

## CHAPTER V

### ELASTIC CONSTANTS IN THE VICINITY OF THE SMECTIC A- NEMATIC TRANSITION

#### Introduction

In the case of a nematic liquid crystal which shows the smectic A phase at lower temperatures strong smectic like short range order builds up as the temperature is lowered. Hence as the nematic-smectic A transition (A-N transition) is approached bend and twist deformations become difficult since they tend to change the layer thickness in the smectic like groups. As a consequence, the corresponding elastic constants are expected to exhibit pretransition anomalies close to the A-N transition point. The effect is particularly pronounced when the transition is second order or quasi-second order. Measurements of bend, splay and twist elastic constants (Cheung *et al.* 1973, Delaye *et al.* 1973) show that  $k_{33}$  and  $k_{22}$  diverge as  $T_{AN}$  is approached. On the other hand  $k_{11}$  shows the normal behaviour.

McMillan (1971) has given a molecular model for a smectic A liquid crystal. Extending the molecular theory of nematic liquid crystals due to Maier and

Saupe (1958, 1959, 1960), he introduced another order parameter  $\psi$ , the amplitude of the density wave in the direction of  $\vec{n}$ . The nematic orientational order parameter  $S$  and the smectic order parameter are coupled. Because of this coupling, greater the value of  $S$  at the A-N transition, less is the entropy change at the transition. This means that a second order transition is favoured if  $T_{AN}^{(1972)} \leq T_{NI}^{(1972)}$  is considerably less than  $T_{NI}$ . In fact McMillan's model (1971) predicts a second order A-N transition if  $\frac{T_{AN}}{T_{NI}} \leq 0.67$ . Later, de Gennes (1973) and McMillan proposed a Landau type of phenomenological description of the A-N transition and of the pretransition phenomena associated with it.

### Theories of de Gennes and McMillan

In a smectic A, one can define a one-dimensional density wave along  $\vec{n}$ , given by

$$\rho(z) = \rho_0 [1 + \frac{1}{(2)^2} |\psi| \cdot e^{-i(q_0 z - \varphi)}] \quad (5.1)$$

where  $\rho_0$  is the average density,  $|\psi|$  the amplitude of the density wave,  $q_0 (= \frac{2\pi}{d}$  where  $d$  is the inter-layer distance) is the wave vector of the density wave and  $\varphi$  an arbitrary phase. The smectic A order parameter can be written as  $\psi = |\psi| e^{-i(q_0 z - \varphi)}$ . Neglecting the background term since we are interested only in

the fluctuations in the smectic order parameter,

$$\psi = |\psi| e^{i\varphi} . \quad (5.2)$$

Thus the order parameter in this case is a two-component function. This brings in an analogy between smectic A and superconductors as pointed out by de Gennes (1972) and McMillan (1972). The analogy is made clearer by the following similarity.

In a smectic A medium  $\text{curl } \vec{n} = 0$  since the line integral  $\int \vec{n} \cdot d\vec{r}$  around a closed loop in a dislocation free space is zero (de Gennes 1969). From Frank's (1958) expression (equation 1.4) for elastic energy density, we see that twist and bend constants involve  $\nabla \times \vec{n}$  which is zero in smectic A. Or in other words  $\text{curl } \vec{n}$  is excluded from smectic A. In superconductors the magnetic flux is excluded. If  $\vec{A}$  is the vector potential, then the magnetic flux =  $\text{curl } \vec{A}$  should vanish. Hence  $\vec{m}$  is similar to the director  $\vec{n}$ . From these arguments, it is clear that the smectic A-nematic transition is analogous to the superconductor-normal phase transition.

As the A-N transition point is approached the size of the smectic like domains increases. The increased size of these clusters can be readily seen

in the increase in the X-ray peak of the scattered intensity related to the liquid structure factor (McMillan 1972, 1973).

In the mean field approximation, the free energy in the neighbourhood of a second order phase transition can be expanded in terms of  $\Psi$  and its gradients. For a fixed orientation of the director  $\hat{n}$ , along  $z$ )

$$F_s = \alpha |\Psi|^2 + \frac{g}{2} |\Psi|^4 + \frac{1}{2M_V} \left( \frac{\partial \Psi}{\partial z} \right)^2 + \frac{1}{2M_T} \left[ \left( \frac{\partial \Psi}{\partial x} \right)^2 + \left( \frac{\partial \Psi}{\partial y} \right)^2 \right] \quad (5.3)$$

where  $\alpha$  is a temperature dependent term and  $M_V$  and  $M_T$  will be defined presently.

For  $T \gg T_{AN}$ , neglecting the term containing  $|\Psi|^4$ , we have from the equipartition theorem, the thermal average of the Fourier components,

$$\langle |\Psi(q)|^2 \rangle = \frac{k_B T}{\alpha + \frac{1}{2M_V} q_z^2 + \frac{1}{2M_T} (q_x^2 + q_y^2)} \quad (5.4)$$

We define the coherence lengths

$$\xi_{||} = \frac{1}{2M_V \alpha}, \quad \xi_{\perp} = \frac{1}{2M_T \alpha} \quad (5.5)$$

$\xi_{\parallel}$  and  $\xi_{\perp}$  signify the size of the smectic like clusters. In the mean field approximation  $\alpha \propto T - T_{AN}$ . As  $T_{AN}$  is approached  $\xi_{\parallel}$  and  $\xi_{\perp}$  diverge.

Now if we allow for director fluctuations, as shown by de Gennes (1973),  $F_s$  takes the general form

$$F_s = \alpha |\psi|^2 + \frac{\rho}{2} |\psi|^4 + \frac{1}{2M_{\nabla}} \left( \frac{\partial \psi}{\partial s} \right)^2 + \frac{1}{2M_T} \left| \vec{\nabla}_1 \psi - i q_s \vec{n} \cdot \vec{\nabla} \psi \right|^2 \quad (5.6)$$

where  $\vec{\nabla}_1$  is the gradient operator in the plane of the layers. This equation is similar to the Landau-Ginsburg free energy for the superconductors.

Now the elastic free energy density can be expressed as

$$F = \frac{1}{2} k_0 (\vec{\nabla} \vec{n})^2 + F_s(\psi) \quad (5.7)$$

where  $k_0$  is the Frank elastic constant in the absence of any smectic like order and  $F_s(\psi)$  is given by equation (5.6) averaged over all  $\psi$ .

If we ignore the difference between  $M_{\nabla}$  and  $M_T$ ,

$$F_s = \frac{q_s^2}{M} \langle |\psi|^2 \rangle \cdot (\vec{\nabla} \vec{n})^2 \xi^2 \quad (5.8)$$

where  $\delta n$  is written as  $\xi \nabla n$  which has the order of the magnitude of the strains in a cluster of size  $\xi$ . In the mean field approximation

$$\langle |\psi|^2 \rangle = \text{const.} \frac{T}{\alpha \xi^3}. \quad (5.9)$$

This corresponds to the correlated fluctuations in a volume  $\xi^3$ . From the above three equations we find that the smectic like order gives rise to a correction for twist and bend constants, the correction being  $\delta k \propto \xi$ .

Now if we take  $M_y \neq M_z$ , it can be shown (de Gennes 1972) that

$$\delta k_{22} = \frac{\pi(2)^{\frac{1}{2}}}{6} \cdot \frac{k_B T}{d^2} \cdot \frac{\xi_\perp^2}{\xi_\parallel} \quad (5.10)$$

and

$$\delta k_{33} = \frac{\pi(2)^{\frac{1}{2}}}{6} \cdot \frac{k_B T}{d^2} \cdot \xi_\parallel$$

In the mean field approximation  $\xi \propto (T - T^*)^{-\frac{1}{2}}$  (For a purely second order transition  $T^* = T_{AN}$ . For a weak first order transition  $T^* < T_{AN}$ ). de Gennes (1972) argued that mean field results may not be applicable to A-N transition. Using Wilson's (1972) calculations he concluded that  $\xi \propto (T - T^*)^{-0.66}$ .

Hence the full expression for the elastic constant can be written as

$$k_{ii} = k_{ii}(0) + \text{const. } (T - T^*)^{-\gamma} \quad (5.11)$$

$i = 2, 3$ .  $\gamma = \frac{9}{2}$  in mean field approximation and  
 $\gamma = 0.66$  in helium analogy.

If  $k_{ii}(0)$  is assumed to obey mean field variation

$$k_{ii}(0) \propto s^2.$$

Hence

$$k_{ii} = C_1 s^2 + C_2 (T - T^*)^{-\gamma} \quad (5.12)$$

These theoretical predictions initiated a large number of experimental studies. Since we had developed a new method to determine  $k_{22}$  we thought it worthwhile measuring the twist constant in some nematics which exhibit the smectic A phase at lower temperature. We have also measured  $k_{33}$  for some of these compounds. However we must emphasize that the experimental set up used here was not specifically designed to measure the critical phenomena (the *temperis-re* control being only  $\sim \pm 0.02^\circ\text{C}$ ) and hence the numerical values that are obtained by the analysis of the data are perhaps only of qualitative significance.

### Experimental

Chemicals: We have measured  $k_{22}$  and  $k_{33}$  for SCB, 10 OMCP, 4'-n-octyloxy-4-cyanobiphenyl (8 OCB)

and p-cyanobenzylidene-p'-octyloxyaniline (CBOOA). Of these 8CB and 10 OMCPC were prepared in our Chemistry Laboratory. 8 OCB was obtained from BDH Laboratories and was used without further purification.  $k_{22}$  measurements were done on CBOOA supplied by Eastman Organic Ltd. after recrystallisation from n-heptane ( $T_{AN} = 82.7$ ,  $T_{NI} = 107$ ). We have already mentioned that McMillan's model (1971) leads to the result that the A-N transition is second order if  $\frac{T_{AN}}{T_{NI}} < 0.87$ . Hence if the nematic range is increased, the nature of A-N transition comes closer to second order. With this in mind, we have prepared two mixtures of 8 OCB and 7CB thereby extending the nematic range considerably. None of the compounds studied here have reached the McMillan limit. However, the differential scanning calorimetric measurements show that in some compounds with large nematic range, the A-N transition is hardly detectable.

The transition temperatures of 8 OCB and the mixtures are given in table 5.1. In this Chapter, we shall give, in addition to  $k_{22}$  and  $k_{33}$ , the  $k_{11}$  data for 8 OCB and the mixtures as well.

The values of S and  $\rho$  necessary for the calculation of elastic constants are given in Chapters III and IV for 8CB and 10 OMCPC respectively. In the

case of other compounds, we have obtained them as described below.

#### Order parameter and density

For CBOOA,  $S$  values were taken from the work of Fernandes and Venugopalan (1976). The temperature variation of density was taken from the data of Torsa and Cladis (1975).  $S$  and  $\rho$  values are given in Table 5.2.

The refractive indices of S OCB and the two mixtures are tabulated in Table 5.3. They are plotted in Figure 5.1.

We have measured the density of S OCB at  $T_{NI} - T = 12^\circ\text{C}$  by the capillary method (see Appendix II). Using this value and the refractive index data its average polarizabilities  $\bar{\alpha}$  for different wavelengths were calculated.

For the mixtures we used the relation (Chandrasekhar and Madhusudana 1969)

$$\bar{\alpha}_{\text{mix}} = p_1(\bar{\alpha})_1 + p_2(\bar{\alpha})_2 \quad (5.13)$$

where  $p_1$  and  $p_2$  are the molar proportions of the components 1 and 2. Using equation (8) of Appendix II, the density of the mixtures at  $T_{NI} - T = 12^\circ\text{C}$  are

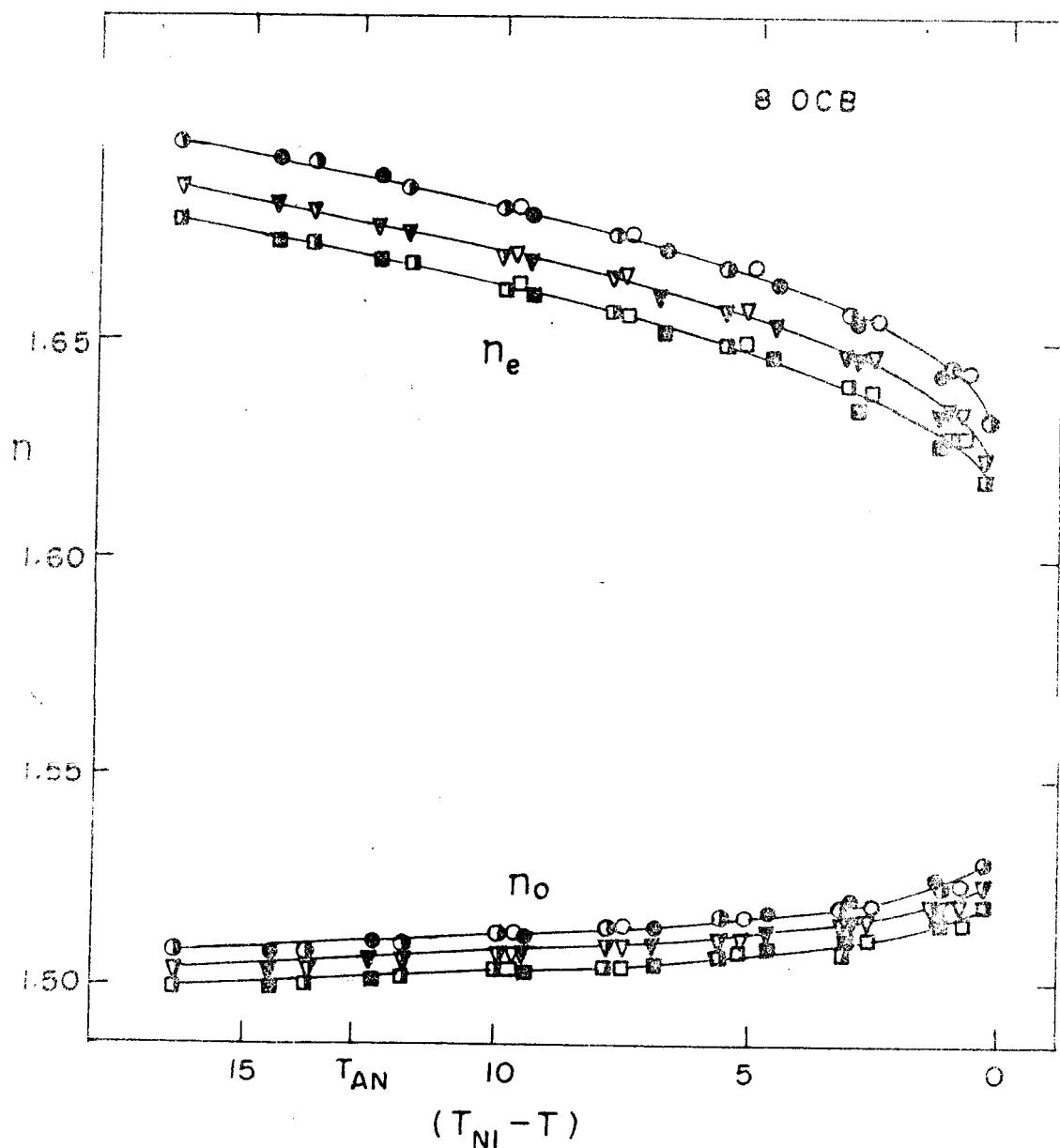


Figure 5.1a

Refractive indices of S OCB as functions of temperature. The circles, triangles and squares are the values for  $\lambda 5461 \text{ \AA}$ ,  $\lambda 5893 \text{ \AA}$  and  $\lambda 6328 \text{ \AA}$  respectively.

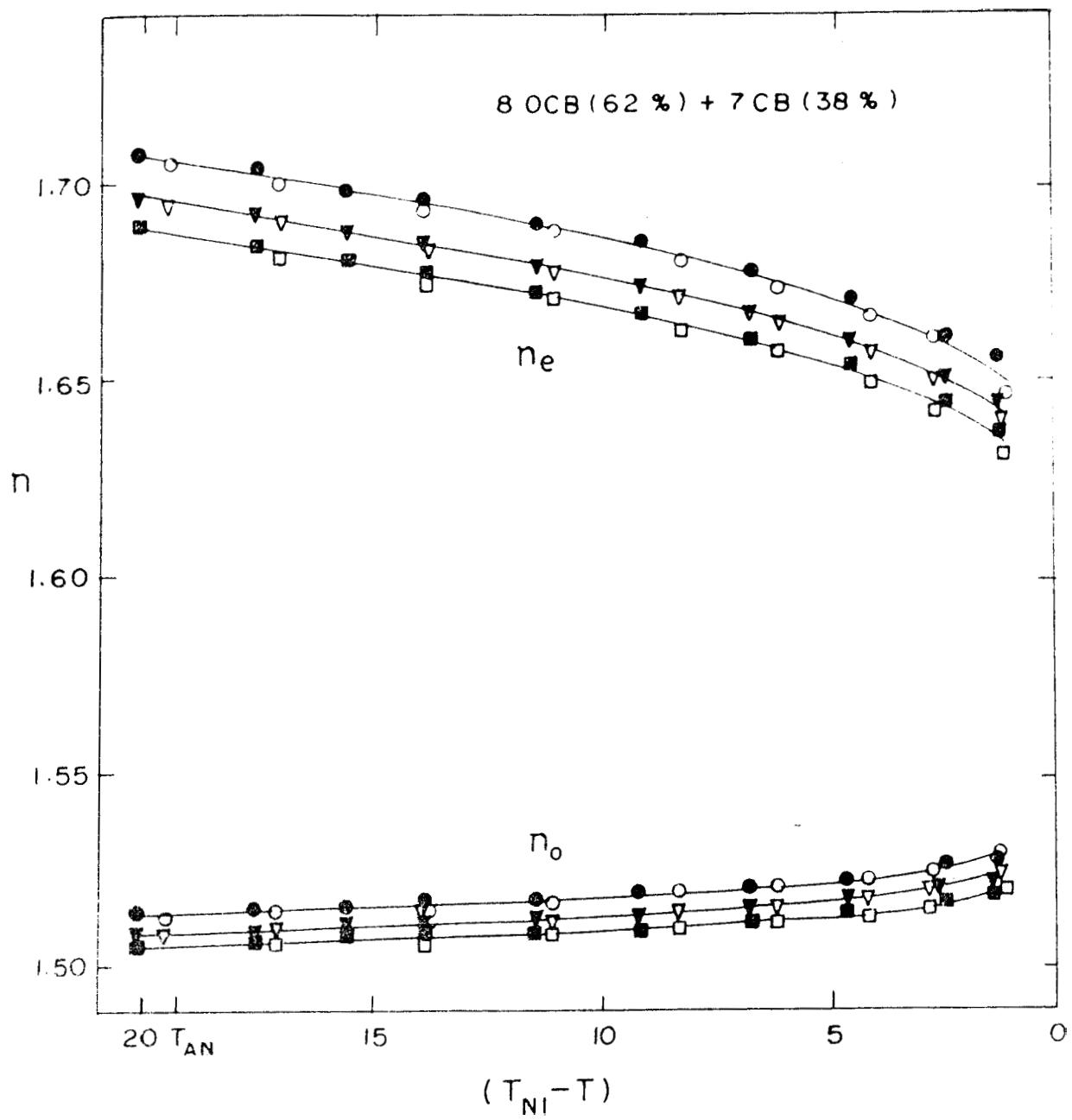


Figure 5.1b

Refractive indices of Mixture I [8 OCB (62%) + 7 CB (38%)] as functions of temperature. The circles, triangles and squares are the values for  $\lambda 5461 \text{ \AA}$ ,  $\lambda 5893 \text{ \AA}$  and  $\lambda 6328 \text{ \AA}$  respectively.

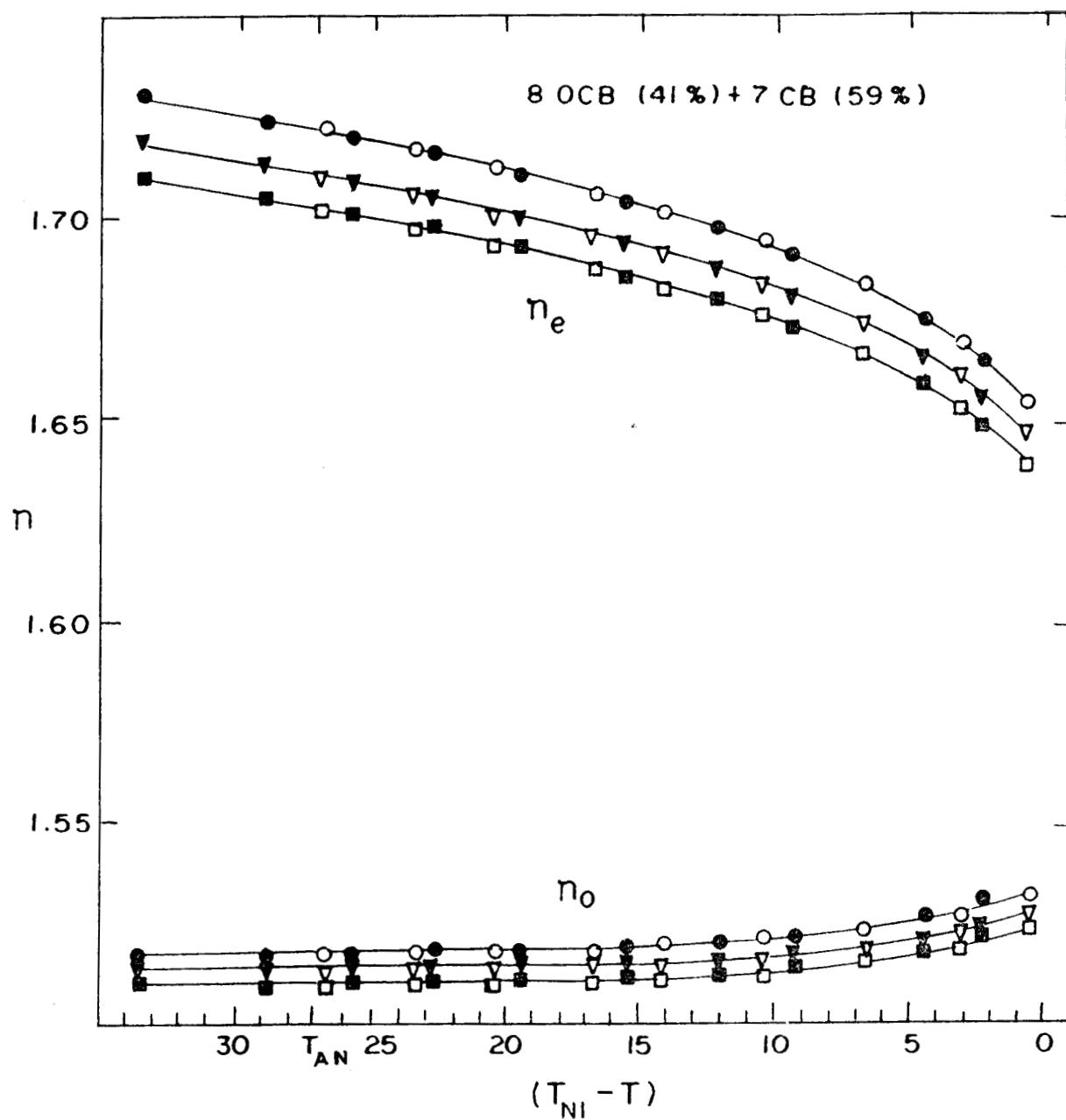


Figure 5.1c

Refractive indices of Mixture II [8 OCB (41%) + 7 CB (59%)] as functions of temperature. The circles, triangles and squares are the values for  $\lambda 5461 \text{ \AA}$ ,  $\lambda 5893 \text{ \AA}$  and  $\lambda 6328 \text{ \AA}$  respectively.  $c = 1.25 \text{ mm}^2 \text{ g}^{-1}$

calculated. The values are given in Table 5.4. The temperature variation of density from the optical data are given in Table 5.5. They are plotted in figure 5.2.

To calculate the order parameter of S OCB, from the optical data, we need the value of  $\Delta\alpha$ . We have estimated the increment in  $\Delta\alpha$  from 7CB to S OCB using bond polarisabilities (see Appendix II). The value of  $(\bar{\alpha}/\Delta\alpha)_{S \text{ OCB}}$  was estimated to be 1.37. Knowing the values of  $S$  for 7CB and S OCB, the order parameter of the mixtures, at any relative temperature, can be calculated using the equation (Chandrasekhar and Nadhusudana 1969)

$$S_{\text{mix}} = p_1(S)_1 + p_2(S)_2 \quad (5.14)$$

The temperature variation of  $S$  for S OCB and mixtures are given in figure 5.3 and Table 5.6.

### Elastic constants

We shall discuss the analysis of  $k_{22}$  and  $k_{33}$  in the next section. For the sake of completeness we have given the splay elastic constants of S OCB and its mixtures with 7CB in Table 5.7. They are represented graphically in figure 5.4.

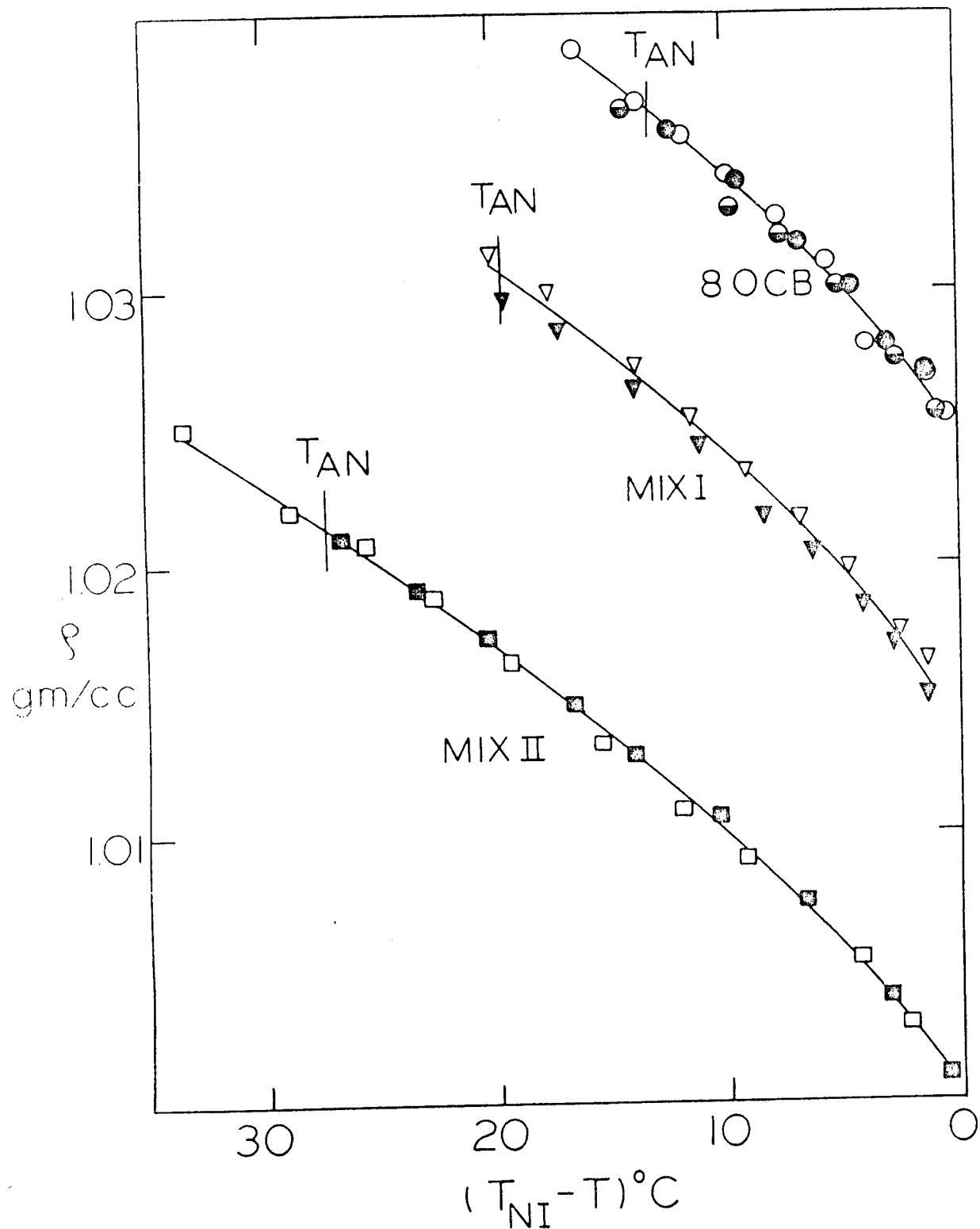


Figure 5.2: Densities of 8 OCB, Mixture I and Mixture II derived from optical anisotropy measurements as functions of the relative temperature. Each symbol represents a value averaged over the calculations for wavelengths  $\lambda 5461 \text{ \AA}$ ,  $\lambda 5893 \text{ \AA}$  and  $\lambda 6328 \text{ \AA}$ .

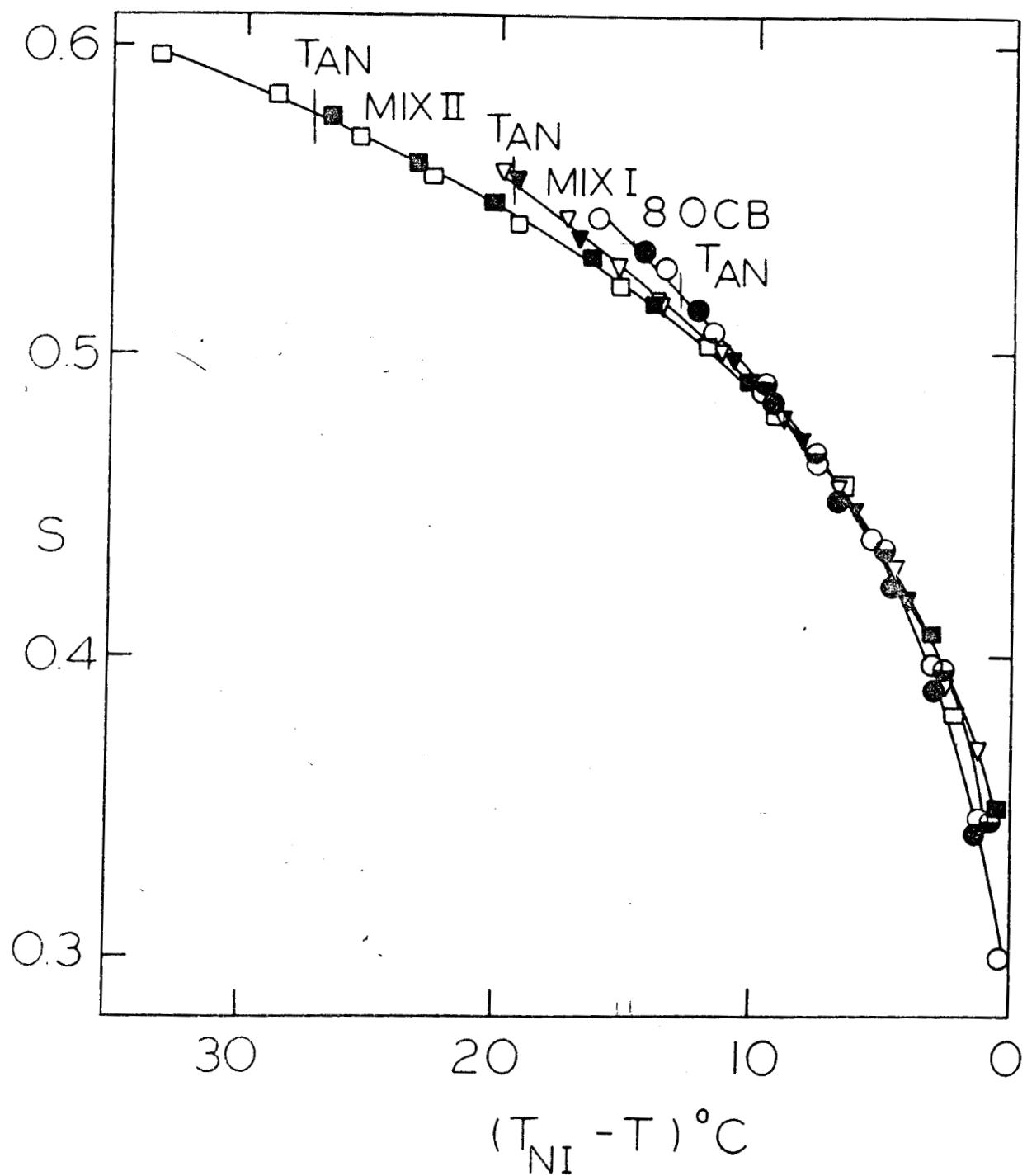


Figure 5.3

Order parameters of 8 OCB, Mixture I and Mixture II as functions of the relative temperature.  $(T_{NI} - T) ^\circ C$

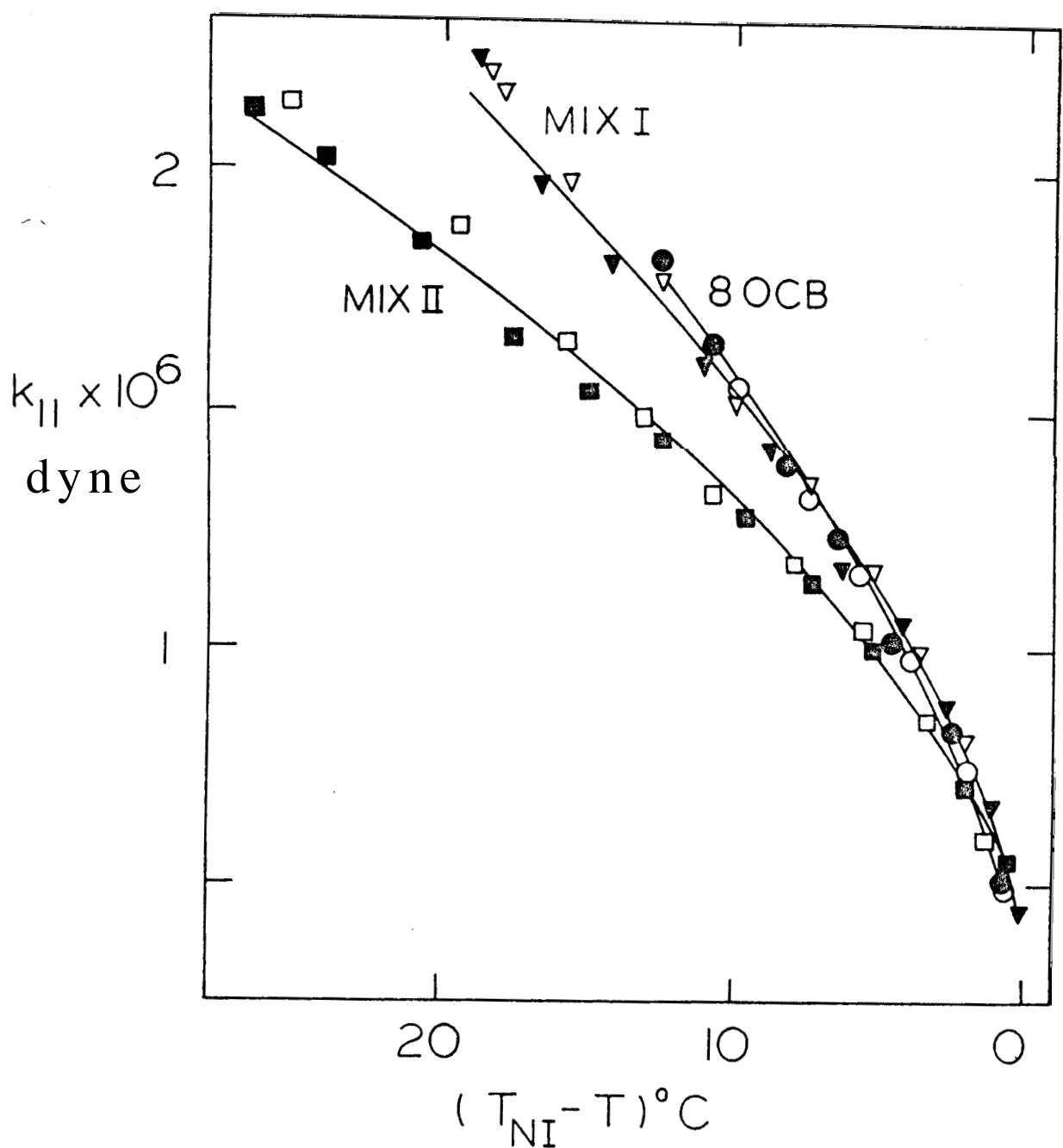


Figure 5.4

Splay elastic constants of 8 OCB, Mixture I and Mixture II as functions of the relative temperature.

### Analysis of $k_{22}$ and $k_{33}$

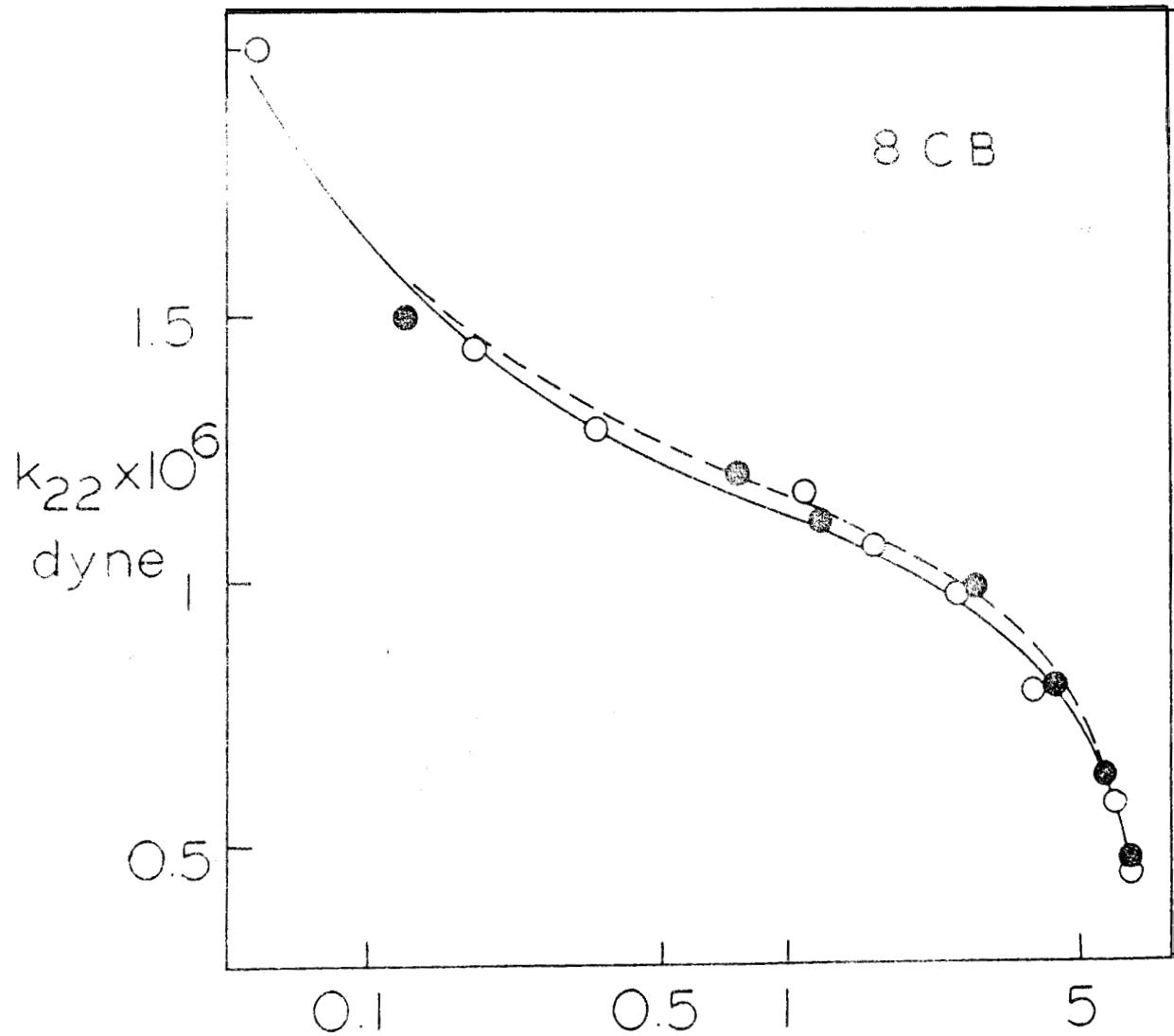
The experimental values of the twist and bend constants can be fitted to the equation (5.12). Since  $T^* = T_{AN}$  only if the transition is second order, we can treat  $T^*$  also as a variable. We have used a 4 parameter fit with variables  $c_1$ ,  $c_2$ ,  $\gamma$  and  $T^*$ .

The data for the full temperature range was first fitted to the equation (5.12). However as we have already discussed in earlier chapters the background term cannot be taken to be, accurately represented by  $c_1 s^2$ . Since the background term makes a predominant contribution near  $T_{NI}$ , it is appropriate to drop data points from higher temperature region until the R.M.S. error is minimised (see e.g., Chu and McMillan 1975). Table 5.8 gives the ratio  $T_{AN}/T_{NI}$ ,  $\Delta H_{AN}$  and  $\gamma$ . The

experimental values of  $k_{ij}$  ( $i = 2,3$ ) along with the least squares fitted values are given in Tables 5.9 and 5.10. They are plotted in figures 5.5 and 5.6 respectively.

There have been a number of experimental determinations of the critical exponent  $\gamma$ . The values are summarized in Table 5.11. Except for light scattering method, all the other determinations make use of the Freedericksz transition technique which is a static method. The method involves the application of an external field to deform the sample. Since the time constant becomes large as the A-E transition is approached, the static equilibrium in this case becomes quite uncertain. In addition, as Cheung et al. (1973)

.... cont'd.



$(T - T^*)$  °C

Figure 5.5a

Twist elastic constants of 8CB as a function of  $(T - T^*)$ . The values for different samples are marked separately. The curves are least square fitted to the equation of the type  $k_{11} = C_1 s^2 + C_2 (T - T^*)^{-\gamma}$ .

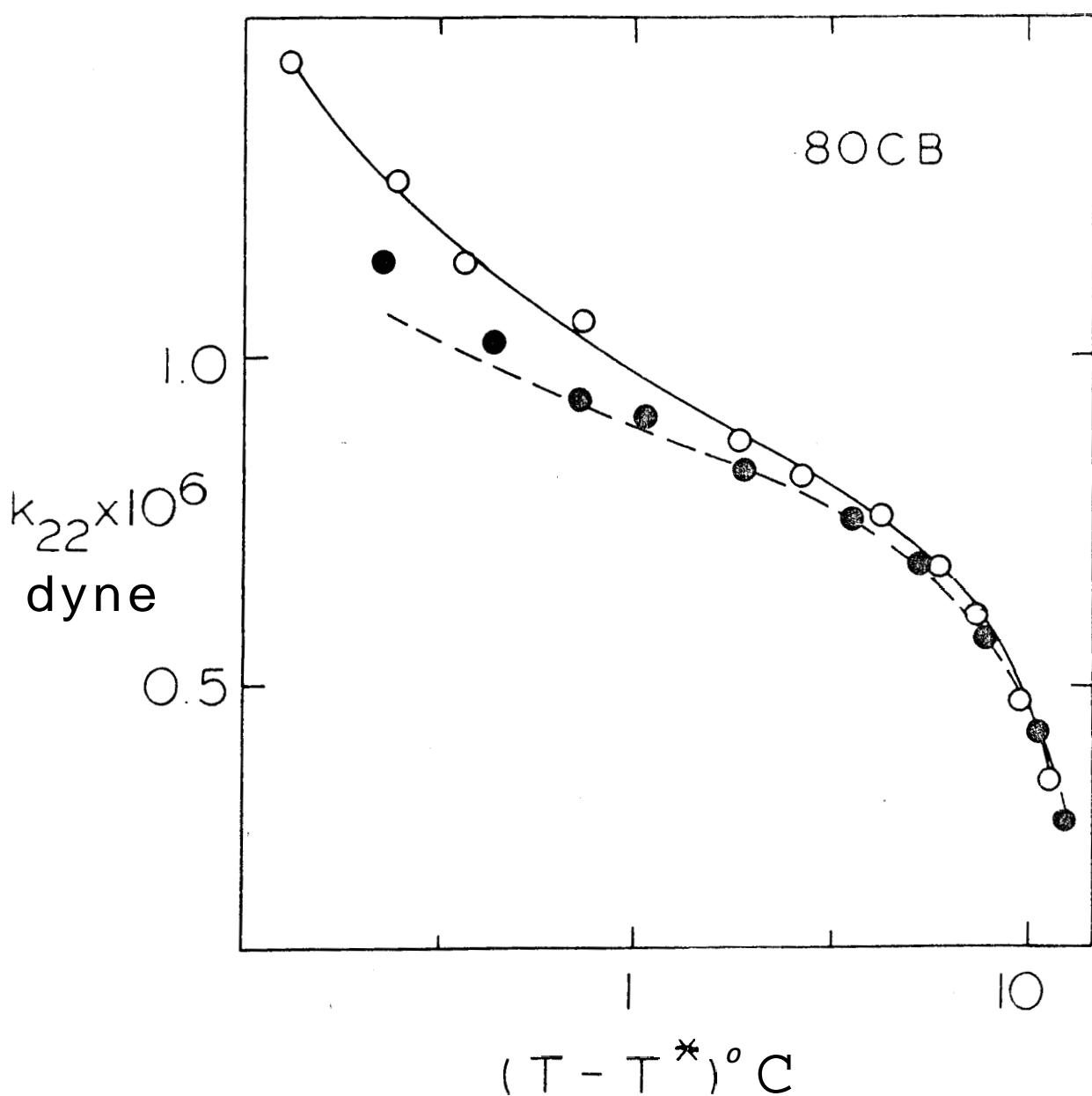


Figure 5.5b

Twist elastic constants of 8 OCB as a function of  $(T - T^*)$ .  
The values for different samples are marked separately.  
The curves are least square fitted to the equation of the  
type  $k_{ij} = c_1 s^2 + c_2 (T - T^*)^{-\gamma}$ .

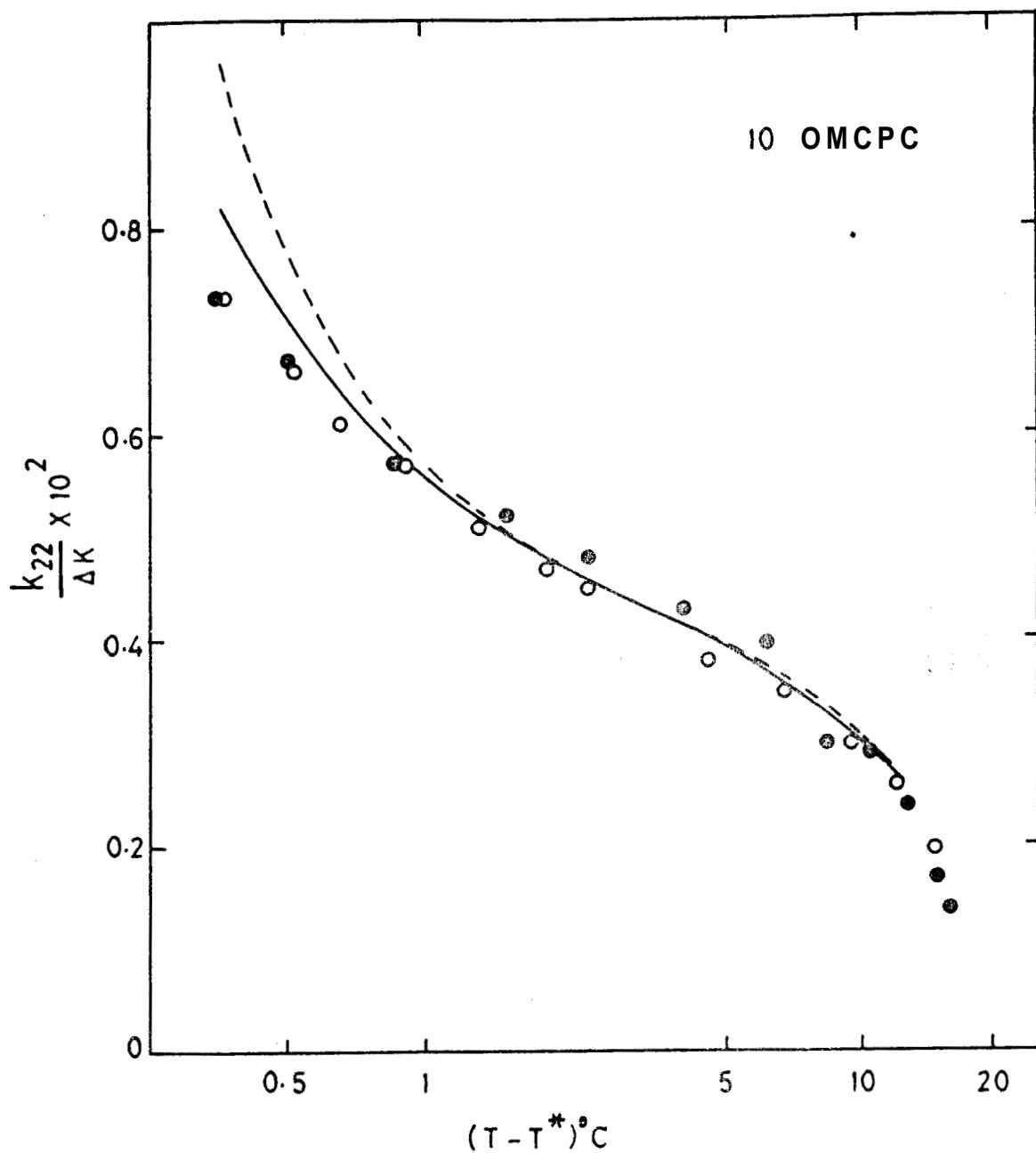


Figure 5.5c

Twist elastic constants of 10 OMCPC as a function of  $(T - T^*)^\circ C$ . The values for different samples are marked separately. The curves are least square fitted to the equation of the type  $k_{11} = C_1 S^2 + C_2 (T - T^*)^{-\gamma}$ .

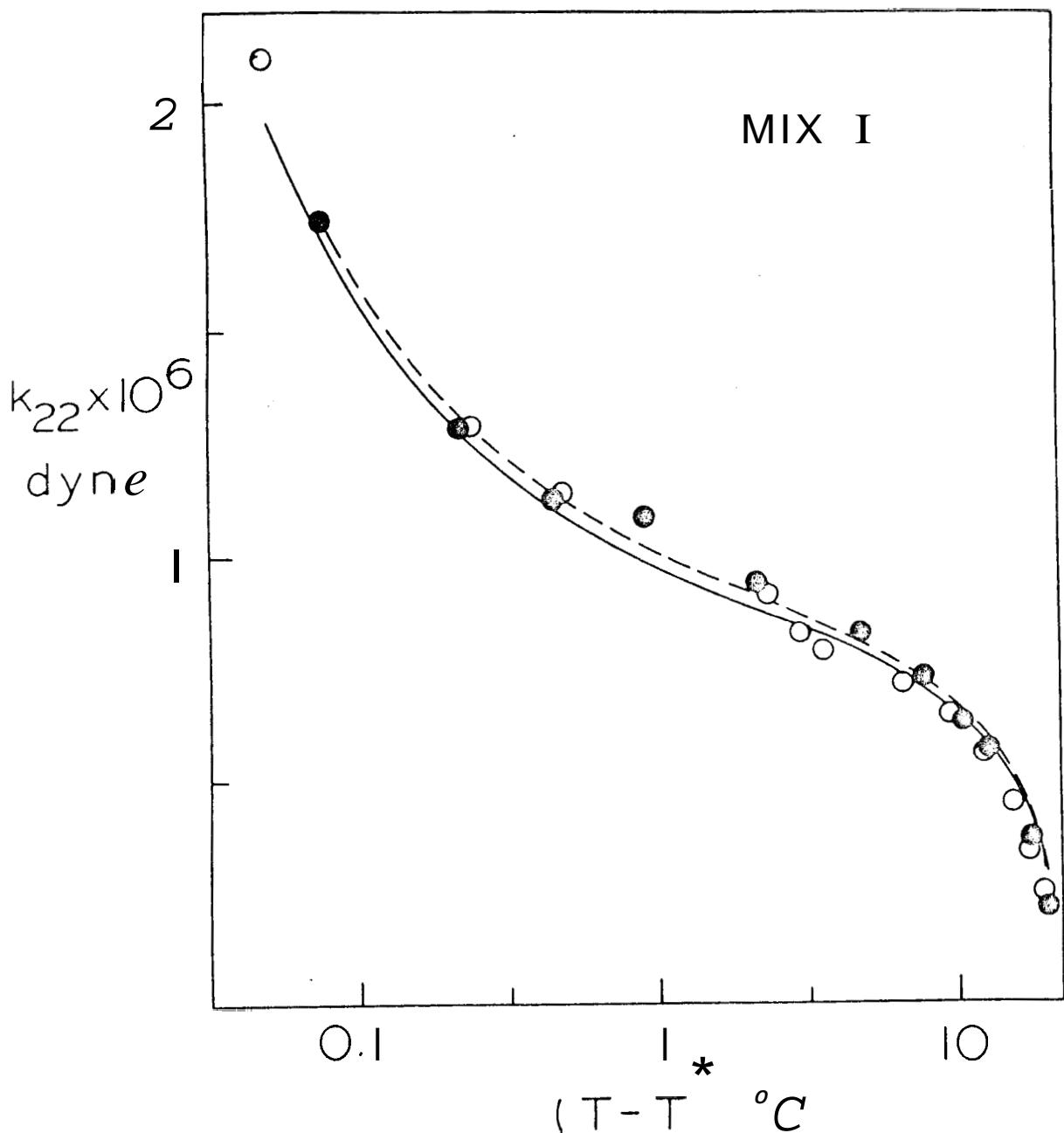


Figure 5.5d

Twist elastic constants of Mixture I as a function of  $(T - T^*)$ . The values for different samples are marked separately. The curves are least square fitted to the equation of type  $k_{11} = C_1 S^2 + C_2 (T - T^*)^{-\gamma}$ .

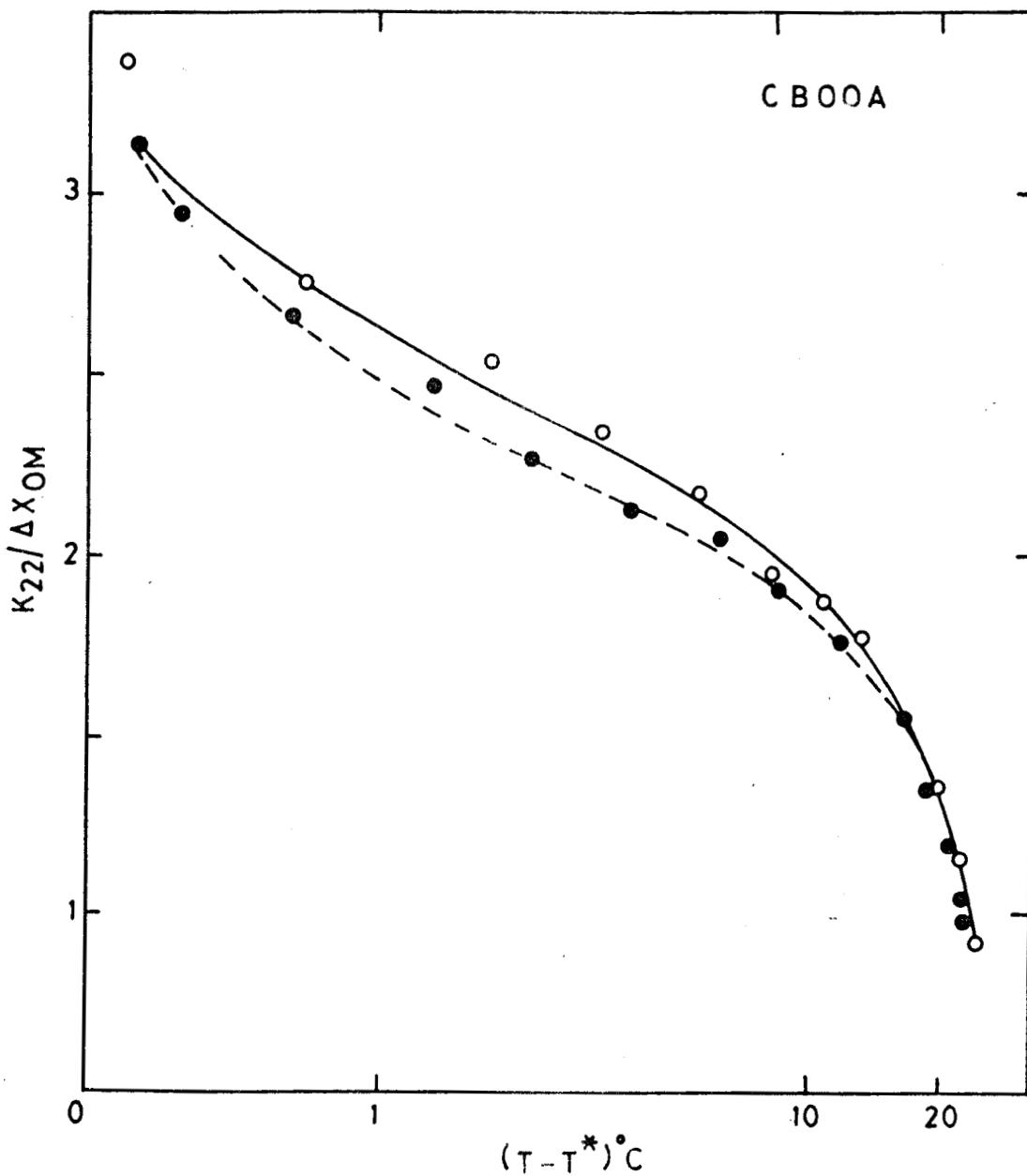


Figure 5.5e

Twist elastic constants of CB00A as a function of  $(T - T^*)$ . The values for different samples are marked separately. The curves are least square fitted to the equation of the type  $k_{11} = C_1 s^2 + C_2 (T - T^*)^{-1}$ .

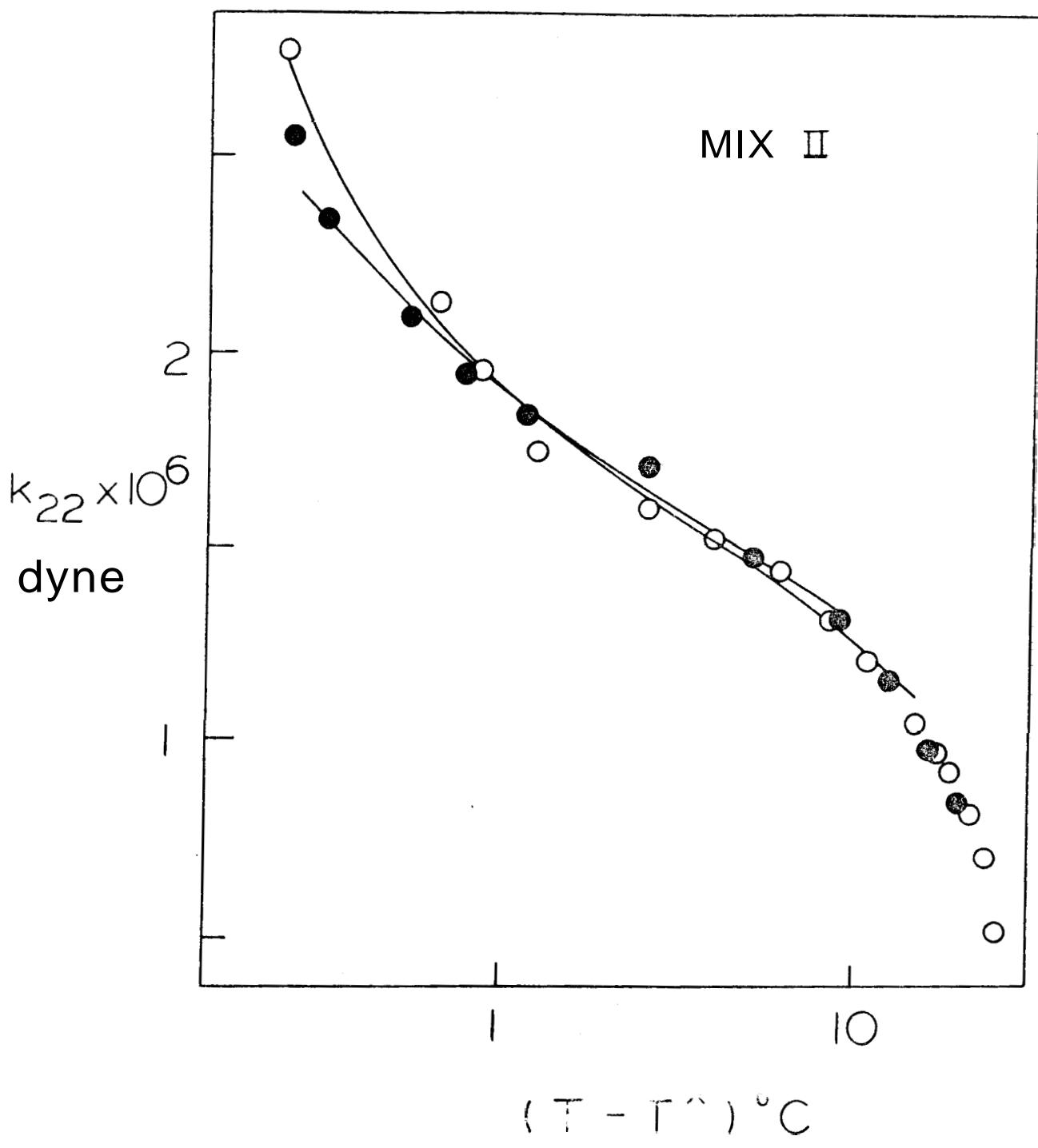


Figure 5.5f

Twist elastic constants of Mixture II as a function of temperature. The values for different samples are marked separately. The curves are least square fitted to the equation of the type  $k_{ii} = C_1 S^2 + C_2 (T - T^x)^{-\gamma}$ .

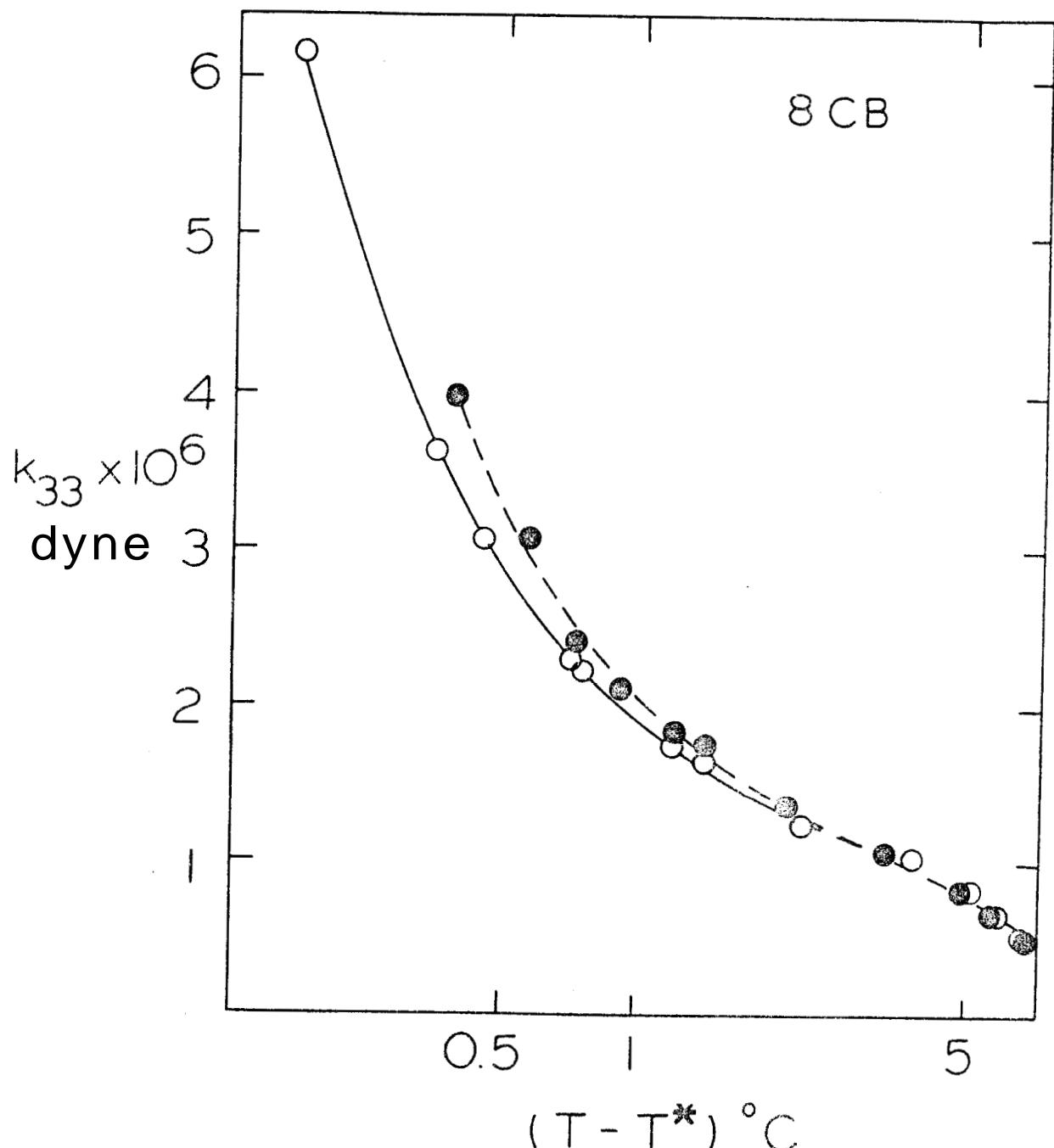


Figure 5.6a

Bend elastic constant of 8CB as a function of  $T - T^*$ .  
The least square fitting is done as mentioned in figure 5.5.

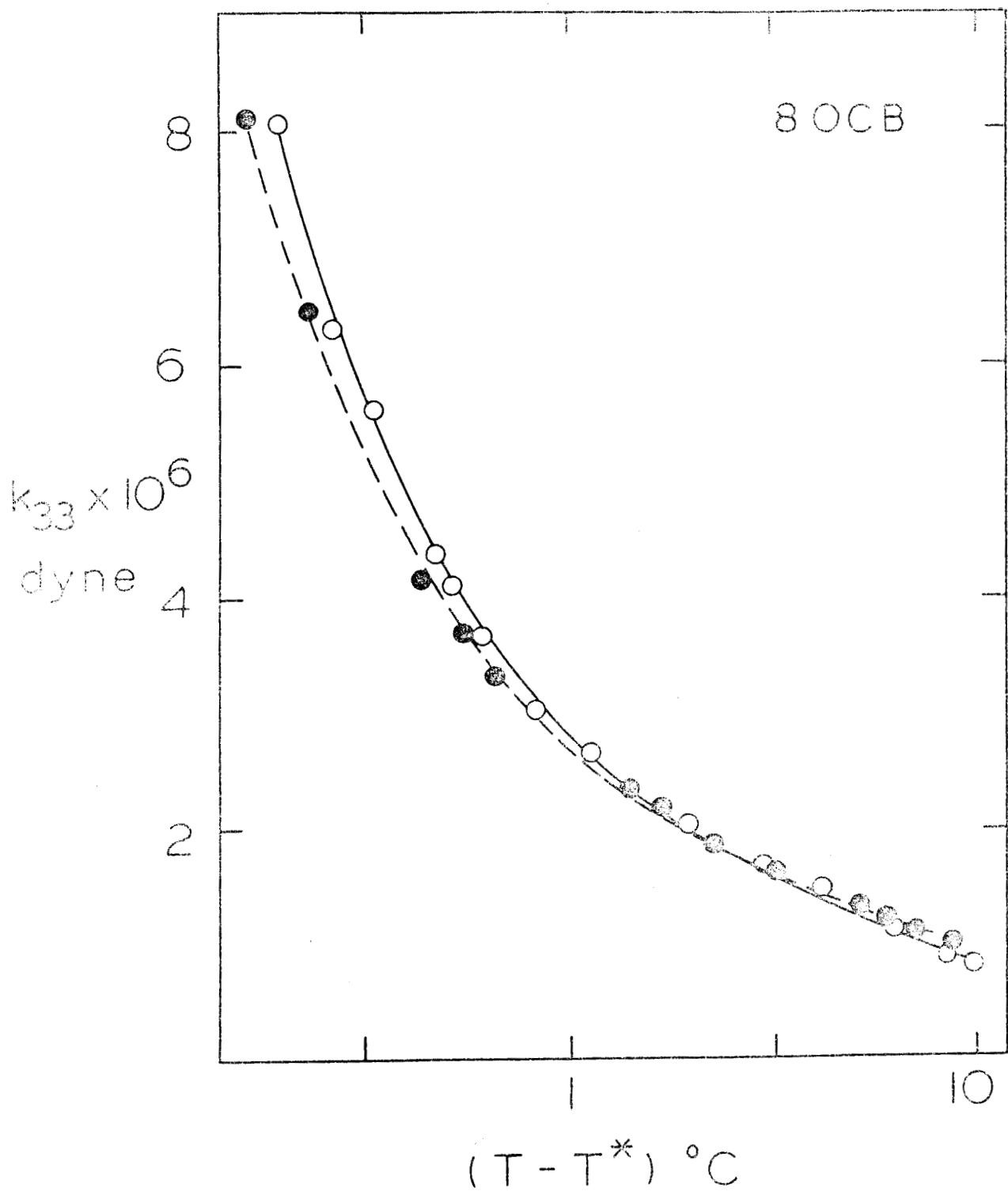


Figure 5.6b

Bend elastic constant of 8 OCB as a function of  $T-T^*$ .  
The least square fitting is done as mentioned in figure 5.5

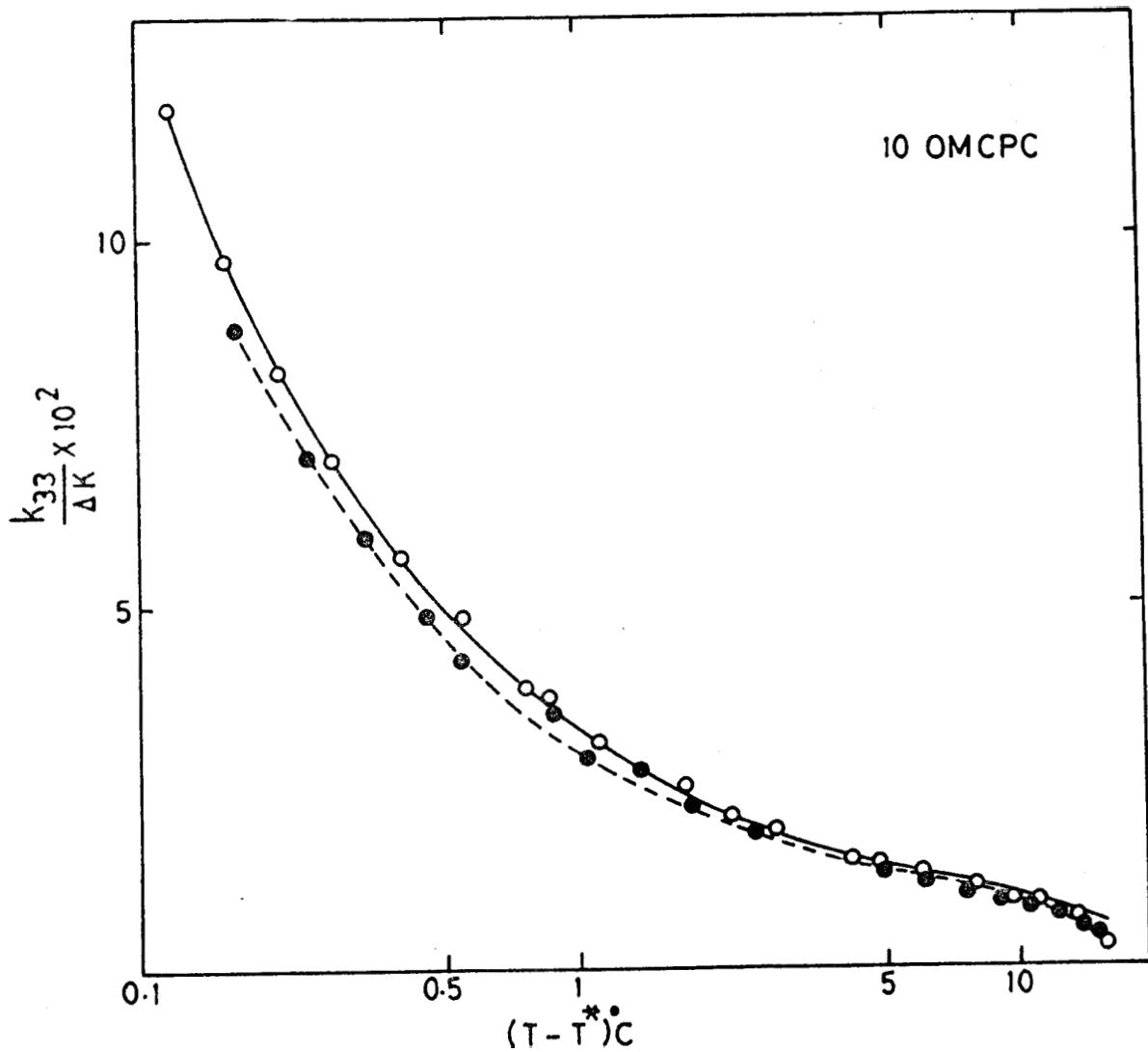


Figure 5.6c

Bend elastic constant of 10 OMCPC as a function of  $T - T_c^*$   
The least square fitting is done as mentioned in figure 5.5

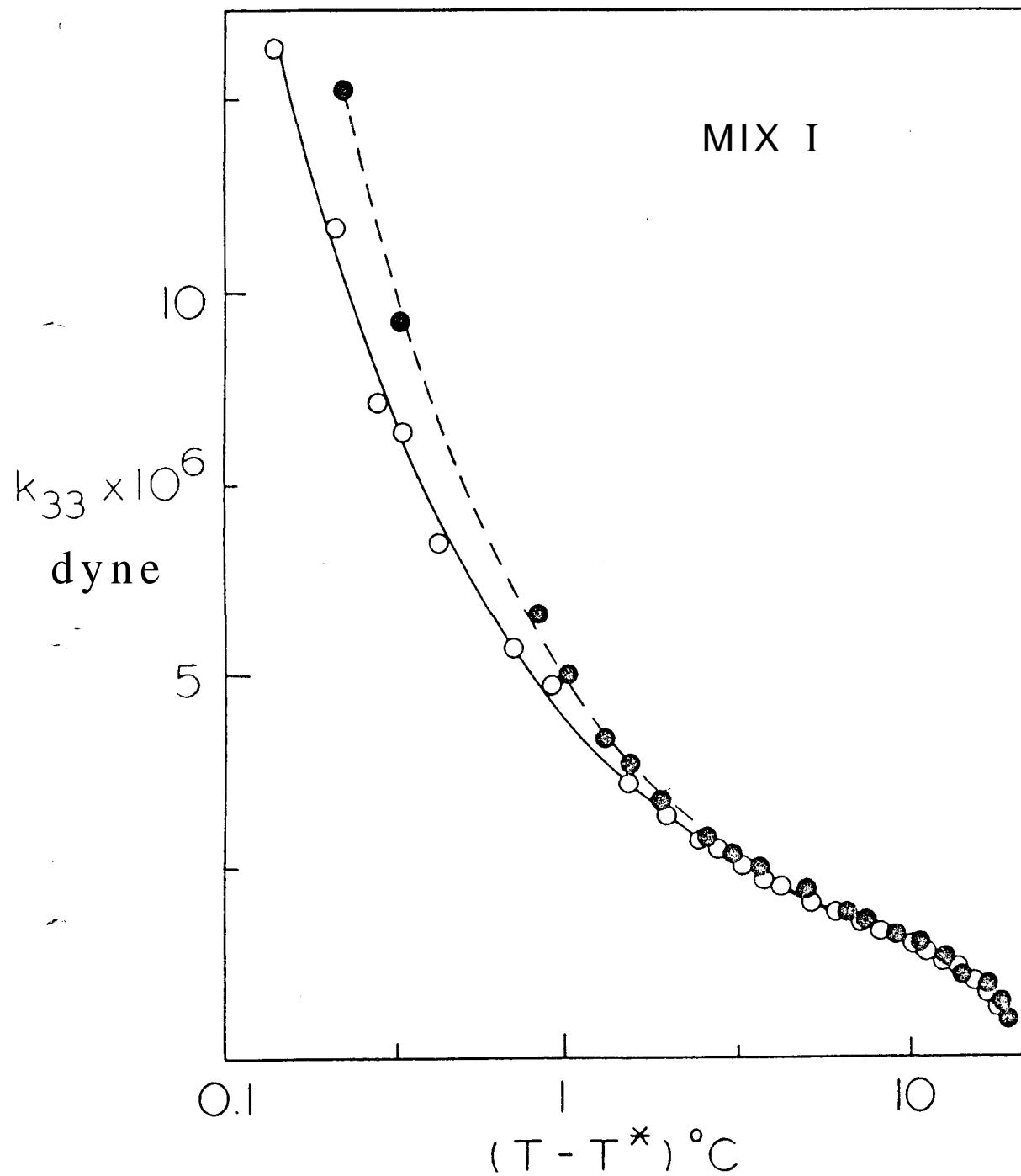


Figure 5.6d

Bend elastic conetant of Mixture I as a function of  $T-T^*$ .  
The least square fitting is done as mentioned in figure 5.5

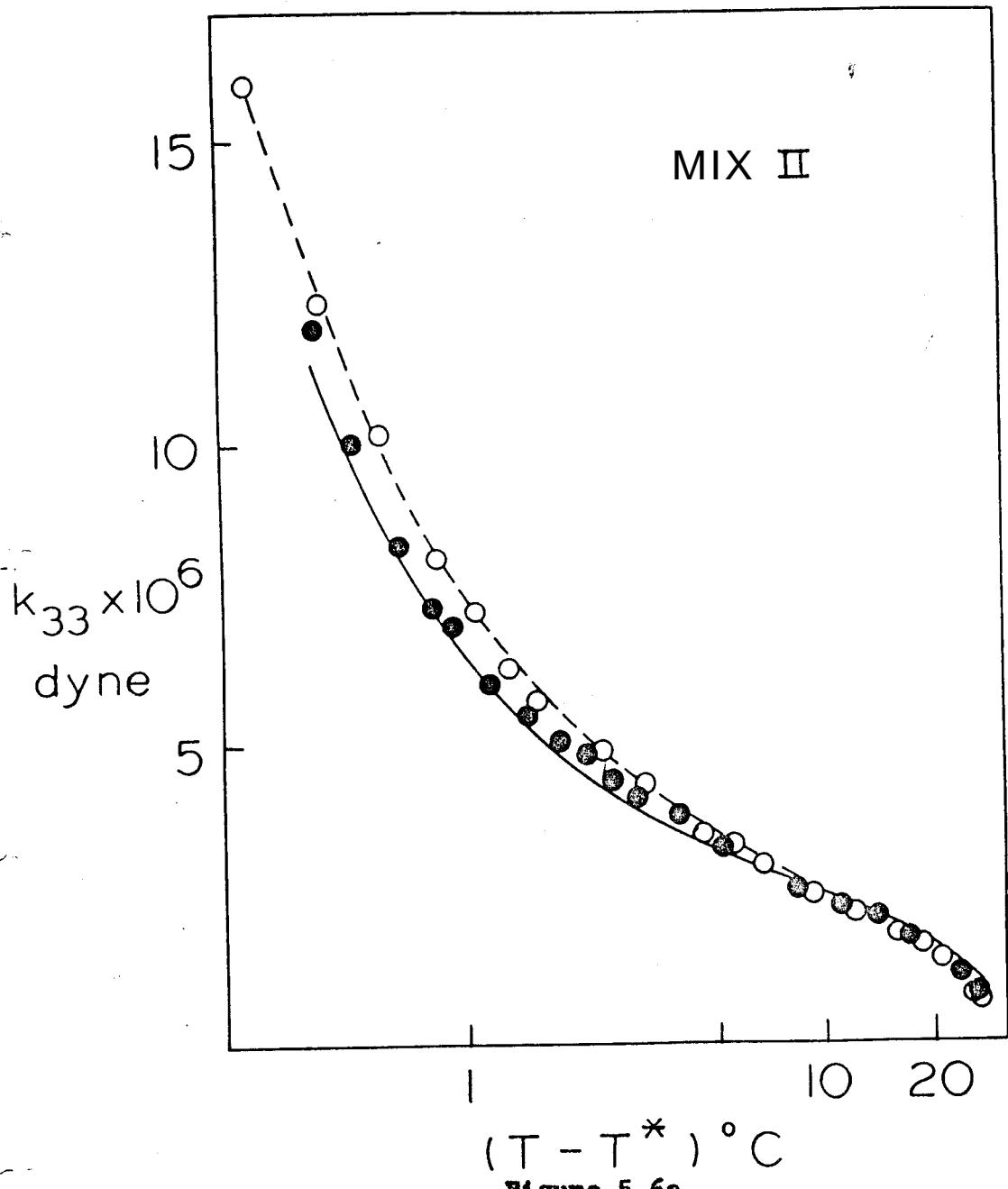


Figure 5.6e

Bend elastic constant of Mixture II as a function of  $T-T^*$ .  
The least square fitting is done as mentioned in Figure 5.5

have pointed out, one cannot approach  $T_{AN}$  very closely because in this region an instability of a certain type sets in. For these reasons, the light scattering method in which no external field is used, is expected to be the most accurate. From the table, we see that an accurate light scattering experiment gives a value  $\gamma = 0.5$  while other methods give higher values.

Another important factor to be considered in the data analysis is the purity of the sample. Gladis (1974) has shown that the value of  $\gamma$  is extremely sensitive to the state of purity of the sample. While a very pure CBBA gave a value  $\gamma = 0.5$ , the one doped with a small amount ( $\sim 1.5\%$ ) of ortho MBBA raised the value of  $\gamma$  to 1.0. Thus it is clear that a value  $\gamma$  other than 0.5 and 0.66 might either be due to the impurity content in the sample or due to the inaccuracies in the experiment.

We must also mention here that de Gennes (1973) has pointed out that some compounds may give  $\gamma = 0.66$  and some  $\gamma = 0.5$ . Also Chu and McKillian (1975) conclude that the value of  $\gamma = 0.5$  for CBBA might be due to the fact that the compound is near its tricritical point.

In all our experiments, we have not made any

special efforts to purify the sample. However since most of the experiments were done on chemically stable compounds, there is little chance of the sample decomposing during the experiment.

Since the temperature controls in our experiments were not specially designed for studying precritical phenomena, we do not put any emphasis on the values of  $\gamma$  obtained. However, we wish to point out that  $\gamma$  is closer to 0.66 rather than to 0.5 in most cases. We also observe from Table 5.8 that  $\gamma$  obtained for  $k_{22}$  in any compound is smaller, in general, than that for  $k_{33}$ . We know that even in nematics which do not have smectic A at lower temperatures, the index  $x$  in the equation  $k_{11} = CS^x$  is larger than 2 for  $k_{33}$  while for  $k_{22}$  it is nearly 2. Therefore for  $k_{33}$  a background tan of  $C_1 S^2$  may not be quite appropriate.

From Table 5.8, it is also seen that as the nematic range is increased by adding 7CB to 8OCB, the heat of A-N transition decreases. Correspondingly,  $\gamma$  has a tendency to decrease. Very close to the tricritical point, one would expect  $\gamma$  to attain the mean field value.

### References

- Gopalakrishnan, S., Madhusudana, N.V. 1969  
J. de Phys. 30, 04-24.
- Cheung, L., and Meyer, R.B. 1973 Phys. Lett. 43A, 261.
- Cheung, L., Meyer, R.B. and Gruler, H. 1973 Phys. Rev. Lett. 31, 349.
- Chu, K.C. and McMillan, W.L. 1975 Phys. Rev. A11, 1059.
- Cladis, P.E. 1974 Phys. Lett. 48A, 179.
- de Gennes, P.G. 1969 J. de Phys. 30, 04-65.
- de Gennes, P.G. 1972 Solid State Commun. 10, 753.
- de Gennes, P.G. 1973 Mol. Cryst. Liq. Cryst. 21, 49.
- Delaye, M., Ribotta, R. and Durand, G. 1973 Phys. Rev. Lett. 31, 443.
- Delaye, M. 1976 (to be published).
- Djurek, D., Baturic-Rubcic, J. and Franulovic, K. 1974 Phys. Rev. Lett. 33, 1126.
- Frank, P.C. 1958 Disc. Faraday Soc. 25, 19.
- Fernandes, J.R. and Venugopalan, S. 1976 Mol. Cryst. Liq. Cryst. 32, 113.
- Leger, L. 1973 Phys. Lett. 44A, 535.
- Maier, W. and Saupe, A. 1958 Z. Naturforsch. 13a, 564
- Maier, W. and Saupe, A. 1959 Z. Naturforsch. 14a, 882

- Maier , W. and Saupe, A. 1960 Z.Naturforsch. 15a, 287
- McMillan, W.L. 1971 Phys. Rev. A, 4, 1238.
- McMillan, W.L. 1972 Phys. Rev. A, 6, 936.
- McMillan, W.L. 1973 Phys. Rev. A, 7, 1419.
- Torza, S. and Cladis, P.E. 1974 Phys. Rev. Lett.  
32, 1406.
- Torza, S. and Cladis P.E. 1975 (Private communication)
- Wilson, K.G. 1972 Phys. Rev. Lett. 28, 548.

Table 5.1

Transition temperatures of 4'-n-octyloxy-4-cyanobiphenyl  
and mixtures

	crystal-smectic or crystal-nematic	@ see%Pc~- nematic	nematic- isotropic
8 OCB	53.3°C	66.9°C	76.7°C
Mixture I	12.2°C	45.7°C	65.3°C
Mixture II	12.9°C	25.2°C	56.5°C
Mixture I : 8 OCB (62 mole %) + 7CB (38 mole %)			
Mixture II: 8 OCB (41 mole %) + 7CB (59 mole %)			

Table 5.2

Order parameter and density of CB60CA

T <sub>NI-T</sub> °C	Order parameter S	density ρ g/cm <sup>3</sup>
24.4	0.625	0.9422
21.5	0.608	0.9406
19.1	0.592	0.9388
14.2	0.574	0.9368
11.8	0.548	0.9355
8.9	0.532	0.9337
7.0	0.508	0.9325
5.5	0.492	0.9315
3.1	0.465	0.9298
2.1	0.434	0.9290
0.7	0.412	0.9277

Table 5.3  
Refractive indices of 8 OCB and its mixtures with 7CB

T <sub>NI-T</sub> °C	λ 5461 Å		λ 5893 Å		λ 6328 Å	
	n <sub>o</sub>	n <sub>e</sub>	n <sub>o</sub>	n <sub>e</sub>	n <sub>o</sub>	n <sub>e</sub>
(i) 8 OCB						
16.3 (II)	1.508	1.695	1.503	1.685	1.500	1.677
14.4 (I)	1.508	1.691	1.503	1.681	1.500	1.673
13.7 (II)	1.508	1.690	1.504	1.679	1.501	1.672
12.4 (I)	1.510	1.687	1.505	1.676	1.502	1.668
11.8 (II)	1.510	1.684	1.506	1.674	1.502	1.667
9.9 (II)	1.512	1.679	1.507	1.669	1.504	1.661
9.7 (III)	1.511	1.679	1.506	1.669	1.503	1.661
9.4 (I)	1.512	1.678	1.508	1.668	1.504	1.660
7.7 (II)	1.513	1.673	1.509	1.664	1.505	1.656
7.6 (III)	1.513	1.673	1.509	1.664	1.504	1.655
6.8 (I)	1.514	1.670	1.510	1.659	1.506	1.651
5.5 (II)	1.516	1.666	1.511	1.656	1.507	1.648
5.1 (III)	1.515	1.665	1.511	1.655	1.507	1.648
4.6 (I)	1.517	1.662	1.512	1.652	1.509	1.645
3.1 (II)	1.519	1.655	1.515	1.646	1.507	1.639
3.0 (I)	1.520	1.654	1.515	1.645	1.511	1.634
2.6 (III)	1.519	1.654	1.514	1.644	1.510	1.637
1.3 (I)	1.525	1.642	1.519	1.632	1.516	1.626
1.2 (II)	1.524	1.643	1.519	1.634	1.515	1.627
0.8 (III)	1.523	1.641	1.518	1.633	1.514	1.626
0.4 (II)	1.529	1.631	1.524	1.622	1.519	1.617
<hr/>						
(ii) Mixture I						
20.1 (I)	1.514	1.707	1.509	1.697	1.506	1.689
19.5 (II)	1.513	1.705	1.509	1.695	-	-
17.6 (I)	1.515	1.703	1.510	1.692	1.507	1.684
17.1 (II)	1.515	1.700	1.510	1.690	1.507	1.682
15.6 (I)	1.515	1.698	1.511	1.687	1.508	1.680
13.9 (II)	1.516	1.694	1.511	1.684	1.508	1.676
13.9 (I)	1.517	1.695	1.512	1.684	1.509	1.677
11.5 (I)	1.517	1.685	1.513	1.679	1.510	1.672
11.1 (II)	1.517	1.688	1.512	1.678	1.509	1.671
9.2 (I)	1.519	1.684	1.514	1.674	1.510	1.666
8.3 (II)	1.519	1.680	1.514	1.671	1.510	1.663
6.8 (I)	1.520	1.677	1.515	1.667	1.512	1.660
6.2 (II)	1.521	1.673	1.516	1.665	1.512	1.658
4.7 (I)	1.522	1.670	1.518	1.660	1.514	1.653
4.2 (II)	1.523	1.666	1.518	1.657	1.514	1.650
2.8 (II)	1.525	1.660	1.520	1.650	1.516	1.642
2.6 (I)	1.526	1.660	1.521	1.650	1.517	1.643
1.4 (I)	1.527	1.655	1.522	1.645	1.519	1.637
1.3 (II)	1.530	1.646	1.524	1.639	1.521	1.631
<hr/>						

Table 5.3 continued

$\frac{3}{d} - T$	$\lambda 5461 \text{ \AA}$	$\lambda 5893 \text{ \AA}$	$\lambda 6328 \text{ \AA}$			
$n_o$	$n_e$	$n_o$	$n_e$	$n_o$	$n_e$	
(111) Mixture II						
33.4 (I)	1.517	1.730	1.513	1.719	1.510	1.710
28.9 (I)	1.517	1.724	1.513	1.714	1.509	1.705
26.7 (II)	1.517	1.722	1.513	1.711	1.510	1.703
25.7 (II)	1.518	1.720	1.514	1.709	1.510	1.701
23.4 (II)	1.518	1.717	1.514	1.706	1.510	1.698
22.8 (II)	1.518	1.716	1.514	1.705	1.510	1.697
20.4 (II)	1.518	1.712	1.514	1.701	1.511	1.694
19.5 (II)	1.518	1.710	1.514	1.700	1.511	1.692
16.6 (II)	1.519	1.706	1.515	1.696	1.511	1.689
15.5 (II)	1.519	1.703	1.515	1.693	1.511	1.685
14.1 (II)	1.520	1.701	1.515	1.691	1.512	1.683
12.1 (II)	1.520	1.697	1.516	1.687	1.512	1.679
10.4 (II)	1.521	1.694	1.517	1.684	1.513	1.676
9.4 (II)	1.521	1.690	1.517	1.680	1.514	1.672
6.7 (II)	1.524	1.683	1.519	1.674	1.516	1.667
4.5 (II)	1.526	1.674	1.522	1.665	1.518	1.658
3.1 (II)	1.527	1.669	1.523	1.661	1.519	1.653
2.4 (II)	1.530	1.663	1.525	1.654	1.521	1.648
0.6 (II)	1.532	1.654	1.527	1.646	1.524	1.635

Table 5.4

Densities and average polarizabilities of 8 OCB and its mixtures with 7CB

Density $\rho$ at $(T_{NI}-T)=12^\circ\text{C}$ in gm/cc	Average polarizability $\bar{\alpha} \times 1024 \text{ cm}^3$		
	$\lambda 5461 \text{ \AA}$	$\lambda 5893 \text{ \AA}$	$\lambda 6328 \text{ \AA}$
8 OCB	1.0354*	38.64	38.28
Mixture I	1.0239	37.92	37.57
Mixture II	1.0301	37.52	37.17

\*measured value.

Table 5.5: Density of S OCB and mixtures

$T_{NI} - T$ °C		Density $\lambda 5461 \text{ \AA}$	Density $\lambda 5893 \text{ \AA}$	Density $\lambda 6328 \text{ \AA}$	Mean
(i) S OCB					
0.8	1.0253	1.0254	1.0258	1.0255	
2.6	1.0274	1.0274	1.0281	1.0276	
5.1	1.0299	1.0296	1.0310	1.0302	
7.6	1.0321	1.0323	1.0320	1.0321	
9.7	1.0326	1.0328	1.0335	1.0330	
1.3	1.0268	1.0264	1.0275	1.0269	
3.0	1.0285	1.0286	1.0273	1.0281	
4.6	1.0298	1.0299	1.0308	1.0302	
6.8	1.0317	1.0314	1.0323	1.0318	
9.4	1.0337	1.0337	1.0346	1.0340	
12.4	1.0360	1.0358	1.0367	1.0362	
14.4	1.0367	1.0362	1.0371	1.0367	
0.4	1.0256	1.0250	1.0259	1.0255	
1.2	1.0271	1.0267	1.0276	1.0271	
3.9	1.0289	1.0289	1.0265	1.0281	
5.5	1.0311	1.0308	1.0311	1.0310	
7.7	1.0323	1.0327	1.0335	1.0328	
9.8	1.0340	1.0338	1.0350	1.0343	
11.8	1.0354	1.0354	1.0367	1.0358	
13.7	1.0365	1.0362	1.0379	1.0369	
16.3	1.0388	1.0386	1.0396	1.0390	
(ii) Mixture I					
1.5	1.0148	1.0148	1.0153	1.0150	
2.8	1.0169	1.0170	1.0168	1.0169	
4.1	1.0181	1.0181	1.0188	1.0183	
6.2	1.0201	1.0203	1.0206	1.0203	
8.3	1.0213	1.0220	1.0218	1.0217	
11.1	1.0242	1.0239	1.0245	1.0242	
13.9	1.0260	1.0263	1.0269	1.0264	
17.1	1.0283	1.0285	1.0287	1.0285	
19.5	1.0294	1.0301		1.0297	
1.4	1.0163	1.0163	1.0165	1.0164	
2.6	1.0174	1.0172	1.0180	1.0175	
4.7	1.0197	1.0196	1.0202	1.0198	
6.8	1.0215	1.0213	1.0219	1.0216	
9.2	1.0234	1.0233	1.0235	1.0234	
11.5	1.0252	1.0250	1.0261	1.0254	
13.9	1.0271	1.0270	1.0278	1.0273	
15.6	1.0276	1.0278	1.0286	1.0280	
17.6	1.0301	1.0296	1.0303	1.0300	
20.1	1.0311	1.0312	1.0318	1.0314	

Table 5.5 continued

$\frac{\% \text{NI}}{-T}$	Density $\rho$ gm/cc				
	°C	$\lambda 5461 \text{ \AA}$	$\lambda 5893 \text{ \AA}$	$\lambda 6328 \text{ \AA}$	Mean
(iii) Mixture II					
0.6	1.0004	1.0007	1.0016	1.0010	
3.1	1.0034	1.0036	1.0045	1.0038	
6.7	1.0069	1.0072	1.0081	1.0074	
10.4	1.0099	1.0106	1.0108	1.0105	
14.1	1.0124	1.0126	1.0136	1.0129	
16.6	1.0142	1.0144	1.0157	1.0148	
20.4	1.0167	1.0168	1.0180	1.0172	
23.4	1.0186	1.0187	1.0197	1.0190	
26.7	1.0206	1.0206	1.0214	1.0209	
2.4	1.0022	1.0026	1.0038	1.0029	
4.5	1.0045	1.0052	1.0063	1.0053	
9.4	1.0085	1.0087	1.0097	1.0090	
12.1	1.0103	1.0107	1.0118	1.0109	
15.5	1.0130	1.0132	1.0139	1.0154	
19.5	1.0155	1.0165	1.0168	1.0164	
22.8	1.0186	1.0188	1.0190	1.0188	
25.7	1.0206	1.0204	1.0210	1.0207	
28.9	1.0214	1.0221	1.0224	1.0220	
33.4	1.0245	1.0248	1.0257	1.0250	

Table 5.6  
Order parameters of 8 OCB and mixtures

$T_{NI} - T$ °C	S			
	$\lambda 5461 \text{ \AA}$	$\lambda 5893 \text{ \AA}$	$\lambda 6328 \text{ \AA}$	Mean
(i) 8 OCB				
0.8	0.346	0.347	0.349	0.347
2.6	0.394	0.395	0.396	0.395
5.1	0.438	0.436	0.436	0.437
7.6	0.467	0.468	0.466	0.467
9.7	0.491	0.490	0.490	0.490
1.3	0.342	0.342	0.343	0.342
3.0	0.391	0.391	0.383	0.388
4.6	0.424	0.423	0.423	0.423
6.8	0.454	0.452	0.450	0.452
9.4	0.484	0.484	0.483	0.484
12.4	0.515	0.514	0.515	0.515
14.4	0.535	0.536	0.535	0.535
0.4	0.299	0.297	0.305	0.300
1.2	0.346	0.348	0.348	0.347
3.1	0.397	0.397	0.410	0.397
5.5	0.440	0.439	0.439	0.439
7.7	0.466	0.467	0.466	0.466
9.9	0.489	0.489	0.487	0.488
11.8	0.507	0.507	0.508	0.507
13.7	0.529	0.528	0.529	0.529
16.3	0.545	0.545	0.545	0.545
(ii) Mixture I				
1.3	0.342	0.346	0.344	0.344
2.8	0.396	0.394	0.392	0.394
4.1	0.419	0.420	0.421	0.420
6.2	0.446	0.449	0.451	0.449
8.3	0.471	0.473	0.473	0.472
11.1	0.497	0.498	0.501	0.499
13.9	0.520	0.519	0.519	0.519
17.1	0.538	0.540	0.540	0.539
19.5	0.558	0.558	-	0.558
1.4	0.375	0.369	0.367	0.370
2.6	0.392	0.392	0.392	0.392
4.7	0.432	0.429	0.430	0.430
6.8	0.459	0.458	0.458	0.458
9.2	0.480	0.481	0.480	0.480
11.5	0.501	0.500	0.501	0.501
13.9	0.518	0.517	0.517	0.517
15.6	0.530	0.528	0.528	0.529
17.6	0.546	0.545	0.543	0.545
20.1	0.561	0.561	0.561	0.561

Table 5.6 continued

$\frac{T_{HI}-T}{^{\circ}C}$	S			Mean
	$\lambda 5461 \text{ \AA}$	$\lambda 5893 \text{ \AA}$	$\lambda 6328 \text{ \AA}$	
(111) Mixture II				
0.6	0.349	0.350	0.352	0.350
3.1	0.406	0.408	0.410	0.408
6.7	0.455	0.457	0.458	0.457
10.4	0.493	0.491	0.491	0.492
14.1	0.517	0.517	0.517	0.517
16.6	0.531	0.531	0.533	0.532
20.4	0.549	0.550	0.550	0.550
23.4	0.563	0.563	0.563	0.563
26.7	0.578	0.578	0.578	0.578
2.4	0.380	0.381	0.384	0.382
4.5	0.422	0.423	0.424	0.423
5.5	0.481	0.480	0.479	0.480
12.1	0.502	0.503	0.503	0.503
15.5	0.522	0.523	0.525	0.523
19.5	0.543	0.544	0.545	0.543
22.8	0.559	0.559	0.560	0.559
25.7	0.571	0.572	0.571	0.571
28.9	0.585	0.586	0.586	0.585
33.4	0.597	0.598	0.598	0.598

Table 5.7

Splay elastic constant of S OCB and mixtures  
(1) S OCB

$T_{NI}-T$ °C	$H_c$ Kgauss	$(k_{11})_{exp}$ dyne	$(k_{11})_{cal}$ dyne
0.6	2.10	0.50	0.49
1.9	2.36	0.74	0.71
3.9	2.56	0.98	0.98
5.7	2.68	1.16	1.18
7.5	2.80	1.32	1.35
10.0	2.93	1.55	1.57
12.5	3.10	1.82	1.79
$x_0 = 30.2 \mu m$			
0.6	2.14	0.51	0.49
2.5	2.46	0.83	0.80
4.5	2.59	1.02	1.05
6.5	2.75	1.24	1.25
8.3	2.85	1.39	1.42
10.9	3.00	1.64	1.64
12.6	3.10	1.82	1.80
$x_0 = 30.1 \mu m$			

## (11) Mixture I

0.5	2.15	0.56	0.51
2.0	2.40	0.81	0.78
3.6	2.54	1.00	0.99
5.2	2.66	1.17	1.16
7.5	2.77	1.35	1.36
10.1	2.87	1.52	1.56
12.6	3.03	1.77	1.73
15.8	3.13	1.98	1.94
18.1	3.22	2.16	2.09
18.5	3.24	2.20	2.11

 $x_0 = 30.2 \mu m$ 

0.1	1.97	0.45	0.42
1.1	2.25	0.67	0.63
2.7	2.43	0.88	0.88
4.2	2.56	1.05	1.06
6.4	2.66	1.17	1.27
8.9	2.80	1.42	1.47
11.2	2.93	1.60	1.64
14.4	3.03	1.81	1.83
16.8	3.10	1.97	1.99
18.9	3.25	2.23	2.15

 $x_0 = 30.2 \mu m$

Table 5.7 continued

$T_{NI}-T$ °C	$H_c$ Kgauss	$(k_{11})_{exp} \times 10^6$ dyne	$(k_{11})_{cal} \times 10^6$ dyne
(iii) Mixture II			
0.6	2.25	0.56	0.51
1.9	2.40	0.71	0.58
3.3	2.53	0.85	0.82
5.5	2.64	1.00	1.00
7.4	2.75	1.14	1.17
9.7	2.84	1.28	1.31
12.5	2.95	1.44	1.46
15.0	3.00	1.54	1.59
17.7	3.07	1.65	1.72
20.9	3.20	1.85	1.86
24.2	3.29	2.02	2.01
26.6	3.34	2.12	2.12
$x_0 = 27.8 \mu m$			
1.3	2.32	0.60	0.60
3.3	2.59	0.89	0.84
5.6	2.75	1.04	1.03
8.0	2.85	1.18	1.20
10.7	2.95	1.33	1.37
13.2	3.07	1.49	1.50
15.9	3.17	1.64	1.64
15.9	3.32	1.86	1.80
25.4	3.45	2.13	2.07
$x_0 = 27.1 \mu m$			

Table 5.8

$T_{AN}/T_{NI}$ , heats of transition and the indices  $\gamma$  for the systems studied

$\frac{T_{AN}}{T_{NI}}$	$\Delta H_{AN}$ cal/gm	$\gamma$	
		$k_{22}$	$k_{33}$
8 CB	0.98	0.74	1.0
8 CCB	0.96	0.64	0.82
10 ONCPC	0.95	<0.01	0.64
Mixture I	0.94	0.63	0.67
CDOCA	0.94	0.60	—
Mixture II	0.92	<0.01	0.69

Table 5.9  
 Twist elastic constants [ $k_{\text{cal}} = C_1 S^2 + C_2 (T - T^*)^{-\gamma}$ ]

T-T*	$k_{\text{exp}} \times 10^6$	$k_{\text{cal}} \times 10^6$	
°C	dyne	dyne	
(I) S CS			
0.06	1.14	1.11	$C_1 = 2.68$
0.18	0.82	0.82	$C_2 = 0.071$
0.36	0.73	0.73	$\gamma = 0.68$
1.13	0.66	0.62	$T^* = 33.27$
1.60	0.60	0.59	RMS error = 0.0210
2.54	0.55	0.55	
3.96	0.44	0.48	
6.17	0.32	0.34	
6.77	0.25	0.27	
(II) S OCO			
0.13	0.85	0.90	$C_1 = 2.93$
0.77	0.68	0.68	$C_2 = 0.045$
1.20	0.63	0.64	$\gamma = 0.79$
2.75	0.56	0.56	$T^* = 33.30$
4.33	0.45	0.47	
5.75	0.35	0.37	
6.47	0.26		RMS error = 0.0223
(III) S OCO			
0.13	1.44	1.44	$C_1 = 3.07$
0.24	1.26	1.25	$C_2 = 0.19$
0.36	1.14	1.16	$\gamma = 0.74$
0.72	1.05	1.02	$T^* = 66.936$
1.83	0.88	0.88	
2.63	0.82	0.83	
4.16	0.76	0.75	RMS error = 0.0146
5.83	0.68	0.68	
7.34	0.61	0.61	
9.52	0.48	0.51	
11.40	0.37	0.38	
0.22	1.14	1.06	
0.43	1.02	0.98	$C_1 = 3.05$
0.71	0.94	0.93	$C_2 = 0.12$
1.03	0.91	0.89	$\gamma = 0.66$
1.86	0.83	0.83	$T^* = 66.984$
3.58	0.76	0.75	
5.30	0.69	0.68	
7.78	0.58	0.58	
10.58	0.44	0.43	RMS error = 0.0150
12.29	0.30	0.29	

Table 5.9 continued

$\frac{1}{T} - \frac{1}{T^*}$	$(k/\Delta K)_{\text{exp}}$	$\times 10^2$	$(k/\Delta K)_{\text{cal}}$	$\times 10^2$
"C	dyne		dyne	
(iii) 10 CMOPC				
0.37	0.73		0.62	
0.53	0.66		0.70	$C_1 = 1.27$
0.67	0.61		0.64	$C_2 = 0.219$
0.93	0.57		0.58	$\gamma = 0.58$
1.37	0.51		0.52	$T^* = 56.915$
1.94	0.47		0.48	RMS error = 0.0060
2.41	0.45		0.46	
4.53	0.38		0.40	
6.66	0.35		0.36	
9.40	0.30		0.31	
12.05	0.26			
14.74	0.20			
0.36	0.73		0.58	
0.52	0.67		0.76	$C_1 = 1.24$
0.91	0.57		0.60	$C_2 = 0.226$
1.58	0.52		0.48	$\gamma = 0.54$
2.44	0.48		0.46	$T^* = 56.837$
4.01	0.43		0.41	RMS error = 0.0195
6.23	0.40		0.37	
8.35	0.30		0.33	
10.42	0.29		0.30	
12.61	0.24		0.26	
14.86	0.17			
15.96	0.14			

Table 5.9 Continued

## (iv) Mixture I

$T-T^*$ °C	$k_{\text{exp}} \times 10^6$ dyne	$k_{\text{cal}} \times 10^6$ dyne	
0.05	2.34	2.19	
0.24	1.44	1.38	$c_1 = 2.97$
0.48	1.28	1.20	$c_2 = 0.177$
2.29	1.02	0.97	$\gamma = 0.70$
2.98	0.92	0.93	$T^* = 45.974$
3.53	0.88	0.92	
6.45	0.80	0.83	
9.36	0.72	0.76	RMS error = 0.0570
12.02	0.62	0.68	
14.95	0.50	0.58	
17.15	0.38	0.48	
18.98	0.28	0.36	
0.07	1.94	1.94	
0.22	1.42	1.46	$c_1 = 2.88$
0.46	1.26	1.26	$c_2 = 0.247$
0.92	1.20	1.12	$\gamma = 0.56$
2.12	1.05	1.00	$T^* = 45.973$
4.74	0.92	0.89	
7.58	0.81	0.81	
10.17	0.70	0.73	RMS error = 0.0422
12.39	0.62	0.68	
17.34	0.40	0.48	
19.43	0.23	0.31	

Table 5.9 continued

## (v) CB00A

$T - T^*$	$(k/\Delta\chi_{\text{cm}})_{\text{exp}}$	$(k/\Delta\chi_{\text{cm}})_{\text{cal}}$	
$^{\circ}\text{C}$			
0.28	3.15	3.12	
0.36	2.94	2.97	
0.63	2.64	2.67	
1.32	2.46	2.41	$C_1 = 5.39$
2.23	2.27	2.27	$C_2 = 0.43$
3.73	2.12	2.13	
6.15	2.04	2.00	$\gamma = 0.70$
8.29	1.90	1.90	$T^* = 82.584$
11.77	1.79	1.75	
15.76	1.58	1.55	RMS error = 0.0370
18.63	1.35	1.38	
20.17	1.19	1.27	
22.25	1.06	1.10	
23.46	0.95	0.99	
0.27	3.37	3.17	
0.70	2.75	2.75	
1.84	2.54	2.45	$C_1 = 5.50$
3.27	2.33	2.29	$C_2 = 0.55$
5.49	2.16	2.14	
8.12	1.94	2.00	$\gamma = 0.61$
10.70	1.85	1.88	$T^* = 82.496$
13.11	1.76	1.76	
16.52	1.54	1.58	
19.45	1.34	1.38	RMS error = 0.0456
21.80	1.15	1.20	
23.70	0.89		

Table 5.5 continued

## (vi) Mixture II

$T - T^*$ °C	$k_{\text{exp}} \times 10^6$ dyne	$k_{\text{cal}} \times 10^6$ dyne	
0.24	2.77	2.77	
0.65	2.12	2.09	
0.88	1.96	1.96	
1.24	1.75	1.82	$c_1 = 2.48$
2.56	1.61	1.61	$c_2 = 0.60$
4.02	1.52	1.49	$\gamma = 0.63$
6.17	1.44	1.39	
8.46	1.31	1.28	$T^* = 29.871$
10.78	1.21	1.24	
15.02	1.05	1.11	RMS error = 0.0345
17.42	0.98		
18.86	0.93		
21.40	0.81		
23.68	0.70		
25.20	0.51		
0.25	2.54	2.41	
0.32	2.33	2.30	
0.55	2.08	2.11	$c_1 = 2.45$
0.78	1.93	1.99	$c_2 = 0.67$
1.17	1.84	1.86	$\gamma = 0.54$
2.58	1.70	1.65	$T^* = 29.956$
5.18	1.47	1.49	
9.15	1.31	1.33	
12.68	1.14		RMS error = 0.0648
16.58	0.98		
19.86	0.84		

Table 5.10

Bond elastic constant [ $k_{\text{cal}} = C_1 S^2 + C_2 (T - T^*)^{-\gamma}$ ]

(1) S CB

T-T*	$k_{\text{exp}} \times 10^6$ dyne	$k_{\text{cal}} \times 10^6$ dyne	
0.185	6.17	6.13	$C_1 = 4.27$
0.365	3.63	3.63	$C_2 = 1.02$
0.465	3.07	3.06	$T^* = 33.216$
0.715	2.30	2.33	$\gamma = 0.97$
0.765	2.23	2.23	RMS error = 0.0245
1.195	1.76	1.74	
1.395	1.64	1.62	
2.245	1.24	1.29	
3.855	1.02		
5.115	0.79		
5.965	0.66		
6.555	0.54		
8.402	3.98	3.97	
0.582	3.07	2.97	
0.732	2.39	2.51	
0.932	2.09	2.13	$C_1 = 3.82$
1.212	1.82	1.80	$C_2 = 1.22$
1.412	1.75	1.64	$T^* = 33.058$
2.112	1.33	1.32	$\gamma = 1.03$
3.382	1.03	1.03	RMS error = 0.0619
4.952	0.79	0.80	
5.852	0.67	0.70	
6.832	0.49	0.53	

Table 5.10 continued

## (ii) S OCB

$T-T^*$ °C	$k_{exp} \times 10^6$ dyne	$k_{cal} \times 10^6$ dyne	
0.20	9.62	9.61	$C_1 = 4.41$
0.27	7.59	7.70	
0.34	6.71	6.54	$C_2 = 2.16$
0.47	5.24	5.25	
0.52	4.91	4.91	$T^* = 66.964$
0.61	4.38	4.44	
0.82	3.60	3.71	$\gamma = 0.83$
1.12	3.14	3.11	
1.54	2.41	2.34	RMS error = 0.077
2.97	1.99	1.92	
4.11	1.72	1.66	
6.17	1.34	1.37	
8.23	1.07	1.15	
9.63	0.94	1.01	
10.38	0.75		
0.16	9.67	9.71	$C_1 = 4.82$
0.23	7.71	7.60	
0.43	4.99	5.11	$C_2 = 1.96$
0.55	4.42	4.41	
0.64	3.97	4.05	$T^* = 66.997$
1.40	2.78	2.71	
1.67	2.59	2.50	$\gamma = 0.81$
2.20	2.26	2.22	
3.16	1.94	1.91	RMS error = 0.0646
5.13	1.54	1.56	
5.95	1.42	1.45	
6.98	1.29	1.33	
8.49	1.12	1.18	

Table 5.10 continued

## (iii) 10 OMCP

$T - T^*$ °C	$(k/\Delta K)_{exp} \times 10^2$	$(k/\Delta K)_{cal} \times 10^2$	
0.12	11.79	11.65	
0.16	9.72	9.80	
0.21	8.18	8.33	
0.28	6.99	7.02	
0.40	5.69	5.68	$c_1 = 1.59$
0.56	4.87	4.67	
0.77	3.94	3.89	$c_2 = 2.95$
0.87	3.76	3.63	
1.12	3.17	3.15	$\gamma = 0.64$
1.78	2.53	2.44	
2.27	2.12	2.15	$T^* = 57.028$
2.88	1.93	1.89	
4.18	1.49	1.56	
4.91	1.43	1.44	RMS error = 0.1160
6.08	1.33	1.29	
8.04	1.12	1.11	
9.73	0.95	1.00	
11.08	0.88	0.92	
13.56	0.69	0.78	
14.94	0.52	0.70	
15.91	0.31	0.65	
0.17	8.75	8.70	
0.24	7.00	7.07	$c_1 = 1.34$
0.33	5.91	5.84	
0.45	4.80	4.86	
0.54	4.22	4.37	$c_2 = 2.72$
0.88	3.51	3.29	
1.06	2.93	2.96	$\gamma = 0.64$
1.38	2.67	2.55	
1.83	2.22	2.18	$T^* = 57.015$
2.56	1.82	1.82	
4.94	1.29	1.28	RMS error = 0.0908
6.08	1.17	1.15	
7.62	1.01	1.02	
9.18	0.90	0.92	
10.60	0.82	0.84	
12.24	0.72	0.76	
13.70	0.60	0.69	
15.36	0.42	0.61	

Table 5.10 continued

## (iv) Mixture I

T-T °C	$k_{exp} \times 10^6$ dyne	$k_{cal} \times 10^6$ dyne	T-T* °C	$k_{exp} \times 10^6$ dyne	$k_{cal} \times 10^6$ dyne
0.22	13.91	13.73	0.14	14.49	14.50
0.32	10.64	10.83	0.21	11.96	11.47
0.81	6.43	6.12	0.28	9.43	9.73
1.00	5.53	5.41	0.33	8.99	8.86
1.28	4.65	4.70	0.42	7.45	7.74
1.52	4.23	4.26	0.70	5.91	5.84
1.84	3.76	3.84	0.89	5.35	5.14
2.53	3.19	3.23	1.50	3.98	3.93
2.97	2.97	2.97	1.95	3.49	3.45
3.61	2.74	2.68	2.42	3.12	3.12
4.06	2.53	2.53	2.73	2.97	2.94
4.90	2.42	2.30	3.24	2.75	2.72
6.36	2.08	2.01	3.74	2.56	2.54
7.21	1.98	1.89	4.18	2.47	2.42
8.86	1.75	1.71	5.10	2.21	2.21
10.20	1.61	1.58	6.00	2.08	2.05
11.23	1.49	1.49	7.10	1.86	1.90
12.20	1.46	1.42	8.00	1.79	1.79
13.82	1.27	1.30	8.96	1.71	1.70
14.86	1.19	1.24	10.04	1.61	1.60
16.24	1.02	1.14	10.94	1.54	1.54
17.96	0.81		12.35	1.35	1.42
18.83	0.61		13.71	1.25	1.25
19.16	0.55		15.31	1.06	
			16.66	0.95	
			17.69	0.79	
			18.96	0.56	

$C_1 = 2.82$

$C_1 = 3.06$

$C_2 = 4.56$

$C_2 = 3.93$

$y = 0.69$

$y = 0.64$

$T^* = 45.889$

$T^* = 45.976$

$RMS\ error = 0.0993$

$RMS\ error = 0.1456$

Table 5.10 continued

## (v) Mixture II

T-T <sup>*</sup> °C	k <sub>exp</sub> $\times 10^6$ dyne	k <sub>cal</sub> $\times 10^6$ dyne	T-T <sup>*</sup> °C	k <sub>exp</sub> $\times 10^6$ dyne	k <sub>cal</sub> $\times 10^6$ dyne
0.26	16.04	16.05	0.40	11.85	11.06
0.41	12.25	12.29	0.50	5.94	5.74
0.59	10.15	9.99	0.68	8.27	8.18
0.85	8.10	8.17	0.83	7.25	7.33
1.08	7.17	7.18	0.93	6.92	6.88
1.33	6.29	6.44	1.19	5.95	6.04
1.59	5.80	5.87	1.52	5.55	5.33
2.40	4.89	4.79	1.85	5.03	4.85
3.16	4.35	4.20	2.16	4.80	4.50
4.52	3.55	3.56	2.56	4.37	4.16
5.40	3.35	3.29	3.04	4.07	3.86
6.63	2.98	3.00	3.90	3.71	3.48
9.24	2.53	2.59	4.56	3.47	3.26
12.03	2.24	2.30	5.11	3.28	3.12
15.08	1.94		6.19	2.94	2.57
17.95	1.69		10.74	2.28	2.34
20.78	1.47		12.95	2.07	2.08
22.68	1.27		16.16	1.82	1.93
24.23	1.09		18.50	1.70	1.79
25.50	0.92		21.13	1.41	1.62
26.86	0.69		22.95	1.13	1.45
			24.65	1.02	1.31
			25.71	0.80	1.08
			26.65	0.71	1.05

$C_1 = 3.65$

$C_1 = 5.34$

$C_2 = 6.25$

$C_2 = 5.00$

$\gamma = 0.63$

$\gamma = 0.75$

$T^* = 32.025$

$T^* = 32.089$

$RMS \text{ error} = 0.0862$

$RMS \text{ error} = 0.2005$

Table 5.11  
Comparison of the index  $\gamma$  obtained by earlier workers

Reference	Measured parameter	Method	Compound	$\Delta H$	$\gamma$
Cheung and Meyer (1973)	$k_{33}$	$V_e$ by capacitance measurement	BEMBA	363 cal/mole	1
Cheung et al. (1973)	$H_c$ by optical method		CBCOA	*	0.66
Delaye et al. (1973)	$k_{22}$	Light scattering	CBCOA	*	0.66
Classis (1974)	$k_{33}$	$H_c$ by conoscopic method	CBCOA	*	0.5 (pure)
Leger (1973)	$k_{33}$	$H_e$ by optical method	DBOA	83 cal/mole	0.66
Chu & McMillan (1975)	$k_{22}$	Light scattering	CBCOA	*	0.5
Delaye (1976)	$k_{22}$	Light scattering	9 OCBA	9 cal/mole	0.5

BEMBA - p-butyrybenzylidene-p'-methoxybutyl enone  
DBOA - p-butyrybenzylidene-p'-octylenone.

\* Different values have been reported by different workers. For example, Torse and Classis (1974) obtained a value  $\Delta H_A = 33$  cal/mole using DSC. Delaye (1976) obtained a value 4 cal/mole from adiabatic calorimetry obtained a value 12 cal/mole. Delaye (1976) obtained a value 4 cal/mole from DSC measurements. However we must mention here that DSC and DSC measurements give slightly higher value for  $\Delta H$  because the increase in specific heat near the transition also gives rise to a bump in the curve.

