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PRELIMINARY COMMUNICATIONS

Evidence of electroclinic effect in some TGBA mesophases

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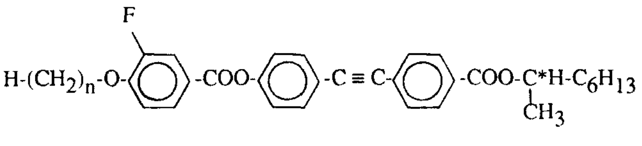
Two members of a chiral tolane series exhibiting a new TGBA phase and a S_C^* ferroelectric phase have been investigated by means of electro-optical measurements. These materials belong to the optically active series of (*R*)-4-(1-methylheptyloxycarbonyl)-4′-(4″-alkyloxy-3″-fluorobenzoyloxy)tolanes and are the tetra- and octa-decyloxy derivatives. Due to the large pitch values in these TGBA mesophases, complete unwinding of the helix is found to be possible in thick cells. This also allows measurements of the electroclinic properties, such as the electric field induced tilt angle, response time, and the ferroelectric properties in the S_C^* phase.

The discovery of new helical smectic phases such as TGBA [1, 2] and TGBC [3] has demonstrated the fascinating manifestations of chirality in liquid crystals and their increasing diversity in this field. Apart from the TGB mesophases, a number of new ferri- and antiferro-electric mesophases [4, 5] have been reported in various chiral compounds. The aim of this paper was (*a*) to check whether it was possible to unwind the helical structure of the TGBA phase by means of boundary conditions in a classical SSFLC cell [6], (*b*) to measure the electroclinic properties of this mesophase and compare the values with the previously published results in the S_A phase [7–9] and (*c*) to evaluate the ferroelectric properties of the smectic C* phases in these compounds.

Two members of the newly synthesized chiral tolane series—the (*R*)-4-(1-methylheptyloxycarbonyl)-4′-(4″-alkyloxy-3″-fluorobenzoyloxy)tolanes [2]—have been used for these investigations. The molecular structure of the homologues is shown below:



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The various phase transition temperatures and the corresponding enthalpies (in italics) are as follows:

n	C		S_C^*		TGBA		I	Units
14	•	66·5	•	94·9	•	104·9	•	°C
		52		*0·23*		*5·3*	•	J g − 1
18	•	67	•	93	•	97	•	°C
		67		*0·29*		*5·47*	•	J g − 1

The TGBA mesophase of these two compounds shows a filament texture for the tetradecyloxy derivative [2] indicating only a moderate chiral twist in the mesophase, whereas the octadecyloxy compound exhibits cholesteric-like textures. The pitch measurements for these compounds were carried out by the classical Grandjean–Cano method [2]. The large values of the pitch in these compounds favour complete unwinding of the helical structured at zero electric field in our cells.

The sample was sandwiched between two ITO coated glass plates (Balzers 30 Ω) of 1·7 × 0·8 cm size. Except in a region of 0·5 cm at the centre of the glass plates, the ITO coating was removed in order to avoid electrical conduction. The effective area which contains the sample was 0·25 cm^2. No spacers were used in order to improve the alignment by sliding the upper plate over the lower plate. The average thickness of the sample was found to be about 5 μm, using the Newton colour method [4]. The homogeneity of the sample was checked from the colour. Both plates were brushed with PVA and the thickness of this coating was about 400 Å. The rubbing direction was parallel for the two plates. A classical electro-optical set-up [7], which allows the measurement of switching current, optical response and apparent tilt angle, was used for these investigations. The 'optical' response time ($\tau_{10/90}$) was determined from the response of the transmitted light, detected by a photodiode.

The apparent tilt angle was measured by a standard method [7], with an accuracy of ± 1°. Square waves of frequency 1 kHz were used for polarization measurements, whereas the frequency of the applied square pulse was 0·1 Hz for apparent tilt angle measurements.

Polarizing measurements: Polarization measurements were performed for various applied fields and temperatures. Figures 1 (*a*) and (*b*) show the polarization values for the two compounds as a function of the applied field at various temperatures in the smectic C* phase. For each temperature, the P_s increases with increasing applied electric field up to a voltage of 20 V (4 V μ^{-1}), whereas a saturation of the P_s is noticed above this field strength. In both compounds, the P_s is found to increase with decreasing temperature. In the compound with $n = 14$ (see figure 1 (*a*)), at a temperature 93°C, the P_s value at low fields is rather high. This may be due to some electroclinic contribution (soft mode) in the S_C^* phase, as this temperature is close to the S_C^*–TGBA transition temperature (1·9°C above). The significantly lower P_s values observed for the second compound ($n = 18$) compared to the first compound ($n = 14$) is due to the increase of the apolar aliphatic chain length.

The variation of the spontaneous polarization P_s, as a function of temperature, for the two compounds, is shown in figure 2. A large difference in the P_s values has been observed for the two compounds. After a sudden fall at the S_C^*–TGBA transition, a rather large value of P_s has been observed in the TGBA phase. These fairly large values (about 70 nC cm^{-2}) for the $n = 14$ compound) near the transition, reveals an unusually large

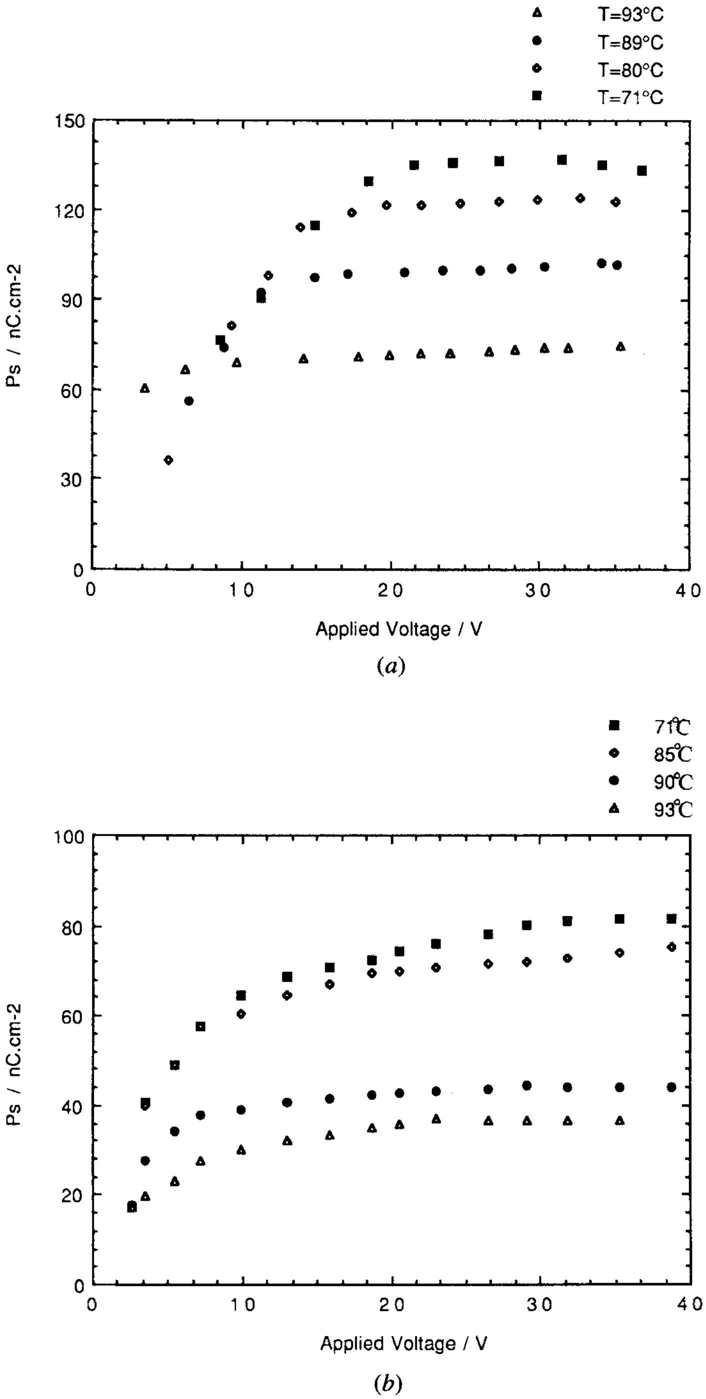

Figure 1. Spontaneous polarization versus field at several temperatures; (*a*), $n = 14$; (*b*), $n = 18$.

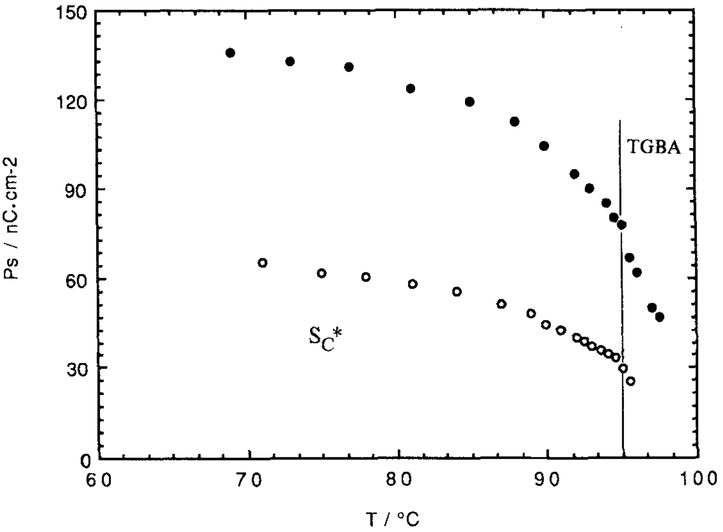

Figure 2. Spontaneous polarization versus temperature. (●) $n = 14$; (○) $n = 18$.

electroclinic effect [5–7, 10] or induced polarization. This has been further confirmed from the response time and the induced tilt angle measurements.

Response time measurements: The response time $\tau_{10/90}$, was measured in the S_C^* and TGBA phase ranges as a function of the applied electric field for different temperatures. Figure 3 shows the response time $\tau_{10/90}$ as a function of field for the compound with $n = 14$ at three different temperatures in the S_C^* phase (76, 81, 93°C) and at a temperature of 96°C in the TGBA phase. In the S_C^* range, the behaviour of $\tau = f(V)$ is rather linear for low fields (up to 20 V), while it is strongly non-linear for high fields, and almost saturated above 20 V. On the contrary, in the TGBA mesophase, τ is independent of the applied field V, which is a clear demonstration of the soft mode behaviour [7]. For instance at 96°C, $\tau = 8\,\mu s$ for the field range from 16 to 40 V. At lower field, the measurement was not possible, as the P_s values were too small. Figure 5 shows the variation of the response time $\tau_{10/90}$ for the whole temperature range. The values are significantly larger for $n = 18$ (small polarization) than for $n = 14$. In the last case, an abrupt change at the S_C^*–TGBA transition is clearly seen, and the τ values drop to a few µs at higher temperatures.

Tilt angle measurements: Figure 5 shows the tilt angle values as a function of temperature for the compounds with $n = 14$ and $n = 18$. The applied voltage across the electrode was 30 V. In the S_C^* phase, over the temperature range 70 to 90°C, the tilt angle is almost constant and decreases very slowly with increasing temperature. Close to the S_C^*–TGBA transition and in the TGBA range, the tilt angle decreases drastically. The tilt angle is fairly large (25°) at the S_C^*–TGBA transition, while its value is more than 30° in compounds exhibiting a S_C^*–N* transition [3]. As a result of the helical character of the TGBA phase, the S_C^*–TGBA transition is found to be second order in nature.

The variations of the measured tilt angle as a function of the applied field for different temperatures in the S_C^* and TGBA phases are shown in figure 6. The tilt angle is found to be independent of the applied field strength over the whole S_C^* range, but it decreases with increasing temperature. Contrary to this, the tilt angle in the TGBA range is almost linear up to 25 V, which is similar to the behaviour observed in the

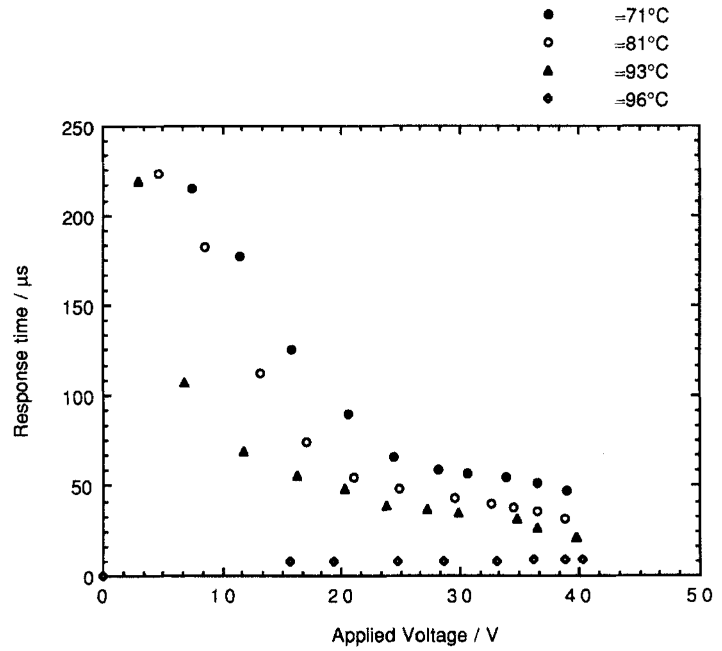

Figure 3. Optical response time τ versus field at several temperatures, $n = 14$.

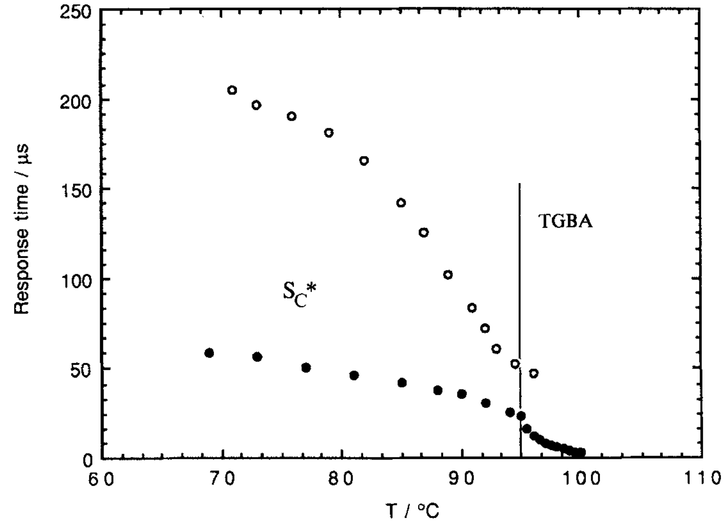

Figure 4. Optical response time τ versus temperature. (●) $n = 14$; (○) $n = 18$.

electroclinic effect [5]. Very close to the S_C^*–TGBA transition (95·3°C), a linear variation of the tilt angle is observed up to 12V, above which a non-linear behaviour is noticed, which is again similar to observations reported earlier [5].

The two compounds studied belong to a new series bearing a 2-octyl chiral chain which results in strong chirality [3, 11, 12]. This strong chirality gives rise to short pitch values in S_C^* and N* phases and induces a helical smectic A phase, although in several cases with rather larger pitch values [11]. This strong chirality and the presence of a COO function near the chiral carbon, induces a strong polarization which is found to

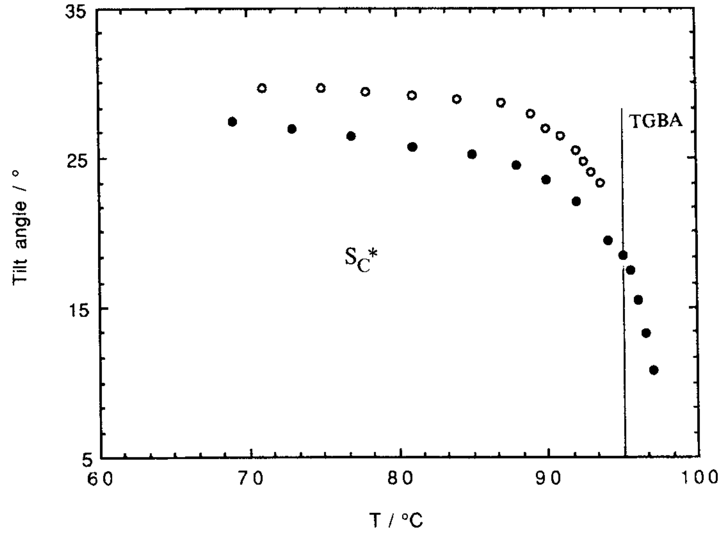

Figure 5. Tilt angle versus temperatures. (●) $n = 14$; (○) $n = 18$.

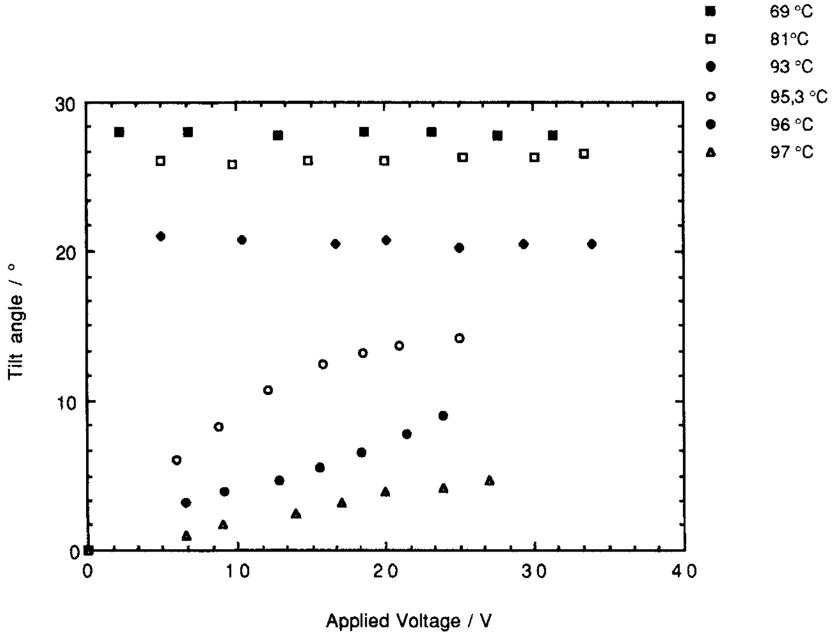

Figure 6. Tilt angle versus applied voltage at different temperatures in the S_C^* and TGBA phases: $n = 14$, S_C^*–TGBA transition at 94·9°C.

be up to 120 nC cm^{-2} in the C_{14} compound, but probably larger in short chain homologues. Another manifestation of this strong chirality is also evidenced in the TGBA phase through the large electroclinic effect (i.e. large field induced tilt angle, short field independent response time, and a fairly large induced polarization up to 70 nC cm^{-2}) which has been unambiguously demonstrated in this work. Although the helical TGBA phase was completely unwound in our cells by means of boundary conditions and thickness, the specific nature of the TGBA mesophase manifests its character as evidenced by the very large value of the tilt angle in the S_C^* phase near the TGBA phase transition. This has also been observed in similar series [2], but with some short pitch TGBA phases.

Now, concerning the electroclinic effect, it will be interesting to explore other TGBA phases in order to check whether increasing helicity enhances the electroclinic properties or gives rise to some other specific behaviour. Moreover, as these compounds are very similar to those giving ferri- and antiferro-electric properties, it should also be interesting to investigate the electro-optical properties in the S_C^* range at low frequencies, in order to check the eventual polystable switching i.e. ferri- and antiferro-electric behaviour.

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