13	71.60
160	41.41	68.01	42.53	68.92	43.36	69.60	45.74	71.55
170	42.01	67.91	43.14	68.84	43.97	69.53	46.35	71.50
180	42.57	67.75	43.70	68.69	44.54	69.38	46.94	71.37
190	43.26	67.64	44.40	68.59	45.24	69.29	47.65	71.31
200	43.71	65.82	44.10	66.97	44.92	67.66	47.29	69.66

α_o and α_e are in units 10^{-24} cm^3

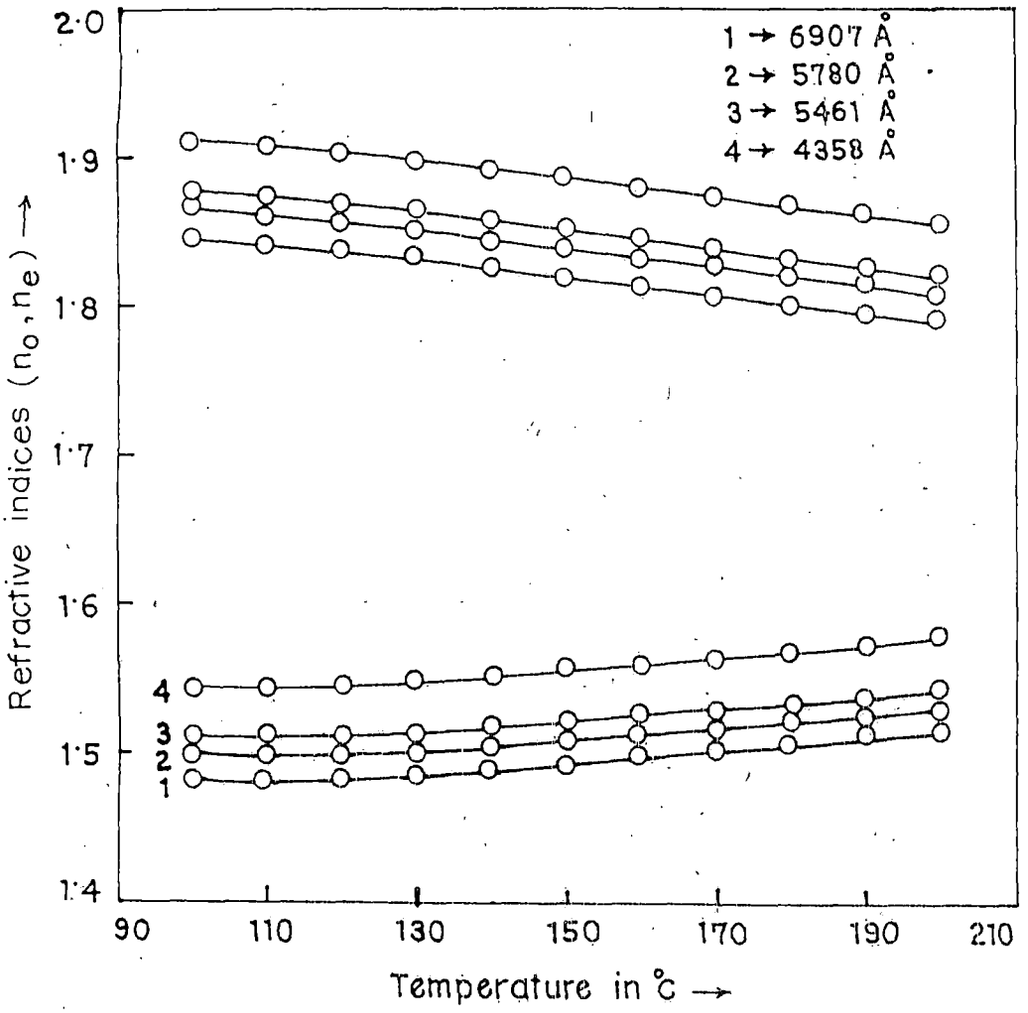

1 → 6907 Å
2 → 5780 Å
3 → 5461 Å
4 → 4358 Å
2·0
1·9
1·8
1·7
1·6
1·5
1·4
Refractive indices (n_o, n_e) →
4
3
2
1
90
110
130
150
170
190
210
Temperature in °C →

Fig. 3.29

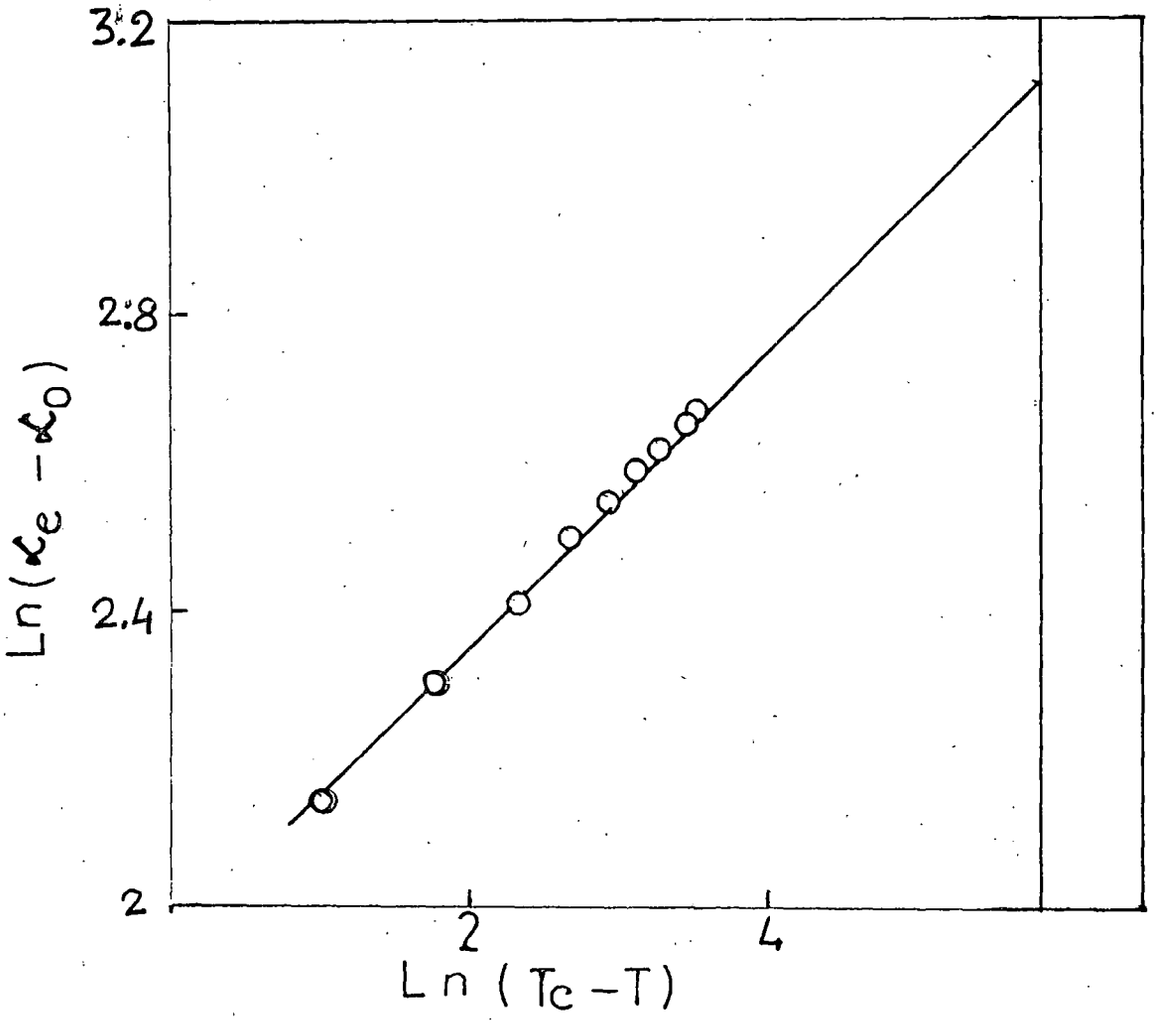


Fig. 3.27

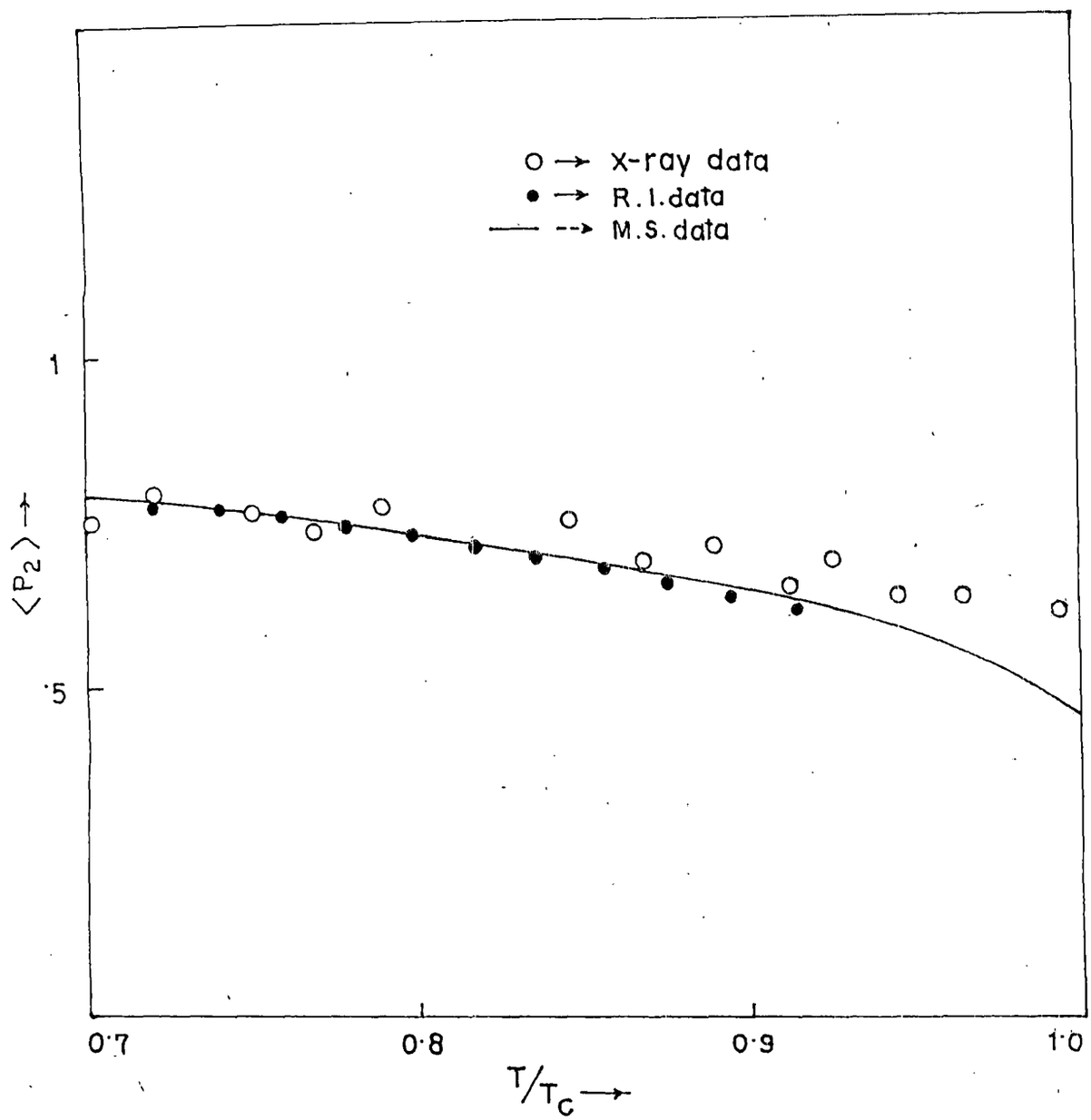


Fig. 3.25

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