Electro-Optical Properties of Ferroelectric Liquid Crystals with a Sulfinate Group as Unique Source of Chirality

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Electro-Optical Properties of Ferroelectric Liquid Crystals with a Sulfinate Group as Unique Source of Chirality

Mohammed Zoubair Cherkaoui, Jean-François Nicoud, Yves Galerne and Daniel Guillon

Institut de Physique et de Chimie des Matériaux de Strasbourg Groupe des Matériaux Organiques 23, rue du Loess B P 20CR 67037 Strasbourg Cedex, France.

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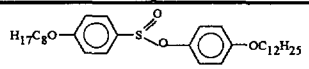
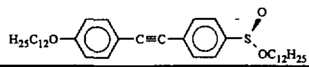
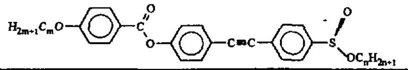
Résumé. — Dans cette communication, nous rapportons les premières mesures électro-optiques sur des cristaux liquides ferroélectriques obtenus à partir de molécules contenant un groupe sulfinate comme centre unique de chiralité Sont présentés la polarisation spontanée, le temps de réponse au champ électrique appliqué et l'angle d'inclinaison des molécules en fonction de la température pour deux molécules typiques de la série homologue. Il est aussi mis en évidence un fort effet électroclinique dans la phase smectique A.

Abstract. — In this communication, we present the first electro-optical measurements performed on ferroelectric liquid crystals materials based on molecules containing a sulfinate group as the unique chiral source Spontaneous polarization, response time to the applied electric field and tilt angle of the molecules as a function of temperature are reported for two representative molecules of the whole series It is also shown the existence of a significant electroclinic effect in the smectic A phase.

Ferroelectric liquid crystals [1] (FLC) are of great interest because of their possible high-technology applications: light valves [2], displays [3], spatial light modulators [4] and pyroelectric detectors [5]. Many requirements for the chiral smectic C* (S_{C^*}) materials to be applicable into electro-optical devices (i.e., chemical stability, a wide S_{C^*} temperature range around room temperature .) have driven and developed the research in the FLC domain; among these requirements, a large spontaneous polarization (P_s) which generally leads to a short response time (τ) is still considered of a fundamental interest [6].

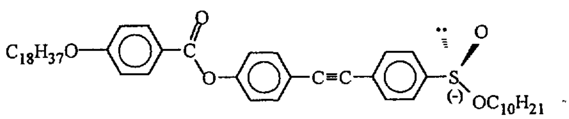
Based on a molecular modeling study, we have shown that a chiral sulfinate group directly attached to the rigid core of the molecule should lead to materials with high P_s [7]. This newly investigated heteroatomic chiral source in liquid crystalline compounds presents a highly polarized S=O bond that should induce a large dipole moment component, transverse to the molecular tilt plane [7]. More recently, we have reported the synthesis and the mesomorphic behavior of new molecules with a sulfinate group as the unique chiral source [8] (see Table I).

Table I. — *Structural formula of the sulfinate compounds investigated for their mesogenic properties; for the series (3), BTS stands for benzenecarbonyloxytolane-sulfinyl; m and n for the number of carbon atoms in the alkyl chains.*

Compound	
	*1*
	*2*
	*3 = m-BTS-On*

Among the series (1), (2) and (3) of Table I, only the compounds of the m-BTS-On series were proved to exhibit smectic A and C* phases in a temperature range between 80 and 120 °C about. Moreover, the study of the thermotropic properties upon varying the nature of the sulfinyl group demonstrated that sulfinates possess a better thermal, as well as a better optical stability than their sulfoxide and sulfinamide homologs. In fact, no degradation, neither thermal racemization were detected, even when these compounds were heated for few hours in the isotropic state (invariance of the transition temperatures and of the specific optical rotation). Thanks to this good stability, the sulfinate compounds have been investigated for their electro-optical properties.

In this communication, we present the first electro-optical measurements performed on the chiral mesogenic sulfinate 18-BTS-O10 (Scheme 1) alone, as an illustration of the general behavior of the series m-BTS-On. (Previous P_s measurements on chiral sulfinyl derivatives have been performed only on mixtures of sulfoxide and host smectic C compounds) [9].



18-BTS-O10 ***ee = 85%***

$K \xrightarrow{95\ 7°C} S_C^* \xleftrightarrow{106\ 4°C} S_A \xleftrightarrow{108\ 1°C} I$

Scheme 1

By applying an electric field of 5 V/μm perpendicular to the plates of a SSFLC cell, filled with 18-BTS-O10 compound, a short response time, τ, of a few μs is measured (Fig. 1), that does not exceed a value of 45 ms near the K-S_{C^*} phase transition. In the same time, the spontaneous polarization, P_s, (represented as a function of temperature in Fig. 2) and the tilt angle, θ, can reach values higher than 90 nC/cm^2 and 30° respectively, far from the S_{C^*}-S_A transition temperature (T_{AC^*}). These results are in agreement with those expected from our molecular modeling studies, and confirm the validity of the choice of the sulfinate group as being an efficient source for providing ferroelectric liquid crystals with high P_s.

In the smectic A phase just above the T_{AC^*} temperature (see Fig. 3), a non zero tilt angle, θ, of the molecules is observed under electric field in the electro-optical cell, indicating the occurrence of an electroclinic effect. This effect is clearly observed when varying the applied

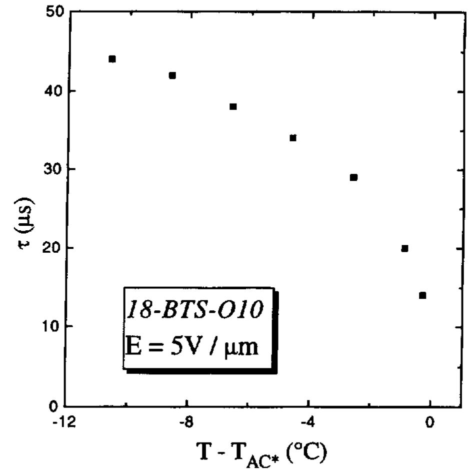
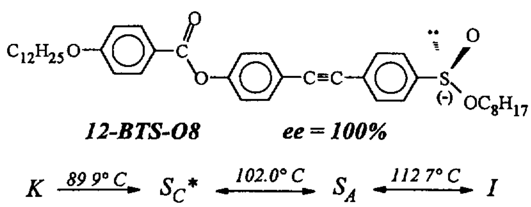


Fig. 1 — Time response as a function of the distance to the T_{AC^*} transition temperature.

electric field at a given temperature; for example, the induced tilt angle varies linearly with the increasing field, and can reach values close to 15° for an applied electric field of 13.5 V/μm at $T = 107$ °C (Fig. 4).

We have to point out that the measured electro-optical properties presented above correspond to a compound having an enantiomeric purity of about 85%. When increasing the enantiomeric purity of the sulfinate, a pronounced increase of the spontaneous polarization is observed. We have investigated precisely the influence of the optical purity on another compound of the m-BTS-On series, namely 12-BTS-O8, the thermotropic behavior of which is shown in Scheme 2:



Scheme 2

We have been able to obtain by asymmetric synthesis both optically pure (R)−(+)− and (S)−(−)−12−BTS−O8 enantiomers [10]. The spontaneous polarization measured with the optically pure enantiomer can reach values of about 270 nC/cm^2 near the K-S_{C^*} transition temperature. By studying different mixtures of both enantiomers, we have found a non-linear relationship between the spontaneous polarization and the enantiomeric purity. In addition, the tilt angle, θ, and the ratio P_s/θ were also found not linearly dependent upon the enantiomeric purity These first observations of the electro-optical properties of the 18-BTS-O10 compound have then been confirmed when studying the whole m-BTS-On series systematically. The following specific features can be deduced: a non-linear coupling between the spontaneous polarization and the tilt angle as a function of temperature, a constant value of the spontaneous polarization whatever the alkyl chain length m, and a considerable increase of θ and τ when

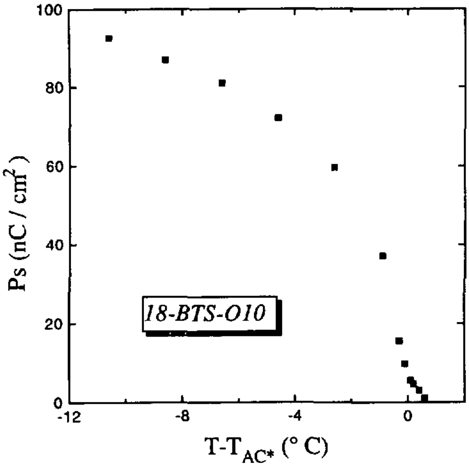


Fig. 2. — Spontaneous polarization in the smectic C* phase as a function of the distance to the T_{AC^*} transition temperature.

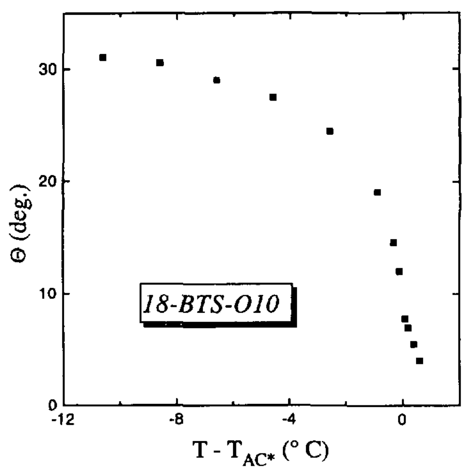


Fig. 3 — Tilt angle of the molecules in the smectic C* phase phase as a function of the distance to the T_{AC^*} transition temperature.

increasing alkyl chain length m, in both cases for a given n (10 and 12). Details of these results will be published in a forthcoming full paper.

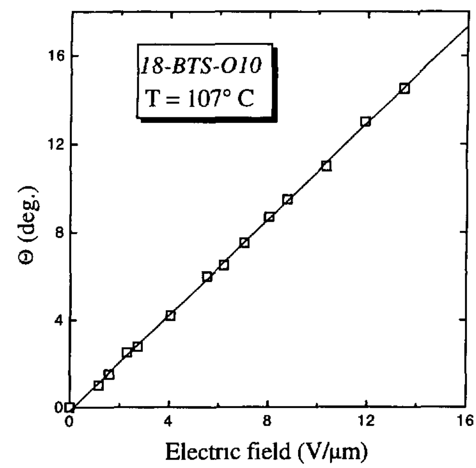


Fig 4 — Induced tilt angle in the smectic A phase at 107 °C phase as a function of the distance to the T_{AC^*} transition temperature

Experimental

The synthesis of the ferroelectric liquid crystals has been reported elsewhere [8]. The spontaneous polarization, tilt angle and optical response time measurements were carried out on a cell consisting of two polytetrafluoroethylene (teflon)-coated ITO- conducting glass plates. The cell thickness was determined by capacity measurements. The liquid crystalline compound was then introduced into the cell by capillarity in its isotropic state. A good orientation (bookshelf geometry) was achieved by slowly cooling from the isotropic state to the S_{C^*} phase without applied electric field. The spontaneous polarization measurements were performed on a calibrated standard bench by applying a triangular voltage across the cell with a wave frequency of 500 Hz. The ferroelectric signal (current *versus* time) was recorded on a HP 54501A oscilloscope. Knowing the active area of the cell, the values of P_s were obtained through the integration of the characteristic peak.

On the above well aligned samples, the tilt angle measurements as a function of temperature were carried out, under a microscope with crossed polarizers, by application of about 0.1 Hz frequency wave rectangular voltage. The tilt angle is equal to half the angle between the two extreme optical states corresponding to the two polarities of the applied electric field. Simultaneously to the spontaneous polarization, the electro-optical response times, τ, were measured; they correspond to the time delay of the ferroelectric peaks referred to the electric field when applied in the rectangular shape

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