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NEW FERROELECTRIC LIQUID CRYSTALLINE SUBSTANCES WITH LATERAL GROUPS IN THE CORE

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New Ferroelectric Liquid Crystalline Substances with Lateral Groups in the Core

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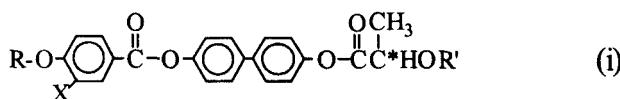
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New series of ferroelectric liquid crystalline materials containing methyl and methoxy lateral groups on the aromatic ring of the core unit, as well as non-substituted materials have been synthesised. All compounds exhibit a wide temperature range of the ferroelectric chiral *SmC** phase. A low temperature ferroelectric phase was detected for some of the investigated compounds probably composed of the *SmC** phase and a crystalline phase. Measurements of spontaneous polarisation and tilt angle, helical pitch and dielectric permittivity has been performed.

Keywords: lateral groups; ferroelectric liquid crystals; spontaneous polarisation; DSC-study; dielectric properties

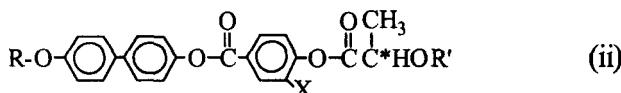
INTRODUCTION

In our previous works [1, 2] the influence of the lateral substitution on the aromatic ring in the core upon the phase transition temperatures have been established. The lateral groups were substituted on the most distant aromatic ring from the chiral centre:



Formula (i) represents *H*, *M* and *MO* series with no lateral substitution group, with methyl (CH_3) and methoxy (CH_3O) groups in *X*-position, respectively [1, 2].

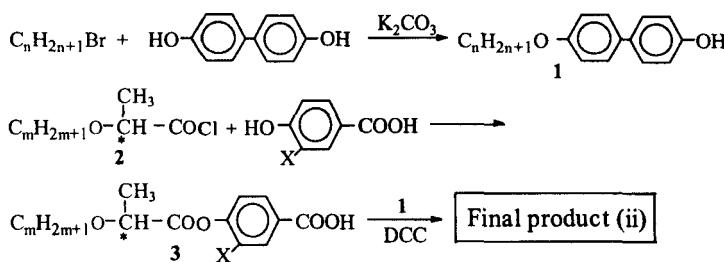
In this study, the influence of the lateral substitution on the aromatic ring nearest the chiral centre has been investigated:



Homologues series with chiral (S)-2-alkyloxypropionic groups bonded with unsubstituted or 3-substituted 4-hydroxybenzoic acids have been synthesised. The same substituents as in [1, 2], namely methyl and methoxy groups were used.

SYNTHESIS

The synthesis was carried out according to the Scheme 1.



SCHEME 1

4-hydroxy-4'-alkoxy-biphenyl (**1**) is prepared by etherification of 4,4'-biphenol with appropriate alkylbromide according to the principles of Williamson synthesis [3]. (S)-2-alkyloxypropionic acids (**2**) are prepared by alkylation of (S)-ethyl lactate in presence of Ag_2O [4] and following hydrolysis of ester group. 4-(2-alkyloxypropionyloxy)-benzoic acids (**3**) are prepared from 4-hydroxybenzoic acid and: (S)-2-alkyloxypropionic chloride [5], or 3-methyl-4-hydroxybenzoic acid, or 3-methoxy-4-hydroxybenzoic acid, respectively. Final product (**ii**) (see Scheme 1) has been obtained by esterification using dicyclohexylcarbodiimide (DDC) as a condensation agent. The products are purified by column chromatography using silica gel as the stationary phase and chloroform-ethanol mixture as eluent.

The synthesised materials (**ii**) were denoted as *ENT 10/m*, *VR 10/m* and *KrR 10/m* for materials with no lateral group, with CH_3O and CH_3 lateral groups in X-position, respectively. The chemical purity of all synthesised compounds is in the range of 98-100%.

MESOMORPHIC PROPERTIES

Mesomorphic properties of all newly synthesised compounds from homologous series *ENT 10/m*, *VR 10/m* and *KrR 10/m* are collected in Table 1. The sequences of phases were determined from texture observations made on planar samples in the polarising microscope. The phase transition temperatures and enthalpies have been evaluated from DSC studies (Perkin-Elmer DSC-7). Typical DSC plots for selected compounds are shown in Figure 1.

All compounds exhibit a wide temperature range of the ferroelectric *SmC** phase, which is shifted to lower temperatures for the substituted compounds. The *SmA* phase as well as the cholesteric phase are absent in studied series.

TABLE 1 Transition temperatures ($^{\circ}\text{C}$) from DSC measured on cooling (5K min^{-1}); values of spontaneous polarisation P_s (nC cm^{-2}) measured at temperatures 10 K below transition to the *SmC** phase and transition enthalpies [ΔH_c in J g^{-1}] for homologous series *ENT 10/m*, *VR 10/m* and *KrR 10/m*. Index m indicates the number of carbon atoms in the hydrocarbon chain of alkoxypropionate unit. Index “**” stands for (S)-2-methylbutyl chain with two chiral centres. (• the phase exists, – the phase does not exist).

	<i>Cr.1</i>	T_c [ΔH_c]	<i>SmC*</i> + <i>Cr.2</i>	T_c [ΔH_c]	<i>SmC*</i>	T_c [ΔH_c]	<i>Iso</i>	P_s
<i>ENT 10/**</i>	•	89 [-8.4]	•	107 [-39.9]	•	142 [-10.9]	•	116
<i>ENT 10/5</i>	•	98 [-48.2]	–		•	141 [-11.2]	•	111
<i>ENT 10/10</i>	•	100 [-78.5]	–		•	135 [-16.6]	•	90
<i>ENT 10/12</i>	•	99 [-56.0]	–		•	129 [-10.9]	•	88
<i>VR 10/7</i>	•	50 [-20.3]	•	63 [-5.8]	•	103 [-9.4]	•	51
<i>VR 10/8</i>	•	52 [-22.7]	•	62 [-3.9]	•	102 [-9.3]	•	36
<i>VR 10/9</i>	•	28 [-21.6]	–		•	98 [-8.4]	•	67
<i>VR 10/10</i>	•	29 [-21.8]	–		•	94 [-8.1]	•	64
<i>VR 10/12</i>	•	40 [-21.9]	–		•	98 [-7.6]	•	65
<i>KrR 10/10</i>	•	57 [-35.4]	–		•	108 [-9.1]	•	90
<i>KrR 10/12</i>	•	62 [-60.3]	–		•	99 [-4.7]	•	83

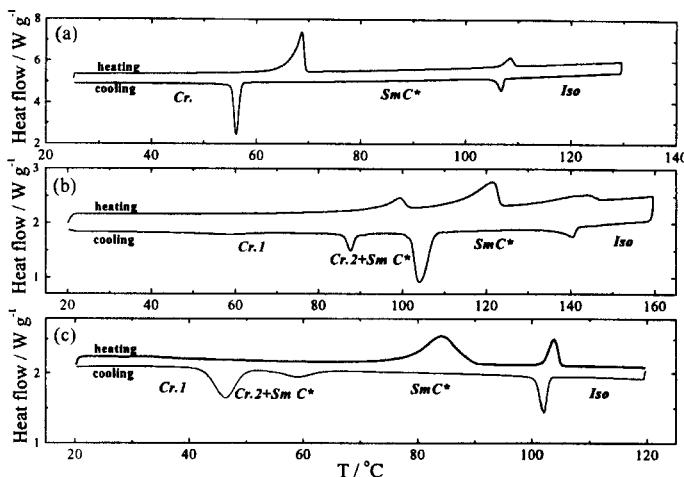


FIGURE 1 Typical DSC plots on heating and cooling (rate 5 K min⁻¹) for *KrR 10/10* (a), *ENT 10/*** (b), and *VR 10/7* (c).

A low temperature ferroelectric phase was detected in three of the investigated compounds (see Table 1). For *ENT 10/***, the X-ray measurements show that on cooling at about 115°C, a single intensity peak corresponding to layer thickness about 30Å occurs (see Figure 2). Then, at about 107°C the intensity of that peak decreases strongly and another peak appears corresponding to 35.5Å. This peak could be related to a crystalline phase. This conclusion is supported by DSC results showing a large enthalpy ($\Delta H_c = 39.9 \text{ J g}^{-1}$) at the onset of this phase (see Figure 1 (b) and Table 1). Such a high value of ΔH_c could correspond to the transition to a crystal phase. On further cooling at about 89°C ($\Delta H_c = 8.4 \text{ J g}^{-1}$) the peak of X-ray intensity related to *SmC** phase disappears and another one corresponding to 32Å appears. It can

be summarised that for *ENT 10/*** there is a region (107-89°C) where the *SmC** and the crystalline phase (*Cr.2*) coexist. In this region, the crystalline phase (*Cr.2*) is seen in the *SmC** phase texture as stripes. The approximate estimation of the *P*_s values shows that this region contains about 25% of the *Cr.2*. Below 89°C the coexistence of two crystalline phases (*Cr.2* and *Cr.1*) occurs.

Qualitatively the same situation is observed with compounds *VR 10/7* (see Figure 1 (c)) and *VR 10/8*. The X-ray study confirms the coexistence of the *SmC** phase and crystalline phase in the temperature ranges 63°C - 50°C (62°C - 52°C), and coexistence of two crystalline phases below 50°C (52°C) for *VR 10/7* (*VR 10/8*). In contrast to *ENT 10/***, for *VR 10/m* homologues the higher temperature DSC peak (at 63°C for *VR 10/7* and at 62°C for *VR 10/8*) corresponds to lower enthalpy than the lower temperature peak. Probably, it means that on cooling the *SmC** phase first recrystallises to another crystalline structure, less ordered than that in the case of *ENT 10/***.

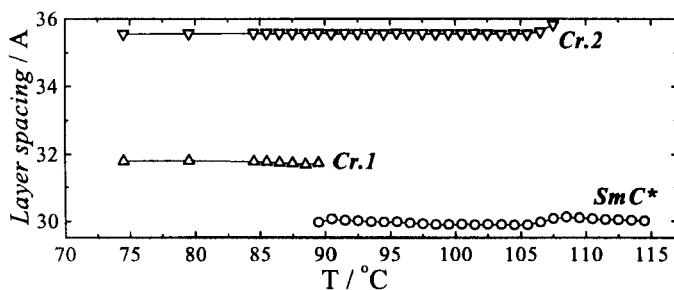


FIGURE 2 Temperature dependence of the layer spacing obtained from the X-ray measurements for *ENT 10/***.

PHYSICAL PROPERTIES

All measurements were performed on samples in the bookshelf geometry (smectic layers perpendicular to the sample plane) 25 μm thick. In the ferroelectric SmC^* phase, temperature dependence of the spontaneous polarisation, P_s , and spontaneous tilt angle, θ_s , as well as helicoidal pitch length, p , have been determined.

The values of P_s have been evaluated from $P(E)$ hysteresis loop detected during P_s switching in a.c. electric field E of frequency 60 Hz (see Table 1). A phase coexistence region of a few degrees has been observed at the $Iso-SmC^*$ phase transition.

The values of θ_s have been determined optically from the difference between extinction position at crossed polarisers under opposite d.c. electric fields $\pm 40 \text{ kVcm}^{-1}$. Tilt angle has been found about 36-39° for different compounds, nearly temperature independent.

Temperature dependences of p have been established by diffraction of He-Ne laser light (630nm) on disclination lines. The line spacing equals p [6]. For the indicated compounds from $VR\ 10/m$ series, temperature dependences of the helical pitch length in the SmC^* phase are shown in Figure 3. The values of p could not be measured in the whole temperature range of the SmC^* phase, because at low temperatures the helix becomes spontaneously unwound. It could not be measured at all for $VR\ 10/12$, because the dechiralisation line spacing was rather high and irregular, showing that the helix remained nearly unwound within the SmC^* phase temperature range.

Temperature dependences of the real part of permittivity at a frequency of 30 Hz have been measured for all studied compounds. There is a great increase of permittivity on cooling from the isotropic to

the SmC^* phase due to the contribution of the Goldstone mode (see Figures 4 and 5). In the temperature range where the SmC^* coexists with the crystalline phase, the values of permittivity are three time lower than at the temperatures of pure SmC^* phase.

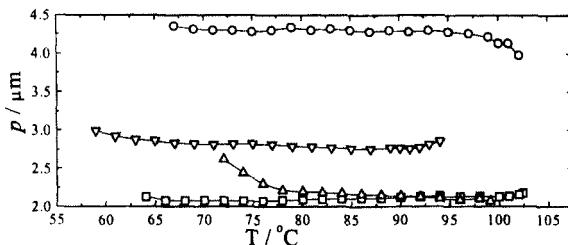


FIGURE 3 Temperature dependence of the helical pitch for indicated $VR\ 10/m$ homologues ($m=7$ (squares); 8 (circles); 9 (up triangles); 10 (down triangles)).

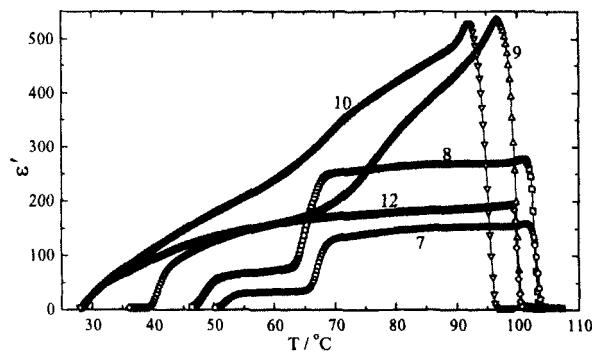


FIGURE 4 Temperature dependences of the real part of permittivity for indicated $VR\ 10/m$ homologues ($m=7$; 8 ; 9 ; 10 ; 12) detected in cooling runs at a frequency of 30 Hz.

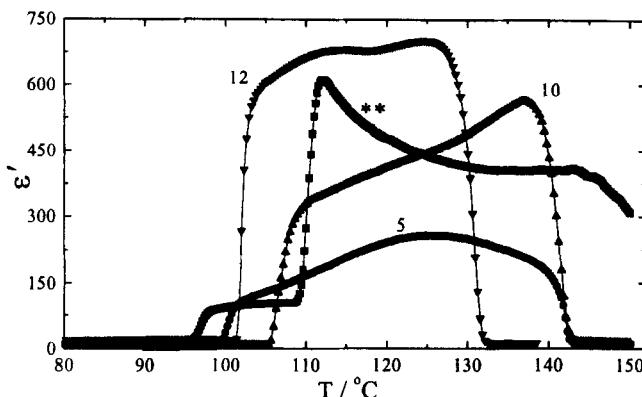


FIGURE 5 Temperature dependences of the real part of permittivity for indicated *ENT 10/m* homologues ($m=**$; 5; 10; 12) detected in cooling runs at a frequency of 30 Hz.

DISCUSSION AND CONCLUSIONS

Similarly as in [1, 2], the phase transition temperatures of *Iso-SmC** phase transition for the substituted compounds are about 30-40°C lower compared to the non-substituted series. This effect can be explained in terms of the steric influence of the methyl and methoxy groups on molecular packing [2]. Moreover, the phase transition to the ferroelectric *SmC** phase originates directly from the isotropic phase. The blue phase, cholesteric and *SmA* phase observed for *H*, *M*, *MO* series [1, 2] are absent. The molecules of *ENT*-series, compare to the molecules of *H*-series [1], have higher dipole moment parallel to the molecular axis, which results in stabilisation of the ferroelectric *SmC** phase at the expense of the cholesteric phase.

A comparison of the P_s values for *ENT 10/m* and *VR 10/m* (see Table 1) shows that the methoxy group substitution results in a slight decrease of the spontaneous polarisation. The methyl substituted series *KrR 10/m* does not show any difference in P_s values with respect to the non-substituted *ENT*-series.

The coexistence of a liquid crystalline and crystal phases is hardly conceivable despite the high value of ΔH_c at the onset of the *Cr.2* phase. From this reason we cannot exclude that the *Cr.2* phase is a highly ordered liquid crystalline phase.

In the ferroelectric *SmC** phase, temperature dependences of the complex permittivity show a strong contribution of the Goldstone mode for all compounds. For some of the studied materials, a very low frequency (~Hz) mode has been detected. The results of dielectric spectroscopy measurements will be published elsewhere.

ACKNOWLEDGEMENTS

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