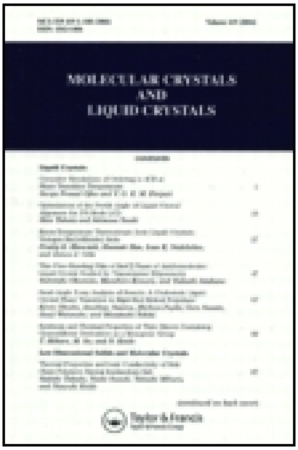

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# New Series of Ferroelectric Liquid Crystals Incorporating Stilbene Unit in the Core

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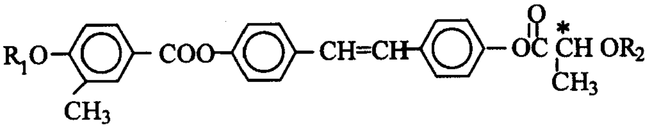
New liquid crystalline materials of the general formula



have been synthesized ($R_1$, $R_2$ are alkyl chains). Mesomorphic properties were determined using polarizing microscopy. All compounds showed very broad smectic C* phase (about 70 – 90 K) and the cholesteric phase. No smectic A phase was observed. In the smectic C* phase the spontaneous polarization is very high, reaching values higher than 300 nC/cm$^2$ at the low temperature limit of this phase for compounds with two chiral centres. The permitivity was measured showing a contribution of the Goldstone mode in the smectic C* phase.

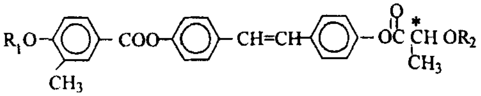
*Keywords:* ferrorelectric liquid crystal; stilbene unit; high spontaneous polarization

## INTRODUCTION

In the previous paper[1] we have described synthesis and physical properties of an FLC series containing a lateral methyl group on the aromatic ring of the alkoxybenzoate unit in the mesogen. The introduction of the lateral methyl group into the molecule caused a strong decrease of all phase transition temperatures in comparison with the non-substituted material. As a result the SmC* phase range was shifted by approximately 40 K to lower temperatures but broadening of the SmC* phase range was not observed. The values of the spontaneous polarization increased moderately due to this substitution.

We have also found that in contrast to the previous case the introduction of an unsaturated bond into the molecule ( in a case of alkylcinnamates[2] ) leads to higher phase transition temperatures for SmC*→ N* and SmC*→ SmA transitions by several tens of degrees. Values of the spontaneous polarization decreased by the introduction of the double bond.

In this study we tried to combine both effects in order to obtain a broadening of the SmC* phase interval without decreasing the spontaneous polarization. We have synthesized a series of compounds containing both a 3-methyl-4-alkoxybenzoate group and a double bond in the 4,4'-dihydroxystilbene unit of the mesogenic part of the molecule. The general formula of these compounds is



1

denoted KrS m/n when $R_1$ and $R_2$ are n-alkyls and KrS m/** when $R_1$ is n-alkyl and $R_2$ is (S)-2-methylbutyl.

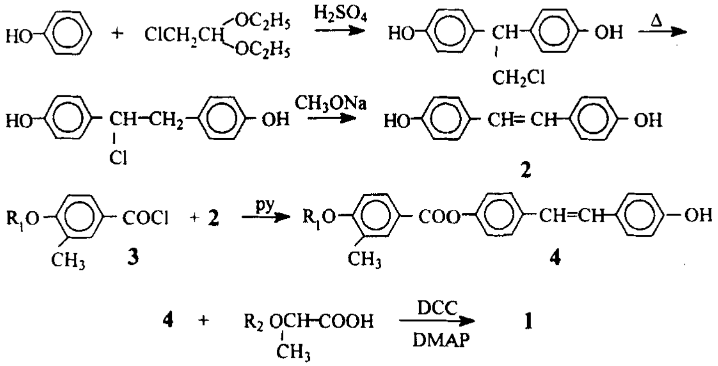
2-Alkoxypropionate group has been used as a chiral part of molecule in all compounds like in our previous works[1,2,3,4].

## SYNTHESIS

The synthesis was carried out as outlined in Scheme 1.

Trans-4,4′-dihydroxystilbene (2) was synthesized in a simple way with excellent yield by condenzation of chloroacetaldehyde diethyl acetal with phenol, and rearrangement of the condenzation product at higher temperature and following dehydrohalogenation.[5] The product, obtained after recrystallization, contained only the trans isomer (confirmed by NMR).

The 4-alkoxy-3-methylbenzoylchlorides (3) were prepared by Grignard synthesis from o-cresyl ethers[1]. The reaction of these compounds with (2) in pyridine yielded mesogenic phenols (4). The o-alkyllactic acids were prepared using the method described by Stevens[6] from ethyl-(S)-(-)-lactate by alkylation with n-alkyliodide, or (S)-2-methylbutyliodide. Esterification of this acids with the appropriate mesogenic phenol (4) in the presence of dicyclohexylcarbodiimide and dimethylaminopyridine in chloroform yielded the crude products (1).



SCHEME 1

The final compounds were isolated from the crude products by column chromatography on silica gel (Kieselgel 60, Merck, Darmstadt) using a mixture of dichloromethane and ethylalcohol (99:1) as the mobile phase. The products were recrystallized at least twice from ethanol. For all compounds the structure was confirmed by $^1$H NMR spectroscopy using a 300 MHz Varian spectrometer. Their purity was checked by high performance liquid chromatography, which was carried out with an Ecom HPLC chromatograph using a silica gel column (Biospher Si 100, 5 μm, 4 x 250, Watrex) and a mixture of 99.9 % toluene and 0.1 % methanol as the eluent, eluting products beeing detected at 290 nm.

## EXPERIMENTAL RESULTS

The sequences of phases have been determined from texture observations using polarizing microscopy. The data is collected in Table I.

TABLE I Phase sequences and phase transition temperatures $T_t$ (°C) for the homologous series KrS n/** and KrS n/m.

| KrS n/m | Cr. | $T_t$ | SmC* | $T_t$ | N* | $T_t$ | Iso |
|---|---|---|---|---|---|---|---|
| **KrS 6/**** | • | 41 | • | 119 | • | 155 | • |
| **KrS 8/**** | • | 38 | • | 121 | • | 145 | • |
| **KrS 6/10** | • | 39 | • | 120 | • | 141 | • |
| **KrS 8/7** | • | 44 | • | 130 | • | 148 | • |
| **KrS 8/10** | • | 41 | • | 127 | • | 138 | • |
| **KrS 8/12** | • | 38 | • | 121 | • | 129 | • |
| **KrS 10/7** | • | 46 | • | 132 | • | 142 | • |

All measurements were done on planar samples (smectic layers perpendicular to the sample plane) 25 μm thick. The compounds exhibit a very broad range of the ferroelectric SmC* phase and the cholesteric phase. All phase transitions observed are of the first order, characterized by a phase coexistence region. In the ferroelectric SmC* phases, the temperature dependence of the spontaneous polarization, $P_s$, and the spontaneous tilt angle, $\theta_s$, have been determined. The values of $P_s$ have been evaluated from the *P(E)* hysteresis loop detected during $P_s$ switching in an a.c. electric field $E$ of frequency 60 Hz. Due to the region of the phase coexistence at the N*-SmC* phase transition, the measurements of the spontaneous polarization could start at the temperature a few degrees below the first appearance of the SmC* phase on cooling. Both series exhibit very high values of the spontaneous polarization, which are significantly higher with the series KrS n/** with two chiral centers (see Fig. 1). For all compounds $P_s$ slightly increases on cooling tending to a saturation at low temperatures.

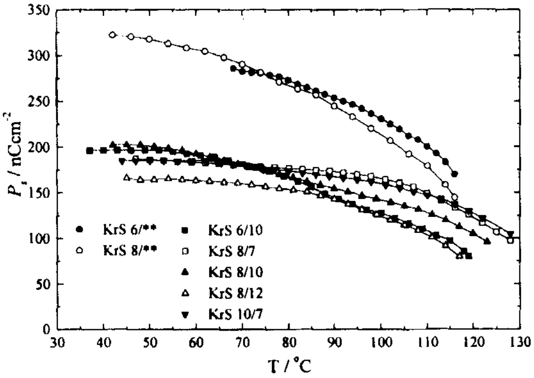


FIGURE 1 Temperature dependence of the spontaneous polarization for indicated KrS n/** and KrS n/m homologues.

The values of $\theta_s$ have been determined optically from the difference between extinction position at crossed polarizers under opposite d.c. electric fields ± 40 kV/cm. Tilt angle of molecules from the smectic layer normal has been found temperature independent and its values is about $40^0$ for all compounds.

The temperature dependence of the helical pitch has been established by the diffraction of the He-Ne laser light (630 nm) on disclination lines in planar cells. The line spacing equals the pitch length.[7] The temperature dependences of the helical pitch in the SmC* phase are shown in Fig. 2 for all compounds. For KrS n/** with two chiral centers the pitch is longer and significantly decreases with decreasing temperature. For KrS n/m the temperature dependence of the pitch length is weak. The pitch could not be measured in the whole temperature range of the SmC* phase, because at lower temperatures it becomes spontaneously unwound.

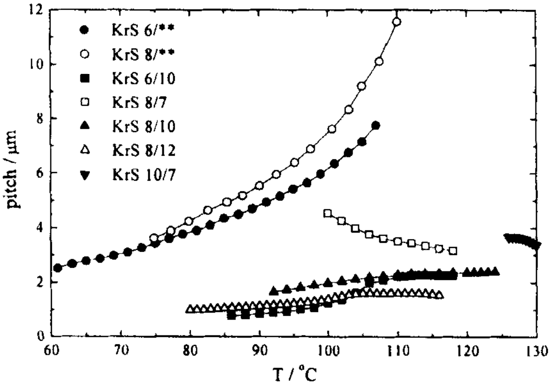


FIGURE 2 Temperature dependence of the helix pitch length in the smectic C* phase for indicated KrS n/** and KrS n/m homologues.

Temperature dependences of the real part of permittivity at a frequency of 40 Hz have been obtained for all studied compounds. There is a great increase in permitttivity on cooling from the cholesteric to the SmC* phase due to the contribution of the Goldstone mode (see Figs. 3 and 4).

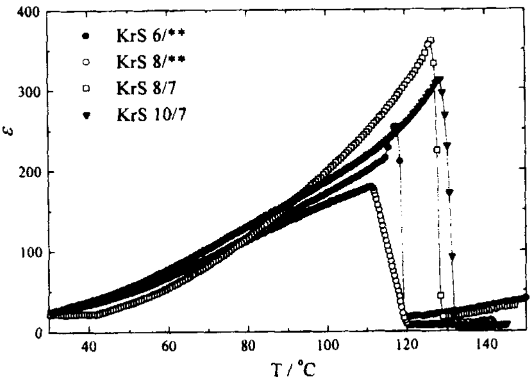


FIGURE 3 Temperature dependences of the real part of the permittivity for indicated KrS n/** and KrS n/m homologues in cooling runs at a frequency of 40 Hz.

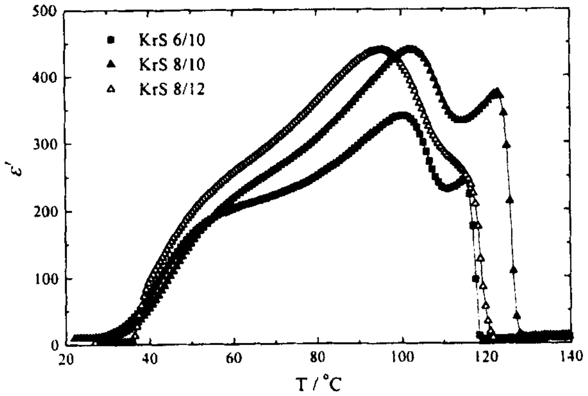


FIGURE 4 Temperature dependences of the real part of the permittivity for indicated KrS n/m homologues in cooling runs at a frequency of 40 Hz.

Two types of temperature dependence are observed in the SmC* phase. For homologues with a short chiral chain a continuous decrease of permittivity is observed on cooling, for homologues with a longer chiral chain the temperature dependence is more complicated with a maximum in the SmC* phase. The reason for this difference is not understood.

## CONCLUSIONS

The new series of liquid crystals reported here exhibit only the cholesteric and very broad ferroelectric SmC* mesophases. The spontaneous polarization in the SmC* phase reaches the values of 200 or 300 nC/cm$^2$ for materials with one or two chiral centres, respectively. These compounds can be very useful as ferroelectric dopants in mixtures for display applications.

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