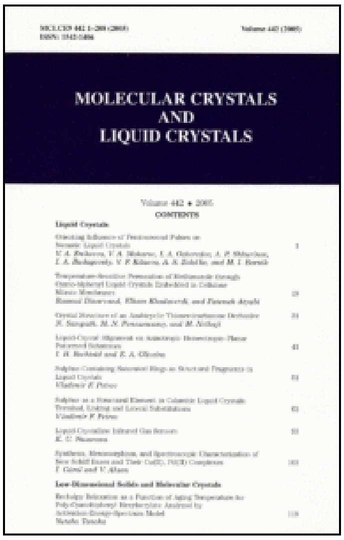

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Spontaneous Polarization and Rotational Viscosity Measurements on Ferroelectric Liquid Crystals Derived from trans-*p*-*n*-alkoxycinnamic Acids†

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We report here the results of systematic measurements of spontaneous polarization and rotational viscosity on four structurally related homologous series derived from trans-*p*-*n*-alkoxycinnamic acids. The influence of alkyl chain length on the magnitude and temperature dependence of the polarization, and the effect of subtle structural changes on the rotational viscosity are discussed.

Keywords: Ferroelectric liquid crystals, spontaneous polarisation, rotational viscosity, tilt angle, response time

INTRODUCTION

Due to their strong electro-optical effects ferroelectric liquid crystals have gained increasing interest during the last few years. Experiments have shown[1] that the electro-optic response depends primarily on the magnitude of the spontaneous polarization (P_s) and the rotational viscosity (γ). In order to obtain fast-response materials it is important to know the influence of molecular structure on P_s and γ. But the delicate interplay between molecular structure and the physical properties is not well understood. Although the literature is abundant with results on polarization, systematic viscosity measurements have been undertaken only relatively recently. The studies reported in this paper are aimed at getting a better knowledge of the structure-property relationship.

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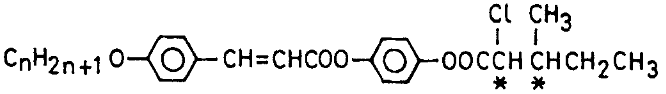
†Presented at the 8th Liquid Crystal Conference of Socialist Countries, Krakow, Poland, August 28–September 1, 1989.

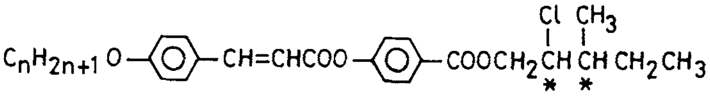
MATERIALS

Studies have been made on four different but structurally related homologous series of compounds. The molecular structures of the four series are shown below.

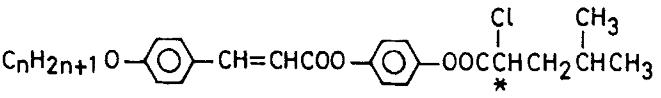
Series I



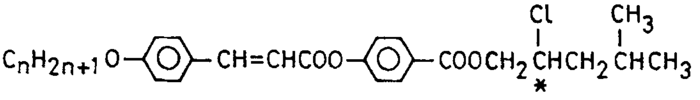
Series II



Series III



Series IV



n = 7–12

Details regarding the synthesis of these compounds, the characterization of the mesophases and phase transition temperatures have been reported in an earlier paper.[2]

As the structural formulae show, compounds of series I and II have a chiral group with two asymmetric carbon atoms while those of series III and IV have only one asymmetric carbon atom. In series I and III at least one chiral group is directly attached to the core (for all practical purposes the COO group at one end of the core is considered to be a part of the core[3]) and in series II and IV it is separated from the core by a spacer CH_2 group.

The investigations of Huang and Lien[4] and of Liu *et al.*[5] have shown that the range of the smectic A phase plays an important role in deciding the nature of the A—C* transition. We will at a later stage compare the thermal variation of polarization very close to the A—C* transition as a function of chain length or the range of the smectic A phase. With this in view, we have presented in Figures 1a–d the temperature range of the smectic A phase as a function of the chain length for the four series.

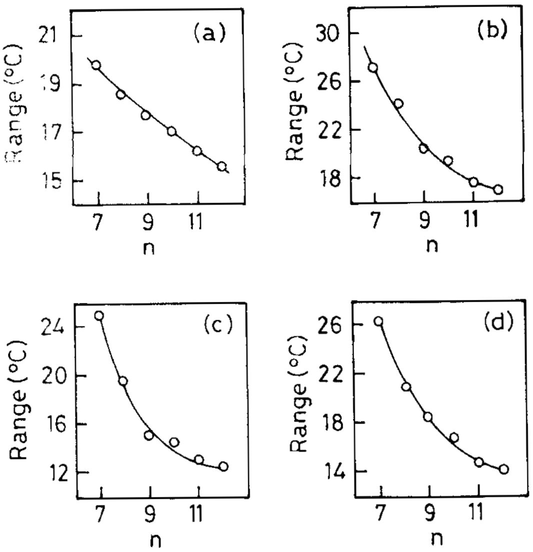


FIGURE 1 Range of the smectic A phase as a function of alkyl chain length for (a) series I, (b) series II, (c) series III and (d) series IV.

EXPERIMENTAL

The sample cell was made up of two ITO-coated glass plates which had the electrode pattern etched on to them. Mylar spacers were used to define the thickness of the cell (care was taken to see that neither the spacers nor the bonding adhesive was present inside the active area). The actual thickness of the cell, typically around 7μm, was measured using an interferometric technique. The active area was calculated by measuring the capacitance of the cell; the calculated area agreed with the area measured visually.

For spontaneous polarization measurements a calibrated Diamant bridge[6] was used. A sinusoidal wave at a frequency of 200 Hz was used to obtain the hysteresis curve. A data acquisition system (HP 7090A) was employed in these experiments. The calibration of the bridge was checked electrically as well as by measuring the spontaneous polarization as a function of temperature for two liquid crystalline systems for which such results have already been reported—by Bahr and Heppke[7] for C7 and by Spruce and Pringle[8] for CE8. The data obtained using our setup agreed to within 5% of the values reported for C7 and within 10% for CE8, over the entire temperature range in both cases. (It may be mentioned, however, that Spruce and Pringle have observed even larger variations between different measurements on the same material.)

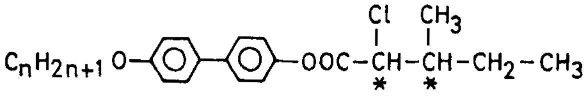
For studying the response time and rotational viscosity we employed the field reversal technique.[9] A square wave driving voltage with an amplitude of 30 kV/cm was used for this purpose. Data was acquired on a storage oscilloscope and for further analysis it was transferred to a computer. The response time and rotational viscosity values obtained using this set up agreed to within 5% of the reported value for CE8[10] over the entire temperature range. Tilt angle data were obtained by the X-ray diffraction method.

RESULTS AND DISCUSSION

Spontaneous Polarization

1) *Compounds with two asymmetric carbon atoms* a) Series I: As already mentioned the asymmetric carbon atoms in these compounds have been directly attached to the core. In this series for the homologues $n = 7$ to 10 a cholesteric phase exists between the smectic A and isotropic phases while for $n = 11$ and 12 there is a direct smectic A—isotropic transition. More importantly, as is evident from Figure 1a also, as the alkyl chain length increases the range of the smectic A phase decreases. This is in contrast to what was observed in compounds which are structurally similar.[7] Figure 2 shows the thermal variation of spontaneous polarization for all the six homologues of series I. It is seen that as the chain length increases, there is a substantial decrease in the magnitude of P_s as well as its rate of variation with temperature close to the A—C* transition point T_c. The inset in Figure 2 is a plot of P_s at $T_c - T = 10°C$ versus chain length: P_s decreases monotonically as the chain length increases. As the molecular structures of series I are very similar to the compounds studied by Bahr and Heppke,[7] MCPnOB whose structural formulae is given below,

MCPnOB



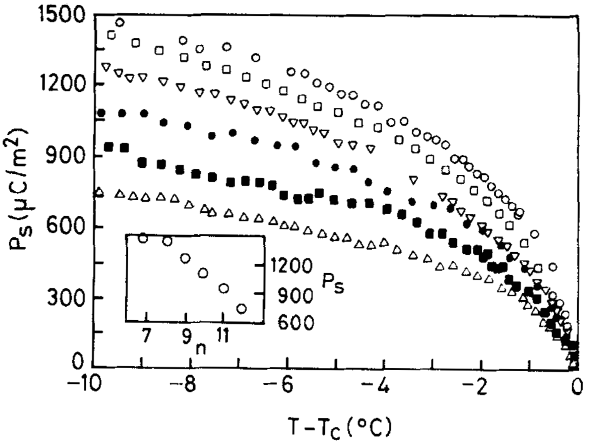


FIGURE 2 Thermal variation of spontaneous polarisation P_s for $n = 7$ (○), $n = 8$ (□), $n = 9$ (▽), $n = 10$ (●), $n = 11$ (■) and $n = 12$ (△) of series I. The inset shows P_s at $T_c - T = 10°C$ versus n.

we can compare the behaviour of P_s in the two cases. Such a comparison shows:

(i) The introduction of a bridging group between the two phenyl rings, albeit a polar one, has brought down P_s by almost a factor of two. The reason for this may be two-fold. Firstly, the increase in the length of the molecule has overcompensated the increase in the transverse dipole moment and secondly, the COO group in the core tilts one phenyl group with respect to the other thus providing an increased degree of freedom of rotation for the chiral part about the rest of the molecule.

(ii) In series I as well as MCPnOB, the rate of variation of P_s as a function of temperature (dP_s/dT) at T_c decreases as n increases. However, in contrast to the MCPnOB series[7] (and also to lactic acid derivatives[11]), the range of the smectic A phase *decreases* with increasing chain length in the case of series I. To our knowledge this is probably the first case of a reverse behaviour.

b) Series II: Here the chiral carbon atoms are separated from the core by a spacer (CH_2) group. P_s measurements done on $n = 7$ to 12 (see Figure 3) seem to answer the basic question viz., does the proximity of the two chiral groups to the core increase the value of polarization? Comparing Figures 2 and 3, one can see that the introduction of a CH_2 group between the core and the chiral parts brings down the value of P_s appreciably. Although the magnitude of P_s has decreased, the overall behaviour within the homologous series is similar to series I, namely, as n increases the range of the smectic A phase, as well as the magnitude of P_s, decrease.

2) *Compounds with only one asymmetric carbon atom* Series III and IV behave essentially similar (see Figures 4 and 5) to their two chiral group analogues, series I and II, except that the difference in P_s between series III and IV—wherein the former has the chiral group directly attached to the core and the latter has a CH_2 spacer group separating the chiral part from the core—is smaller than that between series I and II. For example, for the 10th homologue at $T_c - T = 10$°C the

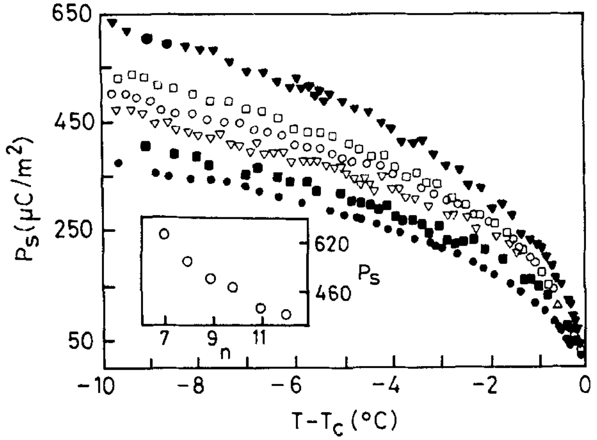


FIGURE 3 Temperature variation of P_s for $n = 7$ (▼), $n = 8$ (□), $n = 9$ (○), $n = 10$ (▽), $n = 11$ (■) and $n = 12$ (●) of series II. The inset is a plot of P_s at $T_c - T = 10$°C versus n.

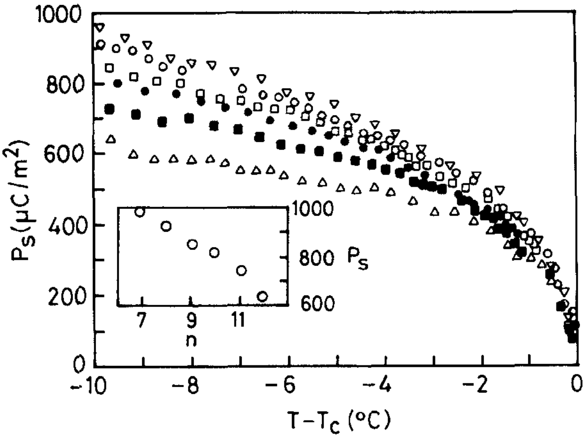


FIGURE 4 Plot of P_s versus temperature for $n = 7$ (▽), $n = 8$ (○), $n = 9$ (□), $n = 10$ (●), $n = 11$ (■) and $n = 12$ (△) of series III. The inset is a plot of P_s at $T_c - T = 10$°C versus n.

difference between series I and II is ~640 $\mu C/m^2$ and that between series III and IV is ~480 $\mu C/m^2$.

Thus, in all the four series of compounds, the value of P_s seems to be sensitive to the positioning of the chiral groups with respect to the core and also to the chain length.

TILT ANGLE

The tilt angle in the C* phase has been evaluated from the expression $\theta = \cos^{-1}(d_{C^*}/d_A)$ (where the subscripts denote the phases in which the layer spacing (d) has

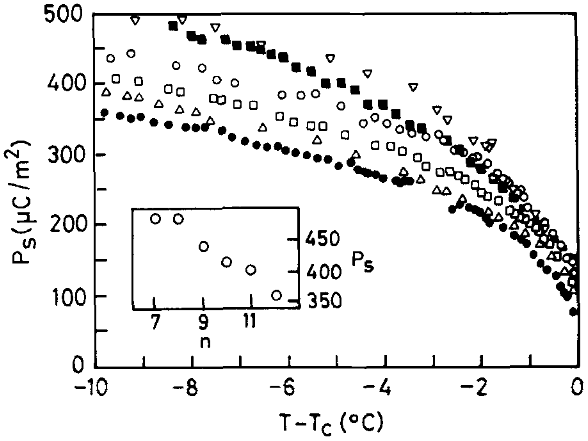


FIGURE 5 Plot of P_s as a function of temperature for $n = 7$ (▽), $n = 8$ (■), $n = 9$ (○), $n = 10$ (□), $n = 11$ (△), $n = 12$ (●) of series IV. The inset shows P_s at $T_c - T = 10$°C versus n.

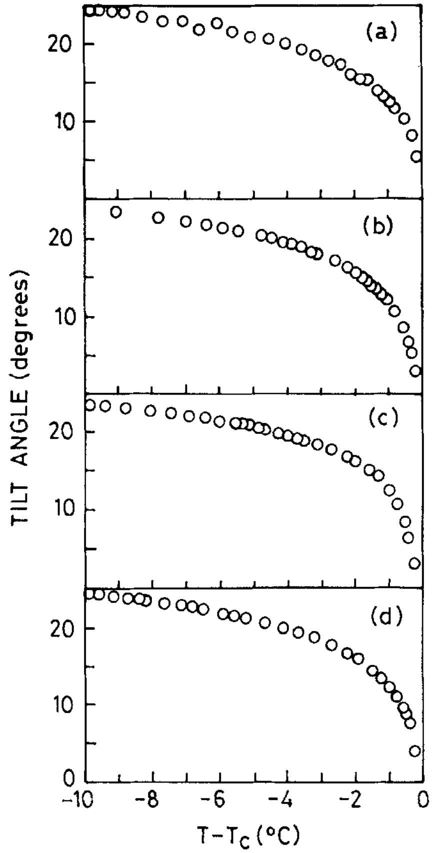


FIGURE 6 Tilt angle as a function of temperature for n = 10 of (a) series I, (b) series II, (c) series III and (d) series IV.

been measured). Figures 6a–d show plots of tilt angle variation as a function of temperature for series I–IV (n = 10) respectively. From the figures it appears that the magnitude and variation of θ is insensitive to the structural differences between the different series.

RESPONSE TIME AND ROTATIONAL VISCOSITY

When an oscillating electric field is applied to a smectic C* sample, the sample responds with a polarization current peak whose full width at half maximum is defined[12] as the switching or response time (τ). All our measurements have been done using a square wave pulse with a frequency of 22.5 Hz and a field strength of 30 kV/cm. Figures 7a–d show the plots of response time versus temperature for representative homologues (n = 10) for series I–IV respectively. The figures show that in all the four series τ varies in a nonlinear fashion as the temperature is

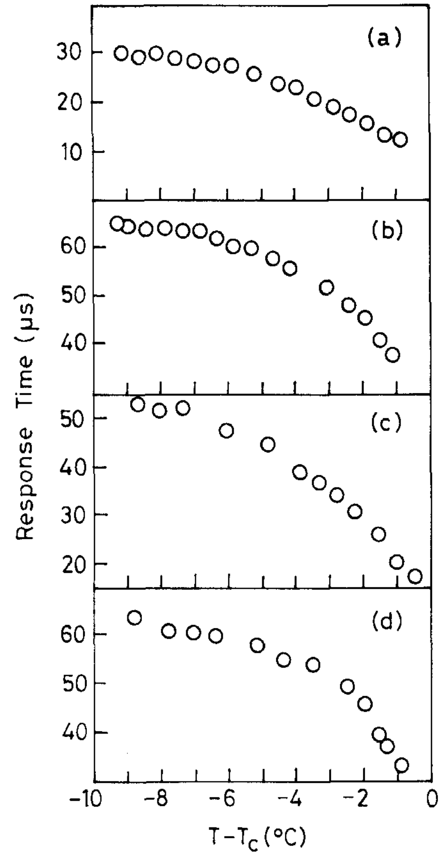


FIGURE 7 Response time as a function of temperature for $n = 10$ of (a) series I, (b) series II, (c) series III and (d) series IV.

changed. In fact, there appears to be a power law behaviour. The variation is steeper in series II and IV compared to series I and III. Comparing the values obtained at $T_c - T = 5°C$ we see that series I has the smallest value ($\simeq 25$ μs), series II and IV have almost the same value ($\simeq 60$ μs) and series III has $\tau \simeq 45$ μs. Thus, one can probably conclude that in order to reduce the switching time it is better to cluster the chiral groups together and attach them directly to the core. This also happens to be the criterion for getting higher polarization values.

We have calculated the rotational viscosities γ_n and γ_ϕ; here γ_n is the viscosity associated with the rotation of the director (**n**) about an axis normal to both **n** and **P**, and γ_ϕ that associated with the director rotation about the layer normal. The viscosities are evaluated by substituting the measured values of switching time (τ), polarization (P_s) and tilt angle (θ) in the following expression[13]:

$$\gamma_n = \gamma_\phi / \sin^2\theta$$

$$\gamma_\phi = \mathrm{P.E}/k \cos \phi$$

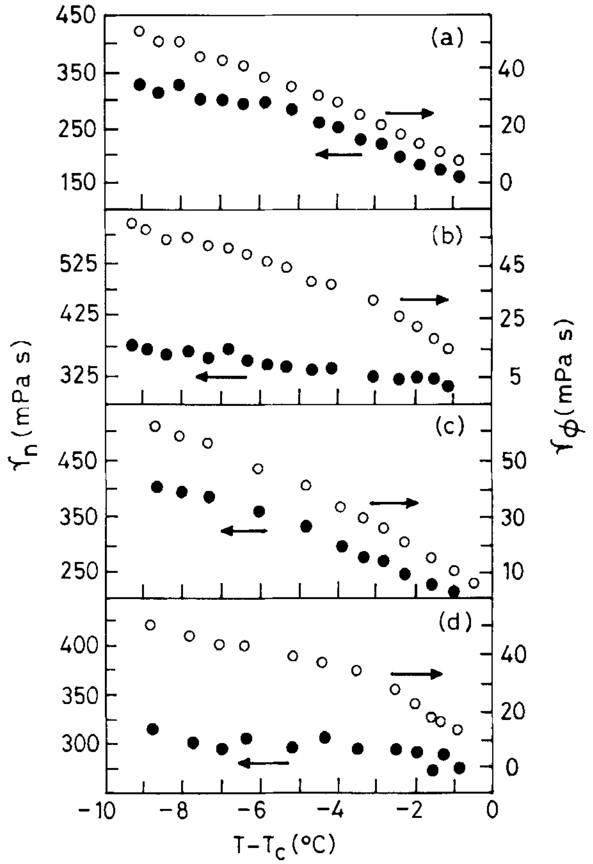


FIGURE 8 Rotational viscosities γ_n and γ_ϕ versus temperature for $n = 10$ of (a) series I, (b) series II, (c) series III and (d) series IV.

where E is the applied electric field,

ϕ is the angle between the P_s vector and the electric field direction and is given by

$$\phi = 2 \sin^{-1} [(\beta - (\beta^2 - 2\beta + 2)^{1/2})/2(\beta - 1)]$$

$$k = \frac{1.76275}{\tau}$$

$$\beta = \exp(k\tau_s)$$

τ_s is the position of polarization current peak with respect to the applied pulse in the time domain.

γ_n and γ_ϕ are plotted against reduced temperature in Figures 8a–d for the 10th homologue of each series. It is seen that in series II and IV γ_n varies slowly as the

TABLE I

P/θ and P/γ_ϕ ratios for $n = 10$ at $T_c - T = 5$°C

Series	P/θ ($\times 10^{-3}$C/m^2)	P/γ_ϕ (C/m^2 Pas)
I	2.35	.025
II	0.97	.008
III	1.7	.015
IV	0.92	.009
Lactic acid derivative[11]	8.0	.06
MHPOBC[15]	—	.04

temperature is changed; over a range of 10°C from the transition it changes by 18% and 15% respectively. But in the case of series I and III the change is appreciably higher for the same temperature range (45% and 50% respectively).

In order to do a quantitative comparison of polarization to tilt coupling and the effect of polarization on viscosity we have tabulated (Table I) the ratios P/θ and P/γ_ϕ for $n = 10$ of each series. The table shows that series I—having two chiral groups nearest to the core—has the highest value of P/θ and P/γ_ϕ. The value of $P/\gamma_\phi = 0.025$C/m^{2}Pas for $n = 10$ of series I compares favourably with two of the best values known to-date reported by Skarp *et al.*[14] and Chandani *et al.*[15] (~0.04 and ~0.06 C/m^{2}Pas respectively).

Tinh *et al.*[16] have also reported P_s values for $n = 8$ of series I and III at $(T_c - 5)$°C and $(T_c - 7)$°C respectively. Our values differ from theirs for both cases. The reason for this is not quite clear, but it must also be mentioned that the transition temperatures reported by them are also different from our values.

In conclusion, the present detailed studies have shown that the value of spontaneous polarization P_s decreases monotonically with increasing chain length. Unlike the trend reported in previous studies on homologous series of compounds, we have observed that the value of P_s as well as dP_s/dT at T_c decreases as the smectic A range diminishes. Further the studies show that the rotational viscosity is also sensitive to subtle changes in molecular structure.

Acknowledgments

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