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Electrooptic investigations of enantiomeric mixtures of the antiferroelectric liquid crystal TFMHPOBC

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Measurements are reported for the polarization in the ordered phase, and for the tilt susceptibility in the 'disordered' smectic A phase, of mixtures of left- and right-handed enantiomers of TFMHPOBC. The tilt susceptibility was found to exhibit a critical exponent $\gamma = 1{\cdot}20 \pm 0{\cdot}05$, and both its magnitude and the polarization were found to be nonmonotonic in enantiomeric excess X of S-TFMHPOBC. Their ratio, however, was found to be approximately constant with X. Several possible explanations are examined.

1. Introduction

Liquid crystals which exhibit an antiferroelectric phase often exhibit ferroelectric and a variety of ferrielectric 'subphases' as well [1]. Understanding and exploiting these subphases have been activities of wide interest during the past few years. The first antiferroelectric material, 4-(1-methylheptyloxy-carbonyl)phenyl 4′-octyloxybiphenyl 4-carboxylate (MHPOBC) [2, 3] was found to have several well-defined ferrielectric phases, as well as the antiferroelectric SmC_A^* phase. Although not fully characterized, one of these ferrielectric phases (the SmC_α^* phase) apparently shows step-like behaviour of the polarization versus both temperature and applied electric field, reminiscent of the 'Devil's Staircase' [4]. Despite—and because of—the richness of the phase diagram of MHPOBC, several interesting phenomena cannot be observed. In consequence other materials possessing purportedly simpler phase diagrams have been synthesized, among them 4-(1-trifluoromethylhexyloxy-carbonyl)phenyl 4′-octyloxybiphenyl 4-carboxylate (TFMHPOBC, see figure 1) [5]. The optically pure material is particularly useful for studying the 'disordered' SmA to 'ordered' SmC_A^* phase transition, as no intermediate ferroelectric or ferrielectric phases are interposed between the SmA and lower temperature SmC_A^* phases. Additionally, over a large enantiomeric excess (ee) range of *mixtures* (*S*-TFMHPOBC + *R*-TFMHPOBC), what has been thought to be a ferroelectric SmC_A^* phase—which we shall now refer to as a SmC_x^* phase—intervenes between the SmA and SmC_A^* phases (see figure 2). The purpose of this paper is to report on experiments at the transition from the SmA phase to the SmC_x^* phase as functions of temperature and enantiomeric excess. Our tilt susceptibility and polarization results show anomalous behaviour, which may suggest that the SmC_x^* region actually consists of several phases.

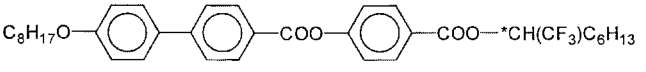

Figure 1. The molecule TFMHPOBC.

2. Experimental

A pair of indium–tin oxide (ITO) coated glass slides was dipped in a mixture of nylon 6/6 and formic acid, allowed to dry, then rubbed unidirectionally. The liquid crystal cell was constructed by cementing together the two slides, which were separated by Mylar spacers of nominal thickness 12·5 μm. The actual cell thickness was determined to within ± 1 μm by measuring the individual glass thicknesses and the overall outer cell thickness with a micrometer. Typical cell spacings were (15 ± 1) μm. The cell was heated and then filled with the TFMHPOBC mixture in the isotropic phase, and slowly

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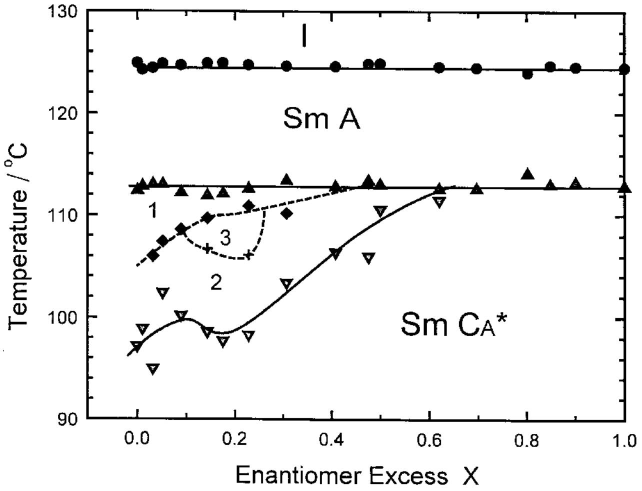

Figure 2. Schematic representation of phase diagram as obtained from separate optical data. The transition temperatures may vary slightly from that of figure 3 as different ovens were used.

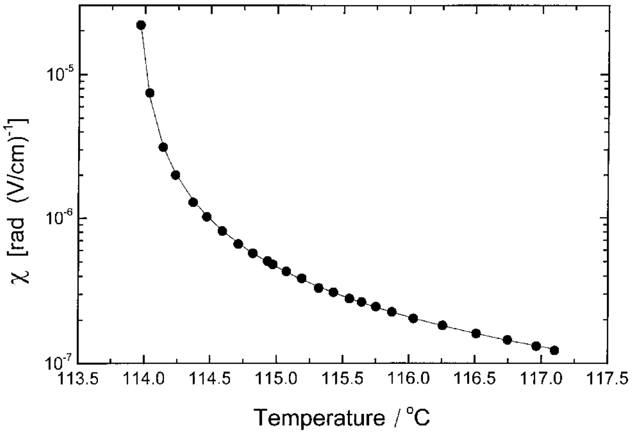

Figure 3. Tilt susceptibility versus temperature in the SmA phase for sample $X=0{\cdot}17$. $T^*=(113{\cdot}89\pm 0{\cdot}02)$°C.

cooled into the SmA phase to avoid the appearance of focal conic textures [6]; a clean bookshelf geometry was thus obtained. The cell was then transferred to an oven that was temperature controlled to approximately 25 mK. In the electroclinic geometry [7], the beam from a He–Ne laser, focused to a diameter $<100\,\mu$m, was incident perpendicular to the cell along the x axis and polarized at an angle $\pi/8$ from the z axis in the yz-plane. After passing through a crossed polarizer, the beam intensity was measured with a photodiode. Applying an a.c. electric field **E** across the sample along the x axis changes the average polar tilt θ [$\propto E$] of the director in the yz-plane. When such a tilt change occurs, there is a concomitant change in the intensity δI at the detector, such that $\theta=\delta I/4I_o$, where I_o is the (much larger) d.c. intensity. To measure the electroclinic coefficient $\chi[\equiv \mathrm{d}\theta/\mathrm{d}E]$, the a.c. voltage at frequency $\nu=317$ Hz was ramped from 0 to 1 $\mathrm{V_{rms}}$ over 120 s and δI [$\propto$ applied voltage] was measured with a lock-in amplifier. The d.c. detector output I_o was measured simultaneously with a d.c. voltmeter. Measurements were performed as a function of enantiomeric excess and of temperature in the SmA phase.

Figure 3 shows a typical set of results for enantiomeric excess $X=0{\cdot}17$ of S-TFMHPOB. [The enantiomeric excess of the mixtures is defined as $X\equiv([S]-[R]/([S]+[R])$, where $[S]$ and $[R]$ refer to the mole fractions of the left- and right-handed enantiomers of TFMHPOBC, respectively. Because of the finite quantities of materials used in the mixtures, all stated values of X have an uncertainty of $\pm 0{\cdot}02$. Moreover, each of the two optically 'pure' compounds has a small amount (<3 per cent) of optical impurity, which introduces a small systematic error in the concentration axis of the figures.] As expected, the electroclinic coefficient χ seems to diverge on approaching the temperature T^*. Although we cannot rule out a first order phase transition, T^* seems to be a second order transition temperature, as data were obtained generally within 25 mK of T^*. To examine the behaviour of χ we performed an algebraic fit of χ versus temperature (for all X) to the form $\chi=\chi_o t^{-\gamma}$, where $t\equiv(T-T^*)/T^*$. As the experimental error in $\log(\chi)$ was approximately constant with temperature, the actual fit was to the form $\log\chi=\log\chi_o-\gamma\log t$. Each set of data typically comprised between 1½ and 2 decades of reduced temperature. Figure 3 shows the best fit for $X=0{\cdot}17$, corresponding to $\gamma=(1{\cdot}20\pm 0{\cdot}05)$. To test the stability of the fits, we used a range shrinking procedure for each set of data, first removing the point closest to T^* and fitting, then the two closest points and fitting, etc. Figure 4 shows the fitted values of γ corresponding to the data in figure 3, where T_{final} corresponds to the temperature of the data point closest to T^*. The susceptibility exponent γ seems to evolve slightly with the range of data being used for the fit. Nevertheless, as this evolution is sufficiently small, several important issues arise (see below). In figure 5 we plot the fitted values of γ versus X using all data points in each set. [For completeness, in figure 6 we show the 'bare susceptibility' χ_o versus X obtained from the three parameter fits.] For enantiomeric excesses $X\leqslant 0{\cdot}6$ the exponent γ clusters around 1·2; it rises sharply for concentrations $X\geqslant 0{\cdot}6$, where the transition is from SmA to $\mathrm{SmC_A^*}$. The scatter in γ for the lower ee range ($0\leqslant X\leqslant 0{\cdot}6$) is consistent with the variation in γ when using the range shrinking procedure. As there is no clear variation in γ with X for $X\leqslant 0{\cdot}6$, we shall take its value to be its average, $\gamma=(1{\cdot}20\pm 0{\cdot}05)$, at the transition from the SmA phase to the $\mathrm{SmC_X^*}$ phase.

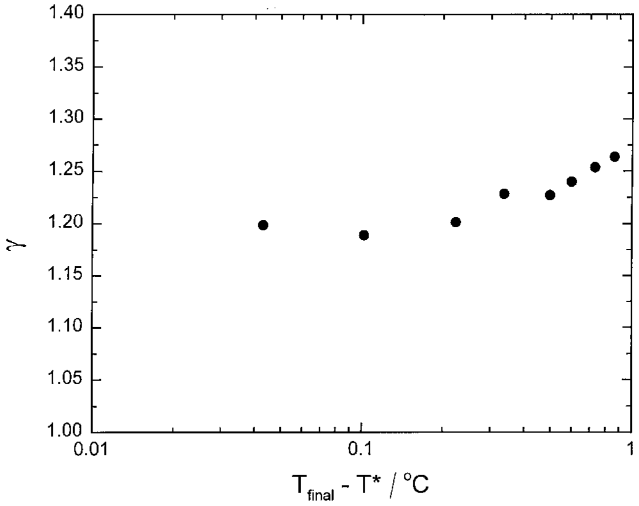

Figure 4. Evolution of susceptibility exponent γ for sample $X=0{\cdot}17$, as obtained by range shrinking. T_{final}-T^* corresponds to the closest approach to the apparent divergence temperature T^* in the fitting procedure.

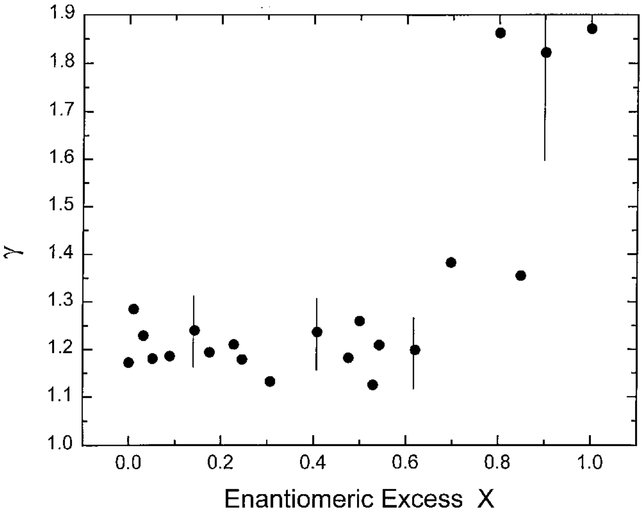

Figure 5. Critical susceptibility exponent γ versus enantiomeric excess X of S-TFMHPOBC. For each point, all data were used, corresponding to the smallest value of T_{final}-T^* (cf. figure 3).

Using this fixed value of $\gamma = 1{\cdot}20$, we then refitted the data using a *two* parameter (χ_o, T^*) fit $\log\chi = \log\chi_o - \gamma\log t$, and display χ_o in figure 7. We note that the general appearance of χ_o versus X is not much different from that of the three parameter fit in figure 6. There are several features to note. First, the bare susceptibility does not vanish for the $X=0$ sample, as one might expect for a racemic mixture. We believe that this is most likely due to the uncertainty in ee, both from the mixing procedure and the optical impurities of the enantiomers. More interesting is the apparent dip in χ_o with X in the neighbourhood of $X=0{\cdot}17$. On performing repeated measurements on several cells and with new mixtures, the dip was reproduced each time. Additionally, we observed an apparent levelling out and perhaps a slight decrease in χ_o for $X>0{\cdot}4$. This behaviour makes it clear that enantiomeric excess is an important parameter affecting the physical properties of the system. Moreover, the nonmonotonic behaviour of χ_o with ee would seem to suggest that the lower temperature SmC$_X^*$ phase(s) may not, in fact, be SmC*. In light of these results, and as the susceptibility depends upon the polarization P, we measured P versus both temperature and ee in the SmC$_X^*$ phase. The measurement was performed using the Sawyer–Tower method with a trian-

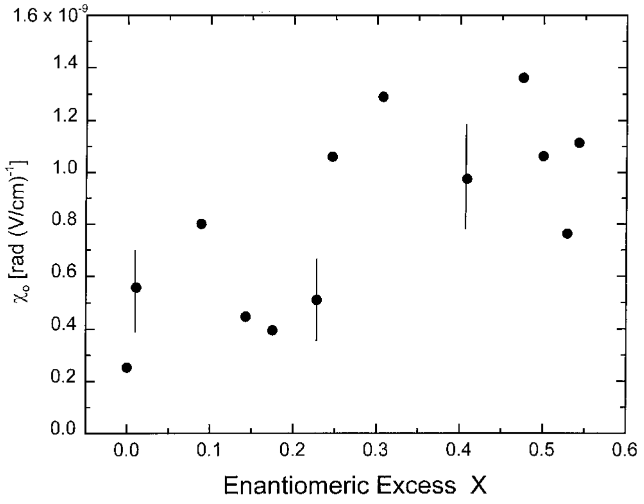

Figure 6. Bare tilt susceptibility χ_o versus X, based upon three parameter fit.

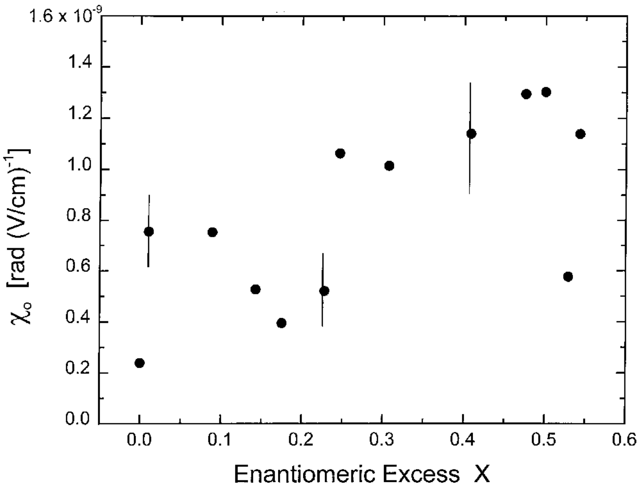

Figure 7. Bare tilt susceptibility χ_o versus X, based upon two parameter fit. To obtain χ_o, a value $\gamma=1{\cdot}20$ was used, and the data at each concentration were fitted to two parameters, namely χ_o and T^*.

gular potential [8]. In order to make a meaningful comparison of the data, we show in figure 8 the polarization versus X at temperature $T = 110°\mathrm{C}$. As T^* throughout the concentration region $0 \leqslant X \leqslant 0{\cdot}6$ is virtually constant and equal to approximately 114°C, the data in figure 8 represent the polarization P_{T} at a fixed value of $T^* - T \approx 4°\mathrm{C}$ in the $\mathrm{SmC}_{\mathrm{x}}^*$ phase. Interestingly, the polarization shows an even larger dip (on a percentage basis) than does χ_{o} around $X = 0{\cdot}17$, and shows a more marked fall off at higher concentrations than the χ_{o} data as well.

In figure 9 we show the ratio $\chi_{\mathrm{o}}/P_{\mathrm{T}}$ versus X, where χ_{o} is the values obtained from the two parameter fits shown in figure 7. Although there is significant scatter in the data, variations of this ratio with ee are considerably less than the large variations in either χ_{o} or P_{T}. In mean field theory above the SmA–SmC* phase transition, the susceptibility χ is equal to $\chi_{\mathrm{P}}\tau/A$, where τ is a coefficient which couples the polarization P and polar tilt angle θ in the free energy term $\tau\theta P$; χ_{P} is a generalized susceptibility coefficient which appears in the free energy term $\frac{1}{2}\chi_{\mathrm{P}}^{-1}P^2$; and $A = a'(T - T^*)$, where a' is a constant and T^* is the physical transition temperature [9]. This temperature, in principle, depends weakly on τ. Below the SmA–SmC* transition, one finds that the polarization $P = \chi_{\mathrm{P}}\tau\theta \propto \chi_{\mathrm{P}}\tau A^{1/2}$. Thus, in mean field theory the ratio χ/P is expected to be proportional to $A^{-3/2}$, so that the role of τ in this ratio is to *shift* the transition temperature. In consequence neither χ/P nor $\chi_{\mathrm{o}}/P_{\mathrm{T}}$ scales with τ within the context of mean field theory. Experimentally we find that, within error bars, the quantity $\chi_{\mathrm{o}}/P_{\mathrm{T}}$ is relatively flat with enantiomer excess [cf. figure 9]. This experimental result would imply that, *if* the lower temperature phase were indeed SmC*, the coefficient A also must be nearly independent of enantiomer excess. [We note that even the two apparently anomalous points differ from the average $\chi_{\mathrm{o}}/P_{\mathrm{T}}$ by much less than the maximum variations of either χ_{o} and P_{T} with enantiomer excess]. But individually χ_{o} and P_{T} are found to vary considerably with ee, and are even nonmonotonic (cf. figures 7 and 8) in ee. This behaviour is inconsistent with τ and the coefficient A being nearly independent of ee, and therefore it is clear that the lower temperature phase is unlikely to be SmC*, or at least is unlikely to be SmC* throughout the entire region $0 \leqslant X \leqslant 0{\cdot}6$.

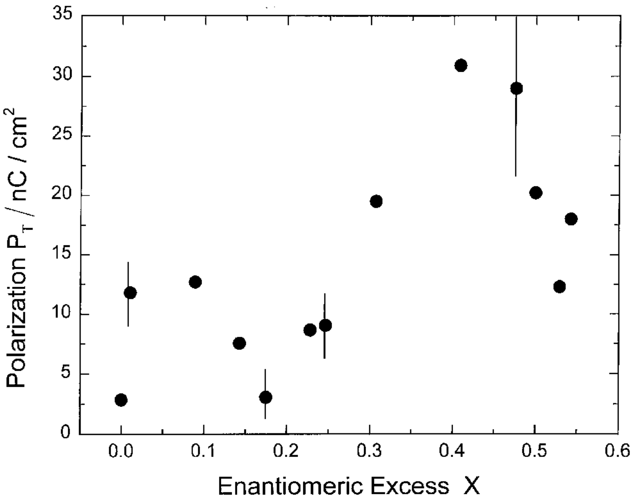

Figure 8. Polarization P_{T} measured in an ordered phase at $T\text{-}T^* = -4{\cdot}0°\mathrm{C}$ versus X.

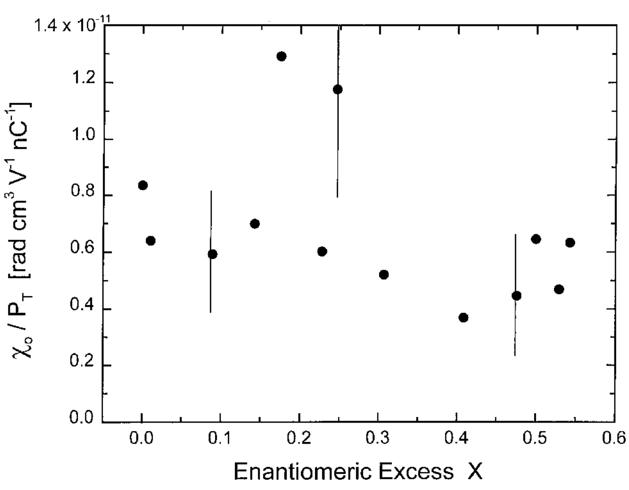

Figure 9. The ratio of bare tilt susceptibility to polarization versus X.

3. Discussion

Taken as a whole, the data raise two interesting questions. First, what is the origin of the nonclassical susceptibility exponent γ, and to what can we ascribe its change in the neighbourhood of $X = 0{\cdot}6$? We remark that we had earlier noted significant deviations from the mean field result $\gamma = 1$ in our initial experiments on the enantiomer S-TFMHPOBC [10]. Second, what is the origin of the nonmonotonic behaviour in χ_{o} and P_{T} with ee?

Interpretation of the critical exponents at the SmA–SmC transition has often been controversial. In the nonchiral material butoxybenzylidene heptylanaline (4O·7) mean-field behaviour was observed [11, 12], whereas in another material, azoxy-4,4′-di-undecyl-α-methylcinnamate (AMC-11), 3D XY critical exponents were found [13–15]. The difference may be ascribed to a material-dependent bare correlation length ξ_{o} which characterizes tilt fluctuations. According to the Ginzburg criterion [16], the temperature region ΔT around T^* in which asymptotic critical behaviour may be observed varies as ξ_{o}^{-6}, and thus a large ξ_{o} may preclude the observation of fluctuation-dominated critical exponents for a particular material. In the first tilt susceptibility measurements of a ferroelectric liquid crystal, Garoff and Meyer observed [9] the anomalous exponent $\gamma = (1{\cdot}11 \pm 0{\cdot}06)$ in the material *p*-decyloxybenzylidene-*p*′-amino-2-methylbutylcinnamate (DOBAMBC), which lies between the mean field value of $\gamma = 1$ and the 3D XY value $\gamma = 1{\cdot}32$. Beresnev, *et al*., conjectured that this result may be due to a temperature-driven coupling between the molecular dipole and the optically polarizable molecular core [17], a suggestion subsequently confirmed in an experiment involving combined electric and magnetic fields [18].

We now examine possible explanations for our results. Figure 5 shows a susceptibility exponent $\gamma = (1{\cdot}20 \pm 0{\cdot}05)$ above the $\mathrm{SmC}_{\mathrm{X}}^{*}$ phase in the region $0 \leqslant X < 0{\cdot}6$, which increases substantially as X approaches 1 above the $\mathrm{SmC}_{\mathrm{A}}^{*}$ phase in the region of high enantiomeric excess. It's unlikely that the value of γ in the region $0 \leqslant X < 0{\cdot}6$ represents a crossover from mean-field to critical. If that were the case one would expect that the range shrinking procedure (see figure 4) would have yielded a *decreasing* exponent (closer to the mean-field value $\gamma = 1$) with increasing T_{final}, as the fitting would involve less of the critical region near T^{*}. This is clearly not the case, as figure 4 shows an increasing trend in γ with T_{final}. Recently Ema, *et al.* [19], performed calorimetry measurements on MHPOBC at the SmA–SmC* phase transition. Fitting their data to a complicated function, they concluded that the behaviour exhibits a crossover from 3D XY to tricritical behaviour. Again, our data is inconsistent with this conclusion, as range shrinking indicates an increasing exponent γ further from the transition. Another possible explanation for the exponent involves molecular effects. As suggested by Beresnev, *et al.* [17], the exponent is nominally either mean-field like or critical, but a temperature-dependent coupling between the molecular dipole and the chromophore near the transition results in a change in the effective exponent. This conjecture may ultimately be tested using the techniques of reference [19], although it is beyond the scope of the present work.

Another possibility is the presence of a chiral interaction term of the form discussed in references [20–23]. Such a term is allowed in a chiral system. If it were sufficiently large, it would result in a phase transition from one ordered phase to another (as a function of enantiomeric excess), but would not greatly affect the transition *temperature* at the order-disorder transition. The effect of this term on the observed exponents is quite complex, as it can result in a large crossover region of slowly varying exponents. Qualitatively, at least, this behaviour is consistent with that observed in our range shrinking analysis. Additionally, this term cannot be present in the racemic mixture, and we would therefore expect the exponent γ to revert to its 3D XY value near $X = 0$. Within error bars, the data in figure 5 seems marginally consistent with this possibility. Therefore, the observed exponent data in the ee region $0 \leqslant X \leqslant 0{\cdot}6$ *may* be due in part to these chiral interactions, although other effects are likely to play a significant role as well.

In the region of large enantiomeric excess, where $0{\cdot}6 < X \leqslant 1$, we find that the exponent γ rises to approximately 1·85. We note that in this region there is a discontinuity between the Neél temperature T_{N} and the supercooling limit T^{*} of the SmA phase, varying continuously from near zero at $X \sim 0{\cdot}6$ to $T_{\mathrm{N}} - T^{*} \sim 1{\cdot}1$°C at $X = 1$ [10]. Considering possible causes for this unusually large exponent, we feel that short range antiferroelectric order in the SmA phase is unlikely, as it requires an order parameter with a large number of spin components. To second order in $\varepsilon[\equiv 4 - d$, where d is the dimension of the system], the isotropic n-vector susceptibility exponent γ is given by [24]

$$\gamma = 1 + \left[\frac{n+2}{2(n+8)}\right]\varepsilon + \left[\frac{n+2}{4(n+8)^{3}}\right](n^{2} + 22n + 52)\varepsilon^{2}.$$

To reach the observed values of $\gamma = 1{\cdot}7$–$1{\cdot}9$ would require in excess of ten spin components. This number is much larger than can be accounted for by the presence of antiferroelectric fluctuations in the SmA phase, which are expected to behave as a four component spin. If Fisher renormalization [25] were a factor, a small increase would be expected if the transition temperature to a tilted phase depended on enantiomeric excess. A larger increase would be expected if the transition between two tilted phases depended on ee, and if this is associated with a non-classical multicritical point. While the phase diagram does have a transition between ordered phases (see below) with a concentration dependent transition temperature, it is inconsistent with a non-classical multicritical point. The large values of γ observed in this concentration remain a mystery.

We now turn to the nonmonotonic behaviour in figures 7 and 8. In a related material, 4-(1-trifluoromethylhexyloxy-carbonyl)phenyl 4′-octylbiphenyl 4--carboxylate (TFMHPOBC), Isozaki and coworkers found that, contrary to the case of MHPOBC, racemization increases the complexity of the phase diagram, at least in the more optically pure region [26]. (Extant models predict subsets of the observed phases [27–29], but we know of no model which predicts the complete set). Our optical and differential scanning calorimetry experiments to be published elsewhere [30] suggest that the ordered $\mathrm{SmC}_{\mathrm{X}}^{*}$ phase in this region is not a single phase but has a number of different subphases. Figure 2 shows a phase diagram obtained from optical measurements which indicates how the $\mathrm{SmC}_{\mathrm{X}}^{*}$ phase seems to be subdivided into at least two phases. [Note that a different oven was used for these measurements, with a systematic depression of T^* by approximately 1°C from the other measurements reported herein.] Dotted lines are used to indicate transitions which are still in question. The actual number of these subphases may be more than two, although the data are equivocal. (We are not certain of the existence of region 3). One of these regions, most likely region 2, may be SmC*. Thus, as a function of concentration the SmA phase may undergo a transition into the $\mathrm{SmC}_\mathrm{A}^*$ phase, the SmC* phase, or other as yet unclassified phases. We remark, however, that the susceptibility above an antiferroelectric transition is not much different from that at a ferroelectric transition, and therefore it is unlikely that the existence of the phase boundaries alone (cf. figure 2) could explain the large variations with X of χ_o and P_T in figures 7 and 8. Moreover simple Landau–Ginzburg analysis does not easily reconcile the observed phase behaviour with the variation of the polarization or susceptibility. We now consider two other possible scenarios: first that there is an unobserved periodicity in the disordered/smectic A phase, and second that there is no such periodicity.

Suppose that there is a periodicity in the smectic A phase longer than the layer spacing—in particular, that alternate layers in the smectic A phase have different concentrations of R and S enantiomers. Then both the SmC and SmC_A order parameters would result in a polarization. It would then be possible that these competing order parameters, together with a change in the enantiomer excess difference between layers, could possibly result in the observed behaviour. An important consequence of this scenario is that an enantiomer segregation transition can be second order for low ee, near the concentration $X=0$. However as enantiomeric segregation is impossible in an optically pure sample, this second order transition must end at a tricritical or critical end point for sufficiently large enantiomeric excess. Such a first order transition may be direct, or may be a virtual transition, preempted by crystallization. The appropriate signature has not yet been observed, although we are currently investigating segregation both experimentally and theoretically.

In the absence of a longer periodicity in the SmA phase, the Landau rules imply that the electric field couples to the uniform SmC order (uniform tilt) order parameter. It is possible for a ferroelectric phase to have the uniform tilt order parameter as a secondary order parameter; this occurs, for example, if there is a tilt order parameter with a period of three layers. However, in all such cases known to us, the secondary order parameter susceptibility—in this case it is the electroclinic susceptibility—diverges, if at all, with an exponent much less than unity. Thus the Landau rules would suggest that: (1) all ordered phases are either a SmC phase or a SmC phase with intralayer modulation [20–23], or (2) the apparent divergence we have observed is eventually cut off at a transition to another phase. Variation of the *polarization* with ee could be explained by intralayer modulation, although the Landau rules do not predict the variation in the bare susceptibility. A cut-off could be consistent with, for example, weak interlayer coupling, resulting in various antiferroelectric ordered phases.

Finally, we consider the role of the coupling τ between the tilt and the polarization. The variation with ee of the bare susceptibility and polarization, and the relative constancy of their ratio, *are* consistent with a variation in the coupling constant τ. Although τ does not play a role—at least within mean field theory—in the ratio $\chi_\mathrm{o}/P_\mathrm{T}$ versus X, it may be important for the polarization and susceptibility individually. A plausible scenario is that the molecular conformations depend on the enantiomeric excess, especially as experimentally there is a change from ferroelectric to antiferroelectric or ferrielectric behaviour with X. This in turn is consistent with differing angles between the pendant chains and the rigid part of the molecule. For example, the two pendant chains may switch from having roughly the same dihedral angle to having essentially opposite angles. As these angles are thought to control the spontaneous polarization, it is plausible that there is a dependence of conformation with X, and that it affects the coupling between tilt and polarization. Such a dependence could be responsible for the nonmonotonic behaviour observed in figures 7 and 8.

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