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LC Acrylic Monomers Incorporating Monothiobenzoate Unit

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The development of LC monophenyl unit is of a great interest for reach low cost LC materials. The aim of this work was to demonstrate the possibility to obtain monomer incorporating single phenyl unit for LC field. We report the synthesis and the characterization of acrylic monomers in fluorinated series which differ by the lengthening of the hydrocarbon spacer linking the acrylic part to the "mesogenic" core. LC behaviour was determined by DSC and POM apparatus. The increasing of the length of this hydrocarbon spacer dramatically decreases the span of the mesophase of type smectic. For a long spacer no mesomorphism is observed.

Keywords: acrylic; monophenyl; perfluoro; smectic; thiobenzoate

1. INTRODUCTION

Low cost polymers need the molecular design of monomers incorporating monophenyl unit [1]. In a previous work, we have described for the first time the possibility of obtaining enantiotropic liquid crystals containing a single phenyl group over a wide temperature range but without hydrogen bonding [2,3]. This kind of behaviour can be explained by the presence of perfluorinated tail as "pro-mesogenic" part linked to a single unit core through a spacer [4]. It is worth noting that the careful choice of the spacer joining the fluorinated chain to the mesogenic core

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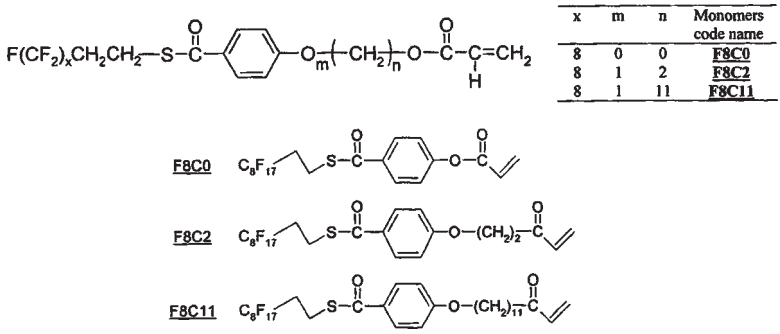

x	m	n	Monomers code name
8	0	0	F8C0
8	1	2	F8C2
8	1	11	F8C11

FIGURE 1 Investigated monomers.

can govern the enantiotropic or monotropic LC character [5–18]. In previous work we have also highlighted the thioester connector as one of the best linking group for the expression of the best segregation into distinct microdomains that is favourable to the appearance of a well organized phase such as a liquid crystal phase [19–22]. In order to reach LC polymers containing a single thiobenzoate unit as rigid core, we present in this work the preparation, the characterization and the LC evaluation of a series of hemifluorinated compounds as described in Figure 1.

The mesomorphic behaviour of all compounds has been studied by a combination of differential scanning calorimetry (DSC) and polarizing optical microscopy (POM). The effect of the hydrocarbon spacer bonding the thiobenzoate core to the acrylic part will be discussed.

2. EXPERIMENTAL PART

2.1. Materials

4-hydroxybenzoic acid (99%), methyl chloroformate (99%), *N*,*N*′-dicyclohexylcarbodiimide (DCC, 99%), 11-bromoundecan-1-ol (97%), Triphenylphosphine (99%), 4-hydroxybenzaldéhyde (98%), 2-hydroxyethylacrylate (95%) were purchased from Aldrich and used as received. Acryloyl chloride (97%) was purchased from Fluka and was used without further purification. Diisopropylazodicarboxylate (95%) was purchased from Merck. 2-(perfluorooctyl)ethane-1-thiol was given by Atofina. Unless specified the solvents were of unpurified reagent grade.

2.2. Methods

Confirmation of the 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. Spectra were recorded using deuterated solvent with TMS as internal reference for ^{1}H NMR and $CFCl_3$ for ^{19}F NMR. MS was carried out using a Thermo Finnigan spectrometer with an EI mode (70 eV) and a direct introduction. The purity of the monomers was determined by thin layer chromatography. The initial phase assignments and corresponding transition temperatures were determined using an Olympus BX 60 optical microscope equipped with crossed polarizers. The samples were thermostated by means of a Linkam Scientific Instruments LTS 350 heating unit and TMS 94 temperature control by the same manufacturer. Temperatures and enthalpies of transition were investigated by DSC using a Mettler Toledo DSC 821 instrument. Samples of 5–10 mg were placed in aluminium capsules and heated in a static nitrogen atmosphere. The heating and cooling curves were obtained at the rate of 5 or 10°C min^{-1}. The phase transition temperatures of the monomers were extrapolated as the onset temperatures. The phase transitions temperatures of the polymers were taken as the maximum temperatures in the DSC enthalpic peaks.

2.3. Synthesis

The synthesis 2-perfluorooctylethyl-4-acryloyloxythiobenzoate (**F8C0**), 2-perfluorooctylethyl-4-(2-acryloyloxyethyloxy)thiobenzoate (**F8C2**) and 2-perfluorooctylethyl-4-(11-acryloyloxyundecyloxy)thiobenzoate (**F8C11**) are described in detail in Figure 2. Yields are reported in Table 1.

4-methoxycarbonyloxybenzoic Acid (1)

To a solution of sodium hydroxide (2.40 g, 60 mmol) in water (60 mL) which was maintained at −10°C, 4-hydroxybenzoic acid (2.76 g, 20 mmol) was added under vigorous stirring. Methyl chloroformate (3.78 g, 40 mmol) was added dropwise at a temperature lower to −5°C. The reaction mixture was allowed to room temperature and stirred overnight. The resulting solution was acidified by HCl (10%) to pH 5 with the formation of a thick precipitate. The solid was filtered off, washed with water and finally dried to yield **1** as a white solid (yield 92%).

^{1}H NMR (CD_3OD/TMS, δ ppm J Hz): 3.91 (3H, CH_3O, s); 7.31 ($2H_{ar}$, d, $J = 9.0$), 8.09 ($2H_{ar}$, d, $J = 9.0$); the acid proton was not observed.

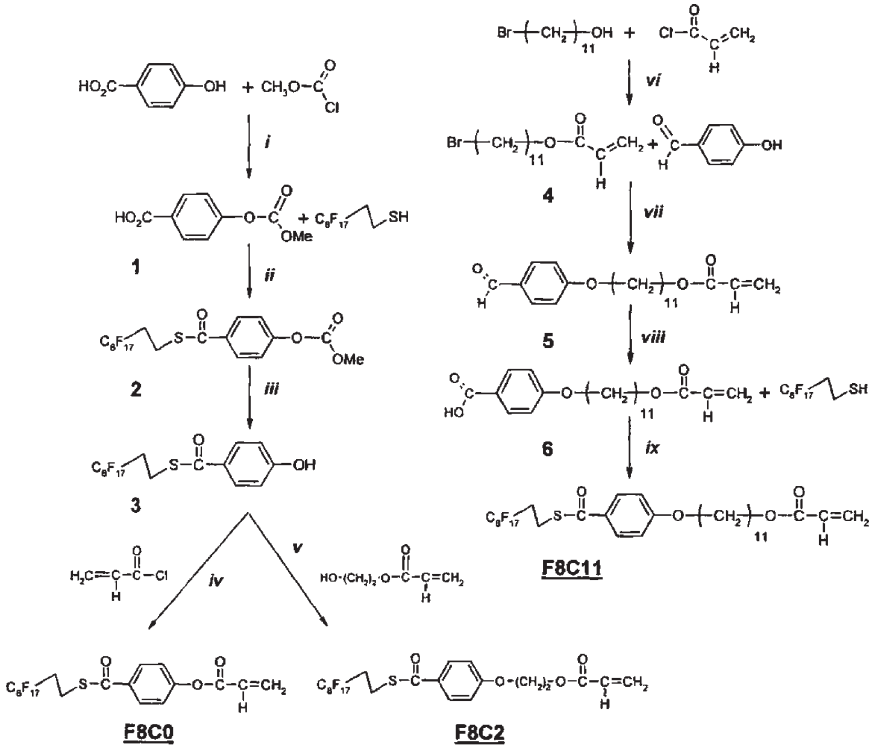

FIGURE 2 Synthetic route to monomers. Reagents and conditions: (i) NaOH, 0°C; (ii) (ix) DCC, CH_2Cl_2; (iii) NH_3, EtOH; (iv) (vi) $Et_2O/N(Et)_3$, 0°C; (v) TPP/DIAD, THF; (vii) K_2CO_3, Acetone, (viii) CrO_3,H_2SO_4, Acetone.

TABLE 1 Yields for Monomers

Cpd n°	R_F value	Spacer length	Yield	Overall
1	–	–	92	–
2	C_8F_{17}	–	93	–
3	C_8F_{17}	–	100	–
F8C0	C_8F_{17}	0	80	68
F8C2	C_8F_{17}	2	56	48
4	–	11	79	–
5	–	11	76	–
6	–	11	75	–
F8C11	C_8F_{17}	11	84	38

2-(perfluorooctyl)ethyl-4-hydroxythiobenzoate (3)

To a dichloromethane solution (50 mL) of 4-methoxycarbonyloxybenzoic acid (1) previously prepared (11 mmol), was added 11 mmol of DCC (*N*,*N*′-dicyclohexylcarbodiimide) and 2-(perfluoro-n-alkyl)ethane-1-thiol (10 mmol). The reaction mixture was then stirred for 12 hours at room temperature and the dicyclohexylurea precipitated was filtrered off. The crude product was finally purified by column chromatography over silica gel using dichloromethane/hexane (3/2) as eluent to give a white solid (**2**). This solid (10 mmol) was then stirred during 4 hours in 15 mL of aqueous ammoniac (30%), 15 mL of dichloromethane and 10 mL of ethanol. Water was eliminated using an azeotropic distillation with ethanol and lyophilization to give a white product (**3**) which can be used without any purification.

3c: ^{1}H NMR ($CDCl_3$/TMS, δ ppm J Hz), 2.48 (2H, $CF_2CH_2CH_2$, tt, $J_{HH} = 8.1$, $J_{HF} = 18.6$); 3.26 (2H, $CF_2CH_2CH_2$, t, $J = 8.1$); 6.93 ($2H_{ar}$, d, $J = 8.95$), 7.82 ($2H_{ar}$, d, $J = 8.95$); 9.36 (phenolic acid proton).

2-(perfluorooctyl)ethyl-4-acryloyloxythiobenzoate (F8C0)

To a stirred solution of **3** (10 mmol), in freshly distilled diethylic ether (30 mL), under inert atmosphere (N_2) and at the temperature of 0°C, we added dropwise acryloyl chloride (17.5 mmol). The solution was maintained at 0°C for 2 hours and then stirred for 12 hours at room temperature. The precipitated salt was filtered off and the solvent removed under vacuum. The crude product was finally purified by column chromatography over silica gel using dichloromethane/hexane (2/1) as eluent to give a white solid (**F8C0**).

F8C0: ^{1}H NMR ($CDCl_3$/TMS, δ ppm J Hz), 2.48 (2H, $CF_2CH_2CH_2$, tt, $J_{HH} = 8.85$, $J_{HF} = 18.30$); 3.22 (2H, $CF_2CH_2CH_2$, t, $J = 8.85$); 6.08 (1H, CH = cis, dd, $J_{HH} = 1.75$, $J_{cis} = 10.10$); 6.22 (1H, CH = gem, dd, $J_{cis} = 10.10$, $J_{trans} = 17.20$); 6.43 (1H, CH = trans, dd, $J_{HH} = 1.75$, $J_{trans} = 17.20$); 7.96 ($2H_{ar}$, d, $J = 8.95$), 7.29 ($2H_{ar}$, d, $J = 8.95$). ^{19}F NMR ($CDCl_3$/$CFCl_3$, δ ppm), −82 (CF_3, m), −115.5 [$(CF_2)_\alpha$, m], −123 [$(CF_2)_{\beta,\gamma,\delta}$, m], −124 [$(CF_2)_\varepsilon$, m], −124.5 [$(CF_2)_\zeta$, m], −127 [$(CF_2)_\eta$, m]. MS (70 eV) m/z (%), 55 (98.2%); 65 (41.6%); 69 (7.9%); 92 (100%); 121 (100%); 175 (100%); 572 (21.6%).

2-perfluorooctylethyl-4-(2-acryloyloxyethyloxy)thiobenzoate (F8C2)

Under Nitrogen atmosphere was added to a solution of 2-(perfluorooctyl)ethyl-4-hydroxythiobenzoate (**3**) (10 mmol), DIAD (diisopropylazodicarboxylate) (10 mmol) in THF freshly distilled, a solution of hydroxyethylacrylate (10 mmol) and TPP (triphenylphosphine)

(10 mmol) in THF freshly distilled. The solution was stirred for 18 hours. The solvent was removed under vacuum and the mix treated with diethylic ether. The crude product was finally purified by column chromatography over silica gel using dichloromethane as eluent to give a white solid (**F8C2**).

F8C2: ^{1}H NMR ($CDCl_3$/TMS, δ ppm J Hz), 2.48 (2H, $CF_2CH_2CH_2$, tt, $J_{HH} = 7.70$, $J_{HF} = 18.30$); 3.23 (2H, $CF_2CH_2CH_2$, t, $J = 7.70$); 4.32 (2H $OCH_2CH_2OC(O)$, d, $J_{HH} = 8.85$), 4.55 (2H $OCH_2CH_2OC(O)$, d, $J_{HH} = 8.85$), 5.95 (1H, CH = cis, dd, $J_{HH} = 1.75$, $J_{cis} = 10.25$); 6.16 (1H, CH = gem, dd, $J_{cis} = 10.25$, $J_{trans} = 17.20$); 6.45 (1H, CH = trans, trans, dd, $J_{HH} = 1.65$, $J_{trans} = 17.20$); 7.96 ($2H_{ar}$, d, $J = 8.85$), 7.00 ($2H_{ar}$, d, $J = 8.85$). ^{19}F NMR ($CDCl_3$/$CFCl_3$, δ ppm), –82 (CF_3, m), –115.5 [$(CF_2)_\alpha$, m], –123 [$(CF_2)_{\beta,\gamma,\delta}$, m], –124 [$(CF_2)_\varepsilon$, m], –124.5 [$(CF_2)_\zeta$, m], –127 [$(CF_2)_\eta$, m]. MS (70 eV) m/z (%), 55 (98.7%); 99 (100%); 121 (15.06%); 92 (100%); 69 (7.74%), 65 (13.62%), 572 (1.0%).

2-perfluorooctylethyl-4-(11-acryloyloxyundecyloxy)-thiobenzoate (F8C11)

To a dichloromethane solution (50 mL) of **6** previously prepared by classical methods (11 mmol), we added 11 mmol of DCC (*N*,*N*′-dicyclohexylcarbodiimide) and 2-(perfluoro-n-alkyl)ethane-1-thiol (10 mmol). The reaction mixture was then stirred for 12 hours at room temperature and the dicyclohexylurea precipitated was filtrered off. The crude product was finally purified by column chromatography over silica gel using dichloromethane/hexane (3/2) as eluent to give a white solid. Yield 38%.

F8C11: ^{1}H NMR ($CDCl_3$/TMS, δ ppm J Hz), 2.48 (2H, $CF_2CH_2CH_2$, tt, $J_{HH} = 7.7$, $J_{HF} = 18.30$); 3.23 (2H, $CF_2CH_2CH_2$, t, $J = 7.7$); 4.07 (ΦOCH_2, t, $J_{HH} = 6.35$); 3.93 ($CH_2OC(O)$, t, $J_{HH} = 6.35$); 4.07 (ΦOCH_2CH_2, q, $J_{HH} = 6.35$); 3.93 ($CH_2CH_2OC(O)$, q, $J_{HH} = 6.35$); 1.25 ($CH_2(CH_2)_7CH_2$ multiplet); 5.95 (1H, CH = cis, dd, $J_{HH} = 1.65$, $J_{cis} = 10.25$); 6.16 (1H, C*H* = gem, dd, $J_{cis} = 10.25$, $J_{trans} = 17.20$); 7.0 (1H, CH = trans, dd, $J_{HH} = 1.65$, $J_{trans} = 17.20$); 7.96 ($2H_{ar}$, d, $J = 8.85$), 7.92 ($2H_{ar}$, d, $J = 8.85$). ^{19}F NMR ($CDCl_3$/$CFCl_3$, δ ppm), –82 (CF_3, m), –115.5 [$(CF_2)_\alpha$, m], –123 [$(CF_2)_{\beta,\gamma,\delta}$, m], –124 [$(CF_2)_\varepsilon$, m], –124.5 [$(CF_2)_\zeta$, m], –127 [$(CF_2)_\eta$, m]. MS (70 eV) m/z (%), 55 (36.81%); 65 (7.58%); 69 (7.9%); 92 (100%); 175 (100%); 345 (4.79%); 572 (1.33%).

3. RESULTS AND DISCUSSIONS

Preparation of the monophenyl monomers was performed according to two different pathways showed in Figure 2.

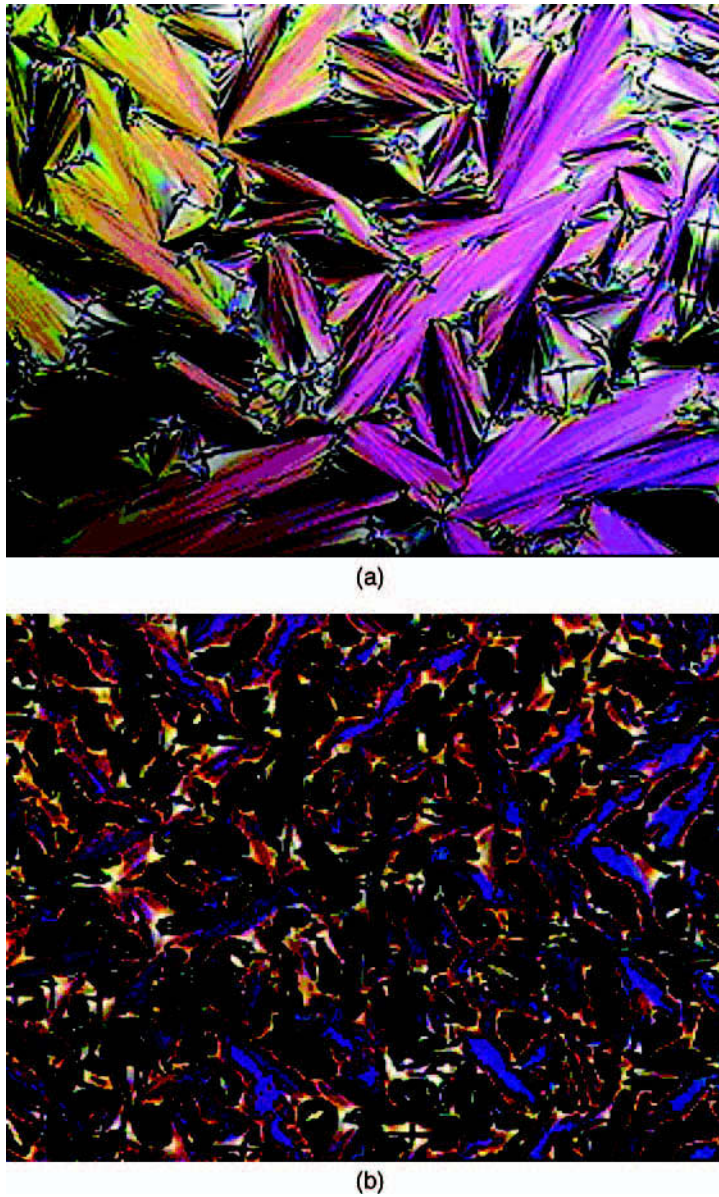

FIGURE 3 (a) Optical polarizing micrograph displayed by **F8C0** on cooling from isotropic melt (temperature 90°C, ×33); (b) Optical polarizing micrograph displayed by **F8C2** on cooling from isotropic melt (temperature 64°C, ×33).

The thioesterification of 4-hydroxybenzoic acid was accomplished by the protection of the hydroxy substituent of the 4-hydroxybenzoic acid, followed by the coupling of the carboxylic acidic group with a fluorinated thiol in presence of *N*,*N*′-dicyclohexylcarbodiimide (DCC) and finally deprotection of the hydroxy group in basic conditions to yield to the intermediate (**3**). The carbonate protecting group was selected because deprotection occurs under mild conditions which do not affect thioester linkage. The deprotection with aqueous ammonia (30%) was carried out in a ethanol/CH_2Cl_2 to solubilized all compounds. This quickly procedure (4 hours) gives quantitatively the hydroxyl derivative.

F8C0 was obtained by coupling **3** with acryloyl chloride in presence of triethylamine. Furthermore **3** yields to **F8C2** by grafting with (hydroxyethyl)acrylate using classical Mitsunobu's conditions [23]. We prepared **F8C11** using another specific synthetic pathway. 11-bromoundecyl acrylate (**4**) is coupled (Williamson mild conditions with the use of potassium carbonate) with 4-hydroxybenzaldehyde to give **5**. The use of 4-hydroxybenzaldehyde eliminated a protection/deprotection step of the carboxylic acid function. Oxidation of aldehyde in corresponding acid (**6**) is carried out with Jones reactant, i.e., relatively mild conditions. Finally coupling **6** with 2-(perfluorooctyl) ethane-1-thiol in presence of DCC gave **F8C11**. The different yields are reported in Table 1.

Monomers were studied by Polarizing Optical Microscopy (P.O.M.) and Differential Scanning Calorimetry (DSC) on heating and cooling with a scanning rate of 10°C/min. F8C0 and F8C2 exhibit an enantiotropic mesophase, identified as smectic by the observation of typical focal conic fans (Figs. 3a and 3b) while F8C11 does not present any L.C. behavior.

Our measurements showed that the L.C. gap of the compounds is dependant of the spacer chain (n = 0, 2, 11). The corresponding

TABLE 2 Transition Temperatures for Monomers Observed on Heating from DSC (Scanning Rate 10°C min^{-1})

	Transition temperature (°C)[a]					Enthalpies ($J.g^{-1}$)	
Compound	C		SmA		I	ΔH_{C-S}	ΔH_{S-I}
F8C0	•	98	•	131	•	−57,98	−11,72
F8C2	•	(83[b])	•	86	•	–	−63,26
F8C11	•	53					

[a]C, crystal; Sm, smectic; I, isotropic

[b]Observed by polarized microscopy; () monotropic transition.

transition temperature and enthalpy from DSC experiments are listed in Table 2.

The effect of the spacer length (x value) was studied for **F8Cx** with x = 0, 2, 11. Increasing the spacer reduces dramatically melting and clearing point temperature and the mesomorphic range (from **F8C0** to **F8C2**) until a total disappearance of the liquid crystal properties for a long chain (**F8C11**). Furthermore, **F8C2** is only monotrope while **F8C0** is enantiotrope.

CONCLUSION

In this paper we have described the preparation and characterization of the mesomorphic properties of a series of acrylic monomers of type monothiobenzoate which differs by the length of the hydrocarbon spacer bonding the acrylic part to the rigid core. Increasing the length of this hydrocarbon spacer strongly influences the clearing point. For a low value of the spacer, smectic A mesophase is recorded. The increasing methylene number of this spacer leads to no LC behaviour. The widest mesomorphic range of this series is obtained when the hydrocarbon spacer is suppressed. The molecular design of such monomers leads us the possibility to the preparation of low cost LC polymers for surface treatment or to reach low surface energy materials.

REFERENCES

[1] Fornasieri, G., Guittard, F., Taffin de Givenchy, E., & Géribaldi, S. (2004). *Polymer*, (submitted).
[2] Fornasieri, G., Guittard, F., & Géribaldi, S. (2003). *Liq. Cryst*., *30*, 663.
[3] Fornasieri, G., Guittard, F., & Géribaldi, S. (2004). *Liq. Cryst*., *31*, 491.
[4] Fornasieri, G., Guittard, F., Taffin de Givenchy, E., & Géribaldi, S. FR Patent, registred number 0300206 (2003).
[5] Takenaka, S. (1992). *J. Chem. Soc. Chem. Commun*., 1748.
[6] Bao, X. & Dix, L. R. (1996). *Mol. Cryst. Liq. Cryst*., *281*, 291.
[7] Okamoto, H., Murai, H., & Takenaka, S. (1997). *Bull. Chem. Soc. Jpn*., *70*, 3136.
[8] Johansson, G., Percec, V., Ungar, G., & Smith, K. (1997). *Chem. Mater*., *9,* 164.
[9] Duan, M., Okamoto, H., Petrov, V. F., & Takenaka, S. (1998). *Bull. Chem. Soc. Jpn*., *71*, 2735.
[10] Okamoto, H., Yamada, N., & Takenaka, S. (1998). *J. Fluorine Chem*., *91*, 125.
[11] Duan, M., Okamoto, H., Petrov, V. F., & Takenaka, S. (1999). *Bull. Chem. Soc. Jpn*., *72*, 1637.
[12] Petrov, V. F., Duan, M., Okamoto, H., & Takenaka, S. (2000). *Mol. Cryst. Liq. Cryst*., *350*, 187.
[13] Taffin de Givenchy, E., Guittard, F., Bracon, F., & Cambon, A. (1999). *Liq. Cryst*., *26*, 1163.
[14] Taffin de Givenchy, E., Guittard, F., Bracon, F., & Cambon, A. (1999). *Liq. Cryst*., *26*, 1371.

[15] Taffin de Givenchy, E., Guittard, F., Géribaldi, S., & Cambon, A. (1999). *Mol. Cryst. Liq. Cryst*., *332*, 1.
[16] Guittard, F., Sixou, P., & Cambon, A. (1995). *Liq. Cryst*., *19*, 667.
[17] Guittard, F., Sixou, P., & Cambon, A. (1997). *Mol. Cryst. Liq. Cryst*., *308*, 83.
[18] Diele, S., Lose, D., Kruth, H., Pelzl, H., Guittard, F., & Cambon, A. (1996). *Liq. Cryst*., *21*, 603.
[19] Tschierske, C. J. (1998). *Mater. Chem*., *8*(7), 1485.
[20] Inoi, T. (1994). *Organofluorine: Chemistry, Principles and Commercial Applications*, New York Plenum Press: New York.
[21] Guittard, F., Taffin de Givenchy, E., Géribaldi, S., & Cambon, A. (1999). *J. Fluorine Chem*., *100*, 85.
[22] Guittard, F. & Géribaldi, S. (2001). In: *Anisotropic Organic Materials – Approaches to Polar Order*, Glaser, R. & Kaszynski, P. (Eds.), ACS Symposium Series, American Chemical Society: Washington D.C., 180.
[23] Mitsunobu, O. (1981). *Synthesis*, *1*, 1.