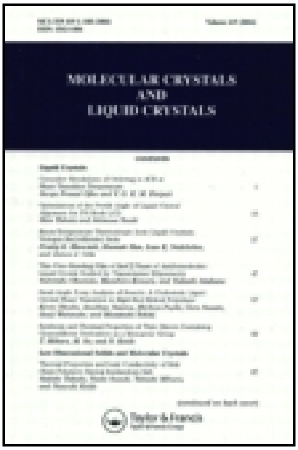

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Bi-Mesogenic Fluorinated Organosiloxanes: Synthesis and Mesomorphic Properties of a Novel Type of Ferro- and Antiferroelectric Liquid Crystal

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Bi-Mesogenic Fluorinated Organosiloxanes: Synthesis and Mesomorphic Properties of a Novel Type of Ferro- and Antiferroelectric Liquid Crystal

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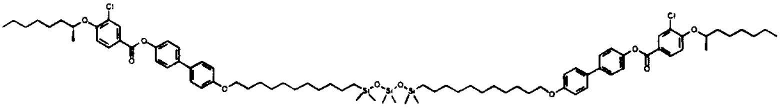
We present a new type of ferro- and antiferroelectric liquid crystal, based on bimesogenic systems with a siloxane spacer as the linking unit. Liquid crystalline materials bearing a perfluorinated chiral lactic acid ester as the terminal chain, were synthesised. We present the mesomorphic properties of these materials and discuss the influence of the siloxane linkage and the fluorine content on the phase behaviour.

Keywords: organosiloxane; ferroelectric; antiferroelectric; spontaneous polarisation; fluorine; lactic acid

INTRODUCTION

Recently we have reported on a series of organosiloxane based bimesogens exhibiting wide temperature range ferro- or antiferroelectric phases, depending only on the length of the siloxane spacer[1]. A representative of these types of compounds is shown in FIGURE 1.



A

FIGURE 1 The three building blocks of a biphenyl benzoate based dimer with a short siloxane spacer as the central linking group

Compound **A** comprises three different building blocks: the highly flexible, polar siloxane spacer, the rigid, highly polarisable aromatic core and the

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flexible, and apolar alkyl chains. Due to the chemical incompatibility of the constituent units, these materials are prone to form smectic phases, where the different units segregate into sub-layers. The objective of the present work is to determine the effect that fluorination of the terminal chains has on these compounds. Due to their unique properties, perfluorinated chains have a pronounced tendency to microphase separate in mixtures with aliphatic and aromatic compounds. Therefore, in siloxane based dimeric biphenyl benzoates a perfluorinated chain would represent a fourth ordering unit and its introduction should strongly influence the mesophase behaviour.

SYNTHESIS

The general synthetic route is outlined in FIGURE 2. Full details of the synthetic procedure will be published elsewhere.

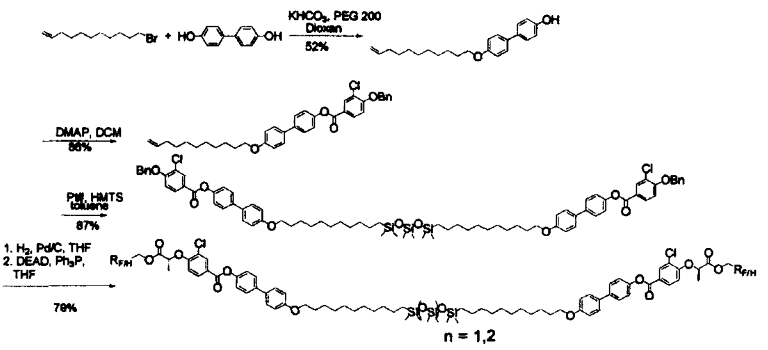


FIGURE 2 General synthetic route

In order to evaluate the influence of the siloxane spacer on the mesomorphic properties, the mono-mesogenic compound **F** was synthesised (FIGURE 3).

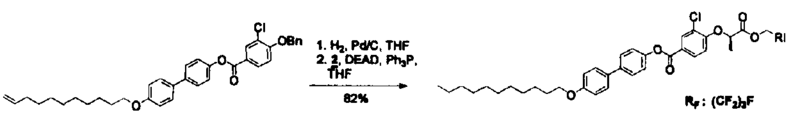


FIGURE 3 Synthetic route for the hydrogenated precursor molecule F

RESULTS

Phase behaviour

Textures and transition temperatures were studied by polarising optical microscopy. Thermal analysis was carried out using a Perkin-Elmer DSC 7 instrument. The electrooptic properties were determined according to ref [2]. Phase transition temperatures and the corresponding enthalpy values of the examined compounds are given in FIGURE 4. The monomesogenic compound **F** forms a modulated SmC_F* antiphase on cooling from the preceeding SmA* phase. The transition is marked by the appearance of a spherulitic texture in the preceding homeotropic areas and exhibits pseudo broken focal-conic defects[3]

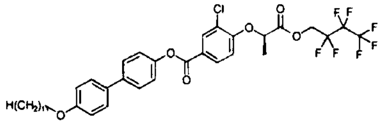
Electrooptic properties

Values for the tilt angle θ, the spontaneous polarisation P_s and the corrected spontaneous polarisation $P_{s,corr}$ ($P_{s,corr} = P_s/\sin\theta$) are given in TABLE 1.

phase	compound	θ [deg]	Ps [nC/cm^2]	Ps,corr
$SmC_{anti,F}*$	F4	38	35	57
SmC_A*	Si3(H)3	36	44	75
SmC_A*	Si3(F)3	42	240	359
SmC_F*	Si4(F)3	44	90	130

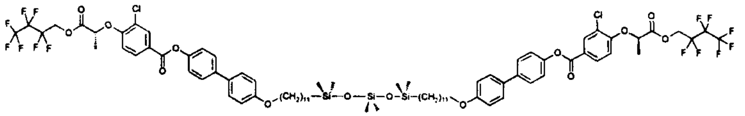
TABLE 1 P_s and θ for the SmC* phases, obtained on cooling 5°C below the phase transition.

Both compounds **Si3(H)3** and **Si3(F)3** which contain the hexamethyltrisiloxane unit as the linking group are antiferroelectric, without showing any high temperature ferroelectric phases. In contrast, using octamethyltetrasiloxane as the linking unit leads to formation of a ferroelectric SmC* phase in **Si4(F)3**. Likewise, the monomesogenic compound **F** which comprises no siloxane unit displays only ferroelectric behaviour in its chiral tilted phase. Comparing **Si3(H)3** and **Si3(F)3** shows, that fluorination of the terminal chain, though having no influence on the general electro optic behaviour, increases the P_s by a factor of 6. In general, introducing the siloxane unit leads to an increase in P_S. Comparing the values for **Si4(F)3** and **Si3(F)3** shows, that this effect is much more pronounced in the antiferro- than in the ferro-electric phase.



F

G* 66 [27.9] (69.4 [3.1] B) $\mathrm{SmC}_{\mathrm{anti,F}}$* 84 [0.7] SmA* 116 [9.5] I



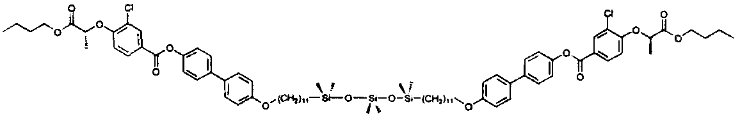
Si3(F)3

heating:

Cr1 35 [4.1] Cr2 71 [12] Cr 3 80 [5.9] $\mathrm{Sm1}_{\mathrm{A}}$* 101 [0.1] $\mathrm{SmC}_{\mathrm{A}}$* 131 [13] I

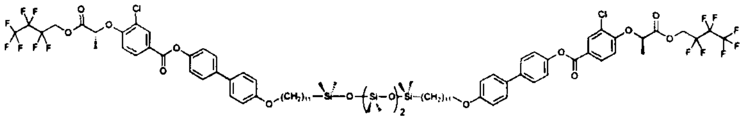
cooling:

I 130[-13.1] $\mathrm{SmC}_{\mathrm{A}}$* 96 [0.1] $\mathrm{SmF}_{\mathrm{A}}$* 32 [-6.4] Cr1



Si3(H)3

B 35 [0.6] $\mathrm{SmC}_{\mathrm{A}}$* 77 [3.7] I



Si4(F)3

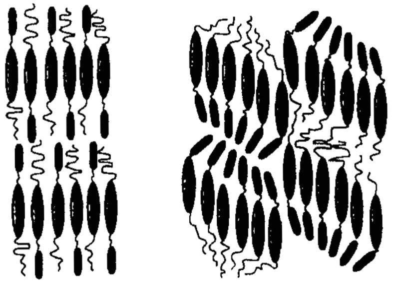
(Cr1 62 [9.0]) $\mathrm{SmC}_{\mathrm{F}}$* 107 [2.1] SmA* 117 [7.1] I

FIGURE 4 Phase transition temperatures [°C] and enthalpies [kcal/mole] for compounds investigated

DISCUSSION

The modulated SmC$_F$* phase of compound F

The formation of an antiphase for the fluorinated material **F** is in line with recent findings for compounds comprising both fluorinated and hydrocarbon chains in one molecule[4]. At high temperatures, fluorinated and hydrocarbon chains are miscible, thus monolayer formation in the SmA phase as depicted in FIGURE 5a is possible.



a) SmA b) SmC* antiphase

FIGURE 5 Possible packing arrangements of compound F in the mesophase

The head-to-tail arrangement allows the different steric requirements of the flexible hydrocarbon chains and the rigid, bulky perfluorinated tails to compensate each other. However, at lower temperature these two units have an increased tendency to segregate due to their chemical incompatibility. Therefore a noncentrosymmetric arrangement of molecules within the smectic layers becomes favourable. This would lead to a build up in packing strain, which can be relieved by the system transforming to a modulated smectic structure (FIGURE 5b)[5].

Spontaneous polarisation

In order to determine why fluorination of the terminal chain leads to a drastic increase in the value of the spontaneous polarisation, molecular modelling

(MM2, MOPAC/PM3) was performed on a model compound, that comprises the terminal chain and the last aromatic unit of the mesogenic core. The energy minimised conformers for the terminal chain were oriented, so that the aromatic core lies in the plane of tilt. It could be shown, that the carbonyl group (C=O) of the lactic acid ester does not adopt the all-trans conformation but is inclined towards the tilt plane, either pointing in the same as or the opposite direction to the chiral methyl group. Calculations of the transverse dipole moments μ of these structures show that μ points into the plane of tilt if the terminal chain is fluorinated, thus producing a positive P_s for all shown conformations. However, for the plain hydrocarbon chain the direction of μ depends on the relative orientation of the C=O group to the methyl group. This gives rise to negative P_s values if both groups lie on the same side of the tilt plane, and vice versa. As all conformers are energetically equivalent (difference in ΔH_f is ~ 0.3 kcal/mole) this results in a low spontaneous net polarisation for **Si3(H)3** compared to its perfluorinated analogue **Si3(F)3**.

Antiferro- and ferroelectric properties in dimers

The antiferro and ferroelectric behaviour in the materials synthesised is governed by the nature of the siloxane spacer. As the behaviour of the monomesogenic compound **F** (no siloxane units) shows, the dipole-dipole pairing energy in adjacent layers is not high enough to stabilise antiferroelectric ordering effectively, thus **F** displays only ferroelectric phases. In contrast, the trisiloxane unit in **Si3(F)3** leads to antiferroelectric behaviour, while introduction of the tetrasiloxane spacer in **Si4(F)3** produces ferroelectric mesophases again. This is in agreement with our earlier finding, that odd numbered siloxane units induce antiferroelectric ordering in liquid crystalline dimers, while even numbered siloxane spacers produce ferroelectric mesophases1[1]. We attributed this behaviour to different molecular shapes. It was assumed that odd numbered siloxane units adopt a bent conformation resulting in anticlinic arrangement and long-range antiferroelectric ordering of the two attached mesogens, while even-numbered siloxane spacers show a preference for straight conformation resulting in ferroelectric alignment. Different molecular shapes would also account for the differing P_s values of **Si3(F)3** and **Si4(F)3**, as a bent conformation imposes a higher hindrance on the reorientation of the molecule around its long axis, compared to a straight molecular structure. In order to test these assumptions, possible energy minimised conformations were generated for compounds **Si3(F)3** and **Si4(F)3**. The high flexibility of the siloxane chain is reflected in the fact that all structures show virtually equal steric energies, thus in the isotropic melt all conformations should be adopted with the same probability. However, in the mesophase possible spatial structures are restricted by their ability to allow effective packing of the mesogens. When the generated conformations were examined accordingly, it was shown, that for the trisiloxane unit a statistical abundance of bent conformers exists, while the tetrasiloxane unit exhibits more straight than bent conformations. However, it is debateable whether a mere statistical preference for bent structures alone is enough to account for the template effect of antiferroelectric siloxane containing dimers in mixtures with their analogue monomesogenic compounds[6]. Recently it has been suggested that in-plane spontaneous polarisation $P_{s,ip}$ parallel to the plane of tilt might contributes to stabilising antiferroelectric alignment[7]. Due to the difference in electronegativity between silicon and oxygen, the trisiloxane unit in its bent conformations exhibits a strong dipole moment parallel to the tilt plane. Interlocking of the bent siloxane spacers on forming the smectic layers orients these dipoles, thus producing in-plane spontaneous polarisation and reducing the Coulomb interaction energy. Additionally, if the sign of the in-plane polarisation alternates from layer to layer, the Coulomb interaction energy between the layers is minimised (FIGURE 6).

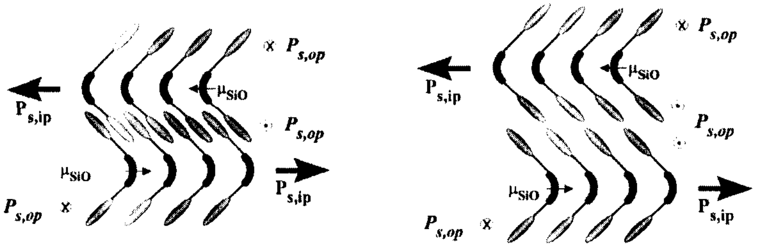


FIGURE 6 Antiferroelectric ordering in bent bi-mesogenic organosiloxanes: molecular dipoles couple to give rise to in-plane spontaneous polarisation

We believe that it is the synergistic interplay between steric requirements of the bent molecular structure and the dipole moments associated with these conformations that stabilises antiferroelectric ordering in bi-mesogenic compounds comprising an odd-numbered, central siloxane spacer.

CONCLUSIONS

We have synthesised novel fluorine containing organosiloxanes, which display a range of ferro- and antiferroelectric mesophases. The electro optic and mesomorphic properties of these materials can be related to their molecular structure. We attribute the occurrence of antiferroelectric behaviour to steric as well as polar interactions, which lead to an in-plane polarisation in the siloxane layers parallel to the tilt plane.

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