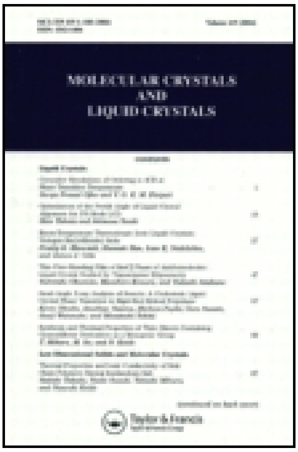

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Synthesis of Rod-Like and Y-Shaped Liquid-Crystalline Compounds with Fluorinated Tail Groups

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A series of the rod-like and Y-shaped liquid-crystalline (LC) compounds with per- and semifluorinated tails was synthesized with variation of the tail length. The perfluoroalkyl tails enhanced stability of the mesophase both for rod-shaped and Y-shaped LC compounds. The effect of semifluoroalkyl tails is different. For rod-shaped compounds such substituents strongly suppress LC properties. For Y-shaped compounds, smectic properties are stabilized.

Keywords Fluorinated tail; rod-like; synthesis; Y-shaped mesomorphic behavior

Introduction

Liquid-crystalline (LC) materials have been known for over a century [1]. It is clear that architecture and functionalization are essential aspects in molecular engineering of liquid crystals for controlling physical properties that give rise to mesophase formation: molecular shape, space filling effects, deformation ability, chirality, minimal interfacial curvature, microphase segregation, and self-assembly. Fluoro substituents have been successfully and usefully incorporated into LC molecules because of the combination of their small size, and high polarity and because the high strength of the C–F bond confers excellent stability. The relatively small size of a fluoro substituent means that it does not significantly alter the desired molecular structure, which helps to maintain the existing LC nature of the compound. However, the important attributes of the fluoro substituent result in subtle but significant changes in physical properties such as melting point, mesophase morphology, and transitions temperatures as well as optical, dielectric, and visco-elastic properties. Such alterations to the attributes of liquid crystals are of great significance in terms of fundamental structure–property relationships and are crucial to the development of commercially successful LC displays [2].

In this study, the influence of fluoro substituents in terminal chains of rod-like and Y-shaped LC compounds on its phase behavior was investigated.

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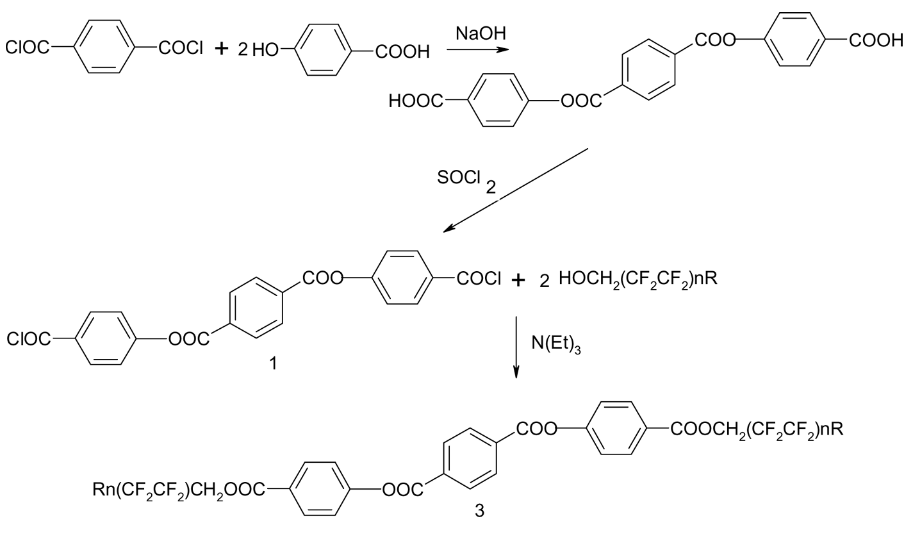
Results and Discussion

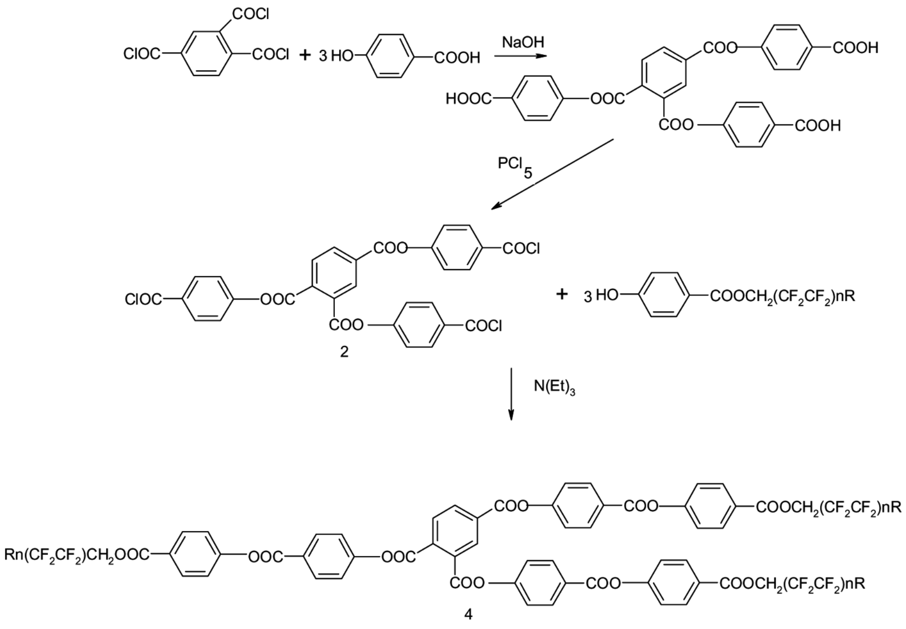
In our study fluoro substituents can constitute a whole terminal chain in the form of a partially fluorinated chain with a perfluorocarbon terminal group or with a semifluorocarbon terminal group with one hydrogen atom located on the end of a pseudo-hydrocarbon chain. In both cases the fluorocarbon moiety is comparatively conformationally rigid. The synthesis of low- and high-molecular-weight polyesters was used as a pathway to a complex acid chloride fragment, which can further react with different alcohols and diols [3]. It allows simplifying a laborious synthesis of a range of compounds with variation of tail groups. Terephthalic acid for rod-like LC compounds (Scheme 1) and a core of 1,2,4-benzenetricarboxylic acid for Y-shaped LC compounds (Scheme 2) were chosen as starting blocks.

The acid chlorides **1** and **2** were prepared in one step from corresponding acids synthesized by interphase condensation of terephthaloyl or 1,2,4-benzenetricarboxylic acid chlorides with p-4-hydroxybenzoic acid [4,5]. The acid chlorides **1** and **2** were used for synthesis of rod-like and Y-shaped compounds **3** and **4,** respectively, by condensation with available semifluorinated alcohols and corresponding p-alkylcarboxyphenols (Schemes 1 and 2). This method was chosen for the preparation of compounds **3–4** because the scale of the reaction may be large and a good yield was essential. The properties of compounds **3–4** are given in Table 1. To complete the reaction, double excess of corresponding alcohol or phenol was required. The reaction time is very fast compared to that with nonfluorinated alcohols or phenols (5–20 min). If the reaction time increases at least twofold (to 40–50 min), thus leads to full destruction of monomers **1–2**. Hence, the ester bonds of monomers **1–2** are sensitive to cleavage by alcohols or phenols with fluorine substituents due to their strong acidity. This property of fluorinated alcohols and phenols is widely used in organic and bioorganic chemistry (for example, for cleavage of protecting groups [6]). The reaction time for the synthesis of compounds **3–4** was optimized to the product yield.

The LC properties of compounds **3–4** were studied under polarizing optical microscopy (POM). The transition temperatures for these compounds were



Scheme 1. The pathway to rod-like LC compounds.



Scheme 2. The pathway to Y-shaped LC compounds.

determined by differential scanning calorimetry (DSC; see Table 1). The melting points increased for all rod-like compounds **3**. The increase of melting temperature and isotropization enthalpy are typical for changes of the alkyl tail on perfluoroalkyls for LC rod-like compounds [2]. Compound **3c** with perfluorinated tails has about the same isotropization temperature as its alkyl analog and the same type of mesophase (smectic A according to POM observations). For compound **3** with semifluorinated tails the situation is different. If compound **3d**, with a relatively long heptyl tail, has practically the same clearing point as its alkyl analog, then compound **3b**

Table 1. Phase transition temperatures and transition enthalpies of compounds **3–4**

Compound	n	R	$T_m{}^a$ (°C)	$\Delta H_m{}^b$ (J g^{-1})	$T_i{}^c$ (°C)	$\Delta H_i{}^d$ (J g^{-1})
3a	1	H	163 (130)^e	5.3 (65.2)^e	−(221)^e	−(1.1)^e
b	2	H	161 (150.5)^e	4.2 (72.0)^e	−(191.6)^e	−(10.5)^e
c	2	F	162.5 (150.5)^e	49.2 (72.0)^e	191.8 (191.6)^e	14.4 (10.5)^e
d	3	H	158.5 (148.5)^e	6.7 (74.5)^e	174 (175)^e	1.2 (11.3)^e
4a	1	H	154 (−)^e	5.5 (−)^e	300 (−)^e	—
b	2	H	142 (86.3)^e	7.4 (28.1)^e	203 (138)^e	1.8 (1.7)^e
c	2	F	144 (86.3)^e	13.5 (28.1)^e	217 (138)^e	2.1 (1.7)^e
d	3	H	118 (17)^e	12.1 (15.6)^e	192 (72.5)^e	1.2 (1.0)^e

[a] Melting point.
[b] Enthalpy at T_m..
[c] Clearing temperature.
[d] Enthalpy at T_i.
[e] Literature data for alkyl analogs for **3** from Leblanc *et al.* [9] and for **4** from Zuev [5] are given in parentheses.

is not liquid crystalline, and **3a** exhibits a monotropic phase between 160°C and 153°C. Hence, replacing one fluorine atom with a hydrogen atom in the terminal methyl group of the perfluoroalkyl tail of compound **3** leads to suppression of the LC behavior of these compounds.

A similar observation was made by Goodby *et al.* [7]. The highly polar nature of the C–F bond can cause polarization of the C–H bond of the same carbon, thus enabling the hydrogen to be involved in hydrogen bonding with the fluorine of a neighboring molecule. Evidently, this interaction leads to destruction of the LC order of calamitic molecules as a result of the formation of a 3D network of hydrogen bonds.

The following trends are observed for series of Y-shaped LC compound **4**. The clearing points of compounds **4a-d** are higher than their nonfluorinated analogs. Y-shaped compounds form a smectic mesophase according to microscopic observations. Furthermore, the clearing temperature for compound **4c** is slightly higher than for compound **4d**. Hence, in this case the perfluoroalkyl tails enhance the thermotropic behavior. In Y-shaped mesogens the mesophase adopts a layered lattice, and the lateral intermolecular attractions help to keep the lateral arrangement in the LC state, hence stabilizing the smectic mesophase. The following conclusions can be made:

1. The perfluoroalkyl tails enhance the stability of the mesophase for both rod-shaped and Y-shaped LC compounds.
2. The effect of semifluoroalkyl tails is different for rod-shaped and Y-shaped LC compounds. For rod-shaped compounds such substituents strongly suppress LC properties. Y-shaped compounds exhibit enhanced smectic properties.

Experimental

Characterization of Materials

The chemical structures for the target materials were identified by ^{1}H nuclear magnetic resonance (NMR) spectroscopy using a Bruker MSL 400 spectrometer and Infrared (IR) spectroscopy using a Bruker Vertex instrument. The purity of the final compounds was assessed by thin-layer chromatography and further confirmed by elemental analysis. The analytical data showed that the percentage errors for the carbon, hydrogen, fluorine, and chlorine contents for the target materials were less than 1% compared with the calculated results. The transition temperatures and enthalpies for all materials were determined by DSC using a Shimadzu 60 calorimeter at a rate of 5°C min^{-1}. Mesophases were identified using a Boetius optical microscope with hot stage (Germany).

Preparation of Materials

4-Semifluoroalkylesters of p-hydroxybenzoic acid were obtained by azeotrope esterification with benzene as solvent and sulfuric acid as catalyst from p-hydroxybenzoic acid and corresponding semifluoroalkyl alcohols. Chloride of 1,2,4-benzenetricarboxylic acid was obtained using the method described in Drechsler and Heidenreich [8]. Chlorides **1** and **2** were obtained according to Bilibin *et al.* [4,5].

Di-5,5′,5″,4,4′,3,3′,2,2′-Nonafluoropentyl-terephthaloyl-bis-4-oxybenzoate ***(3c)***. A solution of 5 g (1 mmol) chloride 1, 0.8 g (4 mmol) 5,5′,5″,4,4′,3,3′,2,2′-nonafluoropentyl alcohol, and 0.4 g (4 mmol) triethylamine in 15 mL of anhydrous dichloroethane was vigorously stirred for 15 min at room temperature. The resulting mixture was poured in 150 mL of ethanol and the residue was filtered off, dried, and twice recrystallized from ethanol to yield white crystals. Yield 550 mg (76%). ^{1}H NMR ($CDCl_3$), δ (J, Hz): 8.36 s (4H); 8.18 d (4 H, J 8.8); 7.39 d (4 H, J 8.8); 4.85 t (4H, J = 13.3). IR (KBr, ν, cm^{-1}): 3103, 3071, 3057, 2892, 1736 (C=O), 1603, 1504, 1433, 1416, 1277, 1200, 1165, 1141, 1119, 1077, 1019, 971, 880, 702. Elemental analysis: Found, %: C 43.45; H 1.50; F 39.01. Calc. for $C_{32}H_{16}O_8F_{18}$, %: C 44.15; H 1.85; F 39.29.

Other compounds **3** were synthesized in a similar way with yields of 45–75%.

Di-5,5′,4,4′,3,3′,2,2′-Octafluoropentyl-terephthaloyl-bis-4-oxybenzoate ***(3b)***. ^{1}H NMR ($CDCl_3$), δ (J, Hz): 8.36 s (4H); 8.18 d (4 H, J 8.8); 7.39 d (4 H, J 8.8); 6.08 tt (2H, $J_1 = 51.9$; $J_2 = 5.4$); 4.85 t (4H, J = 13.5). IR (KBr, ν, cm^{-1}): 3103, 3071, 3057, 2892, 1736 (C=O), 1603, 1504, 1433, 1416, 1277, 1200, 1165, 1141, 1119, 1077, 1019, 971, 880, 702. Elemental analysis: Found, %: C 45.95; H 2.17; F 36.81. Calc. for $C_{32}H_{18}O_8F_{16}$, %: C 46.06; H 2.17; F 36.43.

1,2,4-Tris(4′-n-5,5′,5″,4,4′,3,3′,2,2′-Nonafluoropentylcarbonylyphenyl-4-oxycarbonylphenyloxycarbonyl)benzene ***(4c)***. ^{1}NMR ($CDCl_3$), δ (J, Hz): fragment of 1,2,4-benzene 8.91 s; 8.60 d (1 H, J 8.08); 8.17 d (1 H, J 8.08); fragment of oxybenzoate 8.31 d (4H, *ortho*, J 8.08); 8.35 d (2H, ortho, J 8.08), 7.45 d (4H, *meta*, J 8.08); 7.47 d (2H, *meta*, J 8.08); terminal fragment of oxybenzoate 7.32 d (6H, ortho, J 8.08); 8.13 d (6H, *meta*, J 8.08); 4.85 t (6H, OCH_2, J = 13.3). IR (KBr, ν, cm^{-1}): 3103, 3080, 3057, 2982, 1743 (C=O), 1603, 1508, 1415, 1359, 1263, 1235, 1160, 1062, 1014, 919, 843, 756. Elemental analysis: Found, %: C 47.80; H 2.00; F 31.01; Calc. for $C_{66}H_{33}O_{18}F_{27}$, %: C 48.72; H 2.05; F 31.53.

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