Chapter 6

An Experimental Study of Smectic A – Smectic C Transitions in Monolayer, Partially Bilayer and Bilayer Systems

6.1 Introduction

The smectic A (Sm A) phase formed of nonpolar molecules is usually of monolayer type (Sm A_1) where the layer spacing d is equal to the length l of the molecule. On the other hand, if the constituent molecules possess strong polar end groups, several types of smectic A phases are observed.[1] As discussed in Chapter 4, depending on the extent of interdigitation between the molecules in the neighbouring layers they are classified as bilayer Sm $A_2(d \sim 2l)$, the partially bilayer Sm $A_d(l < d < 21)$ and monolayer Sm $A_1(d - 1)$ phases. The corresponding tilted modifications are referred to as Sm C_2, Sm C_d and Sm C_1 phases respectively. Figure 6.1 shows a schematic representation of the molecular arrangement in these phases.

From a symmetry point of view, transition from Sm A to Sm C can be either first order or second order. Since the Sm C phase can be represented by a two component complex order parameter, de Gennes[2] proposed that the transition might be continuous (second order) and may exhibit helium like critical behaviour (3D XY model). Since most of the experiments[3] showed mean-field behaviour, Safinya et al.,[4] argued that the bare correlation length characterizing tilt fluctuations are usually so large in these systems that the true critical region is unobservably small and consequently the transition is mean-field like. However, the strong pre-transition heat capacity variation on the Sm C side remained to be explained. Analysing high resolution specific heat data, Huang and Viner[5] pointed out the importance of retaining the sixth-order term in the Landau mean-field free-energy expansion in order to provide a quantitative

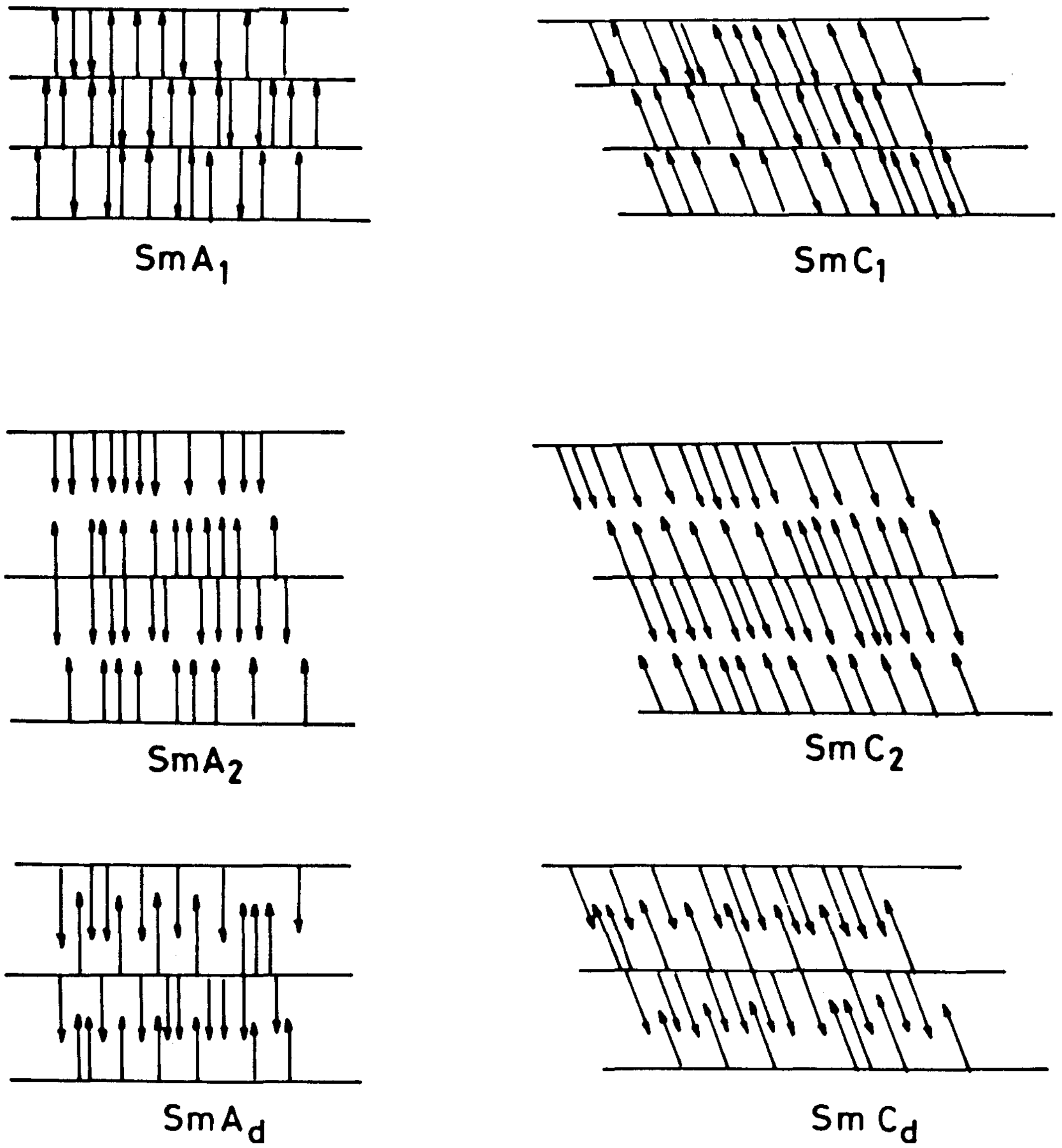


Figure 6.1: Schematic diagram of the molecular arrangement in different types of smectic A and smectic C phases.

explanation of heat capacity data obtained near Sm A-Sm C transition. Subsequent experimental results[6,7] showed that the Sm A-Sm C transition is well described by a Landau model with a large sixth order term in the free energy expression. This would mean that the Sm A-Sm C transition in all these materials lies close to a tricritical point. Furthermore it is seen that the tricritical influence increases with decrease in the temperature range of the smectic A phase[8] and/or by an increase in the strength of the transverse dipole moment of the constituent molecule.[9] An important point to be noted here is that all these experiments have been performed on monolayer systems and none of them showed a simple mean-field behaviour, i.e., with a negligible tricritical influence. Interestingly, the recent heat capacity measurements of Garland et al.,[10] exhibited such a behaviour for two compounds having bilayer Sm A_2-Sm C_2 transition. We have confirmed these results further by doing order parameter (tilt angle) measurements in the vicinity of the bilayer Sm A_2-Sm C_2 transition in one of these compounds. In the light of this, we feel that it would be interesting to see whether such a mean-field behaviour with negligible tricritical influence can be observed for partially bilayer and monolayer Sm A-Sm C transitions also. This Chapter presents high precision X-ray tilt angle measurements in the vicinity of the bilayer Sm A_2-Sm C_2, partially bilayer Sm A_d-Sm C_d and the monolayer Sm A_1-Sm C_1 transitions.

6.2 Experimental

The compounds[11] used are 4'-n- heptacylphenyl -4'-(4"- cyanobenzoyloxy) benzoate (7APCBB) [Sm A_2-Sm C_2], 4-cyanoethylphenyl- 4'- decyloxycinnamate

(CEPDOC) [Sm A_d-Sm C_d], *trans*-1,4-cyclohexane-di-n- octyloxybenzoate (TCOB) [Sm A_1-Sm C_1]. The structural formulae and transition temperatures of these compounds are given in Table 6.1. The experiments were conducted using the computer controlled X-ray Guinier diffractometer described in Chapter **2.**

6.3 Results and Discussion

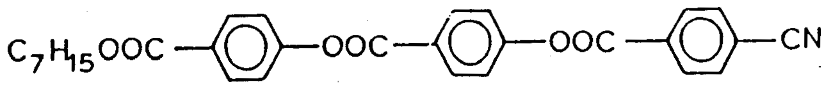
Figures **6.2-6.4** show the temperature variation of the layer spacing near Sm A_2-Sm C_2, Sm A_d-Sm C_d and Sm A_1-Sm C_1 transitions in 7APCBB, CEPDOC and TCOB respectively. The continuous variation in layer spacing in all these compounds indicates that the transitions are second order. The tilt angle in the Sm C phase has been evaluated using the expression

$$\phi = cos^{-1}\left(\frac{d_C}{d_A}\right) \qquad (6.1)$$

where d_C and d_A are the layer spacing values in the Sm C and Sm A phases respectively. It was observed that for these compounds the temperature dependence of the layer spacing in the Sm A phase is not negligible. Hence, instead of considering the value of d_A to be constant in equation 6.1, it was evaluated at each temperature by linearly extrapolating the data in the Sm A phase. Figure 6.5 shows a representative plot in which the value of d_A is evaluated at each temperature.

Figure 6.6 shows the variation of tilt angle, ϕ, obtained in this way for 7APCBB as a function of temperature. The efficacy of using equation 6.1 was verified by determining ϕ directly from a photographic *(four spot* pictures) technique. It was found that the values evaluated from the two methods are in very

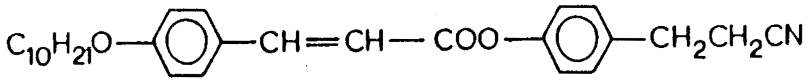
7APCBB



4-n- heptacylphenyl -4′-(4″- cyanobenzoyloxy) benzoate

Isotropic $\xrightarrow[209.4]{}$ N $\xrightarrow[144.5]{}$ Sm A_2 $\xrightarrow[141.6]{}$ Sm C_2

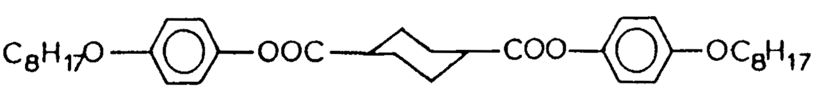
CEPDOC



4-cyanoethylphenyl- 4′- decyloxycinnamate

Isotropic $\xrightarrow[109.5]{}$ N $\xrightarrow[109.0]{}$ Sm A_d $\xrightarrow[59.5]{}$ Sm C_d

TCOB



trans-1,4-cyclohexane-di-n- octyloxybenzoate

Isotropic $\xrightarrow[178.3]{}$ Sm A_1 $\xrightarrow[118.8]{}$ Sm C_1 $\xrightarrow[110.4]{}$ Cry B

Table 6.1: Structural formulae and transition temperatures (in °C) of 7APCBB, CEPDOC and TCOR.

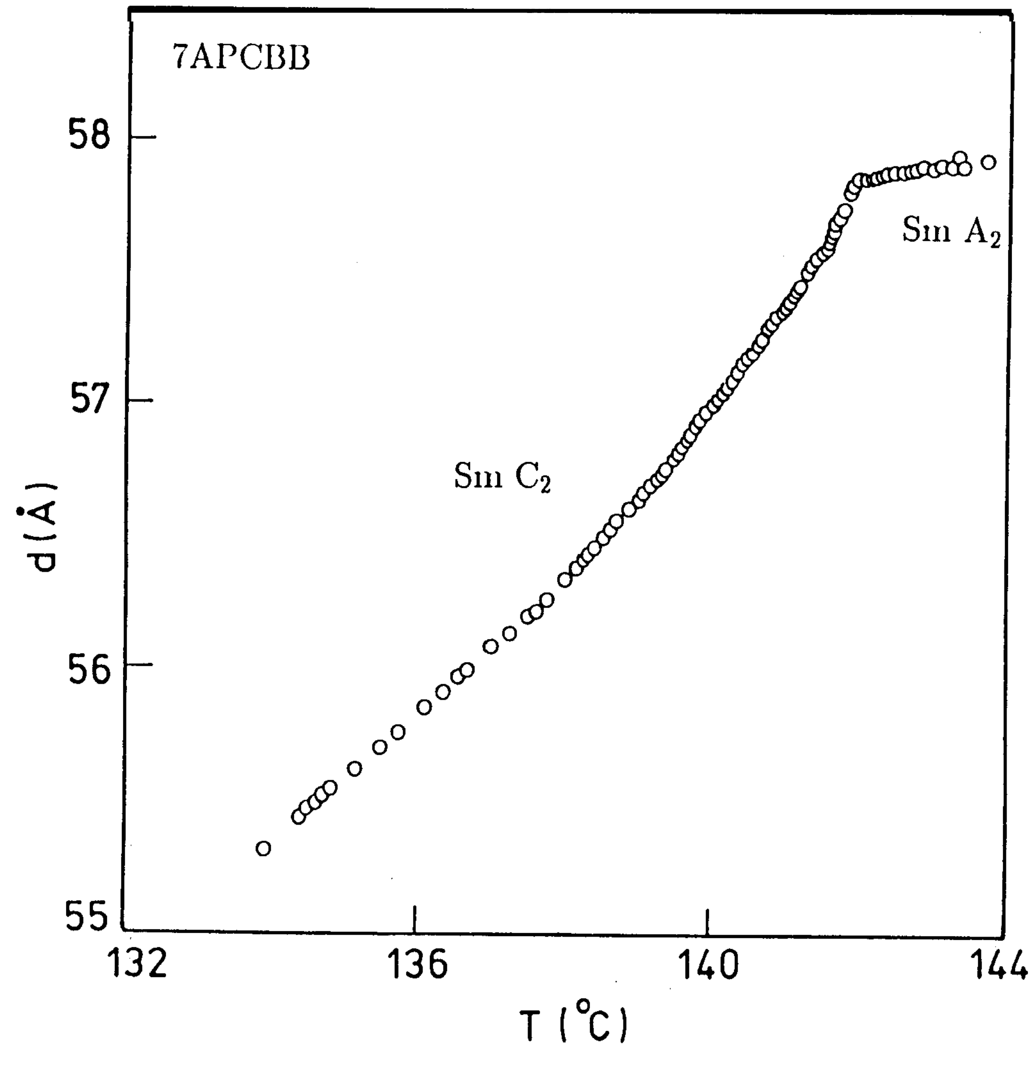


Figure 6.2: Thermal variation of layer spacing d across the Sm A_2-Sm C_2 transition in 7APCBB.

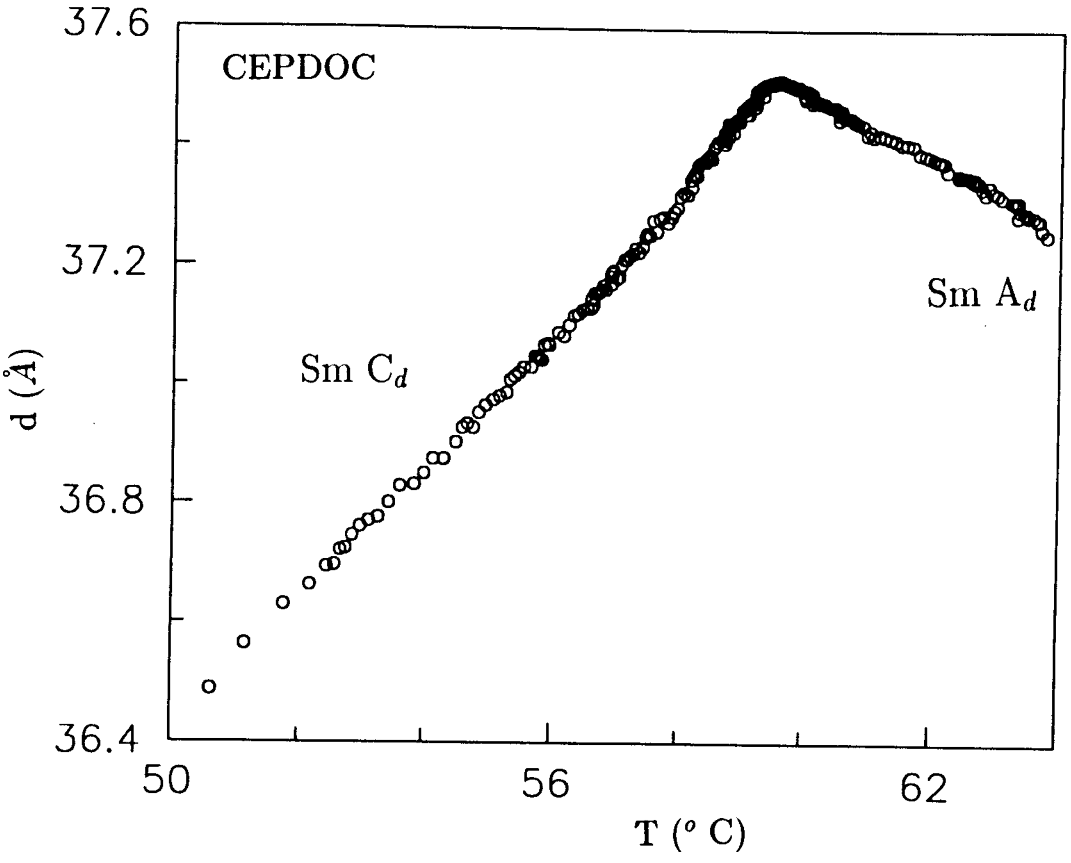


Figure 6.3: Thermal variation of d across the Sm A_d-Sm C_d transition in CEPDOC.

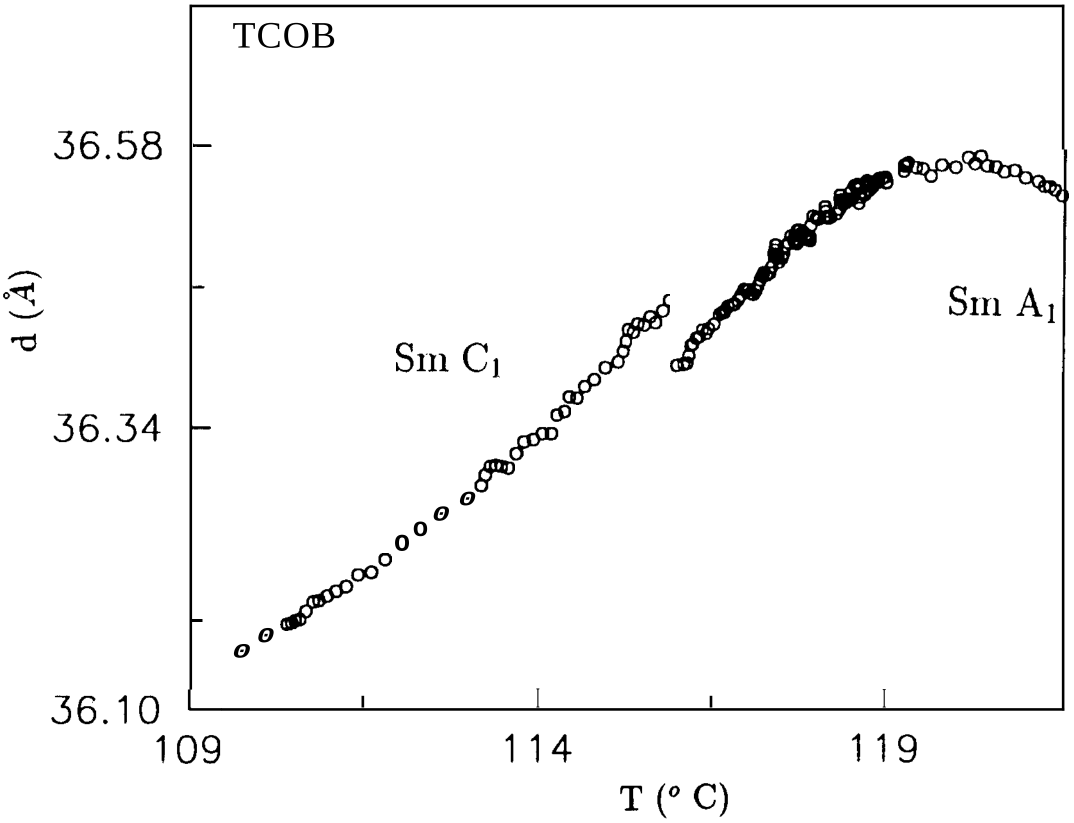


Figure 6.4: Temperature dependence of d across the Sm A_1-Sm C_1 transition in TCOB.

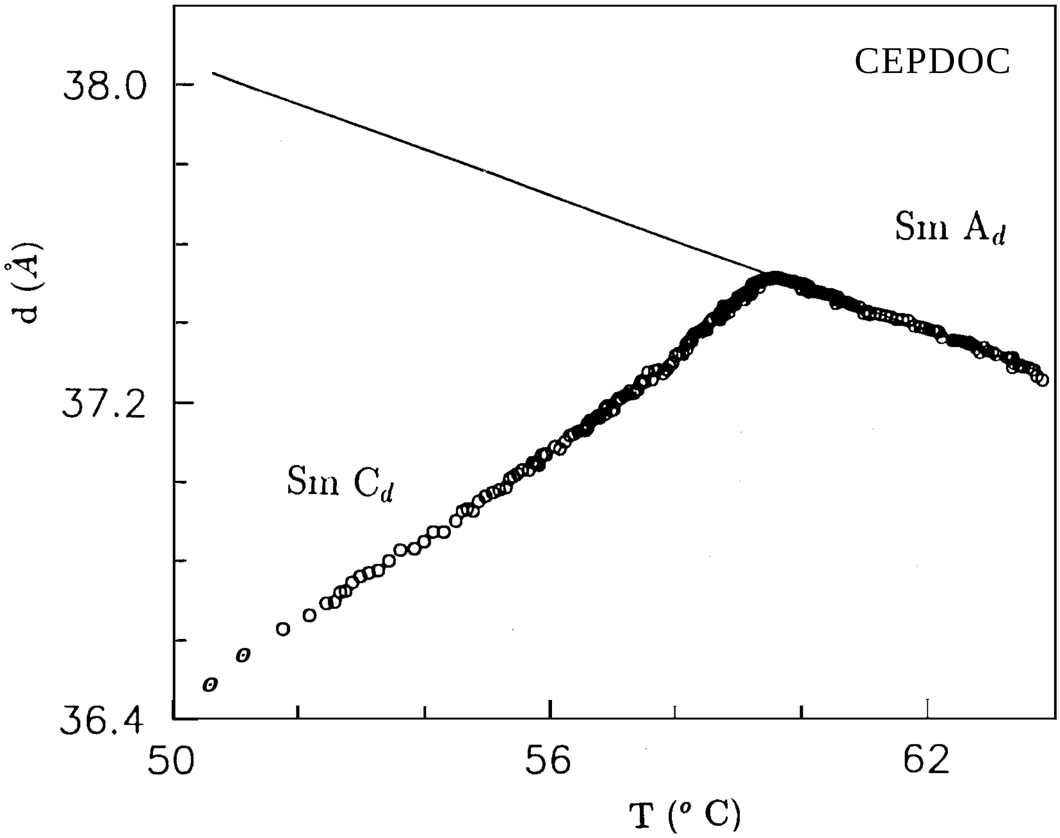


Figure 6.5: Plot showing the extrapolation method used to correct for the temperature dependence of d in the smectic A phase. Circles are the data points. Solid line is a linear fit for the data in the Sm A phase.

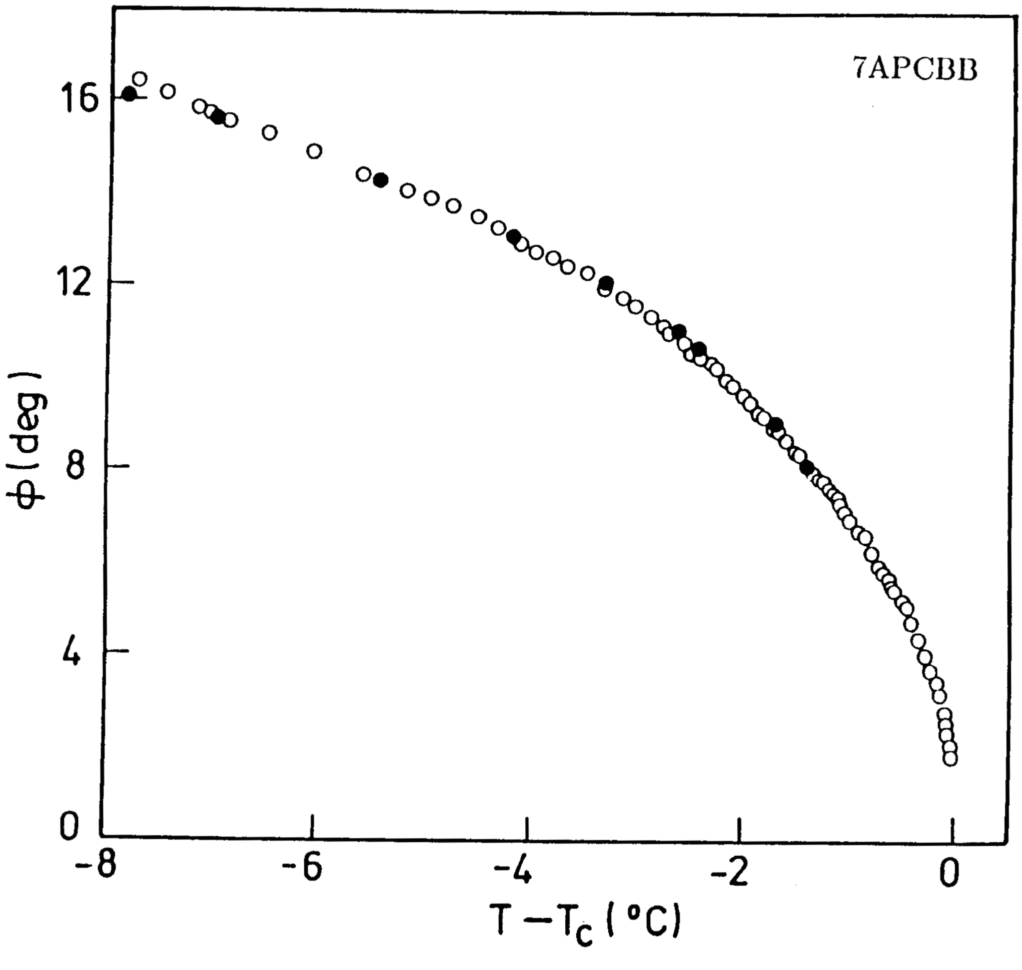


Figure 6.6: Plot showing agreement between tilt angle ϕ in the Sm C_2 phase obtained from diffractometer experiments (open circles) and four spot photographs (filled circles) in 7APCBB.

good agreement with each other (see figure *6.6).*

As mentioned earlier, the Sm A-Sm C transition can be well described by a Landau model with a sixth order term in the free energy expression. This extended mean field expression can be written as

$$F = F_o + at\phi^2 + b\phi^4 + c\phi^6 \tag{6.2}$$

where F_o is the non-singular part of the free energy, t = $\left(\frac{T_c - T}{T_c}\right)$; T_c being the Sm A-Sm C transition temperature. a, b and c are positive coefficients for a continuous transition.

Minimising equation 6.2 with respect ϕ we get

$$\phi = 0 \qquad \text{for } t > 0 \quad (\text{Sm A phase})$$

$$\phi = R^{1/2}\left[(1+3t/t_o)^{1/2} - 1\right]^{1/2} \qquad \text{for } t < 0 \quad (\text{Sm } C \text{ phase}) \tag{6.3}$$

where R $=(b/3c)$ and $t_o = (b^2/ac)$. The parameter t_o is also identified as the full width at half-maximum of the heat capacity curve. From equation 6.3 one can *see* that

1. for $|t| \ll t_o$, $\phi \sim |t|^{1/2}$ implying a simple mean field behaviour, i.e., contribution from the 6th order term in equation 6.2 is negligible.

2. for $|t| \gg t_o$, $\phi \sim |t|^{1/4}$ which describes the mean field-tricritical like behaviour.

Thus, in this model the dimensionless parameter t_o assumes an all important character in describing the cross-over from a simple mean field region near the transition to a tricritical-like region away from the transition. The temperature range over which the simple mean-field behaviour can be observed is controlled by the magnitude of t_o; the smaller this value, narrower is the mean field region. The interesting fact is that in the monolayer cases t_o was found to be small,[5-7,12] in comparison with other mean field transitions,[13] the highest reported value being ~ 6.5 × 10^{-3} for a compound referred to as $\bar{8}$S5.[5] This would mean that in all these substances, the mean field region is quite small.

With these facts in mind, the thermal variation of tilt angle data for 7APCBB is fitted to equation 6.3. Figure 6.7 shows that the fitting is excellent. Remarkably, the value of t_o obtained (=1.5 x 10^{-2}) is larger than any of the previously obtained values for the monolayer cases. This large value of t_o indicates that the mean field region is substantial. The specific heat data obtained by Wen et al.,[10] on the same compound, 7APCBB, showed a step like variation across the transition (see figure 6.8), supporting our observation. The excess heat capacity ΔC_p which has a zero value in Sm A_2 phase increases abruptly at T_c and then levels off to a temperature independent value below T,. The large value of t_o combined with the absence of any pretransitional increase of specific heat on the Sm C_2 side, suggests that the coefficient c in equation 6.2 is very small. In the limiting case of c=0, e.g.,

$$F = F_o + at\phi^2 + b\phi^4, \tag{6.4}$$

the temperature variation of tilt angle can be described by a simple power law:

$$\phi = \phi_o|t|^{1/2} \tag{6.5}$$

where $\phi_o = (a/b)^{1/2}$ and the specific heat will have a step-like jump at the transition.

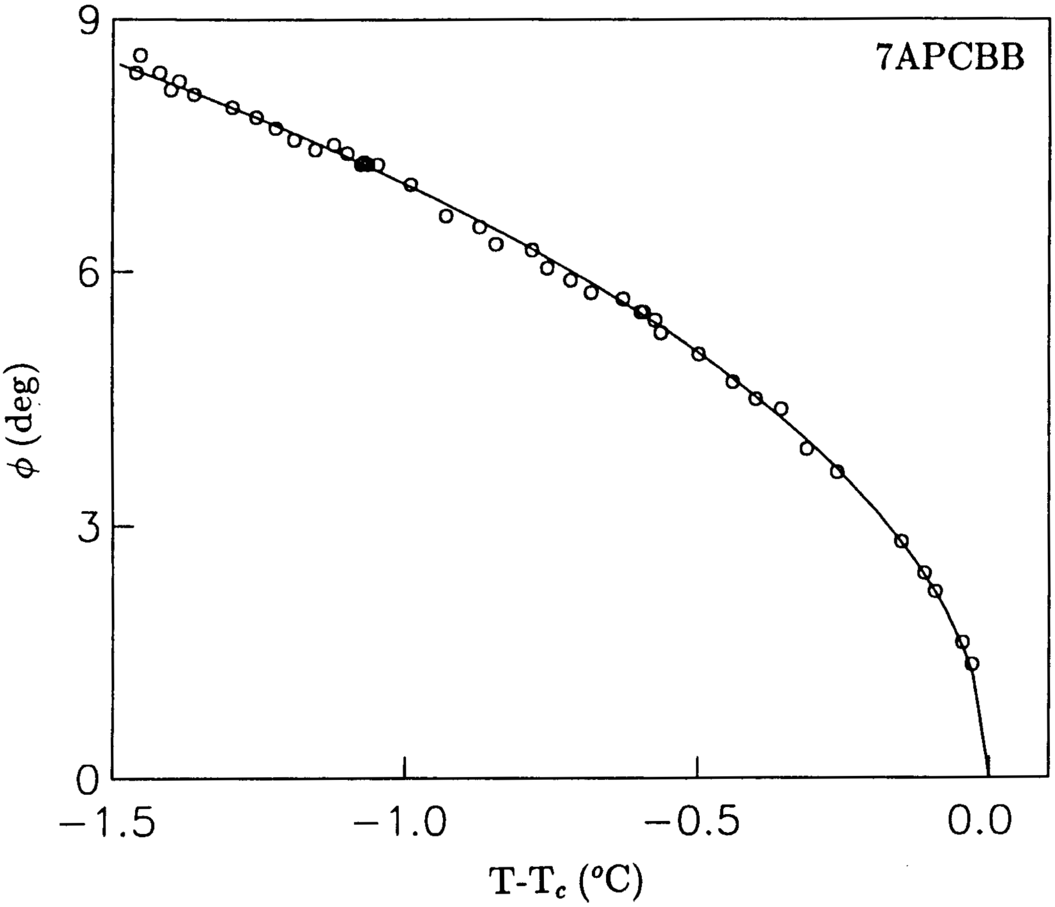


Figure 6.7: ϕ vs. T-T$_c$ plot for 7APCBB showing fit to an extended mean-field expression (EMF) equation 6.3. (solid line).

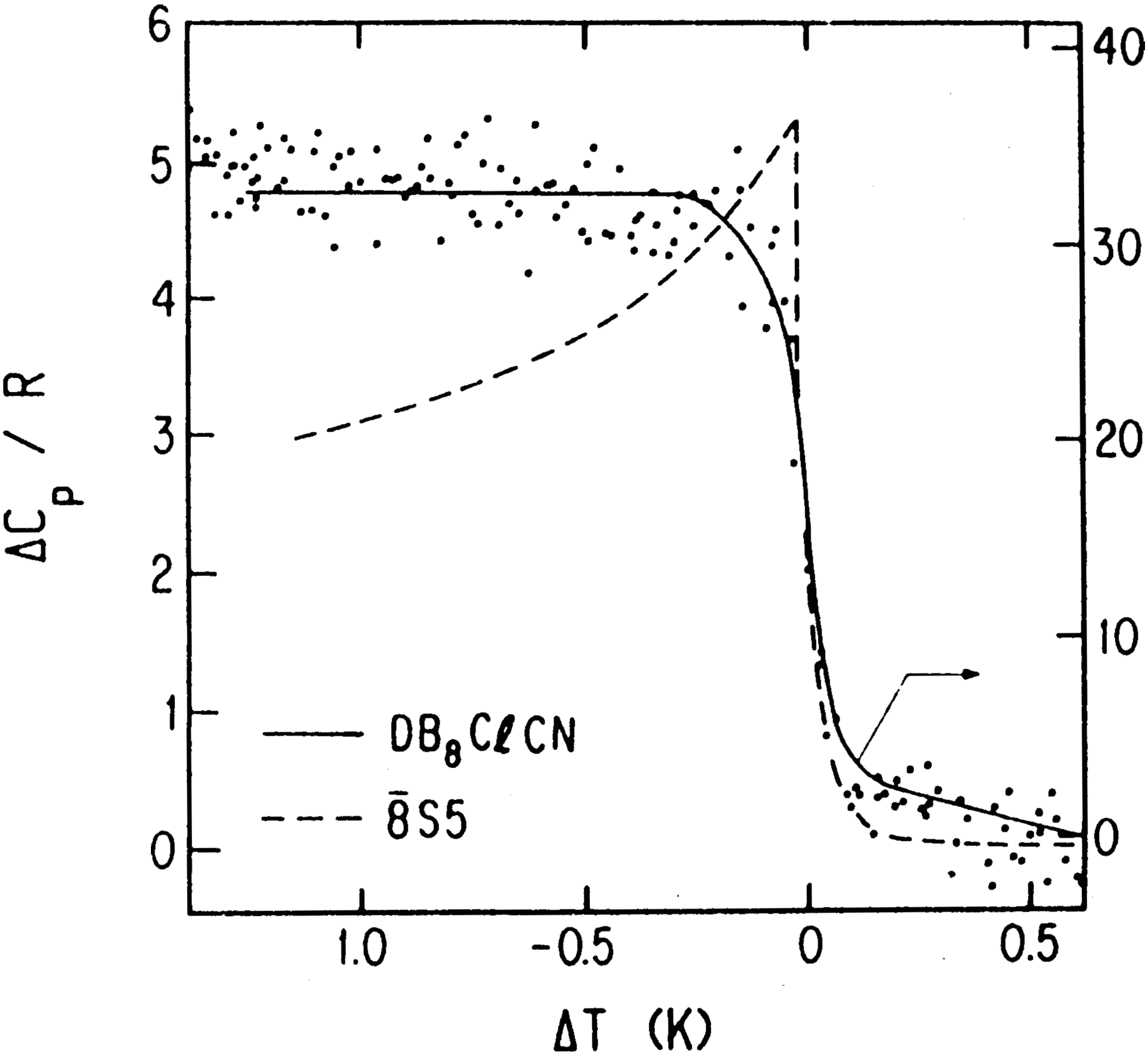


Figure 6.8: Temperature dependence of the excess molar heat capacity associated with the Sm A_2-Sm C_2 transition in 7APCBB. The absence of pretransitional increase on the Sm C_2 side is indicative of a simple mean field transition. Also shown for comparison are the data for the Sm A_2-Sm C_2 transition in DB_8ClCN (solid line) which shows simple mean field behaviour arid the Sm A_1-Sm C_1 transition in $\bar{8}S5$ (dashed line) which has appreciable contribution from the 6th order term in the free energy expression. (From Ref. 10).

Figure 6.9 shows the fitting of the tilt angle data to equation 6.5. Again the fit is very good. From the goodness of fitting of the data to both equations 6.3 and 6.5, and the step-like specific heat variation, we can conclude that for this compound the coefficient c is indeed negligibly small and a mean field expression with up to *4th order terms only* is sufficient to describe the data.

A point to be noted is that the value of t_o obtained for 7APCBB is smaller than the value for another compound (DB8ClCN) having Sm A_2 - Sm C_2 transition[10] (see Table 6.2). A possible reason for this could be the narrow temperature range of the smectic A phase in 7APCBB (2.9 °C) as compared to DB8ClCN ($\simeq$ 38°C).

Having observed that a simple mean field model can describe the tilt angle data in the bilayer Sm C_2 phase, it is interesting to see whether this could be true even in partially bilayer and monolayer Sm C phases also. Since, at least in the monolayer systems it has been demonstrated that the temperature range of Sm A phase influences the nature Sm A-Sm C transition,[8,12] compounds (CEPDOC and TCOB) having a large temperature ($\gg$ 50°) range of Sm A phase were selected (see Table 6.1). Figures 6.10 and 6.11 show the thermal variation of tilt angle for CEPDOC (Sm A_d - Sm C_d transition) and TCOB (Sm A_1 - Sm C_1 transition) respectively along with the fit to an extended mean-field free energy expression (equation 6.3). Fit defines the data very well for both the compounds with fairly large values for t_o, viz., 9.45×10^{-2} and 1.57×10^{-1} for CEPDOC and TCOB respectively.

The data is also fitted to a simple mean field model (equation 6.5) and the

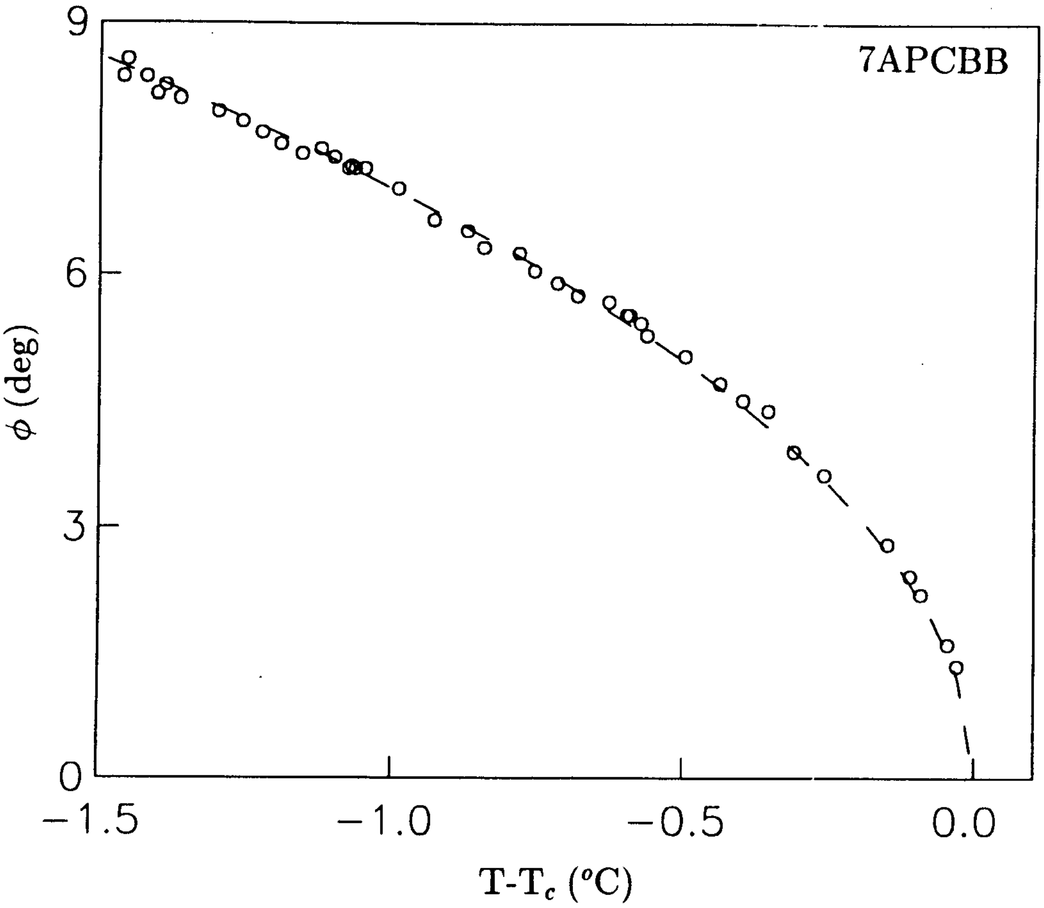


Figure 6.9: Simple mean field fit (SMF) for tilt angle data of 7APCBB. Circles are the data points and dashed line is a fit to equation 6.5.

Table 6.2: Sm A phase temperature range and mean field parameters. The number underlined in the third column indicates that the range of the smectic A phase is given by $T_{isotropic-A}$-T_{AC}.

Compound	Transition	(T_{NA}-T_{AC}) °C	ϕ_o	R	t_o
7APCBB	Sm A_2-Sm C_2	2.9	2.48	0.067	1.45×10^{-2}
DB8ClCN	Sm A_2-Sm C_2	37.9			[a]2.65×10^{-2}
CEPDOC	Sm A_d-Sm C_d	49.5	1.59	0.222	9.45×10^{-2}
TCOB	Sm A_1-Sm C_1	$\underline{59.3}$	1.23	0.168	1.57×10^{-1}
$\bar{8}$S5	Sm A_1-Sm C_1	8.0	[b]2.43	-	[c]6.5×10^{-3}

a: Ref. 10, b: Ref. 4, c: Ref. 5.

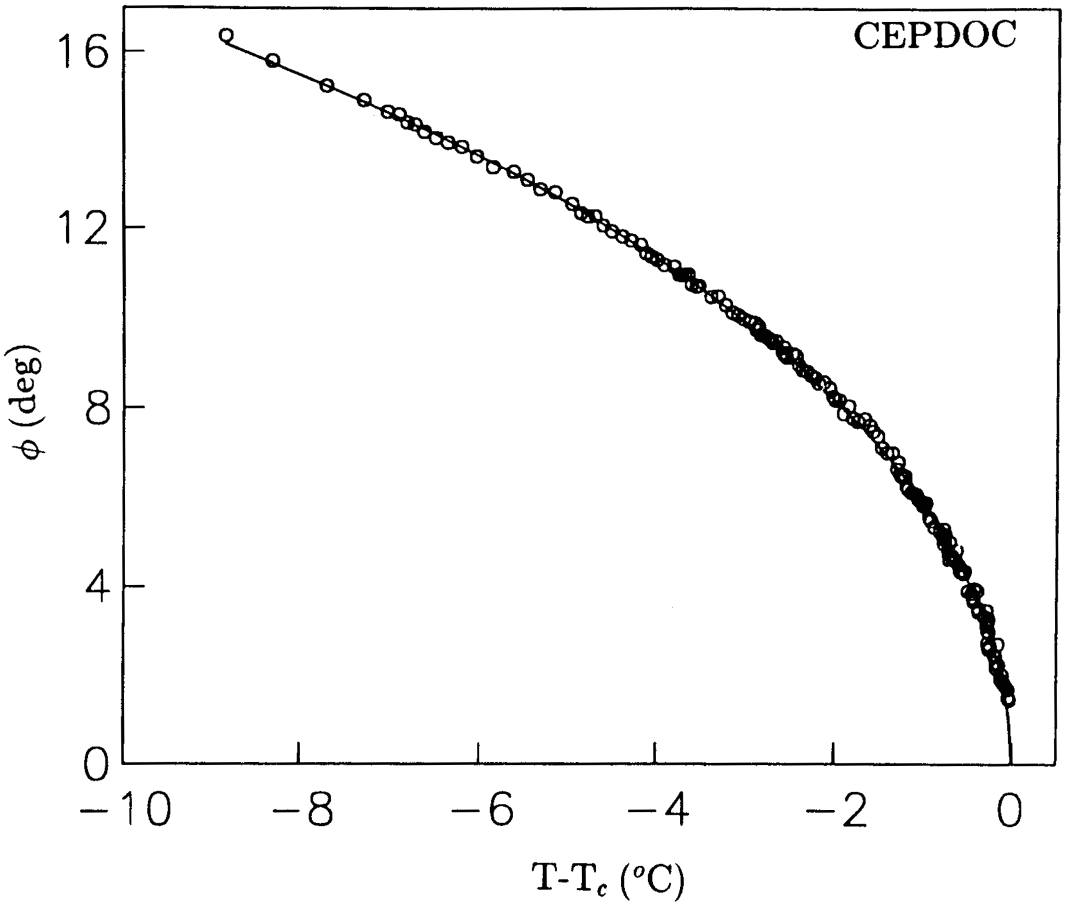


Figure 6.10: ϕ vs. T-T$_c$ plot for CEPDOC. Circles are the data points and solid line is a fit to EMF model (equation **6.3**).

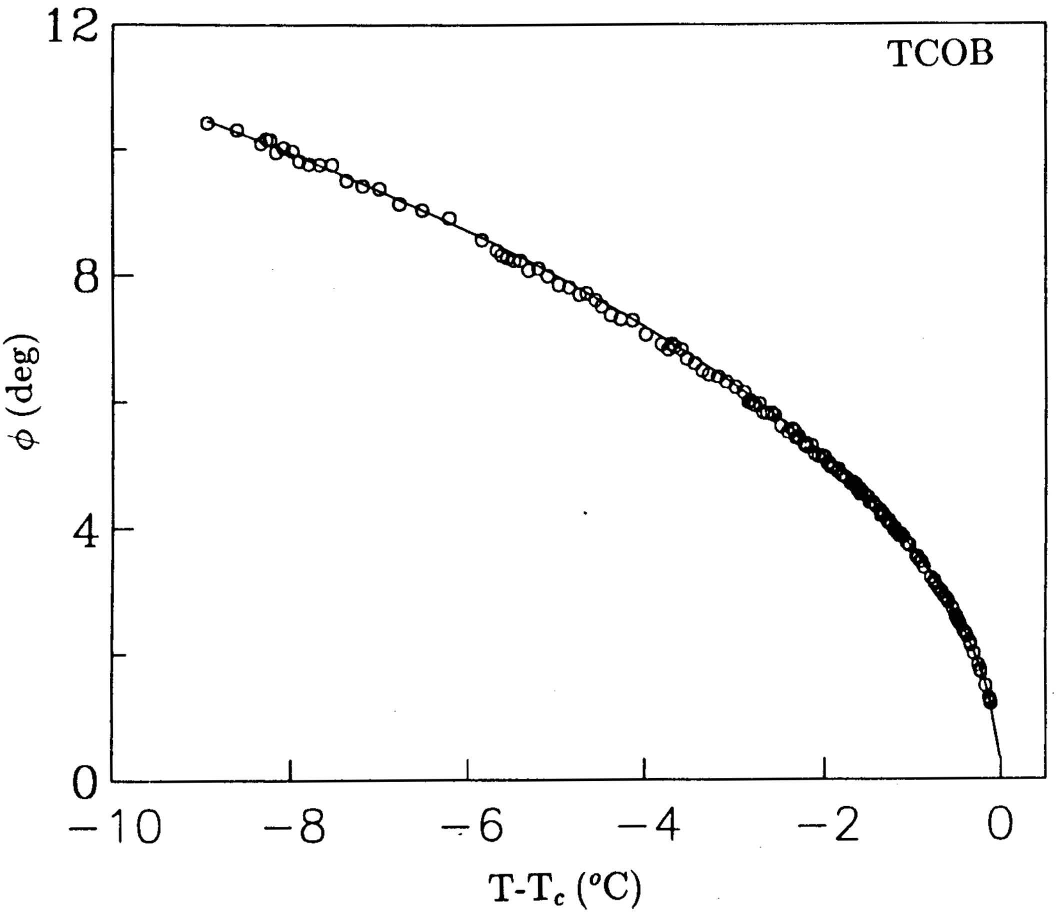


Figure 6.11: ϕ vs. T-T$_c$ plot for TCOB. Circles are the data points and solid line is a fit to equation 6.3.

fits are shown in figures 6.12 and 6.13 for CEPDOC and TCOB respectively. From these plots it is evident that the thermal variation of ϕ for both CEPDOC and TCOB can be quite well described by a simple mean field expression implying that, just as in the case of 7APCBB, the influence of the 6th order term in equation **6.3** is negligible.

Both TCOB and CEPDOC have t_o values higher than any reported so far. Computed values of t_o along with the Sm A phase temperature range for the compounds exhibiting Sm A_2-Sm C_2, Sm A_d-Sm C_d and the Sm A_1-Sm C_1 transitions are tabulated in Table 6.2. Two important points worth noting are

- TCOB has a small tilt angle even deep in the Sm C phase; $\phi \sim$ 11" at $(T_c - 10)$°C. This appears to be due to a small a/b ratio (or ϕ_o), which together with larger values of b/c (e.g.,R), suggest that the coefficient b is large.

- In the bilayer phases (7APCBB and DB8ClCN), an increase of the Sm A phase range by a factor of about 10, increases t_o by a factor of about 2 whereas in the monolayer case (TCOB) an increase of the Sm A phase range by a factor of about 7 increases t_o by a factor of about 25, the reason for which is not quite clear at the moment.

A possible explanation for the observation of a simple mean-field behaviour in the bilayer compounds even when the temperature range of the Sm A phase is quite small is that the smectic A order parameter is saturated before the transition to the Sm C phase takes place, thus reducing the mean field-tricritical crossover effect. At the same time it appears that a larger temperature range is required to saturate the smectic A order in the partially bilayer and monolayer cases.

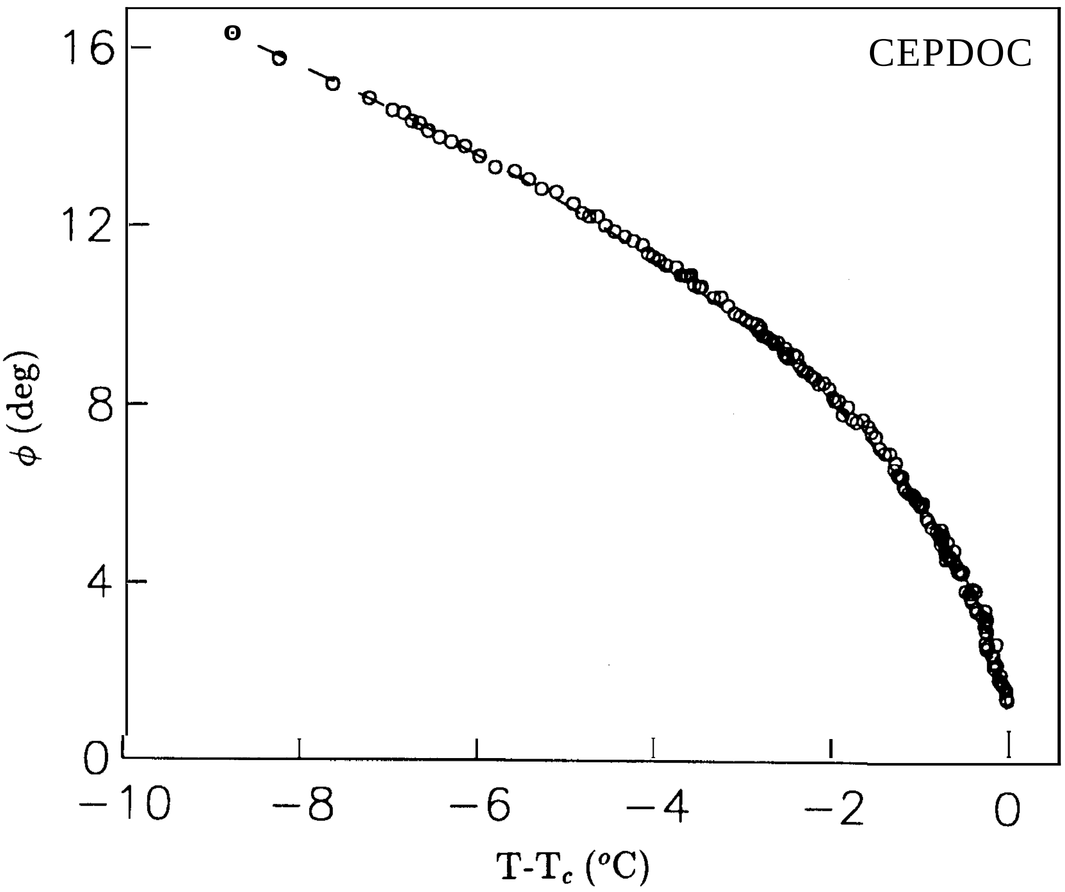


Figure 6.12: ϕ vs. T-T, plot for CEPDOC. Circles are the data points and dashed line is a fit to SMF model (equation G.5).

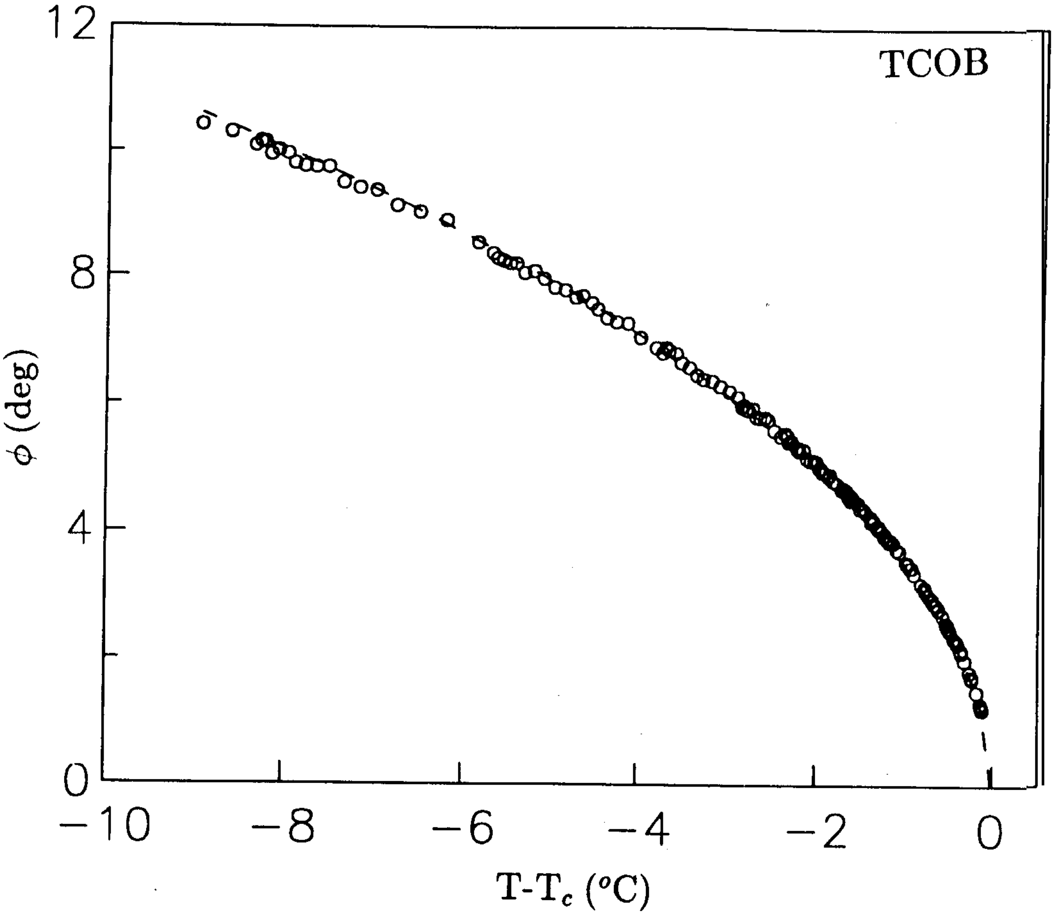


Figure 6.13: ϕ vs. T-T$_c$ plot for TCOB. Circles are the data points and dashed line is a fit to equation 6.5.

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[11] The compounds 7APCBB, CEPDOC and TCOB are kindly provided to us Prof. G.Heppke, Prof.Demus and Prof. M.E.Neubert respectively.

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