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

Microphasic separation-induced enantiotropic liquid crystal behaviour single phenyl unit series based on the fluorophobic effect

G. Fornasieri[a]; F. Guittard[a]; S. Géribaldi[a]
[a] Laboratoire de Chimie des Matériaux Organiques et Métalliques, Faculté des Sciences de Nice Sophia Antipolis, Parc Valrose, 06108 Nice cedex 2, France,

To cite this Article Fornasieri, G. , Guittard, F. and Géribaldi, S.(2003) 'Microphasic separation-induced enantiotropic liquid crystal behaviour single phenyl unit series based on the fluorophobic effect', Liquid Crystals, 30: 6, 663 — 669
To link to this Article: DOI: 10.1080/0267829031000114998
URL: http://dx.doi.org/10.1080/0267829031000114998

LIQUID CRYSTALS, 2003, VOL. 30, NO. 6, 663–669

Microphasic separation-induced enantiotropic liquid crystal behaviour single phenyl unit series based on the fluorophobic effect

G. FORNASIERI, F. GUITTARD* and S. GÉRIBALDI

Laboratoire de Chimie des Matériaux Organiques et Métalliques, Faculté des Sciences de Nice Sophia Antipolis, Parc Valrose, 06108 Nice cedex 2, France

(*Received 28 October 2002; in final form 23 January 2003; accepted 27 February 2003*)

The aim of this work was to demonstrate the possibility of obtaining enantiotropic liquid crystals containing a single phenyl group over a wide temperature range but without hydrogen bonding. We report the synthesis and characterization of several alkoxy monophenyl compounds linked by a thioester group to a 2-(perfluoro-*n* alkyl) ethyl chain. Compared with previous work using monophenyl cores, the synthetic pathway provides compounds is high yields from cheaper raw materials, i.e. 4-hydroxybenzoic acid. The mesomorphic properties were characterized using polarized light microscopy and differential scanning calorimetry. The effects of lengthening the substituents on the phenyl core were considered: varying the length of the alkyloxy groups had a marked effect, with the formation of enantiotropic mesomorphic phases with a maximum temperature range of 70°C. The temperature range of the mesomorphic phase is inversely proportional to the length of the alkyl chain and exhibits an odd–even effect. Decreasing the fluorinated chain length leads to a regular decrease in both the melting and clearing temperatures, giving room temperature transitions. This design approach using a single ring as the mesogenic core is of great interest in the development of low cost LC materials based on the fluorophobic effect.

1. Introduction

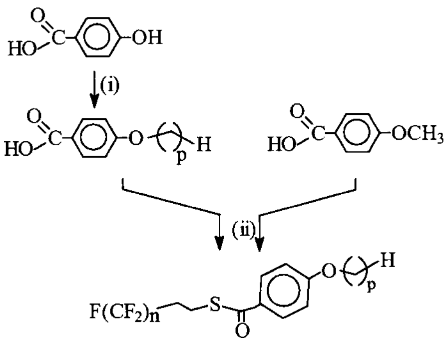
Liquid crystalline materials are characterized by very unusual properties which may be exploited in a range of different applications, not only in electro-optical devices but also as tools for surface reconstruction [1–4]. In such an area, the availability of low cost materials is a key factor in the further development of polymer or surface grafting; and the liquid crystal character can be tuned by appropriate molecular design. A general approach to obtain a mesomorphic material is the introduction of amphiphilic character: the presence in the molecular structure of elements with different degrees of compatibility can produce a segregation into distinct microdomains that is favourable to the appearance of a well organized phase such as a liquid crystal phase [5, 6]. This may be obtained by different possible combinations including, for example, hydrophilic–hydrophobic, aromatic–aliphatic, hydrocarbon–fluorocarbon and rigid–flexible. The last example is the most common and leads to calamitic liquid crystals that consist of two or more rings, which are bonded directly or by a linking group to each other, and to which are attached one or more flexible chains. Hence the replacement of one alkyl chain by a perfluorinated chain, which by comparison is rigid and incompatible (hydrophobic and oleophobic), can be considered as an element of incompatibility which favours the formation of well organized liquid crystalline phases, mostly smectic phase [7–9].

This general molecular approach may be used for the preparation of monophenyl derivatives with mesogenic properties. This is remarkable because such behaviour would not be expected for hydrocarbon series without additional hydrogen bonding. Thus, the development of a liquid crystal having just a single benzene ring [10–17] is a very interesting challenge because it would allow the possibility to access raw precursor materials less expensive than biphenyl derivatives and would lead to products with lower transition temperatures. However, it is worth noting that the careful choice of the spacer joining the fluorinated chain to the mesogenic core can govern the enantiotropic or monotropic LC character [18–22]. Thus, in this work we report the preparation of hydroxythiobenzoate derivatives, shown in figure 1, and characterize their LC properties. The mesomorphic behaviour of all the compounds has been studied by a

---

*Author for correspondence; guittard@unice.fr

Liquid Crystals ISSN 0267-8292 print/ISSN 1366-5855 online © 2003 Taylor & Francis Ltd
http://www.tandf.co.uk/journals
DOI: 10.1080/0267829031000114998



Cpd	n	p
B$_{1\sim2}$	4	1~2
C$_{1\sim14}$	6	1~14
D$_{1\sim2}$	8	1~2

Figure 1. Synthetic route to 2-(perfluoro-*n*-alkyl)ethyl-4-alkyloxythiobenzoate (**B$_{1\sim2}$**, **C$_{1\sim14}$**, **D$_{1\sim2}$**). Reagents and conditions: (i) $H(CH_2)_mBr$ $m=2$–14, KOH, EtOH/H_2O, reflux; (ii) $F(CF_2)_nC_2H_4SH$ $n=4,6,8$, DCC, DMAP, CH_2Cl_2, room temperature.

combination of differential scanning calorimetry (DSC) and polarizing optical microscopy (POM). The effects of lengthening the fluorinated chain or the hydrocarbon chain will be discussed.

2. Experimental

2.1. *Characterization*

Confirmation of the proposed structures of the intermediates and products was obtained by nuclear magnetic resonance (NMR) and mass spectrometry (MS). NMR spectroscopy was carried out using a Bruker AC 200 MHz spectrometer. All spectra were recorded using $CDCl_3$ or CD_3OD as solvent, with TMS as internal reference for ^{1}H NMR and $CFCl_3$ for ^{19}F NMR. MS was carried out using a Finnigan Matt INCOS 500E mass spectrometer coupled with a gas chromatograph (Varian 3400). The purity of the compounds was determined by thin layer chromatography (TLC) and by gas phase chromatography (GPC). The initial phase assignments and corresponding transition temperatures were determined using an Olympus BX60 polarizing microscope equipped with crossed polarizers and a Linkam TMS 94 – LTS 350 hot stage. Smectic to isotropic phase transition temperatures (clearing temperature) and the associated enthalpies of transition were investigated by DSC using a Perkin-Elmer PC series DSC7 calorimeter equipped with a TAC 7/DX thermal analysis controller from 25 to 190°C. The heating and cooling curves were obtained at the rate of 10°C min^{-1}. Zn and In were used as calibration standards. In all cases, the heating and cooling rates were reported as the maxima and minima of their endothermic and exothermic peacks.

2.2 *Synthesis*

4-Hydroxybenzoic acid (99%), 1-bromoalkane (>97%), 4-anisic acid (99%), *N*,*N'*-dicyclohexylcarbodiimide (DCC, 99%) and 4-(*N*,*N*-dimethylamino)pyridine (DMAP, 99%) were purchased from Aldrich and used as received. 2-(Perfluoro-*n*-butyl)ethyl-1-iodide, 2-(perfluorohexyl)ethane-1-thiol and 2-(perfluoro-*n*-octyl)ethane-1-thiol, obtained from Atofina, were also used as received. Unless specified the solvents were of unpurified reagent grade.

The synthesis of 2-(perfluoro-*n*-butyl)ethane-1-thiol from 2-(perfluoro-*n*-butyl)ethyl-1-iodide has been described previously [23].

2.2.1. *4-Alkyloxybenzoic acid (A$_{2\sim14}$)*

To a solution of 4-hydroxybenzoic acid (10 mmol) in water/ethanol (4 ml/11 ml) was added a solution of potassium hydroxide (20 mmol) in water (5 ml). The reaction mixture was stirred under reflux until solubilization took place, then alkyl bromide (11 mmol) was added slowly and stirred under reflux for 12 h. To the resulting precipitate was added a solution of potassium hydroxide (5 mmol) in water (1 ml); the mixture was then stirred for 2 h under reflux. The reaction mixture was dried under vacuum; the solid was acidified with HCl (10%) to pH 3, then washed three times with water and finally with light petroleum (40–60°C) to give a white solid. For **A$_8$**, 4-octyloxybenzoic acid: ^{1}H NMR (CD_3OD/TMS δ ppm, J Hz), 0.89 (3H, CH_3, t, $J=6.8$), 1.31 (10H, $(CH_2)_5CH_3$, m), 1.80 (2H, OCH_2CH_2, m, $J=6.8$), 4.01 (2H, OCH_2, t, $J=6.8$), 6.92 (2H$_{ar}$, d, $J=9.0$), 7.92 (2H$_{ar}$, d, $J=9.0$), (carboxylic acid H not detected).

2.2.2. *2-(Perfluoro-*n*-alkyl)ethyl-4-alkyloxythiobenzoate (B$_{1\sim2}$, C$_{1\sim14}$, D$_{1\sim2}$)*

To a solution of 4-alkyloxybenzoic acid (10 mmol) previously prepared, DCC (11 mmol) and DMAP (1 mmol) in freshly distilled dichloromethane (50 ml), 2-(perfluoro-*n*-alkyl)ethane-1-thiol (9 mmol) was added. The reaction mixture was stirred at room temperature for 6 h, after which the dicyclohexylurea was filtered off. The solvent was removed under vacuum from the resulting solution and the crude product purified by column chromatography over silica gel using dichloromethane/hexane (3/2) as eluent to give a white solid. For **C$_8$**, 2-(perfluorohexyl)ethyl-4-octyloxythiobenzoate: ^{1}H NMR ($CDCl_3$/TMS, δ ppm, J Hz), 0.89 (3H, CH_3, t, $J=6.8$), 1.31 (10H $(CH_2)_5CH_3$, m), 1.80 (2H, OCH_2CH_2, m, $J=6.8$), 2.48 (2H, CF_2CH_2, tt, $J_{HH}=8.1$, $J_{HF}=18.6$); 3.26 (2H, CH_2S, t, $J=8.1$); 4.01 (2H, OCH_2, t, $J=6.8$), 6.92 (2H$_{ar}$, d, $J=9.0$), 7.92 (2H$_{ar}$, d, $J=9.0$). ^{19}F NMR ($CDCl_3$/$CFCl_3$, δ ppm), -81.2 (CF_3, m), -114.9 [$(CF_2)_\alpha$, m], -122.3 [$(CF_2)_\beta$, m], -123.3 [$(CF_2)_\gamma$, m], -123.9 [$(CF_2)_\delta$, m], -126.6 [$(CF_2)_\omega$, m]. MS (70 eV) m/z (%), 593 ([M-F]$^+$, 0.5%); 233 (100%); 121 (42.7%), 69 (25.1%).

3. Results and discussion

3.1. *Synthesis*

The linker connecting the semifluorinated chain to the phenyl core is a thioester group. In previous works onto highly fluorinated liquid crystals, Taffin de Givenchy *et al.* studied the effect on mesomorphic behaviour of the spacer connecting the mesogenic core to the fluorinated chain for a series of partially fluorinated 4-biphenyl derivatives [18–20]. This study showed the strong impact of the connecting group: specifically, imine [22], ester and thioester groups to the appearance of mesomorphic behaviour over a wide temperature range, the thioester derivative, showing the widest smectic range (100°C). Therefore our design approach was to prepare a series of monophenyl compounds joined by a thioester group to a 2-(perfluoro-*n*-alkyl)ethyl group and having a alkyloxy substituent in the 4 position.

All the compounds were prepared from 2-(perfluoro-*n*-alkyl)ethane-1-thiol. It is worth noting that the 2-(perfluoro-*n*-butyl)ethane-1-thiol was synthesized from 2-(perfluoro-*n*-butyl)ethyl-1-iodide according to a method reported elsewhere [23]. The formation of the thioester was achieved through the reaction of a substituted benzoic acid with 2-(perfluoro-*n*-alkyl)ethane-1-thiol in the presence of DCC and DMAP. Thus, the preparation of the 2-(perfluoro-*n*-alkyl)ethane-4-alkyloxythiobenzoates was carried out in two steps. Firstly, the synthesis of the 4-alkyloxybenzoic acids ($\mathbf{A}_{2\sim14}$) involved the reaction of 4-hydroxybenzoic acid with an alkyl bromide in the presence of potassium hydroxide (Williamson reaction). The subsequent thioesterification of $\mathbf{A}_{1\sim14}$ with 2-(perfluoro-*n*-alkyl)ethane-1-thiol gave the 2-(perfluoro-*n*-alkyl)ethane-4-alkyloxythiobenzoate ($\mathbf{B}_{1\sim2}$, $\mathbf{C}_{1\sim14}$ and $\mathbf{D}_{1\sim2}$). The synthetic pathway is shown in figure 1. All the compounds are colourless and chemically stable. Yields are listed in table 1.

Table 1. Yields of monophenyl derivatives.

Compound	*n*	*p*	Yield % 1st step	2nd step	Overall
$\mathbf{B}_1$	4	1	—	84	84
$\mathbf{B}_2$	4	2	51	83	42
$\mathbf{C}_1$	6	1	—	93	93
$\mathbf{C}_2$	6	2	51	88	45
$\mathbf{C}_3$	6	3	68	83	56
$\mathbf{C}_4$	6	4	67	82	55
$\mathbf{C}_5$	6	5	62	85	53
$\mathbf{C}_6$	6	6	70	83	58
$\mathbf{C}_7$	6	7	77	82	63
$\mathbf{C}_8$	6	8	73	91	66
$\mathbf{C}_9$	6	9	77	85	65
$\mathbf{C}_{10}$	6	10	65	85	55
$\mathbf{C}_{11}$	6	11	57	83	47
$\mathbf{C}_{12}$	6	12	52	88	46
$\mathbf{C}_{13}$	6	13	63	84	53
$\mathbf{C}_{14}$	6	14	46	85	39
$\mathbf{D}_1$	8	1	—	89	89
$\mathbf{D}_2$	8	2	51	85	43

3.2. *Thermal and optical characterization*

The alkyloxy compounds were studied by polarizing optical microscopy (POM) and differential scanning calorimetry (DSC). These observations revealed enantiotropic

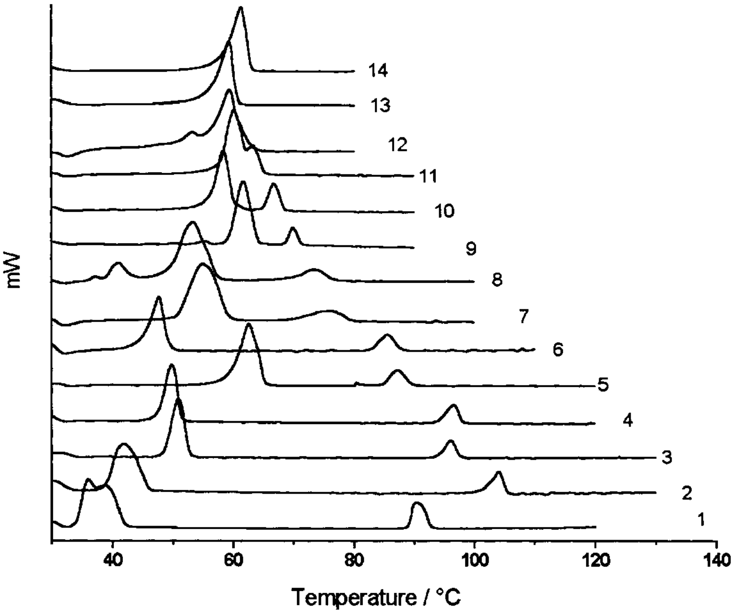


Figure 2. DSC heating curves for 2-(perfluorohexyl)ethyl-4-alkyloxythiobenzoate, *p* varied between 1 and 14 ($\mathbf{C}_{1\sim14}$).

behaviour dependent on the hydrocarbon chain length. The DSC curves of the 2-(perfluorohexyl)ethyl-4-alkyloxythiobenzoates (the hydrocarbon chain length varied from 1 to 14) are shown in figure 2. The phase transitions see on heating these new materials from the crystalline state are shown in figure 3. This diagram has been constructed by studying samples using DSC and POM. The transition temperatures and associated enthalpy changes are listed in table 2. In the phase diagram, the magnitude of the even–odd effect on varying *p* seems to be strongly attenuated after *p* reaches eight methylene units. The existence of two chemically different chains may give rise to intramolecular interactions which influence the total anisotropy of the system. Several points should be highlighted in figure 3. The general trends of the lines joining the points reveal two types of behaviour on varying the nature of the chains. Varying the length of the hydrocarbon group significantly influences the isotropization temperature, which ranges from 102 to 62°C for an *F*-hexyl perfluorinated chain. We observe that increasing the hydrocarbon chain length reduces the liquid crystal range up to the compound with thirteen methylene units for which no mesomorphic behaviour is observed. Indeed, except for the thirteen and fourteen methylene group compounds all the members of the series are enantiotrope. Decreasing the length of the hydrocarbon chain leads to an increase (with an odd–even effect) of the clearing point but a decrease of the melting point.

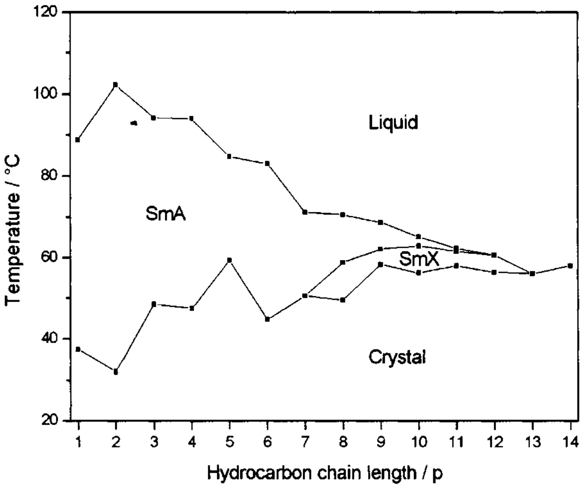
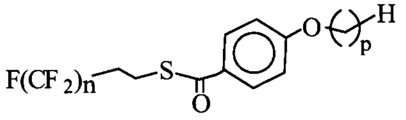


Figure 3. Dependence of the transition temperatures on the length of the hydrocarbon chain (*p* varied between 1 and 14 ($\mathbf{C}_{1\sim14}$)) for the 2-(perfluorohexyl)ethyl-4-alkyloxythiobenzoates.

Table 2. Transition temperatures for the alkyloxy derivatives (compounds $\mathbf{B}_{1\sim2}$; $\mathbf{C}_{1\sim14}$; $\mathbf{D}_{1\sim2}$); enthalpies of transitions (J g^{-1}) in square brackets. Cr, SmX, SmA and I indicate crystal, smectic X, smectic A, and isotropic phases, respectively. Parentheses indicate a monotropic transition (cooling).



			Transition temperatures /°C						
Compound	*n*	*p*	Cr		SmX		SmA		I
$\mathbf{B}_1$			●	17.7[a]			●	57.0[10.4]	●
$\mathbf{B}_2$			●	18.2[a]			●	78.2[11.8]	●
C	6	1	●	37.5[39.8]			●	88.9[10.4]	●
$\mathbf{C}_2$	6	2	●	32.1[45.0]			●	102.2[11.7]	●
$\mathbf{C}_3$	6	3	●	48.6[43.2]			●	94.3[11.2]	●
$\mathbf{C}_4$	6	4	●	47.5[33.4]			●	94.1[10.5]	●
$\mathbf{C}_5$	6	5	●	59.4[52.7]			●	84.9[10.4]	●
$\mathbf{C}_6$	6	6	●	44.8[35.2]	(●	47.0[a])	●	83.1[10.1]	●
$\mathbf{C}_7$	6	7	●	50.7[42.5]	(●	51.8[a])	●	71.2[9.3]	●
$\mathbf{C}_8$	6	8	●	49.6[46.7]	●	58.9[a]	●	70.6[9.6]	●
$\mathbf{C}_9$	6	9	●	59.6[64.4]	●	62.2[a]	●	68.7[9.8]	●
$\mathbf{C}_{10}$	6	10	●	56.3[54.0]	●	62.9[a]	●	65.1[10.4]	●
$\mathbf{C}_{11}$	6	11	●	58.1[18.4]	●	61.6[a]	●	62.4[10.9]	●
$\mathbf{C}_{12}$	6	12	●	56.5[15.6]	●	60.7[4.5]			●
$\mathbf{C}_{13}$	6	13	●	56.1[77.0]					●
$\mathbf{C}_{14}$	6	14	●	58.1[86.0]					●
$\mathbf{D}_1$	8	1	●	52.8[50.0]			●	109.0[9.4]	●
$\mathbf{D}_2$	8	2	●	50.2[45.6]			●	120.6[11.2]	●

[a] Transitions observed from optical microscopy.

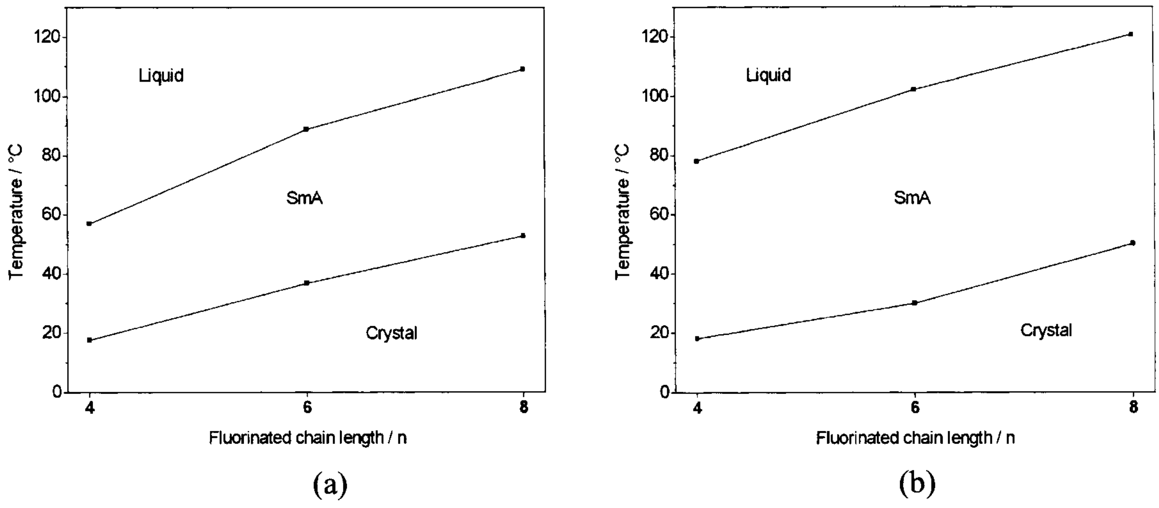


Figure 4. Comparison of the mesomorphic properties seen on heating for the 2-(perfluoroalkyl)ethyl-4-methyloxythiobenzoate (**B**$_1$, **C**$_1$, **D**$_1$), and 2-(perfluoroalkyl)ethyl-4-ethyloxythiobenzoate (**B**$_2$, **C**$_2$, **D**$_2$).

In consequence, the maximum range of the mesophase is obtained for a lower hydrocarbon, i.e. one or two methylene units. In fact the maximum range of the mesophase is 70°C on heating, compound C2, which is the first example of such a wide LC range within a monophenyl series.

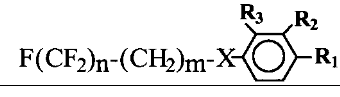
The effect of the fluorinated chain length was studied for the 2-(perfluoro-*n*-alkyl) ethyl-4-methyloxythiobenzoates, **B**$_1$, **C**$_1$, **D**$_1$, and the 2-(perfluoro-*n*-alkyl)ethyl-4-ethyloxythiobenzoates, **B**$_2$, **C**$_2$, **D**$_2$, (figure 4 and table 2). The change in transition temperatures on varying the perfluorinated chain length (from *F*-butyl to *F*-octyl with an increment of two fluoromethylene units) yields an almost constant mesomorphic range. Reducing the fluorinated chain length simultaneous decreases the melting and clearing points. The consequence of this is the ability of this system to produce room temperature LC materials, stimulateing important research focused on the development of omega functionalized monophenyl derivatives [24].

These data can be compared with previous works. In fact, increasing the temperature range of the mesophase is not straight forward in monophenyl series. In fact the literature contains many reports of examples of monophenyl derivatives with a long perfluoroalkyl group, and one, two or three substituents in the *ortho*, *meta* or *para* positions [10–17]. Nevertheless all these compounds are only slightly enantiotropic and indeed essentially monotropic. We show in table 3 and in figure 5 the ranges of mesophases exhibited by monophenyl derivatives from the literature, and for some compounds described in the present work, all of which show enantiotropic behaviour without hydrogen bond formation.

From these results, it seems clear that lateral substitution [10] is not a necessary condition for LC appearance, in agreement with previous studies [11, 13]. Furthermore, the nature of the linking group, i.e. the thioester function in our case, affects in a favourable manner the mesomorphic behaviour.

Concerning the optical observations, the mesophases of all the members of this series appear as bâtonnets on cooling from the isotropic liquid; these merge to give a well developed fan-shaped texture that is typical of a smectic mesophase (figure 6). The miscibility studies

Table 3. Monophenyl enantiotropic LCs from the literature [10, 13, 15, 16].



Compound	*n*	*m*	*X*	*R*$_1$	*R*$_2$	*R*$_3$	Ref
1a	6	2	O	NO_2	H	H	[16]
1b	8	2	O	NO_2	H	H	[16]
1c	10	2	O	NO_2	H	H	[16]
2	10	2	O	H	NO_2	H	[16]
3a	6	2	O	CN	H	H	[16]
3b	8	2	O	CN	H	H	[16]
3c	10	2	O	CN	H	H	[16]
4	10	2	O	H	CN	H	[16]
5	8	4	O	CN	H	H	[13]
6a	6	4	O	CO_2CH_3	H	H	[13]
6b	8	4	O	CO_2CH_3	H	H	[13]
7	8	4	O	CN	H	CH_3	[13]
8	10	2	OC(O)	H	NO_2	H	[10]
9	10	2	OC(O)	H	CN	H	[10]
10	8	2	OC(O)	H	H	NO_2	[15]
11	8	2	OC(O)	OC_6H_{13}	NO_2	H	[15]
12	8	2	OC(O)	OC_6H_{13}	Br	H	[15]
13	8	2	OC(O)	OC_8H_{17}	Br	H	[15]

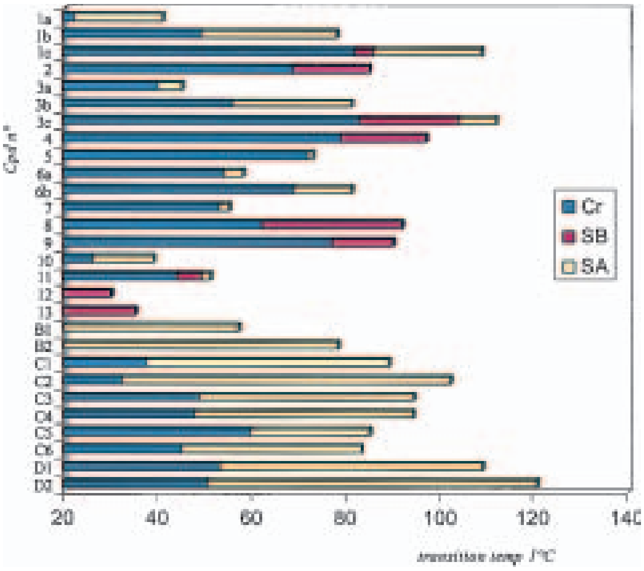


Figure 5. Mesophase behaviour of enantiotropic compounds without hydrogen bonds from the literature, cpd **1**$\sim$**13** [10, 13, 15, 16] and for some compounds investigated in this work ($\mathbf{B_{1\sim2}}$, $\mathbf{C_{1\sim6}}$, $\mathbf{D_{1\sim2}}$).

carried out using standard materials [25] showed that the phase described is of the smectic A type. The compounds with a long hydrocarbon chain ($p \geqslant 6$) show dimorphism with a SmA–SmX transition observed by microscopy. The characteristic textures of the phases observed are shown in figure 7. The POM micrographs (figures 6 and 7) were recorded for exactly the same sample position.

4. Conclusion

In this paper we have described the synthesis, and characterization of the mesomorphic properties, of a new class of monophenyl derivatives that show enantiotropic liquid crystalline behaviour, with mesophases stable over wide temperature ranges. The study of these series has allowed us to show two structure–property relationships. Increasing the length of the fluorinated moiety only weakly influences the melting temperatures, while increasing the number of methylene units in the hydrocarbon chain ($p = 1$–12) strongly decreases the temperature range of the mesophase. Furthermore it is clear that the length of the hydrocarbon chain is important, giving either enantiotropic ($p \leqslant 12$) or no LC behaviour ($p = 13,14$). Finally, smectic thermotropic dimorphism has been observed when $6 \leqslant p \leqslant 12$ with the *F*-hexyl tail. The straight forward synthetic method used demonstrates our ability to obtain low cost materials having useful LC behaviour. The molecular design approaches used for this series lead us to the possibility of using this thiobenzoate core in the preparation of low cost LC polymers for improving surface passivation [26, 27] or for the control of anchoring on solid matrices.

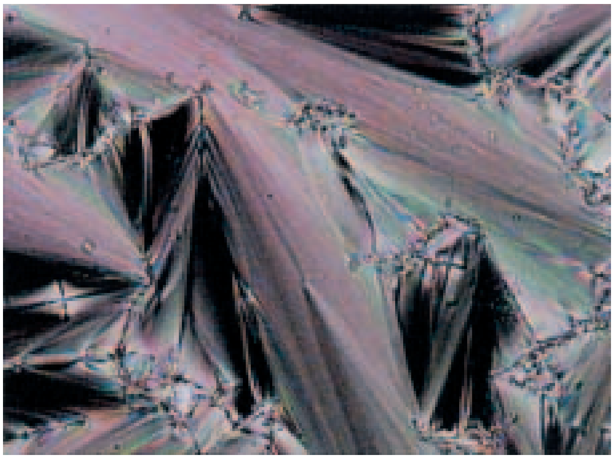


Figure 6. Optical polarizing micrograph of 2-(perfluorohexyl) ethyl-4-octyloxythiobenzoate, $\mathbf{C_8}$, (66×): $T = 64$°C, Cr–SmA.

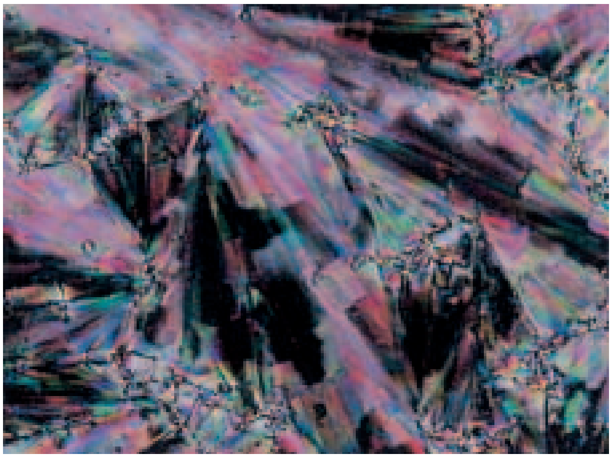


Figure 7. Optical polarizing micrograph of 2-(perfluorohexyl) ethyl-4-octyloxythiobenzoate, $\mathbf{C_8}$ (66×): $T = 59$°C, SmA–SmX (same position of the sample as in figure 6).

The authors thank Atofina for the gift of 2-(*F*-butyl)ethyliodide, 2-(*F*-hexyl)ethane-1-thiol, 2-(*F*-octyl) ethane-1-thiol. G.F. thanks MURST for financial support.

References

[1] Wang, J., Mao, G., Ober, C. K., and Kramer, E., 1997, *Macromecules*, **30,** 1906.

[2] Xiang, M., Li, X., Ober, C. K., Char, K., Genzer, J., Sivaniah, E., Kramer, E. J., and Fischer, D. A., 2000, *Macromolecules*, **33,** 6106.

[3] Kawata, K., 2002, *Chem. Record*, **2,** 59.

[4] Skaife, J. J., and Abbott, N. L., 2001, *Langmuir*, **17,** 5595.

[5] Thiemann, T., and Vill, V., 1998, *Handbook of Liquid Crystals*, Vol1, edited by D. Demus, J. Goodby, G. W. Gray, H.-W. Spiess and V. Vill (Weinheim: Wiley-VCH), p87.

[6] Tschierske, C., 1998, *J. mater. Chem.*, **8,** 1485.

[7] Inoi, T., 1994, *Organofluorine Chemistry Principles and Commercial Applications*, edited by R. E. Banks, B. E. Smart and J. C. Tatlow (New York: Plenum Press), p. 263.

[8] Guittard, F., Taffin de Givenchy, E., Géribaldi, S., and Cambon, A., 1999, *J. Fluorine Chem.*, **100,** 85 and references therein.

[9] Guittard, F., and Géribaldi, S., 2001, *Anisotropic Organic Materials – Approaches to Polar Order*, edited by R. Glaser, P. and Kaszynski, ACS Symposium Series (Washington DC: American Chemical Society), p. 180.

[10] Takenaka, S., 1992, *Chem. Commun.,* 1748.

[11] Bao, X., and Dix, L. R., 1996, *Mol. Cryst. liq. Cryst.*, **281,** 291.

[12] Okamoto, H., Murai, H., and Takenaka, S., 1997, *Bull. chem. Soc. Jpn.*, **70,** 3136.

[13] Johansson, G., Percec, V., Ungar, G., and Smith, K., 1997, *Chem. Mater.*, **9,** 164.

[14] Duan, M., Okamoto, H., Petrov, V. F., and Takenaka, S., 1998, *Bull. Chem. Soc. Jpn.*, **71,** 2735.

[15] Okamoto, H., Yamada, N., and Takenaka, S., 1998, *J. fluorine Chem.*, **91,** 125.

[16] Duan, M., Okamoto, H., Petrov, V. F., and Takenaka, S., 1999, *Bull. chem. Soc. Jpn.*, **72,** 1637.

[17] Petrov, V. F., Duan, M., Okamoto, H., and Takenaka, S., 2000, *Mol. Cryst. liq. Cryst.*, **350,** 187.

[18] Taffin de Givenchy, E., Guittard, F., Bracon, F., and Cambon, A., 1999, *Liq. Cryst.*, **26,** 1163.

[19] Taffin de Givenchy, E., Guittard, F., Bracon, F., and Cambon, A., 1999, *Liq. Cryst.*, **26,** 1371.

[20] Taffin de Givenchy, E., Guittard, F., Géribaldi, S., and Cambon, A., 1999, *Mol. Cryst. liq. Cryst.*, **332,** 2511.

[21] Guittard, F., Sixou, P., and Cambon, A., 1995, *Liq. Cryst.*, **19,** 667.

[22] Guittard, F., Sixou, P., and Cambon, A., 1997, *Mol. Cryst. liq. Cryst.*, **308,** 83.

[23] Szonyi, F., and Cambon, A., 1989, *J. fluorine Chem.*, **42,** 59.

[24] Fornasieri, G., Guittard, F., and Géribaldi, S., 2003, *Lig. Cryst.*, **30,** 251.

[25] Diele, S., Lose, D., Kruth, H., Pelzl, H., Guittard, F., and Cambon, A., 1996, *Liq. Cryst.*, **21,** 603.

[26] Fornasieri, G., Guittard, F., and Géribaldi, S., 2003, *Polymer* (submitted).

[27] Fornasieri, G., Guittard, F., Taffin de Givenchy, E., and Géribaldi, S., 2003, FR Patent, 0 300 206.