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FERROELECTRIC LIQUID CRYSTALS: SOME NEW RESULTS ON A COMPOUND WITH HIGH SPONTANEOUS POLARIZATION*)

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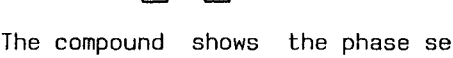
Abstract Recent results concerning the behaviour of the SmC*-SmA transition in electric fields and the dielectric properties of the ferroelectric liquid crystal 4-(3-methyl-2-chlorobutanoyloxy)-4'-heptyloxybiphenyl are summarized.

Last year new ferroelectric liquid crystals were found showing very high values of the spontaneous polarization up to 300 nC/cm², i.e. exceeding the values of DOBAMBC and most other compounds by two orders of magnitude /1, 2/. In this paper some results on one compound of this class of ferroelectric liquid crystals are reported comprehensively. The compound under investigation is 4-(3-methyl-2-chlorobutanoyloxy)-4'-heptyloxybiphenyl with its structural formula given below:



The compound shows the phase sequence I 81.6°C SmA 73.4°C SmC* 71°C SmG 64°C SmH. The spontaneous polarization in the SmC*-phase is in the range from 150 nC/cm² at the SmG-SmC* transition to 80 nC/cm² 0.1 K below the transition to the SmA-phase. The spontaneous polarization decreases discontinuously to zero at the SmC*-SmA transition. This as well as DSC studies and X-ray measurements of the layer spacing indicates that the SmC*-SmA transition of this compound is of first order.

*) Paper presented at the 5. European Winter Conference on Liquid Crystals, Borovets, Bulgaria, 1987.

The SmC*-SmA transition was found to shift to higher temperatures by the application of an external dc electric field analogous to the behaviour of solid ferroelectrics. For these materials the shift of the Curie point by an electric field is a well known phenomenon in the case of a first order ferroelectric-paraelectric transition /3/. The induction of the ferroelectric SmC*-phase by the application of an electric field is demonstrated by the recording of double hysteresis loops at temperatures above the SmC*-SmA transition. The electric field dependence of the SmC*-SmA transition temperature, which can easily be detected by observing the texture change corresponding to the transition while a constant dc field is applied, is shown in figure 1:

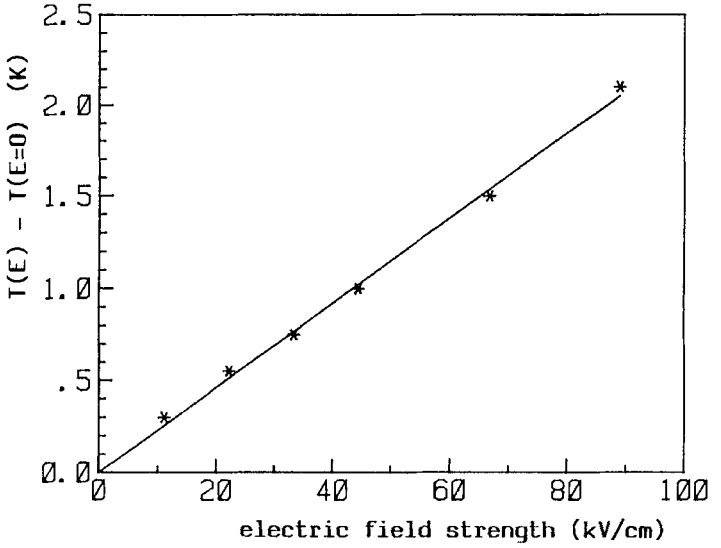


FIGURE 1: Shift of the SmC*-SmA transition temperature versus electric field strength as detected optically with a polarization microscope. The texture change, which is very sharp at zero field and low field strength, becomes continuous at higher field strength indicating that the transition, which is characterized by a jump of the tilt angle at zero and low field, becomes continuous at high field.

Analogous to solid ferroelectrics a linear relation is established which can be described by a Clausius-Clapeyron type of equation /3/

$$\frac{T(E) - T(E=0)}{E} = \frac{\Delta P}{\Delta S}$$

where ΔP and ΔS are the discontinuity of the spontaneous polarization and the entropy change at the SmC*-SmA transition (for the compound under investigation one gets the following values from polarization and DSC-measurements: $\Delta P \approx 80$ nC/cm^2 and $\Delta S \approx 0.0035$ J/gK). The calculated value of $(T(E)-T(E=0))/E$ is in good agreement with the experimental observed (figure 1) temperature shift.

The compound under investigation shows a diverging dielectric constant $\varepsilon_\perp$ in the SmA-phase, the values increasing from 6 at the SmA-I clearing point to about 50 near the transition to the SmC*-phase. The corresponding racemate exhibits a nearly constant value of $\varepsilon_\perp$ in the SmA-phase (figure 2).

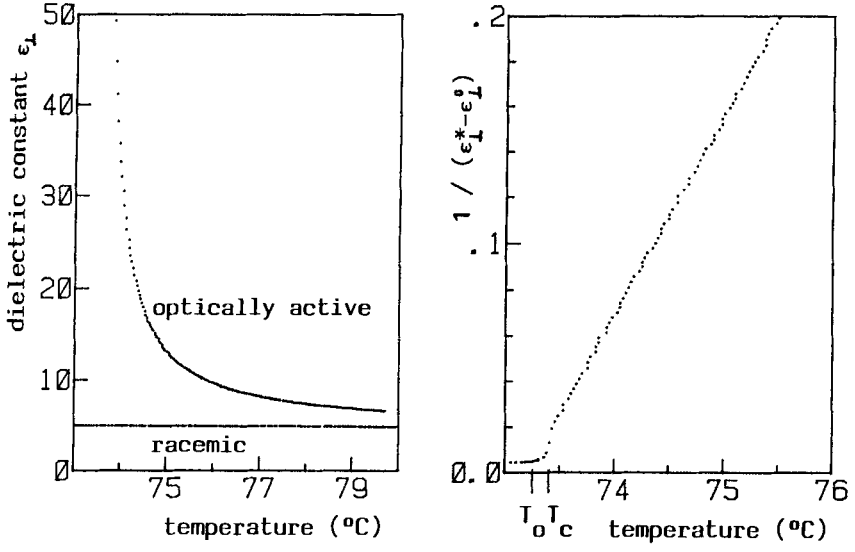


FIGURE 2: a) Temperature dependence of $\varepsilon_\perp$ in the SmA-phase. b) Plot of $1/(\varepsilon_\perp^*-\varepsilon_\perp^0)$ versus temperature.

The inverse of the difference $\varepsilon_\perp^*$(optically active) - $\varepsilon_\perp^0$(racemic) shows a linear dependence on temperature. It should be noted that extrapolating $1/(\varepsilon_\perp^* - \varepsilon_\perp^0)$ to zero gives a temperature To which lies sligthly below the first order transition temperature Tc (figure 2).

A 50% optically active mixture exhibits a value of $\varepsilon_\perp^* - \varepsilon_\perp^0$, which amounts to only 25% of that of the pure optically active enantiomer. Assuming that the tilt-polarization coupling constant varies linearly with chirality (the 50% optically active mixture exhibits 50% of the spontaneous polarization of the pure optically active compound), this indicates a quadratic relation between the dielectric constant and the coupling constant. The dependences of $(\varepsilon_\perp^* - \varepsilon_\perp^0)$ on temperature and chirality are in agreement with corresponding Landau descriptions of the SmC*-SmA transition /4/.

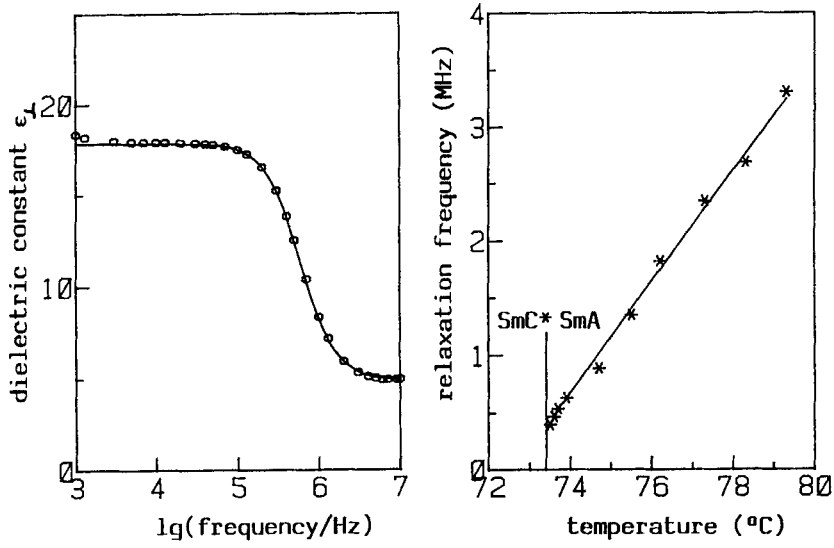


FIGURE 3: a) Plot of $\varepsilon_\perp$ versus frequency. The solid line is calculated according to the relation

$$\varepsilon = \varepsilon(hf) + \frac{\varepsilon(lf) - \varepsilon(hf)}{1 + (f/f_r)^2}$$

b)Temperature dependence of the relaxation frequency.

The frequency dependence of $\varepsilon_\perp$ in the SmA-phase obeys a simple Debye-law, at high frequencies the value of the racemate is approached. The relaxation frequency varies linearly with temperature confirming the theoretically predicted /4c, 4d, 4f/ soft mode behaviour (figure 3).

Details of the results reported will be published in forthcoming papers /5, 6/.

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