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SPONTANEOUS POLARISATION MEASUREMENTS ON CE8 AND CE3, TWO COMMERICALLY AVAILABLE FERROELECTRIC LIQUID CRYSTALS.

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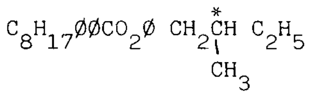
Abstract: Measurements of the spontaneous polarisation are presented on two commercially available chiral esters, both of which have a smectic 'C' phase. Experimental results for the spontaneous polarisation in chiral tilted smectic phases other than the SmC* are also included for one of the materials. It is shown that a dramatic difference exists in the ferroelectric properties of the two structurally very similar materials.

The occurrence of ferroelectricity in liquid crystals was first discovered by Meyer[1]. On the basis of the symmetry arguments all chiral tilted smectic phases are expected to be ferroelectric. In this letter we present the results of spontaneous polarisation measurements on two commercially available smectogenic materials CE8 and CE3 from BDH Ltd., Poole.

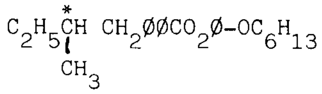
CE8 and CE3 are esters, with a central core consisting of the phenyl 4-biphenyl-4'-carboxylate moiety. Structures and phase transitions are listed overleaf.



$C_8H_{17}\text{ØØ}CO_2\text{Ø}\ CH_2\overset{*}{\underset{CH_3}{C}}H\ C_2H_5$

CE8

$$\text{Crystalline} \xrightarrow{48} \text{SmX} \xrightarrow{61} \text{SmG*} \xrightarrow{67} \text{SmI*} \xrightarrow{70.3} \text{SmC*} \xrightarrow{87} \text{SmA} \xrightarrow{135} \text{Ch} \xrightarrow{140} \text{I}$$



$C_2H_5\overset{*}{\underset{CH_3}{C}}H\ CH_2\text{ØØ}CO_2\text{Ø}\text{-}OC_6H_{13}$

CE3

$$\text{Crystalline} \xrightarrow{65} \text{SmC*} \xrightarrow{79} \text{Ch} \xrightarrow{162} \text{I}$$

The phase transitions obtained by optical microscopy and DSC, for CE8 are the same as those reported by Brand and Cladis[2].

For the purposes of this discussion we have adopted the above nomenclature; however it should be noted that Gray and Goodby[3] report this material to have the following sequence of phase transitions; I - Ch - S_A - S_{C*}- S_{I*} - S_{J*} - S_{G*}.

Both these materials derive their chirality from the presence of the optically active 2-methylbutyl unit. The position of the chiral centre with respect to the central core has been shifted from one end of the molecule to the other on going from CE8 to CE3. An alkoxy group has also been introduced at one end of the CE3 molecule and an alkyl group in CE8. Despite structural similarities, their phase transitions do differ significantly, though both have chiral SmC and cholesteric phases. The occurrence of tilted smectic phases has been discussed by Goodby et al [4] for similar materials, in terms of molecular structure and molecular dipole moments.

In the chiral smectic C phase, and any other tilted smectic phase, the spontaneous polarisation is considered to arise from orientational ordering of the transverse component of the molecular dipole. Dielectric measurements by Klingbiel et al[5] have shown that molecular dipole moments may be accurately estimated by vector addition of group dipole moments. The results of such calculations are that CE8 is predicted to have a transverse molecular dipole of 5.6×10^{-30} Cm, while the presence of an alkoxy group in CE3 is expected to increase this value to 6.9×10^{-30} Cm. Experimental results for alkoxyphenyl alkylbenzoates have shown that predicted values of the transverse molecular dipole are invariably slightly less than measured values[6].

If, as described above, the spontaneous polarisation arises from orientational ordering of the transverse component of the molecular dipole, then CE3 might be expected to have a larger Ps than CE8, or at least one of comparable magnitude. The experimental measurement of Ps and results are presented.

EXPERIMENTAL PROCEDURE

Measurement of the spontaneous polarisation is carried out by the hysteresis method on a Diamant bridge[7]. An a.c. signal is supplied by a Hewlett Packard 3312A signal generator, which is then passed through a voltage amplifier capable of delivering 300 volts peak to peak, at up to 1kHz.

Samples of the liquid crystal were placed between conducting glass plates which had been treated with rubbed polyimide to induce uniform planar alignment. 7 μm mylar was used as a spacer between electrodes, the active area of which was 2.5 cm^2. Cell and sample were placed in a Mettler FP52 hot stage which was controlled to an accuracy of ±0.1°C.

This experimental set up has enabled us to routinely observe switching and texture changes, while also making measurements of the spontaneous polarisation, and coercive field, of a number of smectogenic materials. Values for the coercive field, Ec, are variable according to measuring conditions used, namely the frequency and applied field and no detailed results for Ec are presented here.

Measurements of Ps for DOBAMBC were made and found to be in good agreement with values quoted by Hoffmann et al,[8], using a similar technique.

EXPERIMENTAL RESULTS FOR CE8 AND CE3

A uniform homogeneous alignment of CE8 was obtained by cooling the sample slowly, at -0.1°C/min, through the cholesteric/smectic A transition. Further cooling into the SmC* phase is accommpanied by the rapid appearance of pitch lines. When a slow sinusoidal field of 50V p.p is applied the pitch unwinds, and the sample clearly switches between a dark and bright state.

We were able to observe a hysteresis loop in the SmC*, SmI* and SmG* phases of CE8 at 50Hz, and 180V peak to peak. Figure 1 shows measured values for the spontaneous polarisation as a function of temperature over the three phases. Values of the Ps in the SmC* phase rise to about 3.5 nC/cm^2, at 71°C. On cooling into the SmI* phase there is a rapid increase in the value of Ps,7 nC/cm^2 at 68°C, and a corresponding increase in the coercive field.

Further cooling into the SmG* phase is accompanied by a continuing increase in the critical field, and it becomes impossible to completely switch the ferroelectric dipole at 50Hz and 180 V p.p. At 64°C the measuring conditions were altered to 30Hz and 180 V p.p. The coercive field is smaller at this frequency, and a Ps of about 8.8 nC/cm^2 is indicated. At lower temperatures measurement of Ps becomes difficult, and eventually we enter the SmX phase.

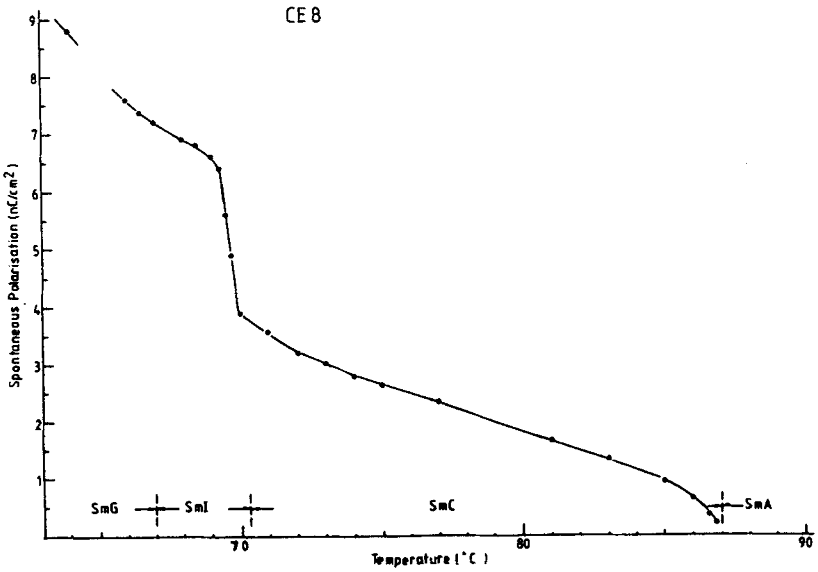


Figure 1.

Switching in the SmX phase is extremely slow and no Ps was measured. Our observation of this phase are consistent with those made by Brand and Cladis[2].

With CE3 it was not possible to obtain uniform homogeneous alignment. When observed through a polarising microscope a fine random texture is seen, made up of very small focal conic groups. No matter how slowly and carefully one cools the sample it is not possible to grow large focal conics. When a slow sinusoidal field of 180 V p.p is applied to this sample the small focal conics merely flicker. It does not appear that there is complete switching as the helical pitch is not seen to unwind, as with CE8.

Using the Diamant bridge we have been unable to measure a value of spontaneous polarisation for CE3. The material has been carefully examined a number of times and no positive identificatiuon of a measurable spontaneous polarisation can be made.

Unwinding of the helical structure in a SmC* liquid crystal by a D.C. electric field is described by the expression:

$$Ec = \frac{\pi.K.\theta}{4.Ps.z^2} \qquad [1]$$

The pitch lengths z, of CE8 and CE3 in their cholesteric phases are similar, of the order 0.3 µm. It might be expected that in comparing the SmC* phases of these two materials they would have pitch lengths of similar magnitude, however this was not the case.

Chiral mesogens with a SmC* to cholesteric transition tend to have a short pitch, and high tilt angle SmC* phase[9] , and indeed CE3 is observed to selectively reflect light in the visible. Therefore CE3 must have a pitch length in the SmC* phase of around 0.3 µm. CE8 is observed to have a pitch length of 3 µm (obtained by microscope observation of pitch lines).

The helical structure of CE8 in the SmC* phase is observed to unwind with a d.c. field of around 5 volts, whereas CE3 required around 150 volts. Using equation 1 to compare these two materials, and assuming a simple proportionality between Ec and $1/z^2$, a pitch length of about 0.5 µm for CE3 might be expected . This is consistent with the observed selective reflection of light in the visible spectrum, and suggests that CE3 has a ferroelectric dipole of similar magnitude to that in CE8.

CONCLUSION

Although it was not possible to directly measure a value for the spontaneous polarisation in CE3, other, less direct, observations indicate that it probably does have a ferroelectric dipole of comparable size to that of CE8. The short pitch length of CE3 in the SmC* phase increases the required unwinding field by such a large amount that no value of Ps is measurable using the routine experimental procedure outlined in this paper.

Work is in progress to characterise the value of spontaneous polarisation for CE8 and CE3 in mixtures, and preliminary results are also consistent with CE3 having a comparable Ps to CE8.

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