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PRELIMINARY COMMUNICATION

Piezoelectric effect in smectic C* and smectic F*

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The piezoelectric response in chiral smectic C* and smectic F* phases of a binary mixture of *N*-(4-*n*-heptyloxybenzylidene)4'-*n*-hexylaniline (7O.6) chiralized by 4-*n*-heptyloxy-4'-hydroxybiphenyl α -chlorocarboxylic acid ester (A7) has been observed by the method of Blinov *et al.*

The investigation of the piezoelectric effect in chiral ferroelectric phases is possible by the measurement of the electric charge resulting from the distortion of the helix of the ferroelectric liquid crystal produced by shear flow. In the method of Blinov *et al.* [1], this flow is induced by oscillating air pressure applied to a liquid crystal drop in contact with two electrodes [1, 2]. In the original experimental geometry [1, 2] two in-plane electrodes were used while in the present study the drop was sandwiched between two tin oxide electrodes. Recently, in the same sandwich geometry the first observation of ferroelectricity in a lyotropic phase was realized [3].

The synthesis of 7O.6 has been described elsewhere [4] and A7 was a gift from G. Heppke [5]; they have the phase sequences:

7O.6: C 39°C S_G 55°C S_F 66°C S_C 68.5°C S_A 80°C I,

A7: C 72°C (S₇ 71°C) S_C* 73.5°C S_A 81.5°C I.

Both the pure substances and a mixture of 4 wt % of A7 in 7O.6 were investigated. The sample cells were placed in a heating stage on a polarizing microscope (Meopta) and the temperature dependence of the transmitted light intensity, between crossed nicols, was recorded in order to detect the transition temperatures following the method of Petrov *et al.* [6]. Air pressure was supplied by a loudspeaker excited by a function generator. The pressure at the end of the pipeline was measured by a calibrated piezoceramic transducer. The piezoelectric signal from the ferroelectric liquid crystal layer was detected by a lock-in amplifier (Unipan 232B) with a 10 dB preamplifier (input resistance 100 M Ω) and recorded on a XY recorder (Endim). The temperature was recorded along the X axis by an analogue signal from a digital thermometer. In the present study unoriented samples were employed but the piezo-

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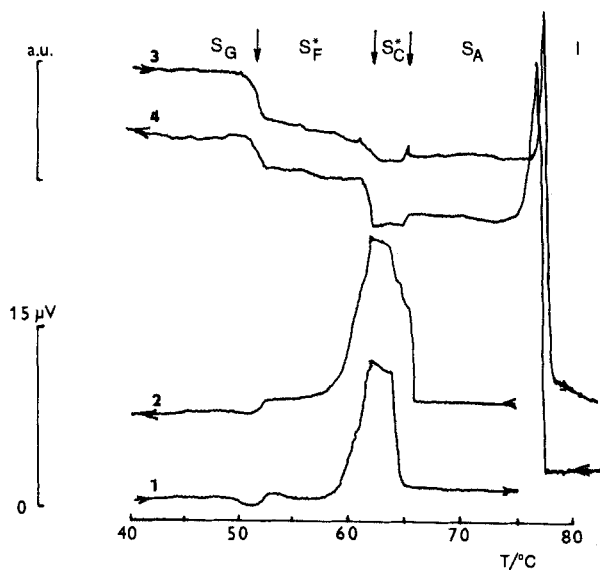


Figure 1. Piezoelectric response and transmitted light intensity of a liquid crystal mixture of 96 wt % 7O.6 and 4 wt % A7 as a function of temperature. Steps in the light intensity trace indicate the transitions (arrows). The layer thickness is $115\ \mu\text{m}$; the electrode area is $50\ \text{mm}^2$; the sound frequency is $110\ \text{Hz}$ giving a pressure maximum at the output of the pipeline and the sound pressure is $2.5\ \text{Pa}$. Trace 1: piezoelectric response in the heating mode; trace 2: piezoelectric response in the cooling mode; trace 3: transmitted light intensity in the heating mode; trace 4: transmitted light intensity in the cooling mode.

electric effect was still observable due to the incomplete averaging of the spontaneous polarization. Both heating and cooling runs were recorded.

Figure 1 shows the records of the piezoelectric signal and transmitted light intensity of a $115\ \mu\text{m}$ thick layer of the mixture of A7 in 7O.6. The transition temperatures of 7O.6 were slightly shifted in the mixture due to the presence of the small percentage of A7. But because of its high spontaneous polarization and chirality the compound A7 is likely to induce a helicoidal arrangement in the tilted smectic phases of 7O.6 making them ferroelectric. The smectic A phase being non-helicoidal did not produce any piezoelectric effect. The often observed electrokinetic effect in the S_A phase (due to its lower viscosity) was minimized by repetitive heating and cooling runs without entering the crystal state. In the S_C^* phase the signal increased with decreasing temperature in accord with the increase of tilt angle typical for $nO.m$ compounds [7, 8]. At the transition to the S_F^* phase there is a break in the curve followed by a marked decrease of the signal due to the higher viscosity of the smectic F^* phase. Still the signal was measurable down to the $S_F^*-S_C^*$ transition.

Measurements on pure A7 were made with cells of a much lower thickness of $15\ \mu\text{m}$ because of the smaller amount of substance. Phase transitions were better resolved in cooling runs (see figure 2). In the heating runs the width of the S_C^* was smaller in agreement with the published transition temperatures [5] and the piezoelectric response was about two times lower (not shown). However, the correspondence between heating and cooling was good only if the cooling was stopped before 64°C where a transition to the crystal state occurs (see figure 2). By heating the sample from the solid state different transition temperatures of 74°C and

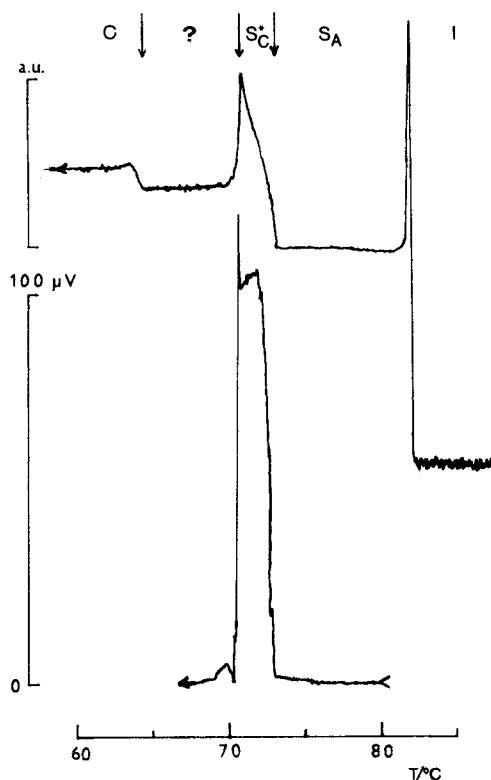


Figure 2. Piezoelectric response and transmitted light intensity of the reference compound A7 as a function of temperature in the cooling mode. The arrows indicate the transitions. The layer thickness is $15\ \mu\text{m}$; the electrode area is $40\ \text{mm}^2$; the sound frequency is $110\ \text{Hz}$ and the sound pressure is $2.5\ \text{Pa}$. Upper trace: transmitted light intensity; lower trace: piezoelectric response. Accounting for the lower thickness of the present sample, this response is much higher than that of the mixture (see figure 1). Note the weaker signal in the S_1 phase demonstrating that it is probably ferroelectric as well.

75.5°C were found with different types of response. This problem deserves further attention.

7O.6 being non-chiral did not display any piezoeffect, showing eventually the electrokinetic effect only. To our knowledge this is the first observation of the piezoeffect in a smectic F^* .

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