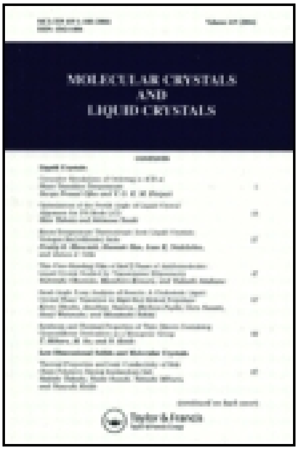

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Synthesis and Mesomorphic Properties of Some Liquid Crystals with Semifluorinated Chains

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Two series of compounds with semifluorinated chains have been synthesized. These compounds were characterized by IR, ^{1}H NMR, ^{19}F NMR, MS, and elemental analysis. Their phase-transition behavior was investigated by differential scanning calorimetry and polarizing optical microscopy. Both the introduction of a triple bond and the decrease of the polarity of the core act to decrease the clearing points and suppress the formation of smectic C phase.

Keywords: ferroelectric; fluorocarbon; liquid crystal; mesomorphic

INTRODUCTION

Fluorinated liquid crystals have received much attention because of their unique properties such as low viscosity, low birefringence, and low conductivity. They are suitable for applications in the mixtures for liquid crystal displays [1–3]. Generally, lateral fluorosubstitution in the core enhances the formation of the nematic phase and decreases clearing points [4]; in contrast, terminal fluorosubstitution in the core enhances the formation of smectic phases and increases clearing points [1].

Recently, attention has turned to liquid crystals with fluorocarbon chains, which are suitable for ferroelectric liquid-crystalline display mixtures [5]. The introduction of perfluoroalkyl or semifluoroalkoxy chains can enhance the formation of smectic mesophases [6–13]. In particular, molecules with semiperfluorinated chains exhibit tilted

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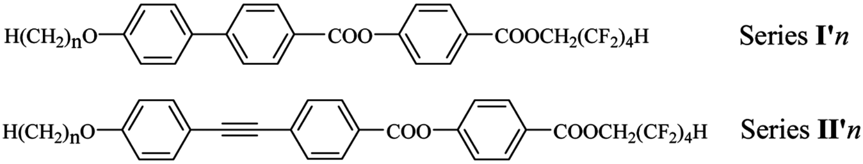


FIGURE 1 Molecular structure of compounds **I'***n* and **II'***n*.

smectic phases, and some are inherently ferroelectric [6]. Several years ago, two series of liquid crystals, series **I'***n* [14] and series **II'***n* [15], which show broad ranges of the smectic C phase, were prepared (Fig. 1). It is well known that liquid-crystalline properties are sensitive to the polarity of the core. Here we synthesized two other series of liquid crystals simply by changing the direction of the ester bond in the cores. This change would affect the polarity of the whole molecule and so would affect the liquid-crystalline properties.

RESULTS AND DISCUSSION

The phase-transition temperatures of all the compounds were determined by differential scanning calorimetry (DSC) with a heating rate of 5°C min^{-1}. The mesomorphic textures were observed on polarizing optical textures for determining the types of mesophases. The transition temperatures shown in Table 1 are the maxima of the transition peaks on each DSC trace.

The compounds were obtained by routes depicted in Scheme 1. The intermediates and final compounds were synthesized according to literature methods [1,2]. The phase-transition behavior of the final compounds is summarized in the table as determined by DSC.

The phase-transition temperatures of compounds **I***n* and **II***n* are summarized in the table. Compounds **I***n* show enantiotropic SmB and SmA phase. When the carbon number (n) of the alkoxy chain is 9, an enantiotropic SmC phase is identified. The clearing points decrease with increasing length of the alkoxy chains. With the introduction of triple bonds to compounds **I***n*, compounds **II***n* were obtained. The SmB phase stability was suppressed by the introduction of triple bonds. Generally, compounds **II***n* show enantiotropic SmA and SmC phases. When the carbon numbers (n) are 4 and 5, enantiotropic nematic phases are identified, with ranges of around 1 to 2°C. Posssibly the triple bond interfered with the conjugation of the molecule; the lateral–lateral interactions are then weakened.

For a clear understanding of the effect of the direction of the ester group in the core, mesomorphic properties of compounds **I***8*, **I'***8*, **II***8*, and **II'***8* are summarized in Fig. 2. The clearing points of **I'***8* and **II'***8*

TABLE 1 Transition Temperatures of Compounds **I***n* and **II***n*

Compounds	n	Transition temperatures (°C)
I*6*	6	Cr 133.9, SmB 140.4, SmA 208.8, I 205.4, SmA 138.4, SmB 131.8 Recr
I*7*	7	Cr 129.4, SmB 141.6, SmA 203.0, I 201.2, SmA 140.1, SmB 127.5 Recr
I*8*	8	Cr 119.4, SmB 141.1, SmA 197.7, I 196.0, SmA 139.6, SmB 117.4 Recr
I*9*	9	Cr 127.6, SmB 129.9, SmC 146.9, SmA 188.2, I 185.8, SmA 146.7, SmC 127.6, SmB 104.6 Recr
II*4*	4	Cr 111.1, SmA 206.5, N 208.3, I 208.0, N 203.9, SmA 101.7, SmB 89.4 Recr
II*5*	5	Cr 103.9, SmC 113.6, SmA 195.9, N 197.1, I 194.5, N 193.5, SmA 111.9, SmC 96.0, SmB 81.3 Recr
II*8*	8	Cr 115.7, SmC 138.3, SmA 183.9, I 182.2, SmA 136.9, SmC 114.3 Recr
II*9*	9	Cr 111.9, SmC 150.5, SmA 179.1, I 177.4, SmA 148.9, SmC 110.4, SmB 88.3, SmX_1 74.4, SmX_2 71.2 Recr
II*12*	12	Cr 109.5, SmB 112.9, SmC 153.4, SmA 168.41, I 166.5, SmA 151.8, SmC 111.1, SmB 81.3 Recr

Notes. Cr = crystal; N = nematic phase; SmA = smectic A phase; SmC = smetic C phase; SmB = smetic B phase; Smx = unclear smetic phase; I = isotropic liquid; Recr = recrystal.

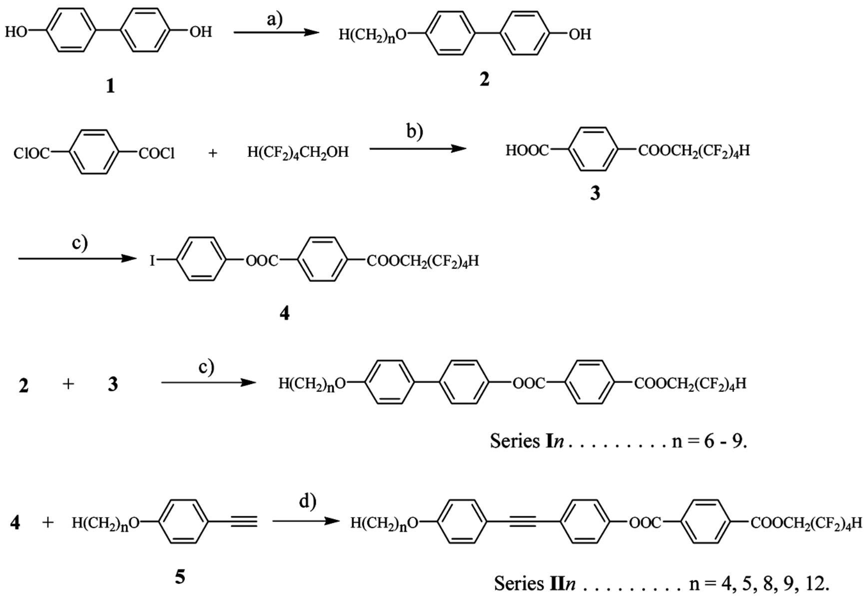
are higher than those of **I***8* and **II***8*, respectively. From the molecular structures, we know **I'***8* and **II'***8* show higher polarity, which is the main reason for the increase of the clearing points. With the increase in the polarity, SmC phases tend to be formed. For example, **I'***8* shows an enantiotropic SmC phase; however, **I***8* does not show the SmC phase. Moreover, the $T_{SmC\text{-}SmA}$ transition of **II'***8* is 34.9°C higher than that of **II***8*. The melting points of **I'***8* and **II'***8* are lower than those of **I***8* and **II***8*, respectively. Molecular symmetry plays an important role in melting points.

In summary, two series of compounds with semifluorinated chains have been synthesized. The introduction of triple bonds suppresses the formation of the SmB phase. The direction of ester bonds strongly affects the melting and the clearing points, as well as the formation of the SmC phase.

EXPERIMENTAL

Characterization

The structures of the final products and intermediates were determined by a variety of spectral methods. IR spectra were taken on a PE-983G spectrophotometer, using KBr pellets of the solids or films



SCHEME 1 Synthesis of compounds **I***n* and **II***n*: a) $H(CH_2)_nBr$/KOH/KI, EtOH; b1) $H(CF_2)_4CH_2OH$, b2) HCl aq.; c) DCC/DMAP, THF; d) $Pd(PPh_3)_2Cl_2$, CuI, PPh_3, THF/Et_3N.

of liquids. ^1H NMR spectra, with TMS as internal NMR standard, were recorded on a Varian EM 360L spectrometer (60 MHz) or a Fx-90Q instrument (90 MHz); ^{19}F NMR spectra, with trifluoroacetic acid (TFA) as external standard, were recorded on a Varian EM 360L spectrometer (60 MHz). For ^{19}F NMR, the high field was positive. MS spectra were measured with a Finnigan-4021 spectroscope.

The phase-transition temperatures of the target compounds were measured by optical microscopy using a polarizing microscope (Olympus PM-6) fitted with a heating stage (Mettler FP-80) and control unit (FP-82) and by DSC (Shimidazu DSC-50 calorimeter with a data system, heating and cooling rate of 5°C min^{-1}). The transition temperatures reported in this article were the peak values of the transition on DSC traces. Phase identification was made by comparing the observed textures with those reported in the literature.

Synthesis

All of the obtained liquid crystals were purified by column chromatography on silica gel using petroleum ether (bp 60–90°C)/ethyl acetate

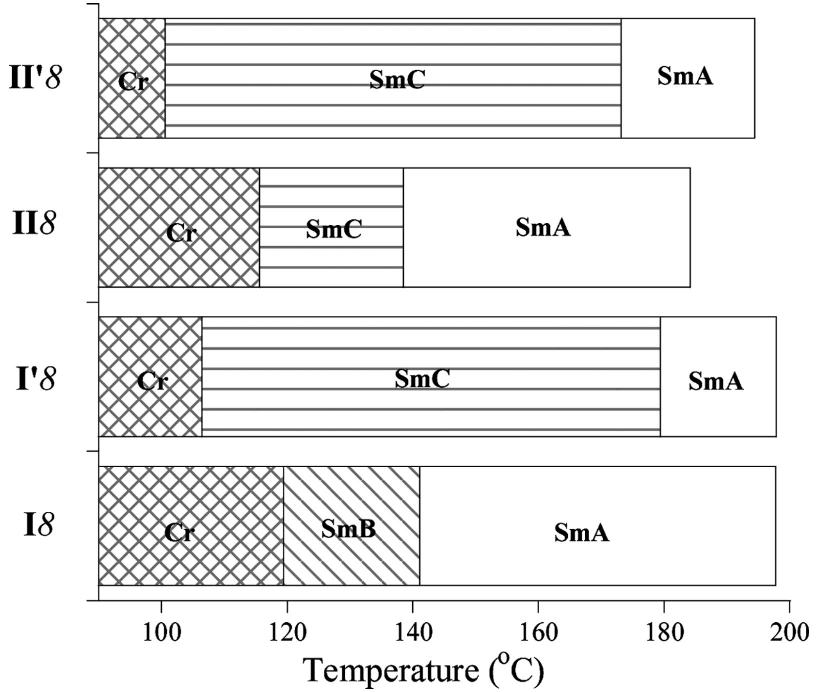


FIGURE 2 Comparison of mesomorphic properties of compounds **I***8*, **I'***8*, **II***8*, and **II'***8*.

(20/1) as eluent and then recrystallized from petroleum ether (bp 60–90°C) and acetone/methanol.

Synthesis of Compound I8

A typical synthetic procedure is as follows: 4-(4′-*n*-octyloxyphenyl)-phenol (0.60 mmol), compound **3** (0.60 mmol), *N,N*′-dicyclohexylcarbodiimide (0.7 mmol), catalytic 4-(dimethylamino)-pyridine, and dry THF (10 ml) were stirred under N_2 at room temperature for 48 h. The mixture was filtered, and the residue was washed with THF. The collected filtrates were evaporated on a rotary evaporator. The residue was purified by flash chromatography and recrystallized from acetone/methanol to give a white solid. Mp 119.4°C. IR (KBr) υ_{max}: 2929, 2853, 1730, 1608, 1278, 1172, 811 cm^{-1}. ^1H NMR (90 MHz, $CDCl_3$/TMS) δ: 0.90 (t, $J = 6$ Hz, 3H, CH_3), 1.27–1.88 (m, 12H), 4.02 (t, $J = 6$ Hz, 2H), 4.90 (t, $J = 14.27$ Hz, 2H), 6.10 (tt, $J = 50$ Hz, 5 Hz, 1H), 6.94–7.67 (m, 8H), 8.17–8.39 (m, 4H) ppm. ^{19}F NMR (56.4 MHz, $CDCl_3$/TFA) δ: 42.1 (s, 2F), 48.0 (s, 2F), 52.7 (s, 2F), 59.9 (d, $J = 50$ Hz, 2F) ppm. MS (m/z): 661 ($M^+ + 1$, 33.19), 362

($HC_4F_8CH_2OOCC_6H_4CO^+ - 1$, 100.00). Elemental analysis: calculated for $C_{33}H_{32}F_8O_5$; C, 60.00; H, 4.88; F, 23.01%; found: C, 59.85; H, 4.68; F, 23.10%.

Synthesis of Compound II8

A typical synthetic procedure is as follows: To a mixture of compound 4-octyloxyphenylacetylene (**5**, 0.44 mmol), compound **4** (0.4 mmol), bis(triphenylphosphine)palladium dichloride (20 mg), triphenylphosphine (60 mg), and CuI (60 mg), under dry N_2, 20 ml of anhydrous triethylamine were added. The obtained mixture was heated under reflux with stirring for 2 h. Analysis by thin-layer chromotography (TLC) revealed completion of the reaction. The precipitate that formed was then filtered off and washed with ether. The solvent was removed *in vacuo*, and the residue was purified by column chromatography on silica gel using petroleum ether/dichloromethane as eluent. The obtained compound was recrystallized from petroleum ether (bp 60–90°C) and subsequently acetone/methanol. Mp 115.7°C. IR (KBr) υ_{max}: 2930, 2853, 2221, 1730, 1607, 1566, 1215, 1168, 838 cm^{-1}. ^1H NMR (90 MHz, $CDCl_3$/TMS) δ: 0.90–1.90 (m, 15H, aliphatic hydrogens), 4.01 (t, $J = 6$ Hz, 2H), 4.90 (t, $J = 14.2$ Hz, 2H), 6.10 (tt, $J = 50$Hz, 5 Hz, 1H), 6.90 (d, $J = 8$ Hz, 2H, ArH), 7.20–7.66 (m, 6H), 8.17–8.39 (m, 4H) ppm. ^{19}F NMR (56.4 MHz, $CDCl_3$/TFA) δ: 42.10 (s, 2F), 47.80 (s, 2F), 52.20 (s, 2F), 59.90 (d, $J = 50$ Hz, 2F) ppm. MS (m/z): 686 ($M^+ + 2$, 45.87), 362 ($HC_4F_8CH_2OOCC_6H_4CO^+ - 1$, 100.00). Elemental analysis: calculated for $C_{35}H_{32}F_8O_5$: C, 61.40; H, 4.71; F, 22.20%; found: C, 61.27; H, 4.64; F, 21.90%.

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