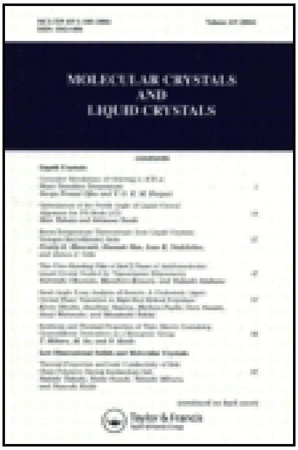

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Synthesis and Liquid Crystalline Properties of (S)-[4-n-Alkyloxy-benzoyloxyphenyl]-4′-[(2-n-alkyloxy)propionyloxy]benzoate

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Synthesis and Liquid Crystalline Properties of (S)-[4-*n*-Alkyloxy-benzoyloxyphenyl]-4′-[(2-*n*-alkyloxy)propionyloxy]benzoate

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New series of chiral liquid crystalline compounds, (S)-[4-*n*-alkyloxy-benzoyloxyphenyl]-4′-[(2-*n*-alkyloxy)propionyloxy]benzoate **(QMn/m)**, were synthesised. Polymorphism of the new compounds was investigated by polarising microscopy and differential scanning calorimetry. All members of the homologous series showed enantiotropic SmC* and N* mesophases except one compound having the longest alkyl chain in both terminal groups. The spontaneous polarisation of these ferroelectric liquid crystalline compounds is about 110–130 nC/cm^2. The temperature dependence of the dielectric permittivity was measured for all the compounds studied. Several ferroelectric binary mixtures were prepared in order to get a wide enantiotropic chiral SmC* phase at ambient temperature.

Keywords: synthesis; lactic acid derivatives; ferroelectric mixtures; spontaneous polarisation; dielectric constant; tilt angle

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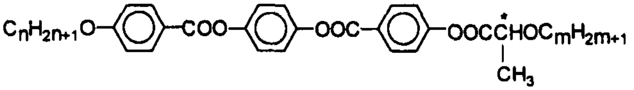
INTRODUCTION

It was described earlier that ferroelectric liquid crystals with a terminal chiral group based on the O-alkyl lactate possess high spontaneous polarisation[1-6]. Here we report on the synthesis and characterisation of a new family of ferroelectric liquid crystals with the same chiral unit but with a different linking group in the core: (S)-[4-*n*-alkyloxybenzoyloxyphenyl]-4'-[(2-*n*-alkyloxy)propionyloxy]benzoate (**QMn/m**). According to this general formula two homologous series were prepared by varying the aliphatic chain length of the chiral part (**m**), while keeping the length of the achiral alkyloxy part fixed at **n=10** and **n=12** respectively. The compounds studied exhibited a broad enantiotropic ferroelectric (SmC*) and N* mesophase, but the cholesteric phase disappeared at the highest homologue **QM12/12**.



QMn/m

n=10,12
m=9,10,12

EXPERIMENTAL

Synthesis

(S)-[4-(2-*n*-Alkyloxy)propionyloxy]benzoic acid (2). A catalytic amount of anhydrous $ZnCl_2$, 11 mmol of α,α-dichloromethylmethylether was added slowly to a solution of 10 mmol of (S)-2-*n*-alkyloxypropionic acid in dry ether. The obtained solution was stirred for 2 hours, then evaporated *in vacuum* and finally dissolved in dry methylene chloride. This solution was added to a stirred solution of 11 mmol of 4-hydroxybenzoic acid in 50 ml of dry pyridine. The mixture was stirred for 8 hours and poured into the diluted solution (100 ml) of hydrochloric acid (1:5). The organic layer was removed and washed with 10 ml of water. The solvents were evaporated and the solid was crystallised from hexane to give the target compounds in 30-40% yields. ***^{1}H NMR*** ($CHCl_3$) δ (ppm): (S)-[4-(2-*n*-decyloxy)propionyloxy]benzoic acid: 0.87 (3H, t, J=6.6 Hz, $C\underline{H_3}CH_2$), 1.18-1.45 (14H, m, CH_2), 1.58 (3H, d, J=6.6 Hz, $C\underline{H_3}C^*H$), 1.65 (2H, m, $OCH_2C\underline{H_2}$), 3.49, 3.68 (2H, 2dt, J_1=8.8 Hz, J_2=6.6 Hz, $OC\underline{H_2}$), 4.20 (1H, q, J=6.6 Hz, C*H), 7.23 (2H, d, J=8.8 Hz, H-Ar *meta* to -COOH), 8.16 (2H, d, J=8.8 Hz, H-Ar *ortho* to -COOH), 9.4-10.5 (1H, br., COOH).

4-Hydroxyphenyl 4'-*n*-alkyloxybenzoate (6). 50 mmol of 4-alkyloxybenzoic acid was refluxed for 3 hours with 100 mmol of thionyl chloride. The excess of thionyl chloride was removed *in vacuum*, and the residue was dissolved in dry methylene chloride (20 ml). The obtained solution was added dropwise to a stirred solution of 50 mmol of 1,4-hydroquinone in 50 ml of dry pyridine. The mixture was stirred for 1 hour and left to stand overnight. After pouring the reaction mixture into the water the precipitate was filtered off and recrystallised from 100 ml of ethanol to give a slightly coloured compound in 60-70% yields.

^{1}H NMR ($CHCl_3$) δ (ppm): 4-hydroxyphenyl 4'-*n*-decyloxybenzoate: 0.88 (3H, t, J=6.6 Hz, CH_3), 1.20-1.53 (14H, m, CH_2), 1.82 (2H, quint., J=6.6 Hz, $OCH_2\underline{CH_2}$), 4.04 (2H, t, J=6.6 Hz, OCH_2), 5.47 (1H, s, OH), 6.79 (2H, d, J=8.8 Hz, H-Ar *ortho* to -OH), 6.97 (2H, d, J=8.8 Hz, H-Ar *ortho* to-OCH_2), 7.02 (2H, d, J=8.8 Hz, H-Ar *meta* to -OH), 8.13 (2H, d, J=8.8 Hz, H-Ar *meta* to -OCH_2).

(S)-[4-*n*-alkyloxybenzoyloxyphenyl]-4'-[(2-*n*-alkyloxy)propionyloxy]benzoate (QMn/m): 5 mmol of 4-hydroxyphenyl 4'-*n*-alkyloxybenzoate (**6**), 5 mmol of (S)-4-[(2-*n*-decyloxy)propionyloxy]benzoic acid, 12 mmol of dicyclohexylcarbodiimide (DCC) and a catalytic amount of dimethylamino pyridine (DMAP) were dissolved in 20 ml of dry methylene chloride. The resultant mixture was stirred for 48 hours, and the precipitate was filtered off. The solvent was evaporated. The solid residue was purified by column chromatography on Kieselgel (0.063-0.02 mm) sorbent eluted by chloroform-ethanol (99:1) system. After evaporation of the appropriate fractions, the residue was recrystallised from ethanol several times.

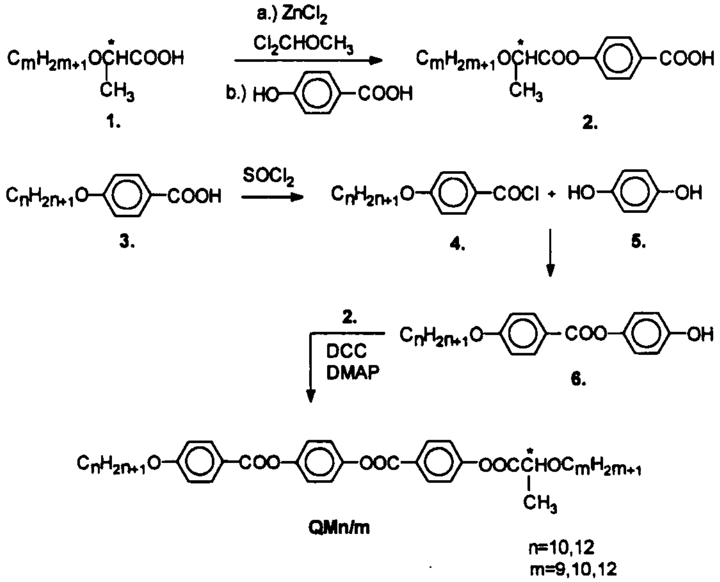
^{1}H NMR ($CHCl_3$) δ (ppm) for **QM10/9:** 0.90 (6H, m, CH_3), 1.2 – 1.5 (26H, m, CH_2), 1.58 (3H, d, J=7.0 Hz, $\underline{CH_3}CH^*$), 1.6 (2H, m, $\underline{CH_2}CH_2OCH^*$), 1.8 (2H, m, $\underline{CH_2}CH_2OAr$), 3.5–3.7 (1+1H, m, $CH^*O\underline{CH_2}$), 4.05 (2H, t, J=6.4 Hz, CH_2OAr), 4.22 (1H, q, J= 6.6 Hz, CH^*), 6.98 (2H, d, J=8.0 Hz, HAr ortho to –$OCOCH^*$), 7.26 (2H, d, J=8.0 Hz, HAr ortho to $OCOCH^*$), 7.28 (4H, d, J=8.0 Hz, HAr ortho to –OCOAr), 8.15 and 8.26 (2H, d, J=8.0 Hz HAr ortho to -COO).

Characterisation

Spectroscopic studies: The structure of the compounds was confirmed in $CDCl_3$ solution by ^{1}H NMR spectroscopy using a 300MHz Varian spectrometer. Tetramethylsilane was used as internal standard.

Texture observations and DSC: The textures of liquid crystals and their mixtures were observed in unoriented thin films between glass slides using an Amplival Pol U polarising microscope equipped with a Boetius hot-stage. The heating rate was 4 °C/min, the cooling rate was not controlled. The phase transition temperatures and the transition enthalpies were determined by a Perkin Elmer DSC7 differential scanning calorimeter in nitrogen atmosphere with a heating and cooling rate of 5 °C/min.

Physical properties: All physical measurements were performed on 25 µm thick planar samples in the bookshelf geometry. The spontaneous polarisation was evaluated from the *P(E)* hysteresis loop detected during switching in an a.c. electric field at a frequency of 60 Hz. The tilt angle was determined optically from the difference between the extinction positions at crossed polarisers under d.c. electric fields of opposite polarity (± 40 kV/cm). The real part of the dielectric permittivity was measured at a frequency of 100 Hz using a Schlumberger 1260 impedance analyser.



SCHEME 1. Synthetic pathway for the preparation of the **QMn/m** series

RESULTS AND DISCUSSION

The synthesis of **QMn/m** was carried out following the reaction scheme outlined in Scheme1. The appropriate (S)-2-*n*-alkyloxypropionic acid derivatives (1) were connected to 4-hydroxybenzoic acid to obtain the (S)-[4-(2-*n*-alkyloxy)propionyloxy]benzoic acid (2). This compound was coupled by dicyclohexylcarbodiimide with 4-hydroxyphenyl 4'-*n*-alkyloxybenzoate (6) derivatives obtained in the reaction of 4-*n*-alkyloxy-benzoyl chloride (4) and 1,4-hydroquinone (5) applied in a large excess. The chemical structure of the resulted title compounds (S)-[4-*n*-alkyloxybenzoyloxyphenyl]-4'-[(2-*n*-alkyloxy)-propionyloxy]-benzoate (**QMn/m**) was characterised by ^{1}H NMR spectroscopy.

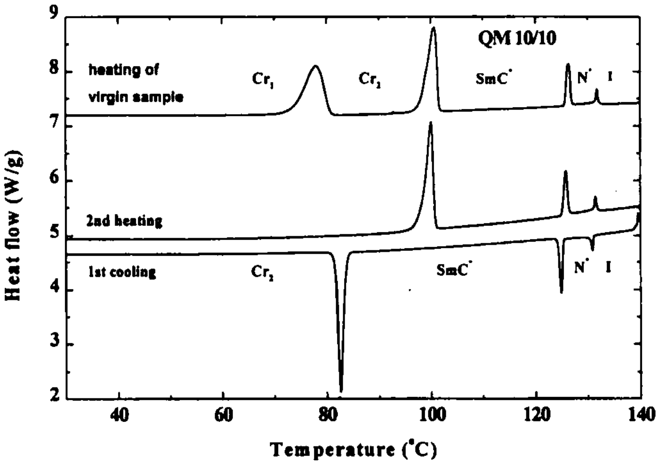


FIGURE 1 Typical DSC curves obtained during the first heating-cooling-heating cycle (compound **QM10/10**).

The mesomorphic properties of the synthesised compounds are summarised in Table 1. The phase transition temperatures and transition enthalpies were determined from the DSC curves (Figure 1 shows a typical example). All observed phase transitions were of the first order. The mesophases were identified from their characteristic textures by polarising microscopy. All compounds exhibited enantiotropic SmC*

	Cr$_1$ (virgin sample)	→ T (°C); *ΔH (kJ/mol)*	Cr$_2$	↔ T (°C); *ΔH (kJ/mol)*	SmC*	↔ T (°C); *ΔH (kJ/mol)*	N*	↔ T (°C); *ΔH (kJ/mol)*	I
QM10/9	● ●	**-** ↑56,8; *47.8*	- ●	**96-104** ↑99.4 ↓83.5; *30.1*	● ●	**125.5** ↑↓125.4; *6.4*	● ●	**132** ↑↓133.2; *1.8*	● ●
QM10/10	● ●	**72** ↑73.8; *33.8*	● ●	**97** ↑98.2 ↓83.6; *29.6*	● ●	**124** ↑↓125.1; *6.1*	● ●	**129** ↑↓131.1; *1.8*	● ●
QM10/12	● ●	**78-80** ↑77.2; *38.8*	● ●	**95.5** ↑95.3 ↓80.3; *29.3*	● ●	**124** ↑↓123.3; *6.4*	● ●	**126.5** ↑↓127.0; *1.7*	● ●
QM12/9	● ●	**-** ↑67.1; *45.8*	- ●	**98** ↑98.8 ↓85.7; *28.4*	● ●	**129** ↑↓128.6; *7.0*	● ●	**130.5** ↑↓130.9; *1.4*	● ●
QM12/10	● ●	**-** ↑77.3; *46.2*	- ●	**97** ↑97.7 ↓84.7; *30.4*	● ●	**127.5** ↑↓127.6; *7.7*	● ●	**128.5** ↑↓128.6; *1.3*	● ●
QM12/12	● ●	**80** ↑78.4; *49.3*	● ●	**97** ↑96.6 ↓83.7; *30.9*	● ●	**124.5** ↑↓125.6; *9.2*	- -	- -	● ●

TABLE 1 Phase transition temperatures (T) and entalpies (*ΔH*) of the **QMn/m** homologous series obtained by optical microscopy (bold values) and DSC in heating (↑) and cooling cycles (↓). ● phase exists, - phase does not exist

and N* mesophases, except the highest homologue **QM12/12** where the N* phase was absent. The phase transition temperatures determined in the polarising microscope were in good agreement with the DSC results. In three compounds a transition between two crystalline modifications ($Cr_1 \rightarrow Cr_2$) could be observed by microscopy. The DSC curves confirmed for all compounds this solid polymorphism in the virgin samples (at the first heating), which was not observable in subsequent cooling and heating cycles.

In Figure 2 the variation of the phase transition temperatures with the terminal chain length (**m**) is presented for both homologous series. The melting behaviour does not seem to show the classical odd-even effect for any of the homologous series. The temperatures of melting ($Cr_2 \rightarrow SmC^*$), clearing ($N^* \leftrightarrow I$) and that of the $SmC^* \leftrightarrow N^*$ phase transition exhibited a slight decrease with increasing number of carbon atoms (**m**) in the aliphatic chain on the chiral side. In contrast to this, however, the temperatures of transition between crystal modifications ($Cr_1 \rightarrow Cr_2$) showed a marked increase with increasing **m**.

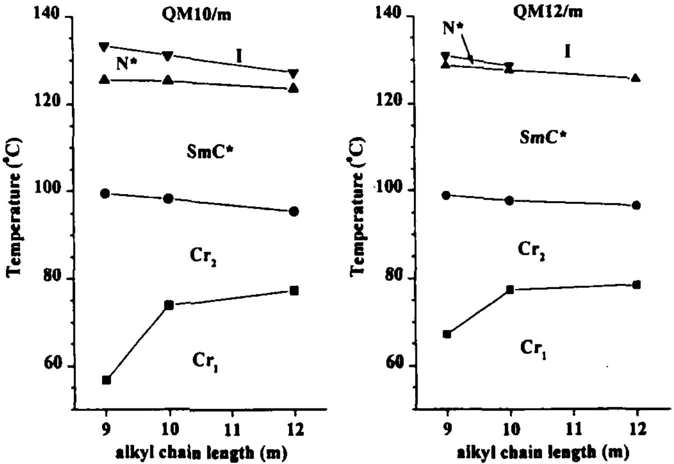


FIGURE 2 Phase diagrams of the homologous series **QM10/m** (left) and **QM12/m** (right).

The ferroelectric SmC* phase was further characterised by measuring the spontaneous polarisation (P_s), the tilt angle (θ) and the dielectric permittivity (ε'). The temperature dependence of the spontaneous polarisation exhibited a regular behaviour (Figure 3). For easier comparison the P_s values measured 5, 10 and 20 °C below the SmC*↔N* phase transition are given in Table 2. There is a slight decrease of P_s with increasing **m** in both homologous series.

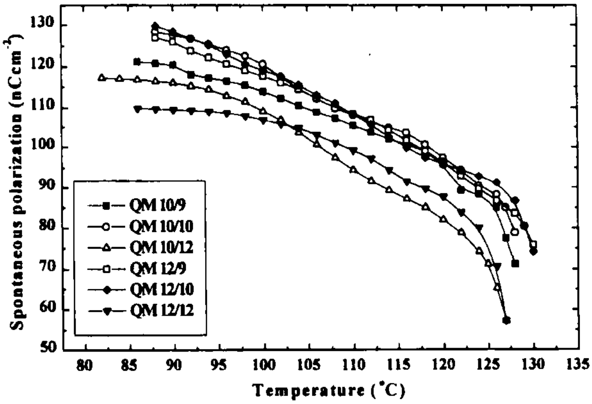


FIGURE 3 Temperature dependence of the spontaneous polarisation in the homologous series **QMn/m**.

	P_s (T_C-5 °C) (nC/cm^2)	P_s (T_C-10 °C) (nC/cm^2)	P_s (T_C-20 °C) (nC/cm^2)
QM10/9	91.2	99.4	107.5
QM10/10	92.0	100.1	110.0
QM10/12	80.7	87.0	100.8
QM12/9	87.7	95.5	107.9
QM12/10	91.1	95.2	107.5
QM12/12	81.8	89.5	101.2

TABLE 2 Spontaneous polarisation (P_s) in the **QMn/m** series measured 5, 10 and 20 °C below the SmC*↔N* phase transition (T_C).

For all compounds the tilt angle was found to be $\theta \approx 43.0$ - 44.7 °, nearly temperature independent. Such a behaviour is quite typical for substances possessing a strongly first order SmC*↔N* phase transition.

The temperature dependence of the real part of the low frequency dielectric permittivity (ε') of the substances is presented in Figure 4. Measured in the bookshelf geometry the large ε' values in the SmC* phase represent the contribution of the Goldstone mode indicating the presence of a helical structure. The small peaks near the SmC*↔N* (or SmC*↔I) phase transitions might be due to the soft mode. In the N* and I phases ε' should drop to low values due to the lack of the Goldstone and the soft mode contributions. The still unusually large ε' values seen in Figure 4 can be due to the relatively high conductivity of the substances or to another parasitic effect connected with the capacitance and the resistance of the surface (e.g. the polyimide) layers which falls down at higher frequencies (~1kHz).

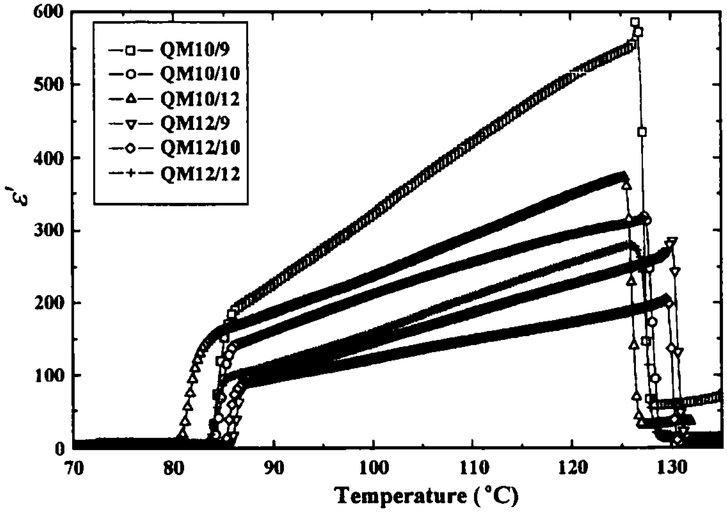
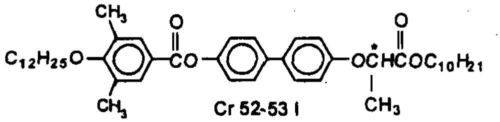


FIGURE 4 Temperature dependence of the real part of the dielectric permittivity (ε') for the **QMn/m** series.

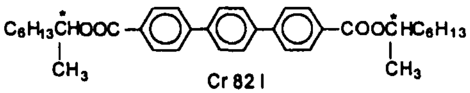
Physical properties of the **QMn/m** series have been compared to those of the earlier synthesised (S)-[4-(2-*n*-alkyloxypropionyloxy)-biphenyl]-4'-*n*-alkyloxy-benzoate (**Hn/m**) series[1,5]. The spontaneous polarisation of all **QMn/m** compounds are considerably higher than that of the **Hn/m** series. This may be due to the presence of the additional polar linking carboxylic group separating the phenyl rings. Comparing the phase sequences of **QM10/10**, **QM10/12** and **QM12/10** with the matching compounds (**H10/10, H10/12** and **H12/10**) one can observe that the change in the core resulted in the appearance of the N* phase and in a preference of crystallisation from the SmC* phase in **QMn/m** rather than forming a more ordered smectic phase (as in **Hn/m**).

The synthesised compounds of the **QMn/m** series melt at high temperatures. In order to lower the melting point several binary mixtures were prepared. Table 3 presents the compositions and the phase sequences of the studied mixtures. The phase transition temperatures for **Mix1** which contains two members of the homologous series **QMn/m**, were almost the same as those of the individual compounds. That indicates a tendency of the members of the **QMn/m** series to form ideal mixtures rather than eutectic ones.

Mixtures	Wt%	Composition	Phase sequence (°C)
Mix1	40.9 59.1	QM12/9 QM10/12	Cr 93 SmC* 124.5 N* 130 I
Mix2	38.9 61.1	DMO12/10 QM12/9	Cr 46 SmC* 91 I
Mix3	12.0 88.0	DMO12/10 QM12/9	Cr 96 SmC* 122 N* 124.5 I
Mix4	12.0 88.0	T8 QM12/9	Cr 60 SmC* 93 N* 94-118 I
Mix5	25.0 75.0	T8 QM12/9	Cr 58 SmC* 92-113 I



DMO12/10



T8

TABLE 3 Composition and phase sequences of the studied ferroelectric binary mixtures determined by polarising microscopy.

Lowering the melting point thus requires mixing with structurally different compounds. We have chosen two chiral but non-mesogenic liquid crystalline compounds for the further studies. One of these substances, (S)-4-*n*-decyl-2-[4'-(3,5-dimethyl-4''-dodecyloxy-benzoyloxy)-4-biphenyloxy]propionate (**DMO12/10**, a member of a homologous series without liquid crystalline properties) is reported here the first time. The other non-mesogenic compound, bis-(R)-(1-methylheptyl)-1,1'-4',1''-terphenyl-1'4''-dicarboxylate (**T8**), has already been used with success in preparing ferroelectric liquid crystalline mixtures with high spontaneous polarisation [7]. **Mix2, Mix3, Mix4** and **Mix5**, which contained these chiral but non-mesogenic substances as guests molecule, exhibited lower melting points than the host compound **QM12/9** itself. The shift of the melting point was larger in mixtures containing guest molecules in higher concentration (**Mix2** and **Mix5**). In **Mix3** and **Mix4** the concentration of the guest molecules **DMO12/10** and **T8** respectively are the same. Although **DMO12/10** melts at lower temperature than **T8**, the melting point of **Mix3** is higher than that for **Mix4**, i.e. **T8** shifts the melting point down more effectively.

We can conclude that a stabilising effect on SmC* phase was observable in all mixtures prepared from structurally different chiral compounds. Presumably the intercalated tail to tail packing of the molecules stabilised the ferroelectric phase in the mixtures.

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