Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

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To cite this Article Kašpar, Miroslav , Bubnov, Alexej , Hamplová, Věra , Málková, Zuzana , Pirkl, Slavomír and Glogarová, Milada(2007) 'Effect of lateral substitution by fluorine and bromine atoms in ferroelectric liquid crystalline materials containing a 2-alkoxypropanoate unit', Liquid Crystals, 34: 10, 1185 — 1192

To link to this Article: DOI: 10.1080/02678290701527461

URL: http://dx.doi.org/10.1080/02678290701527461

Liquid Crystals, Vol. 34, No. 10, October 2007, 1185–1192

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Effect of lateral substitution by fluorine and bromine atoms in ferroelectric liquid crystalline materials containing a 2-alkoxypropanoate unit

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(*Received 14 March 2007; accepted 1 June 2007*)

Two homologous series of ferroelectric liquid crystalline compounds with 2-alkoxypropanoate chiral unit containing biphenyl benzoate core laterally substituted by fluorine and bromine have been synthesized and studied. All compounds possess the ferroelectric smectic C* phase over a broad temperature range. For bromine-substituted compounds values of spontaneous polarization reach high values up to 250 nC cm^{-2}. The effects of the lateral substitution on the phenyl ring far from the chiral centre by methyl and methoxy groups, fluorine, chlorine and bromine atoms on mesomorphic properties and on values of the spontaneous polarization are discussed.

1. Introduction

While designing new liquid crystal molecules with definite properties, it is necessary to have in mind that their mesogenic behaviour is strongly influenced by the structure of the rigid molecular core and by the lateral substitution on the aromatic rings, with the position of the substituted ring in the molecular core being important [1]. During the last few years, several series of ferroelectric liquid crystalline materials containing biphenyl benzoate core and chiral 2-alkoxypropanoate unit have been synthesized and studied with the aim of obtaining new materials responding to the applications demands and contributing to a better understanding of the chemical structure to physical property relationship. A series of such liquid crystalline materials without any lateral substituent [2] was followed by three different series possessing the lateral methyl [3], methoxy [4] or chlorine [5] substitutions in the meta position to the carboxylic group of the 4-alkoxybenzoate unit, i.e. far from the chiral centre. All these materials possess a broad ferroelectric phase, which is shifted to lower temperatures for substituted compounds. However, the lateral substitution in all the cases studied resulted also in an increase of the melting points with respect to non-substituted materials and, hence, narrowing of the enantiotropic range of the SmC* phase occurs. Spontaneous polarization, which is an important parameter in particular for ferroelectric liquid crystalline materials used in mixtures responding to application demands, in the case of lateral methoxy substitution slightly decreases [5], while methyl and chlorine substitutions lead to a strong increase in values of the spontaneous polarization [3, 5]. The π-electron density of the substituted aromatic rings, which is strongly influenced by the character of the atom used for substitution, affects intermolecular interactions in the smectic layers of the ferroelectric SmC* phase due to donor–acceptor coupling. As in all those cases the lateral substitution was carried out far from the chiral centre and the direct influence upon the chiral centre was not expected.

The fluorine atom combines the properties of its large electronegativity and small size so that fluorination has a dramatic effect on the properties of liquid crystal molecules. The influence of the fluorine substitution at different positions of the phenyl ring close to the chiral centre for the phenylbiphenyl carboxylate series of antiferroelectric liquid crystalline (AFLC) materials based on the 4-(4'-nonyloxybiphenyl-4-yl-carbonyloxy)-benzoate core has already been studied [6, 7]. It was shown that the mesophase appearance as well as values of the spontaneous polarization, spontaneous tilt angle and switching times are strongly influenced by the position of the fluorine substituent on the phenyl ring closest to the chiral centre. Moreover, the frustrated

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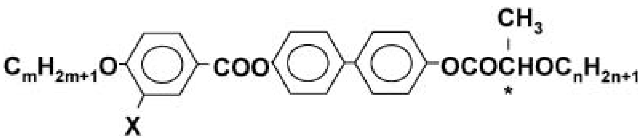
Liquid Crystals
ISSN 0267-8292 print/ISSN 1366-5855 online © 2007 Taylor & Francis
http://www.tandf.co.uk/journals
DOI: 10.1080/02678290701527461

twist grain boundary smectic A, smectic C and the blue phases of different structure were detected in tolane derivatives laterally substituted by fluorine atoms far from the chiral centre [8]. Fluoro-substituted alkyl ether compounds [9] were intensively studied as liquid crystalline materials responding to the definite application demands. These compounds possess a high voltage holding ratio, a low threshold voltage, high birefrigence and excellent miscibility with liquid crystal materials of different molecule stucture, especially at low temperatures.

The bromine atom is used very rarely as a lateral substituent for the molecules forming liquid crystalline materials. Comparison of stability of the orthogonal phases for non-chiral compounds substituted by different halogen atoms including bromine was carried out in [10]. It was found that decreasing of the electron accepting properties of halogen atoms and the larger size of the halogen atom lead to the preference for tilted hexatic phases. A study of various non-chiral liquid crystalline compounds with very simple molecular structure possessing bromine substitution was presented in [11]. The only case of chiral compounds with substitution by bromine near the chiral centre exhibits the highly tilted SmC* phase [12, 13]. Appearance of the highly tilted SmC* phase was also confirmed for three phenyl ring compounds with bromine lateral substitution near the chiral centre [14, 17]. Antiferroelectric phases were observed with bi-mesogenic organosilane liquid crystal materials with either fluorine, chlorine or bromine lateral substituent [12]. For these compounds the highest spontaneous polarization was found for chlorine-substituted compounds [13].

In the present study we have used two significantly different halogen atoms, namely fluorine and bromine, as a lateral substituent on the aromatic ring of the alkoxybenzoate unit far from the chiral centre. The general chemical formula of the studied compounds is

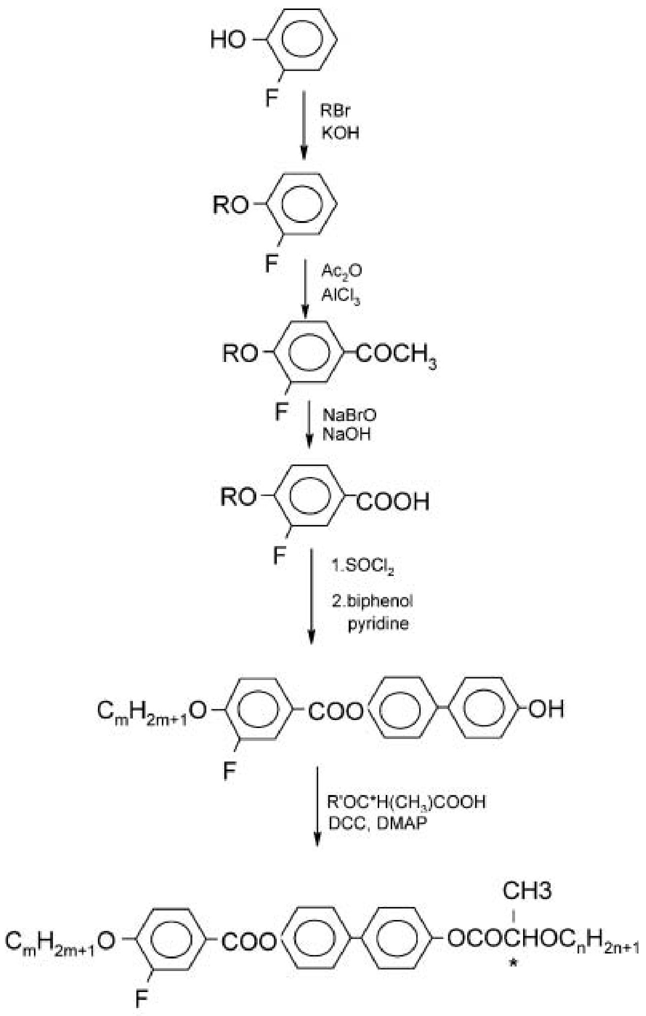


denoted as **Br m/n** and **F m/n** where **X** is the bromine (Br) and fluorine (F) atoms, respectively. The chiral centre of all the studied compounds is in the (S)-configuration. The effects of such a substitution on the mesomorphic behaviour and values of the spontaneous polarization have been established and compared to those for compounds with the same molecular core but different lateral substituents, namely chlorine [5], and the methyl [3] and methoxy groups [4] and are discussed in comparison to those obtained on the non-substituted compounds [2].

2. Synthesis

The general procedure of the synthesis of the compounds possessing fluorine as the lateral substituent is presented in Scheme 1.

Initial o-fluorophenol was alkylated with alkyl bromide in ethanolic solution of potassium hydroxide. The mixture was refluxed for 3 days. After evaporation the residue was distilled at a reduced pressure (1-decyloxy-2-fluorobenzene boiling point (b.p.) 192°/12 mm; 1-fluoro-2-octyloxybenzene b.p. 161°/11 mm). The acylation complex was prepared by dissolving the aluminium chloride in acetic anhydride in dry 1,2-dichloroethane previously cooled in an ice-water bath.



F m/n

Scheme 1. General procedure for synthesis of **F m/n** homologues series.

Then the reaction mixture was stirred at 0°C and the 1-fluoro-2-alkyloxybenzene was added drop wise during 1 hour. Stirring continued at room temperature for 5 hours and then the mixture was treated with ice and HCl with further solvent removal. Reaction with NaOBr was carried out by the Johnson method [15]. The fluorinated acids were crystallized from chloroform, transformed to an appropriate acid chloride and then reacted with biphenol by the method described in [2]. The (S)-(-)-2-alkyloxypropionic acids were obtained by alkylation of (S)-(-)-ethyl lactate with 1-alkyl iodide in the presence of Ag_2O [16] followed by hydrolysis with NaOH. The final products **F m/n** were obtained by esterification using dicyclohexylcarbodiimide as a condensation agent in dichloromethane in the presence of dimethylaminopyridine and crystallized from ethyl alcohol.

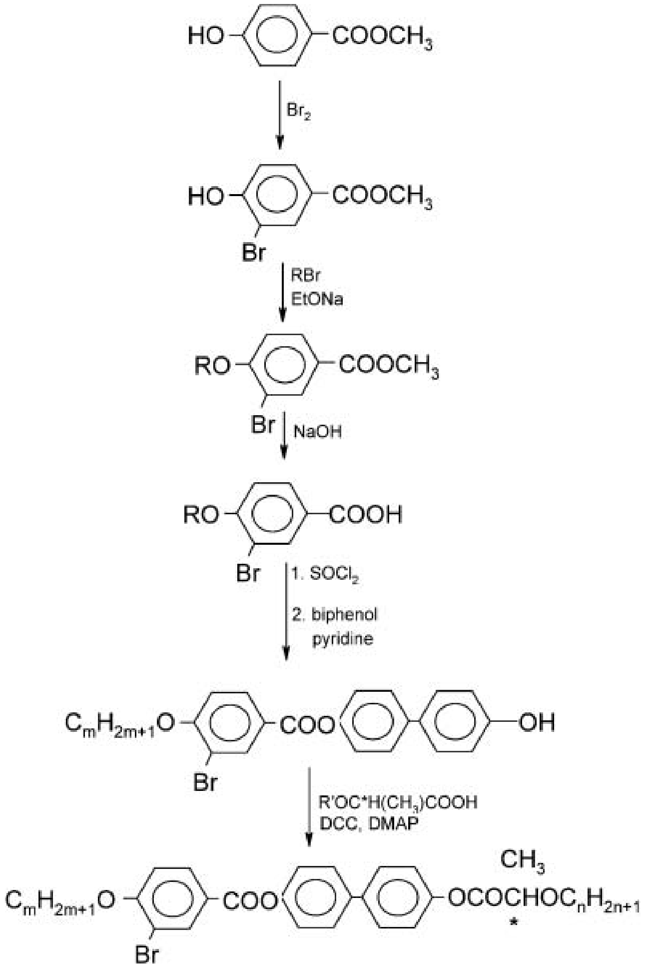
The general procedure of the synthesis of the compounds with bromine as a lateral substituent is presented in Scheme 2.

3-bromo-4-alkyloxybenzoic acids were prepared by bromination of methyl 4-hydroxybenzoate in chloroform at 0°C in the presence of a small amount of iron powder, and this was followed by alkylation and hydrolysis in the usual way. Further reactions were carried out under the same conditions as for fluorinated series (see Scheme 1) and the final products **Br m/n** were finally crystallized from ethyl alcohol.

All raw products were purified by column chromatography on silica gel using a mixture of 99% dichloromethane and 1% ethanol as an eluent. The chemical purity of the compounds was checked by high-pressure liquid chromatography (HPLC) carried out using an Ecom HPLC chromatograph with a silica gel column (Separon 7 μm, 3 × 150, Tessek) with a mixture of 99.9% toluene and 0.1% methanol as eluent, and detection of the eluting products by a UV-VIS detector (λ=290 nm). The chemical purity of all synthesized compounds was found within 99.6–99.9%.

The structures of the intermediate and final products were confirmed by ^1H nuclear magnetic resonance (NMR) spectroscopy using a 300 MHz Varian Spectrometer and solutions in $CDCl_3$ with tetramethylsilane as an internal standard. Spectral data for some intermediates and for the substances **F 8/7** and **Br 10/7** are presented below as an example (given in the order chemical shift multiplicity, number of protons, J/Hz/ and identification):

^1H-NMR ($CDCl_3$, 200 MHz [in ppm]) for 3-fluoro-4-octyloxybenzoic acid: 0.90 t (3H, CH_3); 1.30–1.60 m (1OH, CH_2); 1.85 quint. (2H, $\underline{CH_2}CH_2O$-) 4.10 t, (2H, -CH_2-O-); 7.00 dd* (1H, meta to F); 7.80 dd (1H para to F); 7.86 dd* (1H ortho to F) [*coupling H–F].



Br m/n

Scheme 2. General procedure for synthesis of **Br m/n** homologues series.

^1H-NMR ($CDCl_3$, 200 MHz [in ppm]) for 4-hydroxy-4'-(3-fluoro-4-octyloxybenzoyloxy)-biphenyl: 0.90 t (3H,CH_3); 1.30–1.80 m (12H, CH_2); 4.12 t (2H, CH_2OAr); 5.00 s (1H, OH) 6.90 d (2H ortho to OH); 7.05 t (1H, meta to F); 7.23 (2H, ortho to -OCO); 7.45 and 7.55 dd (4H ortho to Ar–Ar); 7.92 dd (1H para to F); 7.97 d (1H, ortho to F).

^1H-NMR ($CDCl_3$, 200 MHz [in ppm]) for 4-hydroxy-4'-(3-bromo-4decyloxybenzoyloxy)-biphenyl: 0.90 t (3H, CH_3); 1.25–1.85 m (16H, CH_2); 4.10 t (2H, CH_2OAr); 5.10 s (1H, OH); 6.90 d (2H, ortho to OH); 6.95 d (1H, meta to Br); 7.22 (2H, ortho to -OCO); 7.45 and 7.55 (4H ortho to Ar–Ar); 8.14 dd (1H, para to Br); 8.40 d (1H, ortho to Br).

^1H-NMR ($CDCl_3$, 200 MHz [in ppm]) for final product **F 8/7**: 0.90–1.00 m (6H, CH_3); 1.20–1.65 (2OH, CH_2); 1.84 m (2H, $\underline{CH_2}CH_2OAr$); 1.58 d (3H,

$\underline{\mathrm{CH}}_3$-C*H); 3.50 and 3.70 m (2H, $\underline{\mathrm{CH}}_2$OC*); 4.12 t (2H, $\mathrm{CH_2}$OAr); 4.20 q (1H, C*H); 7.05 t (1H, meta to F); 7.19 d (2H, ortho to -OCOC*); 7.27 d (2H, ortho -OCOAr); 7.60 m (4H, ortho to Ar–Ar); 7.92 dd (1H, para to F); 7.97 dd (1H, ortho to F).

^{1}H-NMR ($\mathrm{CDCl_3}$, 200 MHz [in ppm]) for final product **Br 10/7**: 0.90 m (6H, $\mathrm{CH_3}$); 1.20–1.70 m (24H, $\mathrm{CH_2}$); 1.58 d (3H, $\mathrm{CH_3}$-C*); 1.85 m (2H, $\underline{\mathrm{CH}}_2\mathrm{CH_2}$OAr); 3.50 and 3.70 m (2H, $\mathrm{CH_2}$OC*); 4.12 t (2H, $\mathrm{CH_2}$OAr); 4.18 q (1H, C*H); 6.97 d (1H meta to Br); 7.18 d (2H ortho to -OCOC*); 7.23 d (2H, ortho to -OCOAr); 7.60 m (4H, ortho to Ar–Ar); 8.12 dd (1H para to Br); 8.40 d (1H ortho to Br).

3. Experimental

Texture observations by polarizing optical microscope, and measurements of the spontaneous polarization, spontaneeous tilt angle and dielectric constant were carried out on planar samples filled in the isotropic phase into 25 μm thick glass cells by means of capillary action. The inner surfaces of the glass plates were covered by Indium Tin Oxide (ITO) electrodes and the polyimide layers unidirectionaly rubbed, which ensured planar (bookshelf) geometry. The further improvement of the alignment was achieved by an electric field (10–20 Hz, 40 kV cm^{-1}) applied for about 5–30 min. The LINKAM LTS E350 heating stage with TMS 93 temperature programmer was used for the temperature control, which enabled temperature stabilization within $\pm$0.1 K. Phase transition temperatures were checked by differential scanning calorimetry (DSC, Pyris Diamond Perkin-Elmer 7) on samples of 3–6 mg hermetically sealed in aluminium pans with cooling/heating runs at a rate of 5 K min^{-1} in a nitrogen atmosphere. Values of the spontaneous polarization, P_s, were evaluated from the $P(E)$ hysteresis loop detected during P_s switching in an a.c. electric field E of frequency 60 Hz. Values of the spontaneous tilt angle, θ_s, were determined optically from the difference between the extinction positions at crossed polarizers under opposite d.c. electric fields of $\pm$40 kV cm^{-1} on well-aligned samples. The X-ray small-angle scattering studies were carried out with a modified General Purpose X-ray Diffractometer (DRON) system equipped with Ge monochromator, working in reflection mode. Samples were prepared on a glass with one surface left free that assured homeotropic alignment (the temperature was controlled within 0.1 K). Temperature dependences of the real part, ε', of the complex permittivity ($\varepsilon^* = \varepsilon' - i\varepsilon''$) have been measured on cooling at a frequency of 120 Hz using a Schlumberger 1260 impedance analyzer.

4. Experimental results

For the materials studied, the sequence of phases and phase transition temperatures were determined by characteristic textures and their changes observed by polarizing microscope and from DSC measurements. All compounds from the **F m/n** or **Br m/n** series show the ferroelectric tilted smectic C* (SmC*) phase in a broad temperature range; the paraelectric smectic A (SmA) phase was not found. Mesomorphic properties of all newly synthesized compounds from the **F m/n** or **Br m/n** homologues series are collected in Table 1.

Compounds from the **F m/n** series (with the exception of **F 8/10**) possess a monotropic non-tilted smectic phase below the SmC* phase. The symmetric peak on the DSC cooling run (see Figure 1) is of characteristic shape for the transitions to the hexatic orthogonal smectic B (SmB) phase. The existence of the orthogonal SmB phase was confirmed also by X-ray studies (wide scattering angles) for the non-substituted compounds [18]. The crystal–crystal (Cr1–Cr2) transition was observed at temperatures below crystallization for all **F m/n** compounds with the exception of **F 10/10** (see Table 1). For bromine-substituted compounds, the ferroelectric SmC* phase can be supercooled down to room temperatures while the melting points do not differ much compared to fluorinated **F m/n** compounds

Table 1. Sequence of phases, phase transition temperatures (°C), transition enthalpies (ΔH (J/g)) from DSC measured on cooling (5 K min^{-1}) and melting point (m.p., °C) measured on heating for all studied compounds. **X** denotes the atom used as a lateral substituent; •, the phase exists, – the phase does not exist.

	X	m.p.	Cr2		Cr1		SmB		SmC*		I
F 8/5	F	89 [36.1]	•	48 [−9.5]	•	77 [−37.0]	•	88 [−4.9]	•	130 [−8.6]	•
F 8/7	F	90 [26.3]	•	52 [−2.5]	•	83 [−34.5]	•	87 [−2.5]	•	127 [−6.8]	•
F 8/10	F	95 [46.7]	•	53 [−10.2]	•	88 [−49.6]	–		•	125 [−8.2]	•
F 8/12	F	97 [44.7]	•	54 [−9.4]	•	80 [−47.0]	•	87 [−5.2]	•	121 [−6.2]	•
F 10/7	F	90 [19.6]	•	76 [−11.7]	•	85 [−19.1]	•	90 [−7.8]	•	128 [−7.2]	•
F 10/10	F	93 [25.4]	•		–	78 [−38.4]	•	89 [−10.4]	•	121 [−3.4]	•
Br 10/7	Br	86 [46.1]	•	17 [−8.3]	–		–		•	104 [−8.6]	•
Br 10/10	Br	87 [48.7]	•	21 [−39.9]			–	–	•	102 [−8.1]	•

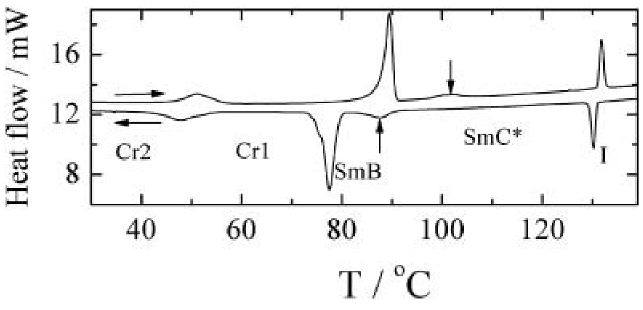


Figure 1. DSC plot recorded on subsequent heating and cooling for compound **F 8/5**. Vertical arrows indicate the peaks corresponding to the phase transition to the non-tilted hexatic SmB phase.

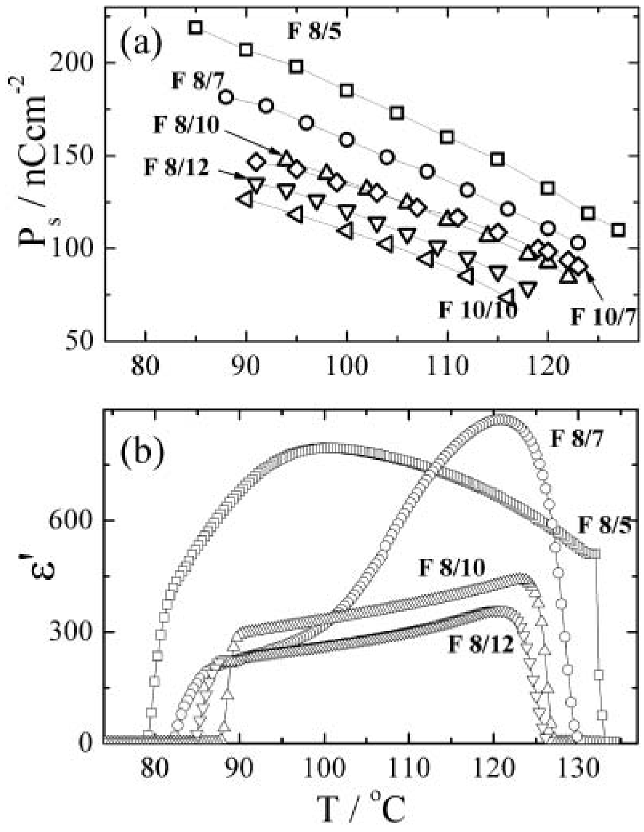


Figure 2. Temperature dependences of (a) the spontaneous polarization, P_s, and (b) the real part of the complex permittivity, ε′, measured at 120 Hz for the indicated compounds.

(see Table 1). The temperature stability of the SmC* phase slightly decreases and the melting point slightly increases with increasing number of carbon atoms **n** in the chiral chain. The Iso→SmC* phase transition is of the first order, possessing a narrow phase coexistence region and temperature hysteresis (the difference between the phase transition temperatures on heating and on cooling).

For **F m/n** compounds, temperature dependences of the spontaneous polarization are shown in Figure 2(a). The values of spontaneous polarization measured in the SmC* phase exhibit a continuous increase on cooling without saturation and they decrease with increasing length of both chiral **n** and non-chiral **m** chains. The temperature dependences of the complex permittivity measured at a frequency of 120 Hz are shown in Figure 2(b). There is a great increase of permittivity on cooling from the isotropic phase to the ferroelectric SmC* phase due to the strong contribution of the Goldstone mode. Depending on the homologue, the values of the spontaneous tilt angle are 38–43° at saturation.

For **Br m/n** compounds, the temperature dependences of the spontaneous polarization, spontaneous tilt angle and real part of the complex permittivity are shown in Figure 3. At the Iso→SmC* phase transition, there is a finite jump up in values of the spontaneous polarization and of the spontaneous tilt angle, which is typical for the first-order phase transition (see Figure 3). For **Br m/n** homologues, the values of the spontaneous tilt angle slightly increase with temperature decrease and are within the interval 43–44° for all compounds. These values are slightly higher than those obtained for **F m/n** homologues**.**

For selected **F m/n** and **Br m/n** compounds, the temperature dependences of the layer spacing, *d*, within the whole temperature range of the tilted ferroelectric SmC* phase are shown in Figures 4 (a) and (b), respectively. Within several degrees below the Iso–SmC* phase transition, there is a decrease in *d* values due to decreasing disorder of the long molecular axes inside the plane of the smectic layers. For **Br m/n** compounds, this decrease is followed by an increase in layer spacing values of the SmC* phase on cooling due to stretching of the aliphatic molecule chains while approaching crystallization (see Figure 4(b)). This increase is not found for the fluorine-substituted compounds due to the narrower temperature range of the SmC* phase (compared to the **Br m/n** compounds).

5. Discussion and conclusions

Two new series of fluorine- and bromine-substituted liquid crystalline materials containing a biphenyl benzoate core and chiral 2-alkoxypropanoate unit have been synthesized and studied.

A bar diagram showing the effect of the substituent type on the sequence of phases and phase transition temperatures for compounds with the same molecule core and with equal length of the chains (**n**=**m**=10) is shown in Figure 5(a). On cooling, the phase transition temperature to the SmC* phase decreases in a sequence

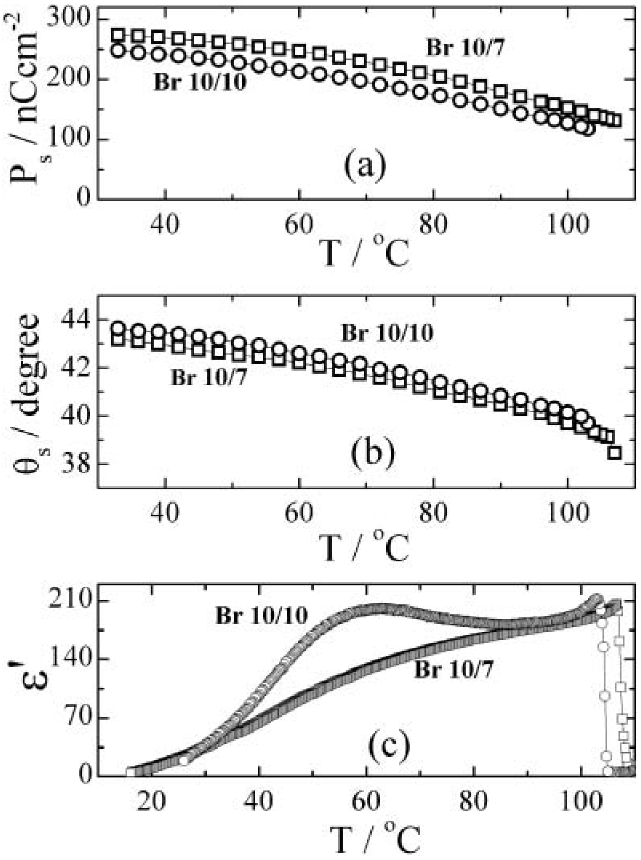


Figure 3. Temperature dependences of (a) the spontaneous polarization, P_s, (b) the spontaneous tilt angle, θ_s, and (c) the real part of the complex permittivity, ε', measured at 120 Hz for indicated compounds.

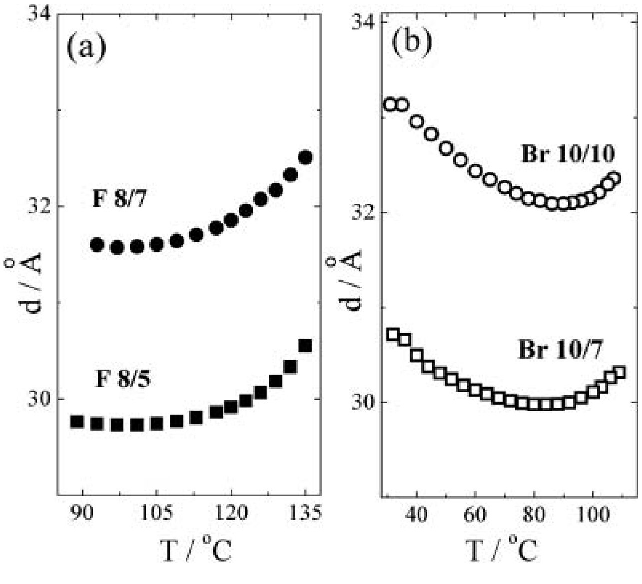


Figure 4. Temperature dependences of the layer spacing, *d*, in the ferroelectric SmC* phase for the indicated (a) **F m/n** and (b) **Br m/n** compounds.

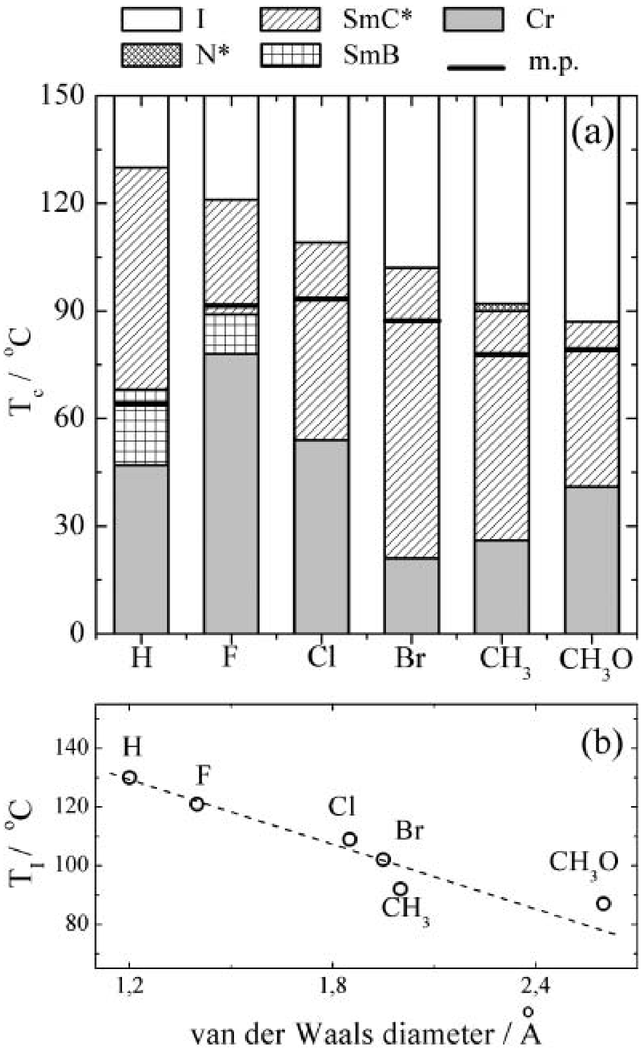


Figure 5. The effect of the substituent type (non-substituted (H), fluorine (F), chlorine (Cl) [21], bromine (Br), methyl (CH_3) [3] and methoxy (CH_3O) [4]) for compounds with equal length of the chains (**n**=**m**=10): (a) a bar diagram of the phases and phase transition temperatures and (b) the temperature of the transition to the isotropic phase (T_{ISO}) versus van der Waals diameter of the substituent.

H>**F**>**Cl**>**Br**>**CH$_3$**>**CH$_3$O**, which corresponds with the van der Waals diameters of teh atoms used as a lateral substituents, namely **H** – 1.20 Å, **F** – 1.40 Å, **Cl** – 1.85 Å, **Br** – 1.95 Å [19] and the calculated diameters [20] for methyl (2.00 Å) and methoxy (2.60 Å) substituents (see Figure 5(b)). This effect can be explained in terms of the steric influence of lateral substitutes on molecular packing. On the other hand, the influence of the bulk-size lateral substituents on melting point is not unambiguous for the materials studied here.

For all the compounds studied, the values of the spontaneous polarization exhibit a continuous increase on cooling and reach the highest value of 260 nC cm^{-2}

Table 2. Comparison of the values of the spontaneous polarization P_s (nC cm^{-2}) measured in the SmC* phase at a temperature 5 K below the phase transition for the compounds differing only in the type of lateral substituent (**X**). Data are presented for two groups of compounds, namely **X 10/10** and **X 8/5**. For **H**, **CH$_3$** and **CH$_3$O** compounds, the P_s values have been taken from [3, 4, 21] as indicated.

X 10/10	P_s	**Ref.**	**X 8/5**	P_s	**Ref.**
H	61	[3]	**H**	73	[21]
F	74	–	**F**	112	–
Cl	118	–	**Cl**	136	[21]
Br	135	–	–	–	–
CH$_3$	83	[3]	**CH$_3$**	121	[3]
CH$_3$O	57	[4]	**CH$_3$O**	66	[4]

for bromine-substituted materials. The spontaneous polarization slightly decreases with increasing length of both molecule chains and is larger for bromine-substituted compounds than for compounds substituted by fluorine.

In Table 2, values of the spontaneous polarization are given at a temperature 5 K below the transition to the ferroelectric SmC* phase for the selected compounds having the same molecular core and differing in the type of lateral substitution group.

For compounds differing only in the type of lateral substituents, the highest values of the spontaneous polarization were detected for chlorine- [5] and bromine-substituted compounds (see Table 2). This is probably caused mainly due to close packing of mesogenic cores, which could take place due to decrease of π-electron density on the phenyl rings drained by halogen atoms. A shorter packing distance of the mesogenic cores results in an increase in mass density of the halogen-substituted compounds, and might also cause more hindered rotation of the molecules around their long axes. In the case of a halogen atom, one should also take into account the relatively high dipole connected with the bond between the carbon atom and the halogen atom, which influences the total lateral dipole moment of the molecule. However, its orientation related to the dipole moment corresponding to the chiral part of the molecule is not fixed, and therefore its contribution to the spontaneous polarization could not be predicted unambiguously.

Values of the spontaneous polarization increase in the following sequence: **CH$_3$O<H<F<CH$_3$<Cl<Br** (see Table 2). For electron-donating substituents such as the CH$_3$O group, the π-electron density in the aromatic ring increases and intermolecular repulsion of negatively charged aromatic rings occurs. This repulsion together with the 'steric effect' of the bulky substituent prevents the closer packing of molecules and thus lowers the spontaneous polarization value.

Recently, this 'steric effect' was also observed by X-ray diffraction studies carried out on compounds with the same molecular core but slightly differing in the type of chiral chain [18]. It was shown that the average distance between the long axis of the neighbouring molecules inside the smectic layer of the ferroelectric SmC* phase increases with the van der Waals diameters of the chlorine, methyl and methoxy substituents.

Acknowledgements

This work was supported by grant Nos. 202/05/0431 from the Czech Science Foundation, No. IAA4112401 and IAA100100710 from the Grant Agency of the Academy of Sciences of the Czech Republic, Research Projects MSM 0021627501 from the Ministry of Education, Youth and Sports of the Czech Republic and AV0 Z10100520 from the Academy of Sciences of the Czech Republic. The authors gratefully acknowledge bilateral Czech–Polish project No. 8 (2006-2007) and, especially, Dr D. Pociecha for the access and help with X-ray measurements.

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