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Preparation and Thermotropic Properties of Partially Fluorinated Acrylates

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New series of monomers which consist of a 4,4'-biphenyl unit linked to a partially linear fluorinated chain on one side and on the other side to an acrylic part which is either directly connected to the core or separated by an oligomethylene spacer, were synthesized. The mesomorphic properties have been characterized by light microscopy and by differential thermal analysis showing the peculiar effect of the fluorinated tail and of the spacer. The overall compounds showed an enantiotropic liquid crystal behavior. However, the series without oligomethylene unit exhibit a smectic behavior over a wide temperature range as compared to the series with a spacer where the mesomorphic behavior appear only on one degree Celsius. Increasing the lengthening of the fluorinated tail simultaneously increases the melting and the clearing points.

Keywords: fluorinated; smectic phase; biphenyl; acrylate

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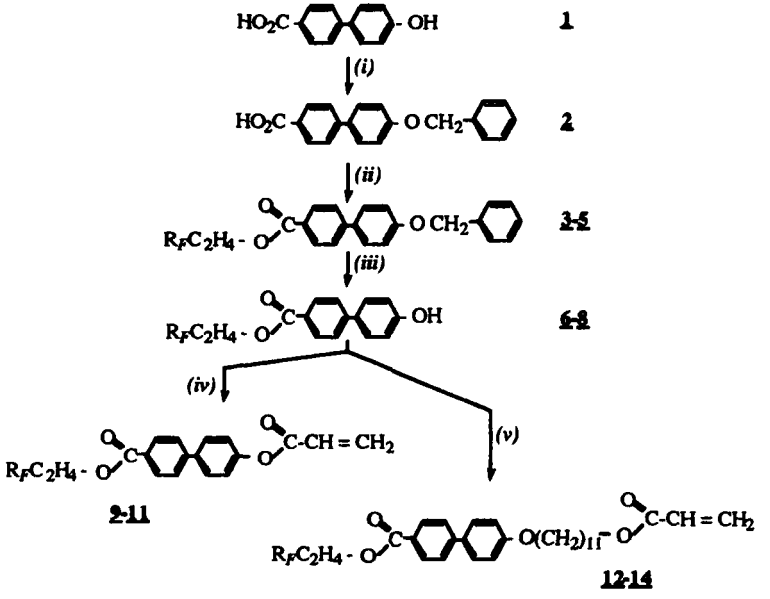
INTRODUCTION

Side-chain liquid crystalline polymers are of pratical interest[1-2] because they combine the anisotropy of a liquid crystal with the intrinsic properties of the polymer backbone such as mechanical properties and glassy state. Several side chain liquid crystal polymers have already been reported such as polyacrylates, polymethacrylates and polysiloxanes[3-4]. Obviously a spacer between the polymer backbone and the mesogenic unit must be present[5]. It must allow an undisturbed organization of the aligned mesogenic units[6]. Thus, the synthesis of molecular rod-like liquid crystals exhibiting calamitic mesophases and possessing unsaturated moiety could be of a great interest especially within fluorinated series. In fact the introduction of perfluorinated tail within LC materials is an interesting alternative to improve mesogenicity[7,8] and lead to smectic phase which are the object of intensitive works [9-13]. The goal of this work is to report the synthesis of rod-like liquid crystal monomers of acrylate type and to evaluate their influence on the span of the mesophase.

EXPERIMENTAL

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 peaks. The transition temperatures and enthalpies registrated from several heating and cooling scans gave identical datas. The heating and cooling cuves were obtained at rates of 10°C in a nitrogen atmosphere. Mass spectrometry (MS) was carried out using a Finnigan Matt INCOS 500E mass spectrometer coupled with a gas chromatograph (Varian 3400). Nuclear Magnetic Resonance (NMR) spectroscopy was carried out using a Brucker AC 200 MHz

spectrometer. All spectra were recorded with $CFCl_3$ for ^{19}F and TMS as internal reference for ^1H NMR. All final compounds gave satisfactory elemental analysis. 4,4'-hydroxybiphenyl carboxylic acid, dicyclohexylcarbodiimide (DCC), dimethylaminopyridine (DMAP), benzyl bromide, acetic acid were purchased from Aldrich and were used without further purification. Compounds 2 to 8 were prepared using standard procedures described in Figure 1.



Reagents and conditions: (i)KOH/H_2O/EtOH; B_2Br reflux, recrist. CH_3CO_2H; (ii) $R_FC_2H_4OH$, DCC/DMAP/CH_2Cl_2 rt; (iii) H_2/Pd/AcOEt; (iv) H_2C=CHC(O)Cl, Et_2O/N(Et)$_3$ 0°C->rt; (v) Br$(CH_2)_{11}$OC(O)CH=CH_2, K_2CO_3/acetone/60°C.

FIGURE 1 Synthetic route to the compounds **9-14**.

2-*F*-alkylethyl-4-(4-acryloyloxyphenyl)benzoates (9-11)

A solution of 2.5 10^{-3} mole of acryloyle chloride in 5 ml of dry diethylether was added dropwise to a stirred solution of 2.0 10^{-3} mole of 2-*F*-alkylethyl-4-(4-hydroxyphenyl)benzoates (**6-8**) previously prepared from standard procedures, in dry diethylether (25 ml) and 3.2 10^{-3} mole

of triethylamine at room temperature under nitrogen atmosphere. The reaction mixture was then stirred for 2 hours at 5-10°C then for 12 hours at room temperature. The crude product was filtered and the residue was purified by column chromatography on silica gel with chloroform/ hexane 8/2 as eluent to yield the pure compounds 9-11 as white solids (table 1). ^{1}H NMR ($CDCl_3$ / TMS) δ (ppm) : 2.64 (tt, 2H, $^3J_{HH}$=6.4Hz, $^3J_{HF}$= 18.3Hz); 4.66 (t, 2H, $^3J_{HH}$=6.4Hz); 6.05 (dd, 1H, $^2J_{HH}$=1.4Hz, $^3J_{cis}$=10.3Hz); 6.35 (m, 1H, $^3J_{cis}$=10.3Hz, $^3J_{trans}$=17.2Hz); 6.65 (dd, 1H, $^2J_{HH}$=1.4Hz, $^3J_{trans}$=17.2Hz); 7,25 (d, 2H, $^3J_{HH}$=8.6Hz); 7,65 (d, 2H, $^3J_{HH}$=8.6Hz); 7,66 (d, 2H, $^3J_{HH}$=8.4Hz); 8.11 (d, 2H, $^3J_{HH}$=8.4Hz); ^{19}F NMR (CDCl3); **9**: -81.6 (m, CF_3); -114.8 (m, CF_2); -124.9 (m, CF_2); -126.6 (m, CF_2); **10**: -81.3 (m, CF_3); -114.6 (m, CF_2); -122.4 (m, CF_2); -123.3 to -124.0 (m, 4F, CF_2); -126.6 (m, CF_2); **11**: -81.3 (m, CF_3); -114.6 (m, CF_2); -122.4 (m, 6F, CF_2); -123.2 to -123.9 (m, 4F, CF_2); -126.6 (m, CF_2); MS (70 eV); m/z (%) : $M^{+\cdot}$ (2.5).

2-*F*-alkylethyl-4-[4-(11-acryloyloxy)undecyloxyphenyl) benzoates (12-14)

A solution of 2.1 10^{-3} mole of 11-acryloyloxyundecylbromide in 5 ml of dry acetone was added dropwise to a stirred solution of 2.0 10^{-3} mole of 2-*F*-alkylethyl-4-(4-hydroxyphenyl)benzoates (**6-8**) previously prepared from standard procedures, and 2.1 10^{-3} mole of potassium carbonate in dry acetone (10 ml) at room temperature under nitrogen atmosphere. The reaction mixture was then stirred for 20 hours at reflux. The crude product was filtered at room temperature. The solvent was removed under vacuum and the residue was purified by column chromatography on silica gel with dichloromethane/hexane 9/1 as eluent to yield the pure compounds **12-14** as white solids (table 1). ^{1}H NMR ($CDCl_3$ / TMS) δ (ppm) : 1.31 (m, 14H); 1.67 (m, 2H); 1.81 (m, 2H); 2.63 (tt, 2H, $^3J_{HH}$=6.4Hz, $^3J_{HF}$= 18.3Hz); 4.00 (t, 2H, $^3J_{HH}$=6.5Hz); 4.15 (t, 2H, $^3J_{HH}$=6.7Hz); 4.65 (t, 2H, $^3J_{HH}$=6.4Hz); 5.81 (dd, 1H, $^2J_{HH}$=1.7Hz,

$^3J_{cis}$=10.3Hz); 6.12 (m, 1H, $^3J_{cis}$=10.3Hz, $^3J_{trans}$=17.3Hz); 6.40 (dd, 1H, $^2J_{HH}$=1.7Hz, $^3J_{trans}$=17.3Hz); 6.99 (d, 2H, $^3J_{HH}$=8.8Hz); 7,56 (d, 2H, $^3J_{HH}$=8.8Hz); 7,63 (d, 2H, $^3J_{HH}$=8.5Hz); 8.07 (d, 2H, $^3J_{HH}$=8.5Hz); ^{19}F NMR (CDCl3); **12**: -81.5 (m, CF_3); -114.8 (m, CF_2); -124.9 (m, CF_2); -126.5 (m, CF_2); **13**: -81.4 (m, CF_3); -114.6 (m, CF_2); -122.4 (m, CF_2); -123.3 to -124.0 (m, 4F, CF_2); -126.6 (m, CF_2); **14**: -81.4 (m, CF_3); -114.6 (m, CF_2); -122.5 (m, 6F, CF_2); -123.1 to -123.9 (m, 4F, CF_2); -126.6 (m, CF_2); MS (70 eV); m/z (%) : $M^{+\cdot}$ (1.4).

RESULTS AND DISCUSSIONS

The synthetic pathways used for the preparation of acrylic derivatives is described in Figure 1. The overall yields of the two series (compounds **9-11** and compounds **12-14**) are reported in table 1.

TABLE 1 Yields for preparation of compounds **9-14**.

Cpd N°	*R_F value*	*yield % †*			
		step (ii)	*step (iii)*	*step (iv)*	*global‡*
9	C_4F_9	92	97	64	37
10	C_6F_{13}	88	95	65	35
11	C_8F_{17}	87	95	64	34
12	C_4F_9	92	97	81	47
13	C_6F_{13}	88	95	85	46
14	C_8F_{17}	87	95	82	44

(†) : yield for step (i) : 65%; (‡) from 4,4'-hydroxybiphenyl carboxylic acid.

Transition temperatures recorded from DSC measurements or microscopy observations are reported in table 2. For compounds **9** to **11**, we can notice that the overall member of this series exhibit mesomorphic properties over a wide temperature range. According to the DSC spectra, the liquid crystal phase is observed from heating and cooling which is

characteristic of an enantiotropic behavior. The phase diagram obtained on heating and plotted against the carbon number of the terminal perfluoroalkylated moieties (**9-11**) is illustrated in figure 2. It is worth noting that the decrease in fluorinated tail length leads to simultaneous reduction of the melting and the clearing temperature. However, the vertical spacing of these points which represent the temperature span of the mesophase is nearly the same as the number of fluoromethylene decrease. The curves obtained from differential thermal analysis are shown in figure 3. No thermic polymerisation or significant change occurs in the transition temperatures after prolongated heating above the istropic melt. The thermogram of compound **9** show a peculiarity. As compared to compounds **10** and **11** which exhibit only one smectic phase of type A from heating or cooling processes (monomorphism clearly shown in figure 3), compound **9** show under cooling process a dimorphism S_A-E. The fluorinated part has an influence in this case : the increase of fluoromethylene unit leads to the suppression of this dimorphism (compounds **10** and **11**).

TABLE 2 Phase transition temperatures obtained from compounds **9-14**.

Cpd N°	R_F	transition temperatures (°C)†				
	value	C		S_A		I
9	C_4F_9	•	74.0 [29.0]	•	151.5 [15.4]	•
10	C_6F_{13}	•	85.4 [29.4]	•	165.0 [13.8]	•
11	C_8F_{17}	•	106.6 [19.6]	•	172.3 [5.6]	•
12	C_4F_9	•	65.5 [51.8]‡	•	66.3*	•
13	C_6F_{13}	•	80.8 [53.3]‡	•	82.0*	•
14	C_8F_{17}	•	102.0 [43.0]‡	•	103.1*	•

(†) from heating; figures in square brackets denote enthalpies of transition ($kJ.g^{-1}$)
(‡)including enthalpies of transition C to I. (*) from microscopy measurement

Compounds **12-14** differ from previous series by the presence of an oligomethylene spacer located between the mesogenic core and the polymerisable moiety. Melting temperature values are with the same

magnitude of the homologous compounds **9-11**. All these compounds with a long spacer exhibit a liquid crystal behavior but the mesophase is visible only over about 1° Celsius (table 2). The optical microscopy allows us to confirm this behavior which is not well defined from DSC measurements even at a rate of 1°C. min^{-1}. The presence of this spacer oligomethylene contribute to destabilize the wide mesomorphic range observed from compounds **9-11**.

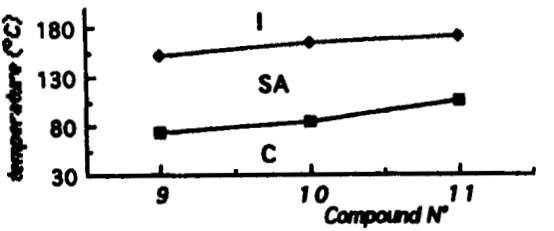


FIGURE 2 Phase diagram of compounds 9-11 on heating

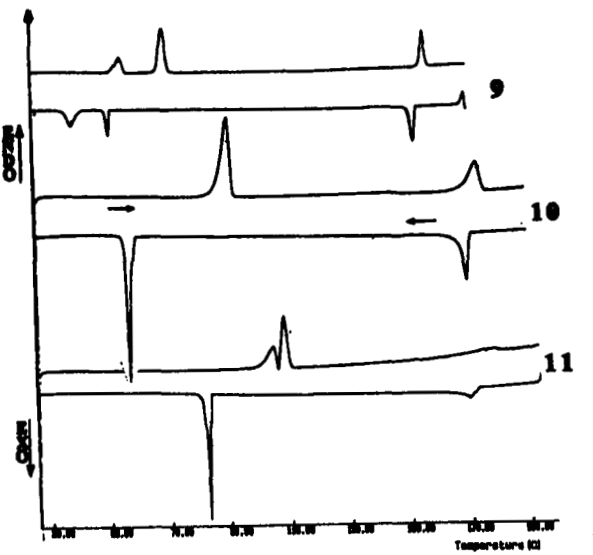


FIGURE 3 DSC curves for compounds **9-11** (heating and cooling rates : 10°C.min^{-1})

CONCLUSION

Two series of acrylates incorporating a linear perfluorinated tail have been synthezised and differ by the presence or not of an oligomethylene unit between the polymerisable part and the rigid core. The decrease of the fluorinated tail affect the clearing and melting temperatures. In the case of F-butyl derivative, a dimorphism was observed for series where the acrylic part is directly bound to the rigid core. Usually the spacer between the rigid core and the polymerisable part enhance the mesomorphic properties of the resulting polymers. Nevertheless, it appears that, in the case of these two series of monomers, this spacer decreases drastically the mesomorphic properties which appears only on few degree Celsius for the series including oligomethylene unit.

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