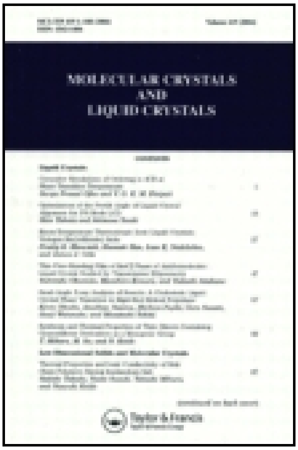

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Synthesis and Dielectric Properties of New Liquid Crystalline Substances with a Lactate Chiral Group

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Two series of new chiral liquid crystalline substances have been synthesized with a lactate chiral group. All compounds exhibit the blue phase, the cholesteric phase and the SmA phase. The ferroelectric SmC* phase was observed for the substance with two chiral centers (n=10) only. The soft mode was detected in the whole range of the SmA phase for all substances and temperature dependences of its relaxation frequency and dielectric strength were determined.

Keywords: lactate chiral group; dielectric properties; soft mode; ferroelectric liquid crystals; liquid crystals

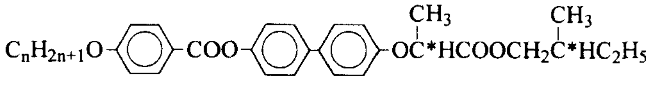
INTRODUCTION

In previous works[1,2] we studied mesomorphic properties of materials (denoted as H-series), where the chiral chain based on lactic acid is connected with the ester group to the rigid core. In this contribution we use the ether linkage group to study the influence of this substitution on mesomorphic properties. A similar exchange has been already studied with the isooctanol chiral chain, which results in a decrease of spontaneous polarization[3].

It can be expected that the transversal dipole-moment of the linkage group has a dominant effect on the conformation of the molecule near the chiral center, which is important for the stabilization of the SmC* phase. The influence of a similar exchange on the stabilization of the antiferroelectric SmC*$_A$ phase has been already established[4].

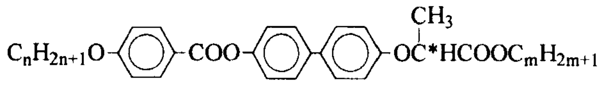
General formulas of the investigated compounds are:

HO n/**:



$$C_nH_{2n+1}O\text{-}C_6H_4\text{-}COO\text{-}C_6H_4\text{-}C_6H_4\text{-}OC^*H(CH_3)COOCH_2C^*H(CH_3)C_2H_5$$

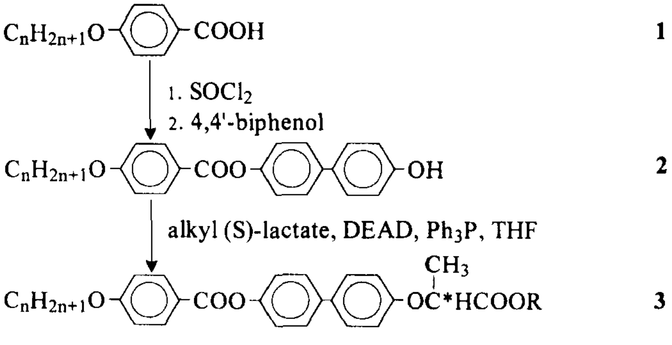
HO n/m:



$$C_nH_{2n+1}O\text{-}C_6H_4\text{-}COO\text{-}C_6H_4\text{-}C_6H_4\text{-}OC^*H(CH_3)COOC_mH_{2m+1}$$

SYNTHESIS

The synthesis was carried out as outlined in Scheme I starting from commercial methyl 4-hydroxybenzoate. Its reaction with corresponding *n*-alkyl bromide in presence of sodium ethanolate in dry ethanol with subsequent hydrolysis allows to obtain 4-*n*-alkoxybenzoic acids **1** in rather high yield.



SCHEME 1

Reaction of prepared compounds with an excess of thionyl chloride yielded benzoyl chlorides, which were then utilized for preparation of 4-(4'-hydroxybiphenyl) 4-*n*-alkoxybenzoate **2** as it was described earlier[1,2,5].

Optically active alkyl lactates have been prepared from commercial (S)-lactic acid by azeotropical esterification with appropriate alcohols.

DEAD supported coupling of the intermediate **2** with the alkyl lactates in the presence of Ph_3P in dry THF[6] followed by column chromatography on silica gel gave the desired compounds **3** of the HO-series.

EXPERIMENTAL PART

4-(4'-Hydroxybiphenyl) 4-n-Alkoxybenzoate **2**. 0.1 Mol 4-*n*-alkoxybenzoyl chloride, prepared from 4-*n*-alkoxybenzoic acid **1** on heating with the the double excess of thionyl chloride, was added drop-wise to a solution of 0.133 mol (20.4 g) 4,4'-biphenol (Aldrich, pure) in 100 ml of pyridine dried over KOH. The reaction mixture was refluxed for 5 hours, stood overnight and washed with dilute hydrochloric acid (150 ml, 1:2), water (twice with 150 ml), 150 ml of 10% aqueous solution of NaOH (for 4,4'-biphenol removal) and, finally, with 100 ml of water. The reaction mixture was acidified with dilute HCl (150 ml, 1:2) and the precipitate was extracted with boiling toluene. Toluene was removed *in vacuo*. The residue was crystallized from ethanol (diester being insoluble) to give a white or light yellow powder in yields about 38-55% (R_f=0.40-0.50 in 5% EtOH, 95% $CHCl_3$; R_f=0.15 in $CHCl_3$).

Alkyl (S)-Lactates. A solution of (120g) (S)-lactic acid (Lachema) and corresponding alcohol (1Mol) (Merck, pure) in 300 ml of benzene was refluxed with a Dean and Stark trap for 10 hours. Benzene was evaporated and the residue was filtered and distilled *in vacuo*. The first fraction being alcohol, the second one being corresponding alkyl (S)-lactate, the third one being α-(alkoxycarbonyl)ethyl lactate, as colourless or slightly yellow liquids.

Final product 3 (HO-series). 4-(4'-Hydroxybiphenyl) 4-alkoxybenzoate **2** (10 mmol), alkyl (S)-lactate (11 mmol), triphenyl phosphine (11 mmol) were dissolved in 30 ml of anhydrous THF. The solution of 11 mmol ethyl azodicarboxylate in 15 ml of THF was added dropwise to the stirred mixture reagents for 30 minutes and left to stand overnight. The solvent was removed under reduced pressure. The residue was chromatographed (CH_2Cl_2 with 1% ethanol, Kieselgel 60) and crystallized from ethanol to produce a white powder.

EXPERIMENTAL RESULTS

The sequences of phases and phase transition temperatures have been determined from the texture observation using polarizing microscopy. All compounds exhibit the blue phase several degrees broad, the cholesteric, SmA, and SmB phases. Only one of the synthesized homologues exhibits the ferroelectric SmC* phase. The data are shown in Table 1.

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

HO n/m	Cr.	T_t	SmB	T_t	SmC*	T_t	SmA	T_t	N*	T_t	BP	T_t	Iso
HO 8/**	•	40	•	56	—		•	66	•	82	•	85	•
HO 10/**	•	41	•	53	•	58	•	65	•	84	•	87	•
HO 8/6	•	32	•	43	—		•	52	•	95	•	98	•
HO 9/6	•	33	•	42	—		•	53	•	87	•	91	•
HO 10/6	•	27	•	44	—		•	64	•	92	•	95	•
HO 10/8	•	39	•	42	—		•	55	•	84	•	87	•
HO 10/10	•	37	•	40	—		•	61	•	77	•	83	•
HO 10/12	•	36	•	40	—		•	59	•	77	•	83	•

In the SmC* phase of the homologue HO 10/** the spontaneous polarization (P_s) and the spontaneous tilt angle (θ_s) have been determined (see Fig. 1) on samples in the book-shelf geometry 25 μm thick. The values of P_s have been evaluated from the *P(E)* hysteresis loop detected during the P_s switching in the electric field of frequency 60 Hz. The values of θ_s have been determined optically from the difference between extinction position at crossed polarizers under opposite d.c. fields ± 40 kV/cm.

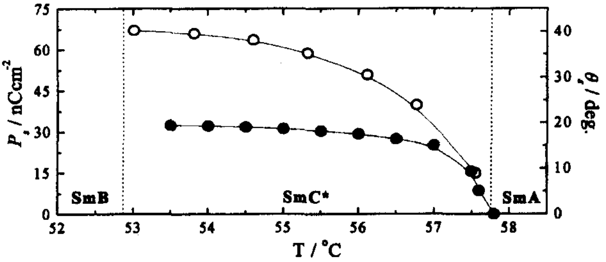


FIGURE 1 Temperature dependences of the spontaneous polarization (open circles) and the spontaneous tilt angle (solid circles) for HO 10/**.

For the ferroelectric compound HO 10/** the temperature dependence of permittivity has been measured at selected frequencies in all liquid crystalline phases (see Fig. 2). Besides, the frequency dispersion of the real (ε') and imaginary (ε'') parts of permittivity has been measured in the frequency range

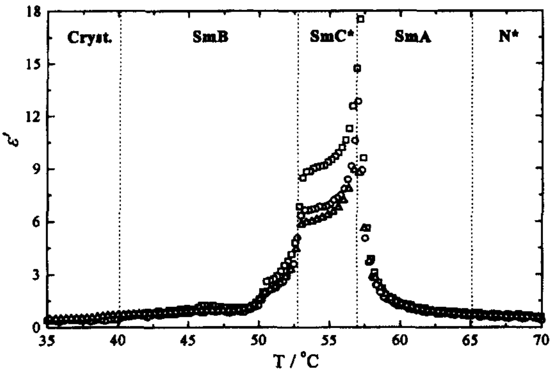


FIGURE 2 Temperature dependences of the real part of permittivity for HO 10/** at frequencies: 30 Hz (squares), 60 Hz (circles) and 100 Hz (triangles).

from 10 Hz to 1 MHz in the SmC* and SmA phases. The dispersion shows a single mode in both phases (see Fig. 3). The fitting[7,8] of the Cole-Cole formula to the $\varepsilon'(f)$ and $\varepsilon''(f)$ dependences (see Fig. 3) gives the relaxation frequencies (f_r) and dielectric strength ($\Delta\varepsilon$) of these modes (see Figs. 4 and 5).

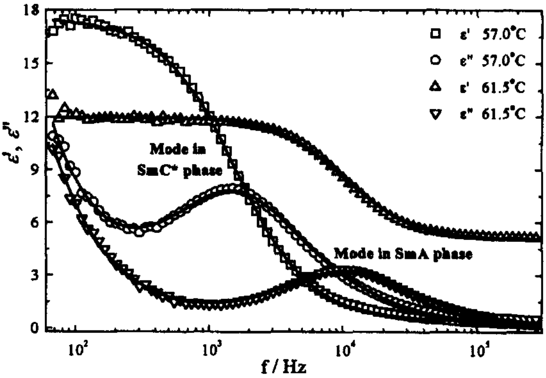


FIGURE 3 Frequency dispersion of the real and imaginary parts of permittivity for HO 10/** at selected temperatures. The solid lines are fits of Cole-Cole formula.

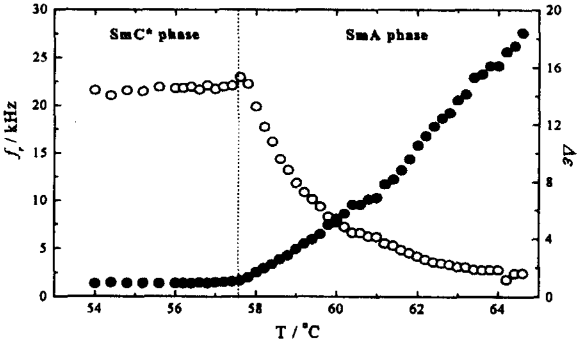


FIGURE 4 Temperature dependences of the fitted relaxation frequency f_r (solid circles) and dielectric strength $\Delta\varepsilon$ (open circles) of the soft mode in the SmA phase and Goldstone mode in the SmC* phase for HO 10/**.

The temperature dependences of both f_r and $\Delta\varepsilon$ in the compound HO 10/** show a typical soft mode and Goldstone mode behavior in the SmA and SmC* phase, respectively. With the other compounds, the soft mode is also observed in the SmA phase, but the ferroelectric phase transition SmA-SmC* does not occur, instead a transition to the SmB phase takes place. In these compounds the relaxation frequency in the SmA phase exhibits two types of temperature dependences. In the compounds HO 8/6 and HO 8/** f_r exhibits a linear softening (Fig. 5 b), the same as in ferroelectric HO 10/**. In the other compounds the linear softening stops several degrees above the transition to the SmB phase and f_r tends to saturation to a constant value (Fig. 5 a).

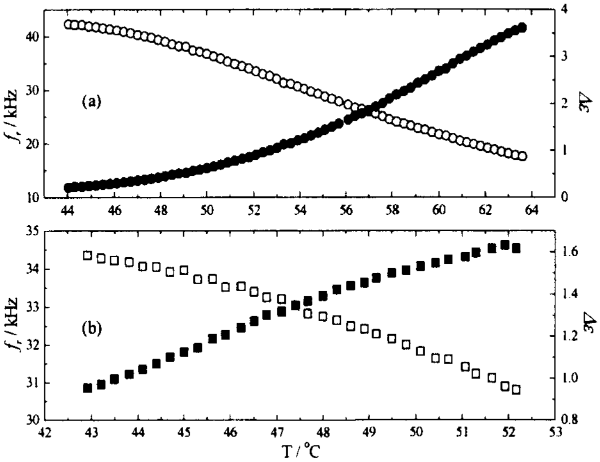


FIGURE 5 Temperature dependences of the fitted relaxation frequency f_r (solid circles and squares) and dielectric strength $\Delta\varepsilon$ (open circles and squares) of the soft mode in the SmA phase for (a) HO 10/6 and (b) HO 8/6.

DISCUSSION AND CONCLUSIONS

Let us compare the properties of the studied HO-series to the similar H-series studied earlier[1,2]. The H-series has a longer core, due to attachment of the chiral end chain by the ester bond. In H-compounds there is a weak conjugation between the aromatic system and the carbonyl group of the chiral acid, which prefers their in-plane conformation. However, the attachment of the chiral chain by the etheral bond does not allow such conformation to exist. Moreover, these compounds have the bulky methyl group of the chiral lactic unit located closer to the core and directed off the plane of the rigid core due to the sp^3 hybridization. This type of hybridization can deteriorate packing of the molecules. This phenomenon can lead to disappearance of the SmC* phase in majority of HO-compounds.

The interesting behavior of the soft mode in the SmA phase of non-ferroelectric homologues is under more detailed experimental and theoretical study.

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