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New fluorinated monomers containing an ester function in the spacer, precursors of side chain liquid crystalline polysiloxanes

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Abstract

Two series of monomers, 2-(perfluoro-*n*-alkyl)ethyl-4-[4-(allyloxy)phenyl]benzoates and 2-(perfluoro-*n*-alkyl)ethyl-4-[4-(allyloxy)benzoyloxy]benzoates have been synthesized. They contain a fluorinated chain obtained from 2-(perfluoro-*n*-alkyl)ethanol, an aliphatic chain containing a double bound on ω and a central mesogenic moiety. Their hydrosilylation by polymethylhydrogenosiloxane give the corresponding polysiloxanes. All of the compounds, characterized by a combination of techniques consisting of differential scanning calorimetry (DSC) and thermal optical polarized microscopy, exhibited high smectogen properties. Monomers, which differ only by the nature of the rigid mesogenic core, showed enantiotropic smectogen mesophases over a wide temperature range. It was shown that the peculiar effect of the biphenyl group leads to a thermotropic polymorphism, while phenyl benzoate group induces a monomorphic character. Transition temperatures are also dependent of the length of the fluorinated moiety.

Keywords: Perfluorinated; Polysiloxane; Smectic

1. Introduction

Side-chain liquid crystalline polymers (SCLCPs) are of both theoretical and practical interest because they combine the anisotropy of a liquid crystal with intrinsic properties of the polymer backbone, such as mechanical properties and glassy state. In such SCLCPs, siloxane polymer is often used as a backbone, because of its low glass transition temperature and great flexibility [1–4]. Thus, such substances develop usefulness for applications in electro-optic devices such as alphanumeric displays, high definition TV displays, projection systems, optical computing and their ability to provide thin films can be applied over very large areas [5,6]. Among the used LC phases, smectic phases are the object of intensive works for these LC displays to the detriment of the nematic phase. On the other hand, the introduction of perfluorinated tail within LC materials can prove useful as short-term prospects as interesting alternatives to avoid defaults or instabilities asserted in hydrocarbon series. In fact one of the most important points for potential use as LC materials is the wide temperature range of mesomorphism, with enantiotropy and reproducibility during the phase transition phenomena, but also chemical stability. The perfluorinated species are chemically stable and possess low viscosity and can in suitable cases, dope the stability of the resulting mesomorphic phases. Such substitutions (fluorine instead of hydrogen) in the flexible extremities of mesogens, such a partial or total fluorination of one of the end chains of a classical rod-like molecule leads to asymmetric mostly smectogen compounds [7–14]. It is worth noting that the nature of spacer, bounding the perfluorinated tail to the rigid core, can govern and exacerbate the potential smectogenic character of the *F*-alkyl tail [15–18]. The synthesis of molecular rod-like liquid crystals which exhibit conventional calamitic mesophases requires generally [19–21] two aromatic, cycloaliphatic, or a combination of one aromatic and one cycloaliphatic groups interconnected either directly or through a suitable linking unit.

These facts suggest to synthesize new compounds containing a fluorinated flexible chain attached to a mesogenic moiety with one reactive terminal group, an ω double bond. The mesogenic moiety is represented by a 4-4′-disubstituted biphenyl group (Fig. 1, class A) or by a 4-substituted phenyl benzoate group (Fig. 1, class B). These mesogenic cores present the advantage of a stability to physical agents such as moisture or UV radiations in comparison to Schiff's bases, diazenes or azoxy compounds [22,23]. Such monomers could lead to new SCLCPs such as polysiloxanes or polyethylenes [24–26]. We decide to synthesize polysiloxanes

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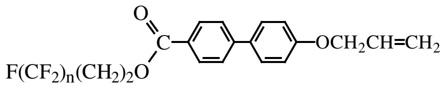
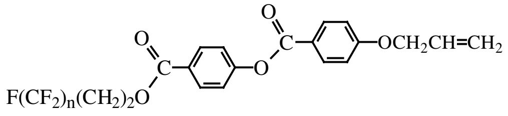


Class A, n = 4, 6, 8



Class B, n = 4, 6 ,8

Fig. 1. Investigated structures.

by hydrosilylation reaction of vinylic groups. The polymer backbone is a poly(methylhydrogeno)siloxane with a degree of polymerization of 35 that can give homogeneous population of polysiloxane molecules.

The goal of this work is to report the synthesis of rod-like LC monomers and the corresponding side-chain polysiloxanes. The LC phases of these new compounds were characterized by a combination of differential scanning calorimetry (DSC) and thermal optical polarized microscopy.

2. Experimental section

2.1. Materials

4′-Hydroxy-4-biphenylcarboxylic acid (99%), 4′-hydroxy-4-benzoic acid (99%), allyl bromide (99%), benzyl bromide (98%), *N*,*N*′-dicyclohexylcarbodiimide (DCC, 99%), 4-dimethylaminopyridine (DMAP, 99%) and palladium on activated carbon (10%), all from Aldrich, were used as received. Poly(methylhydrogeno)siloxane from Merck and hexachloroplatinic acid hydrate (38% Pt) from Fluka were used as received. 2-(Perfluoro-*n*-alkyl)ethanol was given by Elf-Atochem. All solvents were dried and distilled prior to use and column chromatography on silica gel were performed using Merck Kieselgel 60 (70–230 mesh ASTM).

2.2. Analysis

The structures of the final products and intermediates were elucidated by a variety of spectral methods. Infrared spectroscopy was carried out using a Perkin–Elmer Paragon 1000 FT IR spectrometer and mass spectrometry was carried out using a Finnigan Mat INCOS 500E mass spectrometer coupled with a gas chromatography (Varian 3400). ^{1}H NMR (200 MHz) and ^{19}F NMR (188 MHz) spectra were recorded on a Bruker AC 200 MHz spectrometer (NMR spectra in deuteriated solvents using tetramethylsilane (TMS) and trichlorofluorocarbon ($CFCl_3$) as the internal standard respectively for ^{1}H and ^{19}F NMR spectra). The melting points were determined using a Büchi Tottoli 510 melting points apparatus. Liquid crystal textures were determined with an Olympus BH-2 polarized microscope (33 × magnification) equipped with a Mettler model FP-52 hot stage. Thermal transitions were measured on a Perkin–Elmer differential scanning calorimeter DSC 7 equipped with a TAC7/DX thermal analysis controller. Zn and In were used as calibration standards. In all case, the heating and cooling rates were reported as the maxima and minima of their endothermic and exothermic peaks. The transition temperatures and transition enthalpies registered from several heating and cooling scans gave identical data. GPC, for determine purity of the polymers, were carried out in tetrahydrofuran (THF) using micro-styragel columns with 10^4, 10^3 and 10^2 particle size at room temperature. The concentration of the polymer solutions were 2 mg/ml. The detection was made with a differential refractometer (Waters 401). Elution volumes were converted to molecular weights based on calibration with narrow molecular weight polystyrene standards.

2.3. Synthesis

2.3.1. 4′-Allyloxy-4-biphenyl carboxylic acid (**1**)

To a solution of 4′-hydroxy-4-biphenyl carboxylic acid (30 mmol) in water/ethanol (10 ml/30 ml) was added a solution of potassium hydroxide (60 mmol) in water (15 ml). The reaction mixture was stirred under reflux until the precipitate disappear and then allyl bromide (33 mmol) was added slowly and stirred overnight under reflux. To the resulting precipitate was added a solution of potassium hydroxide (33 mmol) in water (15 ml) and then stirred for 1 h. under reflux. The resulting precipitate was filtered at room temperature, recrystallized from acetic acid, then from ethanol, and dried under vacuum to give a white solid. Yield, 65%; IR (KBr disc): 3200–2600, 2923, 1685, 1422, 996, 944, 847 cm^{-1}; ^{1}H NMR (CD_3SOCD_3/TMS, δ ppm), 4.63 (2H, OCH_2CH, t, $J = 5.1$ Hz), 5.28 (1H, OCH_2CHCH_2, dd, $J = 10.5$ Hz, $J = 1.5$ Hz), 5.42 (1H, OCH_2CHCH_2, dd, $J = 17.2$ Hz, $J = 1.5$ Hz), 6.03 (1H, CH_2CHCH_2, m, $J = 10.5$ Hz, $J = 5.1$ Hz, $J = 17.2$ Hz), 7.07 ($2H_{ar}$, d, $J = 8.7$ Hz), 7.68 ($2H_{ar}$, d, $J = 8.7$ Hz), 7.75 ($2H_{ar}$, d, $J = 8.3$ Hz), 8.00 ($2H_{ar}$, d, $J = 8.3$ Hz), 12.8 ($1H_{ac}$, s).

2.3.2. 2-(Perfluoro-n-alkyl)ethyl-4-[4-(allyloxy)phenyl]benzoates (**2a–2c**)

A solution of dicyclohexylcarbodiimide (DCC, 24 mmol) in dichloromethane (5 ml) was added to a solution of 4′-allyloxy-4-biphenyl carboxylic acid (**1**) (21 mmol), 2-(perfluoro-*n*-alkyl)ethanol (20 mmol) and dimethylaminopyridine (DMAP, 2 mmol) in dichloromethane (10 ml). The reaction mixture was stirred at room temperature (6 h) after which the dicyclohexylurea that had formed was filtered off. The solvent was removed under vacuum from the resulting solution and the crude product was purified by column chromatography over silicagel using dichloromethane as the eluent to give a white solid. **2c**: Yield, 90%; IR (KBr disc): 3077, 1730, 1415, 790 cm^{-1}; ^{1}H NMR ($CDCl_3$/TMS, δ ppm), 2.63 (2H, CH_2CF_2, tt,

$J_{\mathrm{HH}} = 6.4$ Hz, $J_{\mathrm{HF}} = 18.3$ Hz), 4.59 (2H, $\mathrm{OC}H_2\mathrm{CH}$, t, $J = 5.3$ Hz), 4.61 (2H, $\mathrm{C}H_2\mathrm{CH_2CF_2}$, t, $J = 6.4$ Hz), 5.33 (1H, $\mathrm{OCH_2CHC}H_2$, dd, $J = 10.5$ Hz, $J = 1.5$ Hz), 5.44 (1H, $\mathrm{OCH_2CHC}H_2$, dd, $J = 17.3$ Hz, $J = 1.5$ Hz), 6.09 (1H, $\mathrm{CH_2C}H\mathrm{CH_2}$, m, $J = 10.5$ Hz, $J = 5.3$ Hz, $J = 17.3$ Hz), 7.01 (2$\mathrm{H_{ar}}$, d, $J = 8.8$ Hz), 7.57 (2$\mathrm{H_{ar}}$, d, $J = 8.8$ Hz), 7.62 (2$\mathrm{H_{ar}}$, d, $J = 8.5$ Hz), 8.07 (2$\mathrm{H_{ar}}$, d, $J = 8.5$ Hz); ^{19}F NMR ($\mathrm{CDCl_3/CFCl_3}$, δ ppm), −81.2 ($\mathrm{CF_3}$,m), −113.9 ($(\mathrm{CF_2})_\alpha$, m), −122.2 ($(\mathrm{CF_2})_{n\beta}$, m), −123.3 ($(\mathrm{CF_2})_\gamma$, m), −123.9 ($(\mathrm{CF_2})_\delta$, m), −126.6 ($(\mathrm{CF_2})_\omega$, m); MS (70 eV), 700 (29.5%), 660 (11.6%), 659 (48.7%), 237 (60.7%), 209 (13.8%), 197 (22.1%), 169 (19.8%), 131 (12.5%), 119 (11.8%), 77 (35.1%), 69 (41.3%), 41 (100%).

Elemental Analysis: calculated for **2a**: $\mathrm{C_{22}H_{17}F_9O_3}$ (500.36): C, 52.81; H, 3.42; F, 34.17; found: C, 52.97; H, 3.56; F, 34.32; calculated for **2b**: $\mathrm{C_{24}H_{17}F_{13}O_3}$ (600.38): C, 48.01; H, 2.85; F, 41.14; found: C, 48.29; H, 3.01; F, 41.26; calculated for **2c**: $\mathrm{C_{26}H_{17}F_{17}O_3}$ (700.39): C, 44.59; H, 2.45; F, 46.11; found: C, 44.81; H, 2.57; F, 46.29.

*2.3.3. 4-(Allyloxy)benzoic acid (**3**)*

The procedure described for (**1**) is applied by using 4-(hydroxy)benzoic acid instead of 4′-hydroxy-4-biphenyl carboxylic acid. Yield, 65%; m.p. 155–158°C; IR (KBr disc): 3200–2600, 2960, 1686, 1428, 996, 944, 847 $\mathrm{cm^{-1}}$; ^{1}H NMR ($\mathrm{CD_3SOCD_3/TMS}$, δ ppm), 4.68 (2H, $\mathrm{OC}H_2\mathrm{CH}$, t, $J = 5.2$ Hz), 5.28 (1H, $\mathrm{OCH_2CHC}H_2$, dd, $J = 10.5$ Hz, $J = 1.6$ Hz), 5.44 (1H, $\mathrm{OCH_2CHC}H_2$, dd, $J = 17.3$ Hz, $J = 1.6$ Hz), 6.10 (1H, $\mathrm{CH_2C}H\mathrm{CH_2}$, m, $J = 17.3$ Hz, $J = 10.5$ Hz, $J = 5.2$ Hz), 7.05 (2$\mathrm{H_{ar}}$, d, $J = 9.0$ Hz), 8.00 (2$\mathrm{H_{ar}}$, d, $J = 9.0$ Hz), (carboxylic acid H not detected).

*2.3.4. 4-(Benzyloxy)benzoic acid (**4**)*

The procedure described for (**1**) is applied by using 4-(hydroxy)benzoic acid and benzyl bromide instead of 4′-hydroxy-4-biphenyl carboxylic acid and allyl bromide respectively. Yield, 65%; m.p. 185–187°C; IR (KBr disc): 3200–2600, 2920, 1683, 1606, 1512, 847, 771, 736 $\mathrm{cm^{-1}}$; ^{1}H NMR ($\mathrm{CD_3SOCD_3/TMS}$, δ ppm), 5.23 (2H, $\mathrm{OC}H_2\mathrm{Ar}$, s), 7.12 (2$\mathrm{H_{ar}}$, d, $J = 9.0$ Hz), 7.42 (5$\mathrm{H_{ar}}$, m), 8.00 (2$\mathrm{H_{ar}}$, d, $J = 9.0$ Hz), (carboxylic acid H not detected).

*2.3.5. 2-(Perfluoro-n-alkyl)ethyl-4-(benzyloxy)benzoates (**5a–5c**)*

The procedure described for (**2a**–**2c**) is applied by using 4-(benzyloxy)benzoic acid instead of 4′-allyloxy-4-biphenyl carboxylic acid. **5a**: Yield, 84%; m.p. 43°C; IR (KBr disc): 2933, 1719, 1608, 1512, 1250, 846, 743, 695 $\mathrm{cm^{-1}}$; ^{1}H NMR ($\mathrm{CDCl_3/TMS}$, δ ppm), 2.59 (2H, $\mathrm{C}H_2\mathrm{CF_2}$, tt, $J_{\mathrm{HH}} = 6.4$ Hz, $J_{\mathrm{HF}} = 18.4$ Hz), 4.60 (2H, $\mathrm{C}H_2\mathrm{CH_2CF_2}$, t, $J = 6.4$ Hz), 5.33 (2H, $\mathrm{OC}H_2\mathrm{Ar}$, s), 7.00 (2$\mathrm{H_{ar}}$, d, $J = 8.8$ Hz), 7.41 (5$\mathrm{H_{ar}}$, m), 7.99 (2$\mathrm{H_{ar}}$, d, $J = 8.8$ Hz); ^{19}F NMR ($\mathrm{CDCl_3/CFCl_3}$, δ ppm), −81.4 ($\mathrm{CF_3}$,m), −114.3 ($(\mathrm{CF_2})_\alpha$, m), −124.9 ($(\mathrm{CF_2})_\beta$, m), −126.3 ($(\mathrm{CF_2})_\omega$, m).

*2.3.6. 2-(Perfluoro-n-alkyl)ethyl-4-(hydroxy)benzoates (**6a–6c**)*

2-(Perfluoro-*n*-alkyl)ethyl-4-(benzyloxy)benzoates (**5a**–**5c**) (30 mmol) was dissolved in ethyl acetate (20 ml) containing 0.1 g of 10% palladium on activated carbon. The solution was hydrogenated until hydrogen uptake ceased. The catalyst was removed by filtration and the solvent was removed under vacuum from the resulting solution. The crude product was used without further purification. **6c**: Yield, 95%; m.p. 122°C; IR (KBr disc): 3361, 2977, 1706, 1607, 1517, 1230, 853 $\mathrm{cm^{-1}}$; ^{1}H NMR ($\mathrm{CD_3COCD_3/TMS}$, δ ppm), 2.82 (2H, $\mathrm{C}H_2\mathrm{CF_2}$, tt, $J_{\mathrm{HH}} = 6.1$ Hz, $J_{\mathrm{HF}} = 19.3$ Hz), 4.62 (2H, $\mathrm{C}H_2\mathrm{CH_2CF_2}$, t, $J = 6.1$ Hz), 6.94 (2$\mathrm{H_{ar}}$, d, $J = 8.8$ Hz), 7.92 (2$\mathrm{H_{ar}}$, d, $J = 8.8$ Hz) 9.31 (1H, s); ^{19}F NMR ($\mathrm{CD_3COCD_3/CFCl_3}$, δ ppm), −80.8 ($\mathrm{CF_3}$,m), −113.1 ($(\mathrm{CF_2})_\alpha$, m), −121.5 ($(\mathrm{CF_2})_\beta$, m), −122.4 ($(\mathrm{CF_2})_\gamma$, m), −123.2 ($(\mathrm{CF_2})_\delta$, m), −125.9 ($(\mathrm{CF_2})_\omega$, m).

*2.3.7. 2-(Perfluoro-n-alkyl)ethyl-4-[4-(allyloxy)–benzoyloxy]benzoates (**7a–7c**)*

The procedure described for (**2a**–**2c**) is applied by using 4-(allyloxy)benzoic acid and 2-(perfluoro-*n*-alkyl)ethyl-4-(hydroxy)benzoates (**6a**–**6c**) instead of 4′-allyloxy-4-biphenyl carboxylic acid and 2-(perfluoro-*n*-alkyl)ethanol, respectively. **7b**: Yield, 90%; IR (KBr disc): 3075, 2924, 1728, 1414, 924, 849, 790 $\mathrm{cm^{-1}}$; ^{1}H NMR ($\mathrm{CDCl_3/TMS}$, δ ppm), 2.63 (2H, $\mathrm{C}H_2\mathrm{CF_2}$, tt, $J_{\mathrm{HH}} = 6.4$ Hz, $J_{\mathrm{HF}} = 18.3$ Hz), 4.64 (2H, $\mathrm{OC}H_2\mathrm{CH}$, t, $J = 5.2$ Hz), 4.64 (2H, $\mathrm{C}H_2\mathrm{CH_2CF_2}$, t, $J = 6.4$ Hz), 5.34 (1H, $\mathrm{OCH_2CHC}H_2$, dd, $J = 10.5$ Hz, $J = 1.6$ Hz), 5.45 (1H, $\mathrm{OCH_2CHC}H_2$, dd, $J = 17.3$ Hz, $J = 1.6$ Hz), 6.07 (1H, $\mathrm{CH_2C}H\mathrm{CH_2}$, m, $J = 10.5$ Hz, $J = 5.2$ Hz, $J = 17.3$ Hz), 7.01 (2$\mathrm{H_{ar}}$, d, $J = 8.9$ Hz), 7.31 (2$\mathrm{H_{ar}}$, d, $J = 8.7$ Hz), 8.11 (2$\mathrm{H_{ar}}$, d, $J = 8.7$ Hz), 8.15 (2$\mathrm{H_{ar}}$, d, $J = 8.9$ Hz); ^{19}F NMR ($\mathrm{CDCl_3/CFCl_3}$, δ ppm), −81.3 ($\mathrm{CF_3}$,m), −114.0 ($(\mathrm{CF_2})_\alpha$, m), −122.2 ($(\mathrm{CF_2})_\beta$, m), −123.3 ($(\mathrm{CF_2})_\gamma$, m), −124.0 ($(\mathrm{CF_2})_\delta$, m), −126.6 ($(\mathrm{CF_2})_\omega$, m); MS (70 eV), 644 (<1%), 281 (3.2%), 161 (100%), 133 (2.4%), 131 (1.7%), 121 (21.9%), 119 (8.4%), 93 (5.8%), 77 (5.4%), 69 (2.2%), 41 (26.6%);

Elemental Analysis: **7a**: calculated for $\mathrm{C_{23}H_{17}F_9O_5}$ (544.37): C, 50.75; H, 3.15; F, 31.41; found: C, 50.83; H, 3.01; F, 31.37; **7b**: calculated for $\mathrm{C_{25}H_{17}F_{13}O_5}$ (644.39): C, 46.60; H, 2.66; F, 38.33; found: C, 46.89; H, 2.85; F, 38.47; **7c**: calculated for $\mathrm{C_{27}H_{17}F_{17}O_5}$ (744.41): C, 43.56; H, 2.30; F, 43.39; found: C, 43.76; H, 2.41; F, 43.53.

*2.3.8. Polysiloxanes (**PAa–PAc, PBa–PBc**)*

In a typical experiment, the unsaturated ester (30 mmol) in dry THF (15 ml) was stirred with poly(methylhydrogeno)siloxane (0.85 mequiv of Si–H) at 60°C under nitrogen, then the catalyst, $\mathrm{H_2PtCl_6{\cdot}6H_2O}$ (20 μl of a 0.1 M solution in isopropanol) was added. The reaction was followed by monitoring the decrease of the Si–H IR absorption band at 2165 $\mathrm{cm^{-1}}$, and was generally complete after 36–48 h. heating. The polymer was recovered after precipitations in

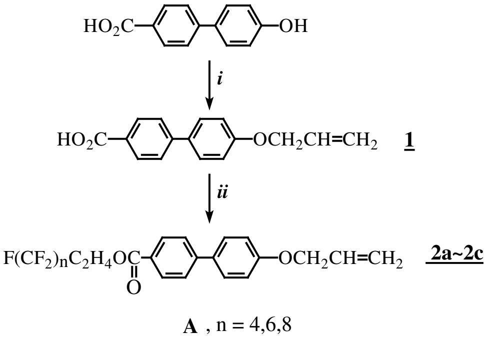


Fig. 2. Synthetic route to 2-(perfluoro-*n*-alkyl)ethyl-4-[4-(allyloxy)phenyl]-benzoates (**2a**–**2c**). Reagents and conditions: (i) $CH_2{=}CHCH_2Br$, KOH, EtOH/H_2O, reflux; (ii) $F(CF_2)_nC_2H_4OH$, DCC, DMAP, CH_2Cl_2, room temperature.

methanol, and purified by dissolution in chloroform and treatment with activated carbon to eliminate the catalyst residues. After filtration and evaporation of the solvent, it was dried at 80°C for 2 h. under vacuum. Analysis example with **PBb**: Yield, 40%; IR (KBr disc): 2965–2875, 1732, 1608, 1512, 1150–1250 cm^{-1}; ^1H NMR ($CDCl_3$, δ ppm), −0.05–0.28 (Si–CH_3), 0.68 (2H, Si–CH_2), 1.83 (2H, Si–CH_2CH_2), 2.58 (2H, CH_2CF_2), 3.82 (Si–C_2H_4CH_2), 4.52 (2H, C$H_2CH_2CF_2$), 6.75 ($2H_{ar}$), 7.10 ($2H_{ar}$), 7.90 ($4H_{ar}$); ^{19}F NMR ($CDCl_3$ δ ppm), −81.4 (CF_3,m), −114.2 ($(CF_2)_\alpha$, m), −122.5 ($(CF_2)_\beta$, m), −123.5 ($(CF_2)_\gamma$, m), −124.1 ($(CF_2)_\delta$, m), −126.8 ($(CF_2)_\omega$, m).

3. Results and discussion

The synthesis of the type A compounds (**2a**–**2c**) was carried out in two steps (Fig. 2). The formation of 4′-allyloxy-4-biphenylcarboxylic acid (**1**) consists in the reaction of 4′-hydroxy-4-biphenylcarboxylic acid with allyl bromide in the presence of potassium hydroxide. Esterification of **1** with 2-(perfluoro-*n*-alkyl)ethanol in the presence of DCC and DMAP give esters 2-(perfluoro-*n*-alkyl)ethyl-4-[4-(allyloxy)phenyl]benzoates (**2a**–**2c**). Yields are collected in Table 1.

Table 1
Preparation of monomers A, B and polysiloxanes

Cpd no.	R_F value	Yield (%)[a]	Yield (%)
(A) **2a**	C_4F_9	85	55[b]
(A) **2b**	C_6F_{13}	91	59[b]
(A) **2c**	C_8F_{17}	90	59[b]
(B) **7a**	C_4F_9	88	46[c]
(B) **7b**	C_6F_{13}	90	48[c]
(B) **7c**	C_8F_{17}	90	48[c]
PAa	C_4F_9	–	29
PAb	C_6F_{13}	–	32
PAc	C_8F_{17}	–	18
PBa	C_4F_9	–	35
PBb	C_6F_{13}	–	40
PBc	C_8F_{17}	–	40[d]

[a] Final step.
[b] Yield from 4′-hydroxy-4-biphenylcarboxylic acid.
[c] Yield from 4-hydroxybenzoic acid.
[d] Crude yield.

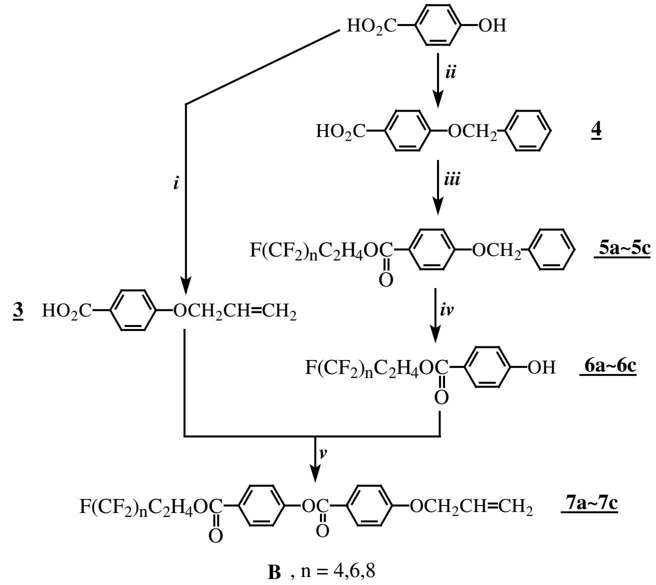


Fig. 3. Synthetic route to 2-(perfluoro-*n*-alkyl)ethyl-4-[4-(allyloxy)benzoyloxy]benzoates (**7a**–**7c**). Reagents and conditions: (i) $CH_2{=}CHCH_2Br$, KOH, EtOH/H_2O, reflux; (ii) $C_6H_5CH_2Br$, KOH, EtOH/H_2O, reflux; (iii) $F(CF_2)_nC_2H_4OH$, DCC, DMAP, CH_2Cl_2, room temp.; (iv) Pd/C, H_2, ethyl acetate, room temp.; and (v) DCC, DMAP, CH_2Cl_2, room temperature.

Preparation of the type B substances (**7a**–**7c**) was realized according to the pathway shown in Fig. 3. 4-(Allyloxy)benzoic acid (**3**) and 4-(benzyloxy)benzoic acid (**4**) were prepared by the alkylation of 4-(hydroxy)benzoic acid with, respectively, allyl bromide and benzyl bromide in the presence of potassium hydroxide. The protected acid (**4**) was esterified with 2-(perfluoro-*n*-alkyl)ethanol in the presence of DCC and DMAP to give esters (**5a**–**5c**). These esters produced (**5**) which were then converted to the corresponding phenols (**6a**–**6c**) by removal of the benzyl protecting group by hydrogenation with palladium on activated carbon. The resulting phenols (**6**) were esterified using DCC and DMAP with acid (**3**) to give the final products, 2-(perfluoro-*n*-alkyl)ethyl-4-[4-(allyloxy)benzoyloxy]benzoates (**7a**–**7c**). Yields are collected in Table 1.

The polysiloxanes (**PAa**–**PAc**, **PBa**–**PBc,** P: polysiloxane, A or B: monomer class, a–c: fluorinated chain length *F*-butyl, *F*-hexyl or *F*-octyl) were prepared according to Fig. 4 by catalytic hydrosilylation with hexachloroplatinic acid hydrate between monomers A or B and poly(methylhydrogeno)siloxane (PMHS). Yields are given in Table 1.

3.1. Phase diagram

The phase sequences were determined by microscopic

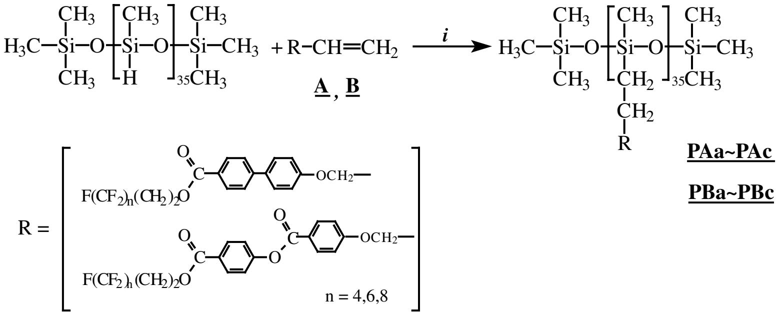


Fig. 4. Synthetic route to polysiloxanes PAa–PAc and PBa–PBc. Reagents and conditions: (i) $H_2PtCl_6{\cdot}6H_2O$/isopropanol, THF, 50°C.

observation, and the transition temperatures were measured by DSC on heating and cooling with a scanning rate of 10°C/min. The DSC curves of monomers A and B are shown in Figs. 5 and 6, respectively. Phase sequences and transition temperatures observed on heating are summarized in Table 2. All compounds showed an enantiotropic mesophase, identified as smectic by the optical microscopic observation of focal conic fans, within a wide temperature range. Miscibililty studies carried out from standard materials show that the smectic phases are of type smectic A and smectic E. When the two series, which differ only by the nature of the mesogenic core, biphenyl ring (Class A, **2a**–**2c**) or phenyl benzoate group (Class B, **7a**–**7c**), are compared, we observe a polymorphism for compounds of class A while monomers B exhibit only a monomorphic character. The S_E–S_A transition temperatures are 119, 121 and 121°C for **2a, 2b** and **2c** monomers, respectively (Table 2). The fluorinated chain lengthening has also low effect on the S_A phase temperature appearance.

3.2. Effect of the nature of the mesogen

From the transitions observed on heating for compounds A and B (Table 2) we can clearly observe that monomers of class A exhibited a wider smectic phase than class B compounds. The difference between these monomers is the nature of the mesogenic core. The biphenyl rigid mesogen leads to a polymorphic and wide smectic phase, from 56°C (**2c**) to 102°C (**2a**), while phenyl benzoate core leads to a monomorphic phase observable only over 50°C (**7a**) to 56°C (**7c**). These results suggest that monomers **2a**–**2c** possess greater propensity to give rise to stable and persistent smectic mesophases than do the monomers **7a**–**7c**, thus indicating that the replacement of the phenyl benzoate

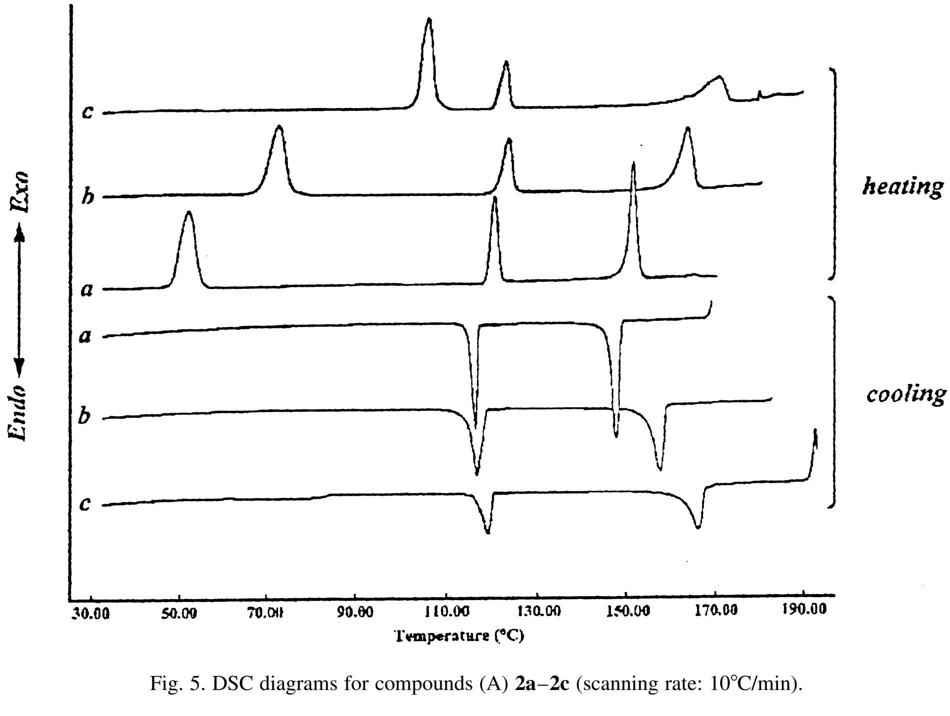


Fig. 5. DSC diagrams for compounds (A) **2a**–**2c** (scanning rate: 10°C/min).

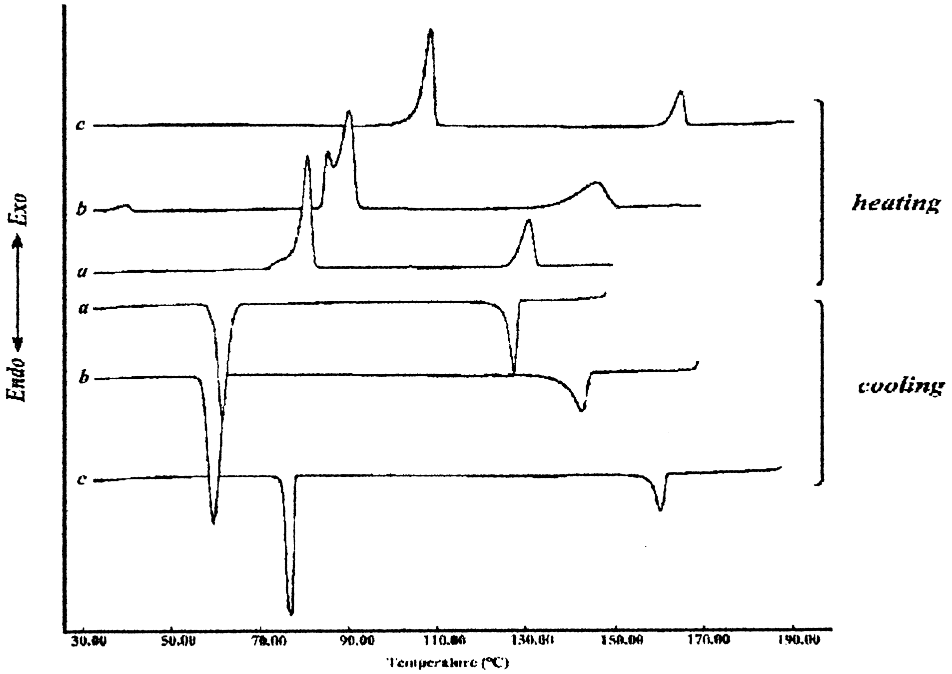


Fig. 6. DSC diagrams for compounds (B) **7a–7b** (scanning rate: 10°C/min).

group by a biphenyl core strongly enhances the smectogenic character in the monomer.

3.3. Effect of the fluorinated tail on phase diagram

As we can observe from data in Table 2 obtained on heating for class A and class B compounds, the transition temperatures are a function of the number of the fluoromethylene units in the fluorinated tail. The decrease of this fluorinated tail length leads to a simultaneous reduction of the melting and clearing temperatures. The comparison of the L.C. phase range against fluorinated chain lengthening shows a completely different mesophasic behaviour between A and B monomers. Compounds A have a wider mesophase with a short fluorinated tail than with a long one, while compounds B exhibited the inverse properties. It seems that there is no systematic behaviour for the mesophase range as a function of the fluorinated chain length.

For compounds A, the S_E phase appearance is favoured with decreasing fluorination extent. Indeed, monomer **2a** with a short fluorinated chain showed a smectic S_E mesophase over 71°C, while a chain with eight perfluoromethylene leads to a S_E phase over only 17°C.

3.4. Polysiloxanes

Polysiloxanes were prepared by hydrosilylation of unsaturated monomers. A typical ^1H NMR spectrum of PMHS modified by monomer **2b** is given in Fig. 7b, the ^1H NMR spectrum of the corresponding monomer **2b** is represented in Fig. 7a. According to these spectra, the most apparent differences between the spectra of polysiloxane with lateral mesogenic part (Fig. 7b) and that corrresponding to the monomer (Fig. 7a) are the suppression of the vinyl signals symbolized par the arrows in Fig. 7, and leads us to determine a grafting rate higher than 98%. This result was confirmed by IR and GPC experiments. All polysiloxanes were studied by DSC and observed by polarizing microscopy in order to

Table 2
Transition temperatures and enthalpies for vinyl derivatives A and B observed on heating (C, crystal; SA, SE, smectic A and E phases; and I, isotropic)

Cpd no.	R_F value	Transition temperatures (°C)							Enthalpies (J/g)	
		C		S_E		S_A		I	ΔH_{C-S}	ΔH_{S-I}[a]
(A) **2a**	C_4F_9	●	48	●	119	●	150	●	30.0	23.7
(A) **2b**	C_6F_{13}	●	68	●	121	●	160	●	26.1	20.3
(A) **2c**	C_8F_{17}	●	104	●	121	●	162	●	27.0	16.6
(B) **7a**	C_4F_9	●	78			●	128	●	34.8	16.0
(B) **7b**	C_6F_{13}	●	84			●	138	●	33.9	13.3
(B) **7c**	C_8F_{17}	●	106			●	162	●	33.7	13.6

[a] Enthalpies at the clearing point.

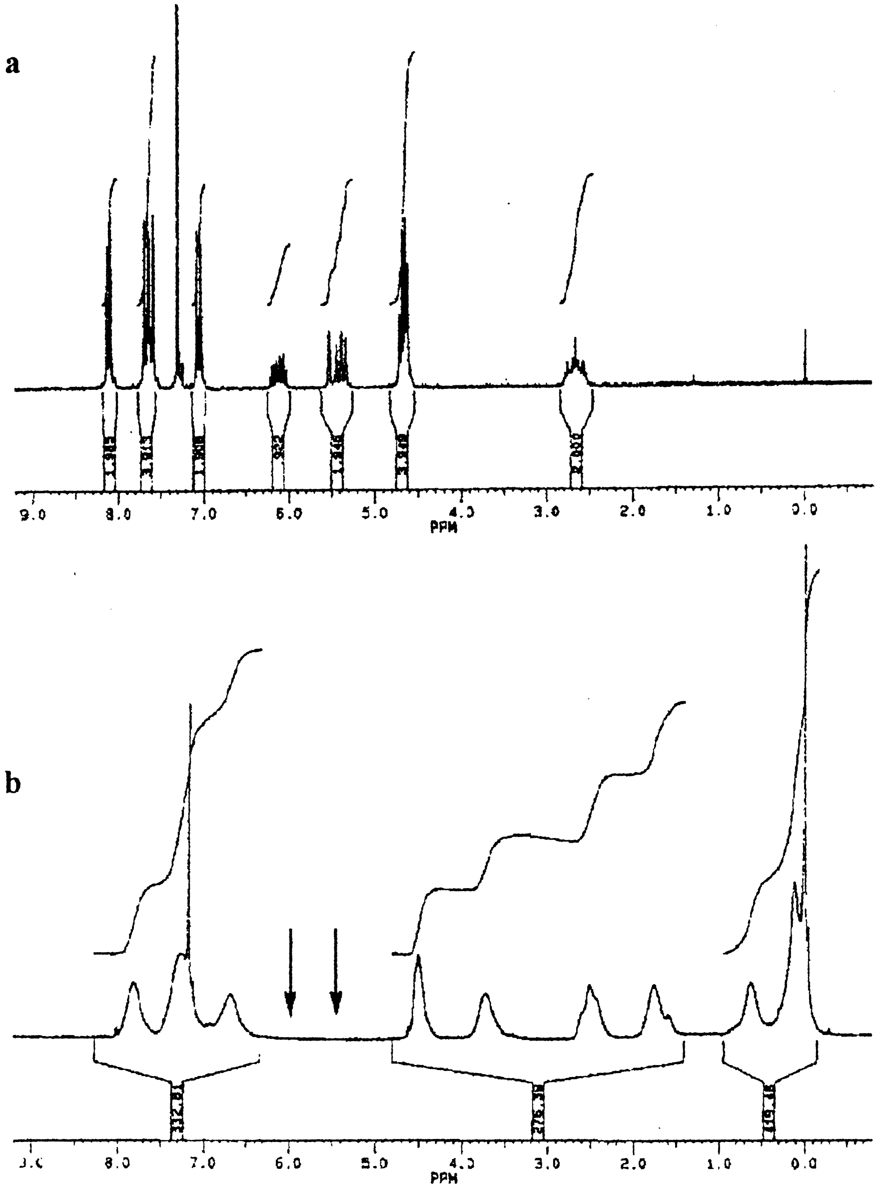


Fig. 7. ^{1}H NMR spectra of: (a) monomer **2a**; and (b) polysiloxane **PAa**.

determine their thermotropic behaviour. A thin layer placed between a microscope slide and a cover glass showed birefringence under a cross-polarizing microscope. By optical observation, the mesophases of all members of these series appear as rods on cooling from the isotropic melt and they coalesce to make well-developed fan shaped textures with focal conic domains that are characteristic of the layer structure of smectic mesophase. The characteristic textures of observed phases are illustrated in Fig. 8. It is worth noting that no significant change occurs in the transition temperatures after prolonged heating above the isotropic transition except for compound **PBb**, where the liquid crystal to isotropic transition is up to 210°C. The clearing temperatures are listed in Table 3.

Polysiloxanes derived from class A monomers (with a biphenyl unit as mesogenic core) have lower clearing temperatures than those obtained from class B monomers. This observation is opposite to the one observed for the monomers, where the biphenyl core strongly enhances the smectogenic character.

Table 3
Clearing temperatures of polysiloxanes PA and PB

Cpd no.	R_F value	T_c (°C)
PAa	C_4F_9	144
PAb	C_6F_{13}	184
PAc	C_8F_{17}	174
PBa	C_4F_9	185
PBb	C_6F_{13}	>210

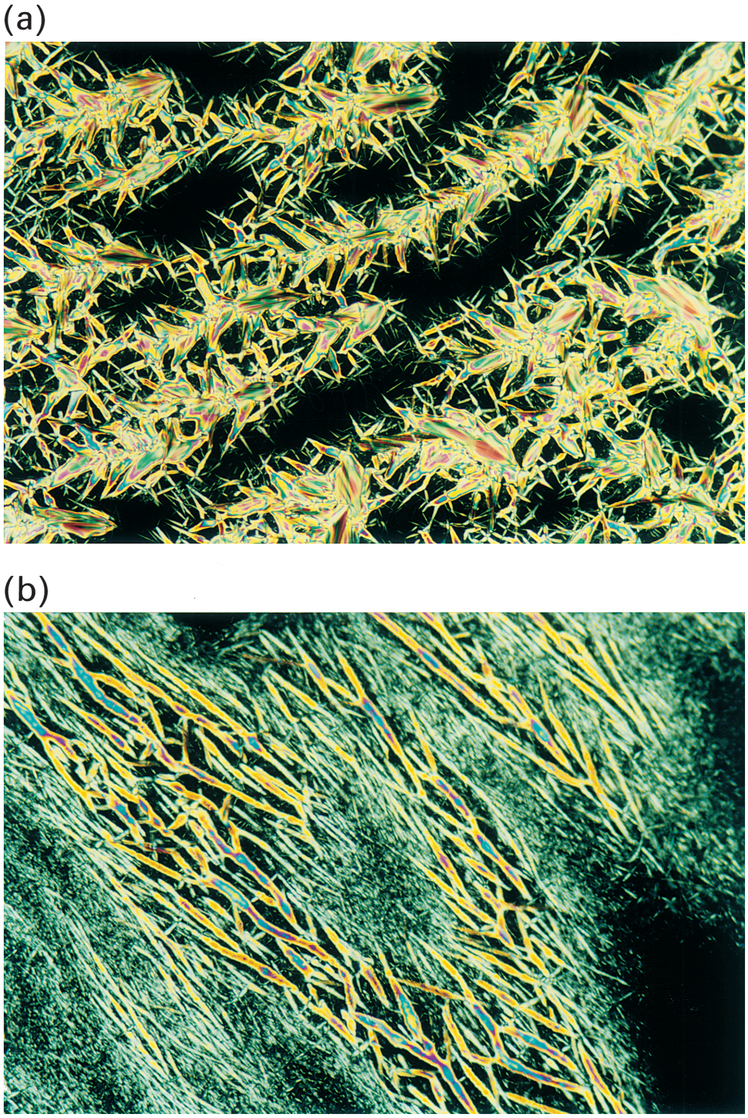


Fig. 8. Optical polarizing micrograph displayed by the polysiloxanes (33 ×): (a) **PAb**, $T = 180$°C, S → I; and (b) **PAc**: $T = 162$°C, I → S.

4. Conclusion

Unsaturated perfluoroalkylated monomers obtained from 2-(perfluoro-*n*-alkyl)ethanol have been prepared with good yields. They present a mesogenic core such as biphenyl ring or phenyl benzoate group. Chemical modification of polymethylhydrogenosiloxane with these compounds leads to a new class of LC fluorinated polysiloxanes. All monomers exhibited mesomorphic enantiotropic properties. The observed smectic mesophases are wide, dependent of the fluorinated chain lengthening, and confer this character to the corresponding polysiloxanes. The biphenyl core strongly enhances the smectogenic character of the monomer and leads to a polymorphism, in comparison with the phenyl benzoate group, that induces only a monomorphic LC character. It is worth noting that the influence of the mesogenic core observed for the monomers is not seen in the corresponding polysiloxane. However, the effect of the fluorinated chain length is the same for monomers and polymers: an increasing of the number of the fluoromethylene units in the fluorinated tail increases melting and clearing temperatures of the monomers and isotropization temperatures of polysiloxanes. The overall results lead us to consider 2-(perfluoro-*n*-alkyl)ethanol as an efficient precursor for the increase of the span of the LC phase, notably for the access of smectic polymers over a wide temperature range.

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