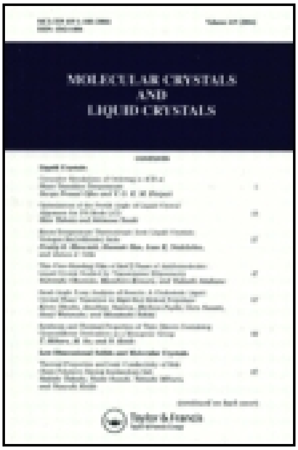

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Mesomorphic Properties of Some Liquid Crystals with Semifluorocarbon Chains

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Mesomorphic Properties of Some Liquid Crystals with Semifluorocarbon Chains

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Three series of chiral compounds with semifluorocarbon chains have been synthesized. These compounds were characterized by infra-red spectra (IR), ^1H nuclear magnetic resonance (^1H NMR), ^{19}F nuclear magnetic resonance (^{19}F NMR), mass spectra (MS), and elemental analysis. Their phase-transition behavior was investigated by differential scanning calorimeter (DSC) and polarizing optical microscopy. To a certain compound, when the terminal hydrogen atom in the semifluoroalkyl chain was substituted by a chlorine atom, both the clearing point and the melting point were increased and the thermal stability of the SmC phase was enhanced. Moreover, with the introduction of a triple bond in the core, both the melting point and the clearing point were increased.

Keywords: fluorocarbon; liquid crystal; mesomorphic

INTRODUCTION

Liquid-crystalline compounds with fluorocarbon chains have been well studied [1–13]. In general, perfluoroalkyl or semiperfluoroalkoxy chains enhance the formation of smectic phases. In particular, molecules with semiperfluorinated chains exhibit tilted smectic phases, and some are inherently ferroelectric [1]. Recently, our group found that a subtle modification of the fluorocarbon chain, the change of the terminal hydrogen atom in the semifluorocarbon chain to a chlorine atom, can enhance the thermal stability of the SmC phase [12]. Here, we study this effect further in two series of compounds.

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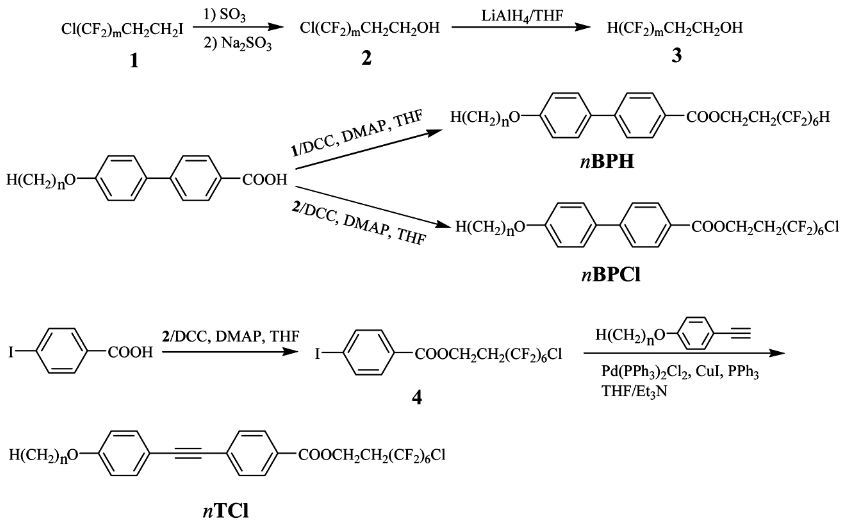
Moreover, another series of compounds with triple bonds in the cores were synthesized. The effect of the triple bond was also studied.

RESULTS AND DISCUSSION

Three series of compounds with semifluorocarbon chains were synthesized according to Scheme 1. Compound **2** was synthesized by dropping **1** into fuming sulfuric acid at 90°C. Then the obtained mixture was dropped into aq. Na_2SO_3 under stirring. After the mixture was refluxed for 1 h, compound **2** was extracted using F113 and purified by distillation in a yield of 75%. Compound **3** was synthesized by the reduction of **2** using $LiAlH_4$. 4-*n*-Alkoxybiphenyl-4′-carboxylic acids and 4-*n*-alkoxyphenylacetylenes were synthesized according to the literature [3,13].

The phase-transition temperatures of *n***BPH** and *n***BPCl** are summarized in Table 1. Only smectic phases were identified. Although the liquid-crystalline temperature ranges are narrow, the SmC phase is formed. When the alkoxy chains are short, enantiotropic SmA and SmC phases are identified. However, when the alkoxy chains are long, compounds *8***BPH** and *10***BPCl** do not form liquid-crystalline phases. In general, the clearing points of the liquid crystals decrease with increasing alkoxy chain length.

By changing the hydrogen atoms in the terminus of the semifluorocarbon chains of *n***BPH** to chlorine atoms (*n***BPCl**), they show similar



SCHEME 1 Synthetic route.

TABLE 1 Transition Temperatures of Compounds *n***BPH** and *n***BPCl**

Compounds	n	Transition temperatures (°C)
*5***BPH**	5	Cr 89.9, SmC 97.6, SmA 108.7, I 106.8, SmA 96.3, SmC 83.0 Recr
*7***BPH**	7	Cr 94.0, SmC 96.2, I 94.3, SmC 82.0 Recr
*8***BPH**	8	Cr 105.2, I 96.9 Recr
*5***BPCl**	5	Cr 95.2, SmC 109.9, SmA 122.1, I 120.3, SmA 108.8, SmC 86.3 Recr
*6***BPCl**	6	Cr 95.0, SmC 111.6, SmA 116.6, I 114.5, SmA 111.0, SmC 88.4 Recr
*7***BPCl**	7	Cr 96.6, SmC 111.1, I 108.9, SmC 90.0 Recr
*8***BPCl**	8	Cr 108.4, I 105.8, SmC 95.2 Recr
*10***BPCl**	10	Cr 112.1, I 105.0 Recr

Note. Cr = crystal; SmA = smectic A phase; SmC = smectic C phase; I = isotropic liquid; Recr = recrystal.

liquid-crystalline properties as *n***BPH**. *8***BPCl** shows a monotropic SmC phase; however, *8***BPH** is not liquid crystalline. When the alkoxy chain numbers are the same, the clearing points and melting points of compounds *n***BPCl** are higher than those of *n***BPH**.

By introducing triple bonds into the cores of *n***BPCl**, compounds *n***TCl** were obtained. The phase-transition temperatures of *n***TCl** are summarized in Table 1 and Fig. 1. The clearing points show a clear odd–even effect. When the carbon numbers of alkoxy chains are 4–6, enantiotropic SmA, SmC, and monotropic SmE phases were identified. When the carbon numbers of alkoxy chains are 7–10, only an enantiotropic SmC phase was identified. *n***BPCl** has longer liquid-crystalline

TABLE 2 Transition Temperatures of Compounds *n***TCl**

Compounds	n	Transition temperatures (°C)
*4***TCl**	4	Cr 89.4, SmC 96.4, SmA 123.6, I 119.7, SmA 96.1, SmC 88.0, SmE 73.2 Recr
*5***TCl**	5	Cr 95.4, SmC 103.0, SmA 115.5, I 111.9, SmA 102.2, SmC 83.2, SmE 78.5 Recr
*6***TCl**	6	Cr 103.6, SmC 111.8, SmA 114.7, I 111.5, SmA 110.8, SmC 82.4, SmE 81.5 Recr
*7***TCl**	7	Cr 100.9, SmC 109.7, I 107.5, SmC 83.6 Recr
*8***TCl**	8	Cr 101.2, SmC 109.4, I 107.4, SmC 84.3 Recr
*9***TCl**	9	Cr 98.9, SmC 106.4, I 104.2, SmC 89.4 Recr
*10***TCl**	10	Cr 102.8, SmC 104.3, I 101.7, SmC 92.7 Recr

Note. Cr = crystal; SmA = smectic A phase; SmC = smectic C phase; SmE = smectic E phase; I = isotropic liquid; Recr = recrystal.

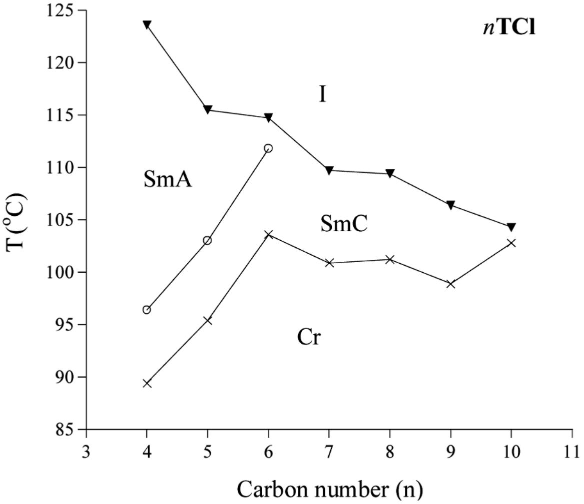


FIGURE 1 Transition behavior of the compounds *n***TCl**: dependence of the transition temperatures on the number (n) of methylene units of the nonfluorinated chain.

cores, increased clearing points, and higher SmC phase temperature ranges than *n***TCl**.

For a clearer understanding of the effects of the H/Cl change at the terminal location of the semifluorocarbon chain and the introduction of a triple bond, the phase-transition properties of three compounds (7**BPH**, 7**BPCl**, and 7**TCl**) are summarized in Fig. 2. From the phase-transition behavior of 7**BPH** and 7**BPCl**, it is found that the substitution of chlorine atom can enhance the tendency for the formation and the thermostability of the SmC phase and increase the clearing and melting points. Such increases are caused by the greater polarity and polarizability of the terminal chlorosubstituent when compared to hydrogen. The substitution of hydrogen for chlorine increases the length of this core. Therefore, the clearing point is increased, and SmC phase temperature range is broader. Turning to 7**BPCl** and 7**TCl**, with the introduction of a triple bond into the core, the clearing point, the melting point, and the SmC phase temperature range are increased, which is as expected because the triple bond increases the molecular length.

In summary, three series of compounds with semifluorocarbon chains have been synthesized. When the terminal hydrogen atom in the semifluoroalkyl chain was substituted by a chlorine atom, both the clearing point and melting point increased, and the SmC* phase

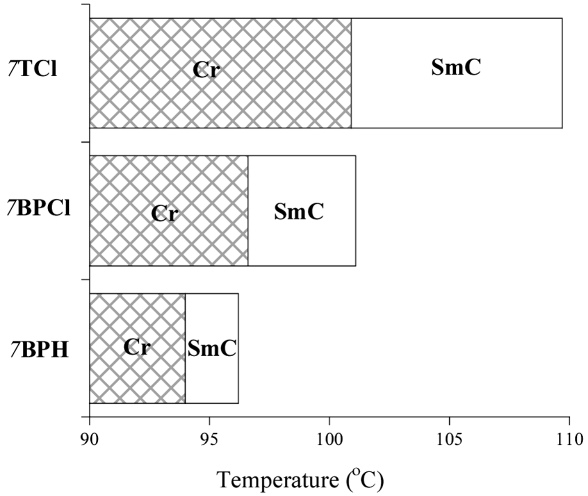


FIGURE 2 Comparison of mesomorphic properties of compounds 7**BPH**, 7**BPCl**, and 7**TCl**.

temperature range was broadened. Meanwhile, both the clearing point and melting point increased with the introduction of a triple bond into the core.

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 of liquids. ^{1}H 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). MS spectra were measured with a Finnigan-4021 spectrometer.

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 differential scanning calorimetry (DSC, Shimidazu DSC-50 calorimeter with a data system, heating and cooling rates 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 (20/1) as eluent and then recrystallized from petroleum ether (bp 60–90 °C) and acetone/methanol.

*Synthesis of Compound 7*BPH

A typical synthetic procedure was as follows. 4-*n*-Heptyloxybiphenyl-4′-carboxylic acid (0.60 mmol), compound **3** (0.60 mmol), *N*,*N*′-dicyclohexylcarbodiimide (0.7 mmol), catalytic DMAP, 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 94.0 °C. υ_{max}(KBr): 2931, 2856, 1715, 1603, 1527, 1200, 1139, 831 cm^{-1}.^{1}H NMR δ_H (90 MHz; $CDCl_3$; TMS): 0.97 (t, $J = 7.0$ Hz, 3H, CH_3), 1.36–1.90 (m, 10H, $5 \times CH_2$), 2.64 (tt, $J_1 = 18.2$ Hz, $J_2 = 6.5$ Hz, 2H, CH_2R_f), 4.01 (t, $J = 6.6$ Hz, 2H, RCH_2O), 4.65 (t, $J = 6.4$ Hz, 2H, RCH_2O), 6.07 (tt, $J_1 = 49.3$, $J_2 = 5.2$ Hz, H, CF_2H), 7.00 (d, $J = 8.7$ Hz, 2H, ArH), 7.57 (d, $J = 8.7$ Hz, 2H, ArH), 7.64 (d, $J = 8.4$ Hz, 2H, ArH), 8.09 (d, $J = 8.4$ Hz, Hz, 2H, ArH) ppm. ^{19}F NMR δ_F (56.4 MHz, $CDCl_3$, TFA): 36.40 (m, 2F), 44.70–46.60 (m, 6F), 52.50 (s, 2F), 60.00 (d, $J = 50$ Hz, 2F) ppm. MS m/z (rel. int.): 641 ($M^+ + 1$, 45.54), 542 ($M^+ - C_7H_{15}$, 100.00), 197 ($HOC_6H_4C_6H_4CO^+$, 45.42). Elemental analysis calculated (for $C_{28}H_{28}F_{12}O_3$): C, 52.51; H, 4.41; F, 35.59%. Found: C, 52.49; H, 4.36; F, 35.51%.

*Synthesis of Compound 7*BPCl

Mp 96.6 °C. υ_{max}(KBr): 2930, 1715, 1603, 1527, 1201, 1147, 830 cm^{-1}. ^{1}H NMR δ_H (90 MHz; $CDCl_3$; TMS): 0.97 (t, $J = 7.0$ Hz, 3H, CH_3), 1.36–1.90 (m, 10H, $5 \times CH_2$), 2.64 (tt, $J_1 = 18.2$ Hz, $J_2 = 6.5$ Hz, 2H, CH_2R_f), 4.01 (t, $J = 6.6$ Hz, 2H, RCH_2O), 4.65 (t, $J = 6.4$ Hz, 2H, RCH_2O), 7.00 (d, $J = 8.7$ Hz, 2H, ArH), 7.57 (d, $J = 8.7$ Hz, 2H, ArH), 7.64 (d, $J = 8.4$ Hz, 2H, ArH), 8.09 (d, $J = 8.4$ Hz, 2H, ArH) ppm. ^{19}F NMR δ_F (56.4 MHz, $CDCl_3$, TFA): −9.30 (s, 2F), 36.40 (s, 2F), 43.10–44.50 (m, 6F), 46.33 (s, 2F) ppm. MS m/z (rel. int.):

674 ($M^+ + 2$, 51.59), 576 ($M^+ - C_7H_{14}$, 100.00), 197 ($HOC_6H_4C_6H_4CO^+$, 79.56). Elemental analysis calculated ($C_{28}H_{27}ClF_{12}O_3$): C, 49.83; H, 4.03; F, 33.77; Cl, 5.25%. Found: C, 49.91; H, 4.01; F, 33.53; Cl, 5.11%.

*Synthesis of Compound 7*TCl

A typical synthetic procedure was as follows: to a mixture of compound 4-*n*-heptyloxyphenylacetylene (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, was added 20 mL of anhydrous triethylamine. The obtained mixture was heated under reflux under stirring for 2 h. Analysis by thin-layer chromatography (TLC) revealed completion of the reaction. The precipitate 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 acetone/methanol subsequently. Mp 100.9 °C. IR (KBr) υ_{max}: 2933, 2857 (s, C–H), 215(s, C≡C), 1715(vs, C=O), 1598 (s, C_6H_4), 1206, 1143 (s, C–O–C) cm^{-1}. ^1H NMR δ_H (60 MHz; $CDCl_3$; TMS): 0.90 (t, 3H, CH_3), 1.33–2.03 (m, 10H, $5 \times CH_2$), 2.60 (tt, $J_1 = 18$ Hz, $J_2 = 6$ Hz, 2H, CH_2R_f), 3.97 (t, $J = 6.0$ Hz, 2H, RCH_2O), 4.60 (t, $J = 6.0$ Hz, 2H, RCH_2O), 6.82 (d, $J = 7.5$ Hz, 2H, ArH), 7.37–7.56 (m, 4H, ArH), 7.94 (d, $J = 7.5$ Hz, 2H, ArH) ppm. ^{19}F NMR δ_F (56.4 MHz, $CDCl_3$, TFA): -9.50 (s, 2F), 35.67 (s, 2F), 42.42–43.75 (m, 6 F), 45.73 (s, 2F) ppm. MS m/z (rel. int.): 699 ($M^+ + 1$, 66.29), 600 ($M^+ - C_7H_{14}$, 100.00), 221 ($HOC_6H_4{-}{\equiv}{-}C_6H_4CO^+$, 36.14). Elemental analysis calculated (for $C_{30}H_{27}ClF_{12}O_3$): C, 51.55; H, 3.89; F, 32.62; Cl, 5.07%. Found: C, 51.56; H, 3.85; F, 32.91; Cl, 5.08%.

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