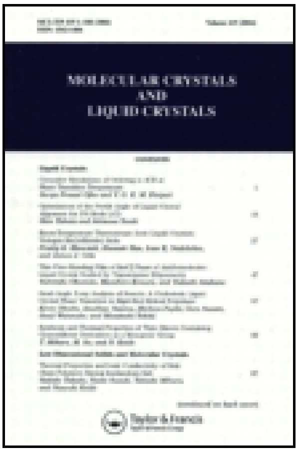

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FERROELECTRIC LIQUID CRYSTALS CONTAINING THE CYANO GROUP

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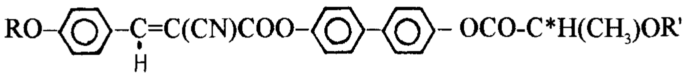
Abstract A new series of ferroelectric liquid crystals having the cyano group in the mesogenic core and with the terminal group based on O-substitued S-(-)-lactic acid has been synthetized and characterized. The compounds exhibit a broad ferroelectric chiral smectic C mesophase with a high spontaneous polarization.

INTRODUCTION

Chiral liquid crystals posessing a broad ferroelectric smectic C mesophase and a high spontaneous polarization are required as very perspective materials for constructing a new type of fast bistable electrooptical devices. It has been described previously[1] that the terminal chiral group based on the O-alkyllactate ensures the high spontaneous polarization in ferroelectric liquid crystals (FLC).

In search of new materials we have synthetized a series of FLC containing the cyano functional group in the mesogenic core and with the terminal group based on the O-substitued S-(-)-lactic acid. A common formula of the series of chiral liquid crystals presented in this contribution is



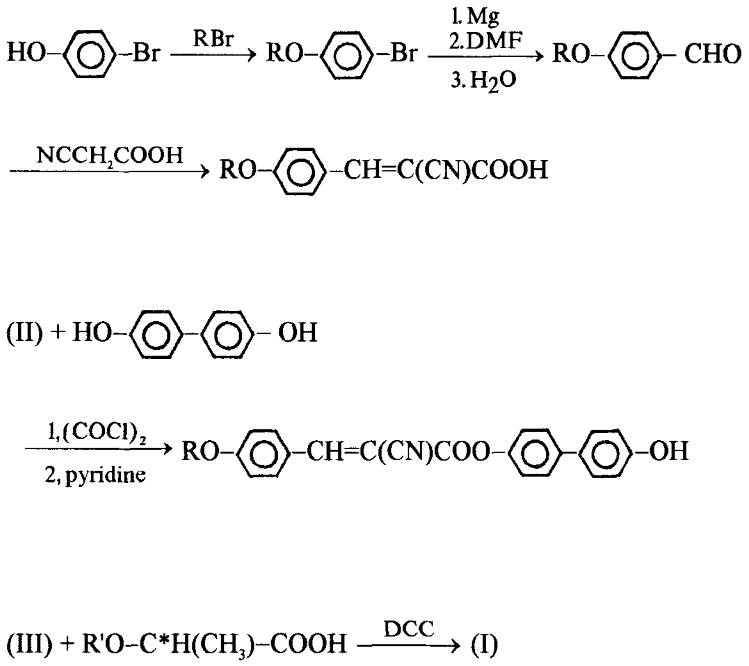
$$RO-C_6H_4-\underset{H}{C}=C(CN)COO-C_6H_4-C_6H_4-OCO-C^*H(CH_3)OR' \qquad (I)$$

where $R = C_nH_{2n+1}$, $n = 6,7,8,9,10,12$; $R' = C_mH_{2m+1}$, $m = 5,7,8,9,10$.

With new substances sequences of mesophases were determined. In the ferroelectric SmC* phases basic characteristics, the spontaneous polarization, P_S, and the spontaneous tilt angle, Θ_S, of molecules from the smectic layer normal, were measured.

SYNTHESIS

The preparations were achieved according to the following scheme



(II)

(III)

The 4-alkyloxybenzylidencyanoacetic acids (see II) were prepared by organomagnesium synthesis from corresponding 4-bromophenylalkylethers and N, N-dimethylformamide (DMF). Subsequent hydrolysis gives the 4-alkyloxylbenzaldehydes. Afterwards these compounds were condensed with cyanoacetic acid by using the Cope method.[2]

The mesogenic phenols (III) were prepared by conventional acylation of 4, 4'-dihydroxybiphenyl with acyl chlorides (II).

2-alkoxypropionic acids were prepared by alkylation of (S)-(-)-ethyl lactate with the appropriate n-alkyliodide in the presence of Ag_2O.[3]

Further reactions were carried out using standard procedures with dicyclohexylcarbodiimide (DCC) as a condensation agent. The resulting materials were purified by column chromatography on silica gel using chloroform-acetonitrile mixture as a mobile phase and by subsequent repeated crystallization from methanol.

RESULTS AND DISCUSSION

The sequence of mesomorphic phases and phase transition temperatures have been determined from characteristic textures and their changes observed in a polarizing microscope. In the ferroelectric SmC* phase the spontaneous values of P_S and Θ_S were measured. The values of P_S were determined from *P(E)* dependences in the form of hysteresis loop detected during P_S switching in the a.c. electric field 40 kV/cm of the frequency 60 Hz. The values of Θ_S were determined optically, from the difference between extinction positions of the planar sample between crossed polarizers under opposite d.c. fields ± 40 kV/cm.

The phases and phase transition temperatures are shown in Table 1 for compounds distinguished by number of carbons in therminal chains *n* and *m* (see I). The observed phase transitions are of the first order. All studied compounds exhibit a broad ferroelectric SmC* phase and a low temperature smectic phase denoted as SmN. In this phase no switching has been observed and also the dielectric constant is much lower than in the ferroelectric phase. This implies a non-polar phase with molecules parallel to the smectic layer normal. It can be assumed that this phase exhibits an arrangement within the smectic layers. X-ray study is necessary to determine the in-layer structure.

TABLE 1 Transition temperatures (°C) and values of the spontaneous polarization P_S (nC/cm^2) at the temperature 20 K below the transition to the SmC* phase. ✱: the phase exists, — : the phase does not exist.

n/m	SmN		SmC*		Ch		Iso	P_S
7/7	✱	63.5	✱	107.8	✱	125.8	✱	82.7
6/9	✱	74.2	✱	108.7	✱	123.8	✱	81.0
8/9	✱	66.9	✱	114.3	✱	117.7	✱	86.8
10/10	✱	70.6	✱	115.8	—		✱	74.2
12/5	✱	71.7	✱	122.1	✱	125.0	✱	76.8
12/8	✱	74.0	✱	123.3	—		✱	86.0
12/9	✱	80.0	✱	118.5	✱	122.3	✱	81.0
12/10	✱	66.6	✱	122.6	—		✱	78.9

It seems that only the substances with odd *m* exhibit the cholesteric phase independently on *n*. For even *m* there is a direct phase transition from the isotropic to the ferroelectric phase. At this phase transition both isotropic and ferroelectric phases coexist without the cholesteric phase would come into appearance. The temperature range of the coexistence of phases can reach up to 10 deg.

The values of P_S measured at temperatures by 20 K lower than the high temperature limit of SmC* phases are rather high (see Table 1). There is a slight regular increase in P_S when cooling, which is 10 ÷ 20 % across the whole SmC* temperature range. The example of the temperature dependence of P_S is shown in Figure 1. The P_S values cannot be measured just below the phase transition (defined here as the first appearance of the SmC* phase on cooling) due to the coexistence of isotropic and SmC* phases.

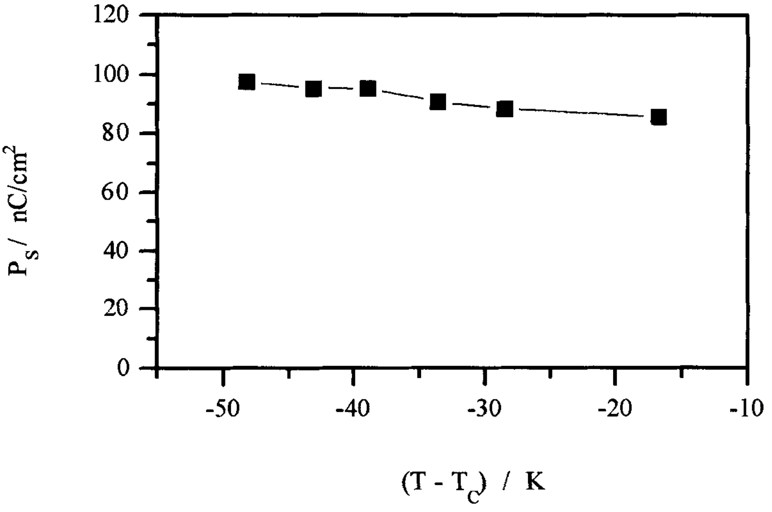


FIGURE 1 The temperature dependence of the spontaneous polarization of the compound *n/m* = 12/8 measured on cooling. T_C is the phase transition temperature, defined by the first appearance of the SmC* phase on cooling.

The values of Θ_S = 43° are the same for all compounds and nearly constant within the SmC* phases. The P_S values are comparable to those obtained with the compounds which do not possess the cyanocinnamic unit in the mesogenic core[1] provided they have similar aliphatic chain length. Comparison of the Θ_S values of the two series shows that introduction the cyanocinnamic unit enhances the Θ_S values by about 2°.

EXPERIMENTAL

4-hexyloxybenzylidencyanoacetic acid

25.7 g (0.1 mol) of 4-bromphenylhexylether (prepared by Williamson method, distilled over calciumhydride) and 5 g magnesium turnings in 200 ml of dry diethylether were stirred at room temperature for 3 hours and then refluxed for 2 hours. The reaction mixture was added dropwise to a solution of 29.2 g (0.4 mol) of dry dimethylformamide in 100 ml of ether under vigorous stirring and cooling by dry ice. Stirring continued for 2 hours at room temperature. The resulting mixture was acidified with dilute HCl while cooled in the ice bath. The organic layer was separated, the aqueous layer was extracted by ether. The extract was washed with dilute hydrochlorid acid and dried over calcium chloride. The solvent was evaporated and the residue was distilled under reduced pressure (B.p. 60°C / 25 mm Hg).

16.5 g (0.08 mol) of 4-hexyloxybenzaldehyde, 8.5 g (0.1 mol) of cyanoacetic acid, glacial acetic acid (1 ml), ammonium acetate (1.5 g) and 300 ml of benzene were refluxed with azeotropical elimination of water. 250 ml of benzene was evaporated, the residue allowed to stand overnight at room temperatute. The precipitate was collected and recrystallized from benzene. The yield was 14.5 g of yellow crystals.

^{1}H NMR ($CDCl_3$, ppm): 8.25 (1H, s, -CH=); 8.1 (2H, d, CH-arom.); 7.0 (2H, d, CH-arom.); 4.08 (2H, t, CH_2-O); 1.3÷1.8 (8H, m, CH_2); 0.92 (3H, t, CH_3).

Mesogenic phenol (III), $R=C_6H_{13}$

A solution of 14.6 g (0.05 mol) 4-hexyloxybenzylidencyanoacetylchloride (prepared from the corresponding acid and oxalylchloride) in methylene chloride (50 ml) was added dropwise to a stired solution of 4,4'-dihydroxybiphenyl (18.6 g, 0.1 mol) in pyridine (50 ml). The resulting solution was stirred overnight at room temperature and evaporated to dryness. The residue was acidified by addition of dilute hydrochlorid acid. Solid product isolated by filtration was extracted by toluene and separated from unsoluble biphenol. Toluene extract was evaporated and mesogenic phenol was crystallized from ethanol.

^{1}H NMR ($CDCl_3$, ppm): 8.33 (1H, s); 8.09 (2H, d); 7.48÷7.58 (4H, m); 7.27 (2H, d); 7.05 (2H, d); 6.92 (2H, d); 4.85 (1H, s); 4.08 (2H, t); 1.3÷1.8 (8H, m); 0.92 (3H, t)

Final product (I), $R{=}C_6H_{13}$, $R'{=}C_8H_{17}$

The preparation was carried out using standard condensation method with DCC. The product was purified by the column chromatography on silica gel with the mixture of chloroform and acetonitrile in the volume concentration ratio 97:3 as an eluent.

^{1}H NMR ($CDCl_3$, ppm): 8.33 (1H, s); 8.09 (2H, d); 7.55÷7.65 (4H, dd); 7.29 (2H, d); 7.20 (2H, d); 7.02 (2H, d); 4.22 (1H, q); 4.08 (2H, t); 3.5 (1H, m); 3.7 (1H, m); 0.9÷1.8 (29H, m).

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