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Semifluorinated Liquid-Crystalline Di- and Triblock Ester Molecules

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ABSTRACT: A series of ester molecules based on rigid fluoroalkyl mesogenic units instead of the classical linked-ring systems has been synthesized and investigated for liquid crystallinity. Aliphatic hydrocarbon chains or substituted single phenyl rings were linked to various perfluoroalkyl segments. The mesophases were investigated by optical microscopy, DSC, and X-ray diffraction. In these compounds smectic A or B phases were observed and identified optically or by X-ray diffraction. The 3,5-dihydroxyphenyl compounds were also found to be lyotropic. Differences in the mesophase transition temperatures were observed which are discussed in terms of the structure. The smectic layer spacings found from X-ray data show monolayers or bilayers. This type of layer ordering is discussed with reference to the structure and considering the molecules as models of main-chain and side-chain polymers.

Introduction

Most liquid-crystalline materials are classically composed of linear rod-shaped molecules[1] based on para-substituted ring systems. Novel structures that are compatible with liquid crystallinity are therefore of interest, and while structure−property relationships for the linked-ring type molecules[2] have been extensively studied, liquid-crystalline behavior in molecules where the mesogenic unit consists of rigid "rodlike" fluoroalkyl segments has been little investigated.

Diblock and triblock carbon−carbon-linked fluorocarbon−hydrocarbon small-molecule compounds, usually with longer fluorinated segments, have been investigated[3−6] and usually show smectic B or very narrow smectic A mesophases.[6] It has been observed that in main-chain polymers composed of short alternating fluorocarbon and hydrocarbon blocks, the "microblock polymers", a mesophase is observed even when the fluorocarbon "rod" is very short (4 carbons in length).[7] Therefore it appears that there is a greater driving force for segregation into an ordered (layered) mesophase than in other nonfluorinated (e.g., phenyl ring) compounds, because of the strong incompatibility of fluorocarbon with hydrocarbon in these materials. A similar observation has been made for the aliphatic hydrocarbon main-chain polyesters with perfluoroalkyl segments, the polymer with perfluoroalkyl units as short as 4 carbons again also showing a mesophase[8] with layer periodicities that are somewhat less than the extended repeat length. Polyphilic linear fluoroalkyl para-substituted aromatic systems have also been investigated, usually containing biphenyls or longer extended ring systems[9,10] and show smectic phases. These have one fluoroalkyl group at one end of the molecule or two such groups, one at each end, which can lead to ferroelectric liquid crystals.[9]

In the case of polymers with mesogenic fluorinated side chains, the acrylates have geen extensively studied[11] and can show a smectic B mesophase. Polyesters with perfluoroalkyl side chains have also been investigated and have been shown to have a smectic phase with an interpenetrated bilayer arrangement of the fluorinated units.[12] Liquid-crystalline polysiloxanes with fluorinated groups on the side chains are known, but these also have mesogenic linear aromatic groups in the side chains.[13]

Chart 1

$\mathbf{HF}_{10}-CH_2O_2C(CH_2)_m-H$
1, $\mathbf{HF_{10}R_8}$, $\mathbf{HF}_{10} = H(CF_2)_{10}$, $m = 8$
2, $\mathbf{HF_{10}R_{12}}$, $\mathbf{HF}_{10} = H(CF_2)_{10}$, $m = 12$
3, $\mathbf{HF_{10}R_{17}}$, $\mathbf{HF}_{10} = H(CF_2)_{10}$, $m = 17$

$\mathbf{HF}_{10}-CH_2O_2C-Ph-O(CH_2)_m-H$
4, $\mathbf{HF_{10}PhOR_4}$, $\mathbf{HF}_{10} = H(CF_2)_{10}$, Ph = phenylene, $m = 4$

$\mathbf{HF}_{10}-CH_2O_2C-Cy-(CH_2)_m-H$
5, $\mathbf{HF_{10}CyR_5}$, $\mathbf{HF}_{10} = H(CF_2)_{10}$, Cy = 1,4-*trans*-cyclohexyl, $m = 5$

$\mathbf{F}_n-CH_2O_2C(CH_2)_mCO_2CH_2-\mathbf{F}_n$
6, $\mathbf{F_6R_{12}F_6}$, $\mathbf{F}_n = F(CF_2)_6$, $m = 12$
7, $\mathbf{F_6R_{20}F_6}$, $\mathbf{F}_n = F(CF_2)_6$, $m = 20$
8, $\mathbf{F_7R_{12}F_7}$, $\mathbf{F}_n = F(CF_2)_7$, $m = 12$
9, $\mathbf{F_7R_{20}F_7}$, $\mathbf{F}_n = F(CF_2)_7$, $m = 20$
10, $\mathbf{HF_{10}R_{20}HF_{10}}$, $\mathbf{HF}_{10} = H(CF_2)_{10}$, $m = 20$

To extend the understanding of fluoroalkyl mesogenic molecules without extended ring systems, the following types of semifluorinated molecules were investigated; linear di- and triblock ester-linked compounds (the ester analogues of the carbon−carbon-linked molecules[3−6]), as small-molecule models of main-chain polymers, containing one or two perfluoroalkyl units of 6, 7, or 10 carbons linked to aliphatic hydrocarbon chains of 8, 12, 17, or 20 methylene units (see Chart 1). Also the perfluoroalkyl diol "monomers" were investigated and showed lyotropic liquid crystallinity in water, in addition to thermotropic liquid-crystalline behavior. However, the 3,5-diacetoxy and dibenzyloxy analogues of these molecules were not liquid crystalline, nor were the perfluorooctylsulfonamido diol (compound **18**) dialkyl esters with *n*-butyl, *n*-octyl, and *n*-heptadecyl alkyl groups. Schematic representations of the compounds are shown in Chart 1. The structures of the perfluoroalkylphenyl compounds are shown in Chart 2.

Experimental Section

The compounds were prepared from aliphatic acids, diacids, or the 3,5-substituted benzoic acid and the corresponding 1*H*,1*H*- or 1*H*,1*H*,2*H*,2*H*-perfluoroalkyl alcohols, using the carbodiimide activated ester forming procedure described previously.[14] A representative synthesis for compound **2** is as follows:

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Chart 2

$\mathbf{F}_n\text{–}\mathrm{CH_2O_2CPh}(\mathbf{OR})_2$
11, $\mathbf{HF_{10}Ph(Ac)_2}$, $\mathbf{R}$ = acetyl, $\mathbf{HF}_n = \mathrm{H(CF_2)_{10}}$
12, $\mathbf{F_7Ph(Bz)_2}$, $\mathbf{R}$ = benzyl, $\mathbf{F}_n = \mathrm{F(CF_2)_7}$

$\mathbf{F}_n\text{–}(\mathrm{CH_2})_m\mathrm{O_2CPh}(\mathbf{OH})_2$
13, $\mathbf{F_6Ph(OH)_2}$, $\mathbf{F}_n = \mathrm{F(CF_2)_6}$, $m = 1$
14, $\mathbf{F_62Ph(OH)_2}$, $\mathbf{F}_n = \mathrm{F(CF_2)_6}$, $m = 2$
15, $\mathbf{F_7Ph(OH)_2}$, $\mathbf{F}_n = \mathrm{F(CF_2)_7}$, $m = 1$
16, $\mathbf{HF_{10}Ph(OH)_2}$, $\mathbf{HF}_n = \mathrm{H(CF_2)_{10}}$, $m = 1$
17, $\mathbf{F_{10}\text{-}2Ph(OH)_2}$, $\mathbf{F}_n = \mathrm{F(CF_2)_{10}}$, $m = 2$

$\mathrm{F(CF_2)_8SO_2N(CH_2CH_2OH)_2}$
18, $\mathbf{F_8(OH)_2}$

1H,1H-Perfluoroundecyl alcohol [1.064 g (2 mmol)] and 0.449 g (2.1 mmol) of tridecanoic acid were added to a stirred solution of 0.19 g (1 mmol) of *p*-toluenesulfonic acid and 0.121 g (1 mmol) of (dimethylamino)pyridine in 25 mL of dry dichloromethane. A little dry THF can also be added to help the solubility of the materials. Then about 0.4 g (3 mmol, about 50% excess) of diisopropylcarbodiimide was added, and the solution was stirred for 24 h. The solvent was then removed on a rotavapor and the mixture washed with methanol (or the solution poured into about 100 mL of methanol to precipitate the product for the less soluble compounds). The products were recrystallized from methanol or a methanol–solvent mixture or methanol/hexane in the case of compounds **13**–**17**.

3,5-Diacetylbenzoic acid was made from 3,5-dihydroxybenzoic acid and acetic anhydride reacted at room temperature for 1 h. 3,5-Bis(benzyloxy)benzoic acid was prepared from 3,5-dihydroxybenzoic acid (0.1 mol) and an excess of benzyl bromide (0.3 mol) and dry K_2CO_3 in dried acetone or MEK, refluxed for 24 h. This product was then hydrolyzed with sodium hydroxide (1.0 M in 1:1 methanol–water) for 2–3 h and recrystallized from acetone/methanol to give the product acid as fine white crystalline needles in high yield; mp 214–215 °C. The perfluoroalkyl 3,5-dihydroxybenzoate products were obtained by debenzylation using 10% Pd on carbon and ammonium formate.[15] The results of chemical characterization and elemental analyses were consistent with assigned structures in all cases.

In the IR, all compounds except **18** showed the ester at 1732–1742 cm^{-1}, except **13**–**17**, which showed the carbonyl at a lower frequency, about 1700 cm^{-1}, and **11**, which showed a second ester peak at 1769 cm^{-1}. All compounds showed fluoroalkyl at 1110–1270 cm^{-1}. In the ^1H NMR, the terminal H in the $\mathbf{HF_{10}}$- group was observed as a triplet of triples (1:2:1 intensity) between 5.84 and 6.26 ppm.

All reagents were obtained from Aldrich Chemical Co., except (perfluorocyclohexyl)methanol/(trifluoromethyl)perfluorocyclopentyl)methanol (mixture of isomers) and 2-perfluorobutyloxy-*1H,1H*-perfluoropropan-1-ol, which were gifts from 3M Research Ltd., and the remaining fluorinated alcohols were obtained from Fluorochem.

Measurements were performed on the following instruments: IR, on a Nicolet 510M spectrometer; NMR, on a Bruker WM250 250-MHz spectrometer; DSC, on a Perkin-Elmer Series 7; polarizing light microscopy, on a Leica Axioscope fitted with a Mettler FP82 microfurnace. The X-ray diffraction measurements were performed on a Philips PW 1710 diffraction system.

The liquid-crystalline samples were prepared by heating to the isotropic phase and cooling down into the mesophase. The samples were then quenched in liquid nitrogen and ground to powders for the X-ray measurements.

Elemental analyses were performed in the Department of Chemistry, University of Cambridge.

Results and Discussion

Typical mesophase textures observed in the polarizing optical microscope (POM) are shown in Figure 1a,b for the liquid-crystalline diblock compounds **1**, **2**, **4**, and **5** and in Figure 1c for the triblock compounds **7**–**10**. The textures in Figures 1a and 1b are clear and characteristic of a smectic B phase.[1] The grainy texture in Figure 1c is very similar to the previously observed fluorocarbon polymer mesophases.[6,7,11] All the triblock compounds (**7**–**10**) showed this texture, but **10** also appeared to show smooth smectic B type conics[1] just below the isotropic phase on cooling. However, this grainy texture is not clearly similar in appearance to any standard smectic (or nematic) phase. X-ray diffraction was performed to elucidate the mesophases. Interestingly, since the textures of the triblock compounds were similar to those of the corresponding polymers, they may indeed be better model compounds, having a mesophase similar to that of the polymers. In **8** and **9** it was not always possible to shear the material in the mesophase temperature range and they do not appear to have liquid crystalline mesophases. It was noted that the crystals of compound **7** ($\mathbf{F_6R_{20}F_6}$) showed a large reversible "swelling" of approximately 15–20% in the microscope at the solid to mesophase transition temperature, then becoming soft and shearable, indicating considerable molecular reorganization.

Thermal (DSC) transition temperatures and enthalpies are shown in Table 1 for the compounds which showed a mesophase. In the linear compounds **1**–**10**, the DSC endotherm peak indicating the onset of the (see above) shearable phase observed in the POM is smaller than the peak indicating the transition to an isotropic liquid on second heating (or about equal in the case of **4**). The enthalpies of these transitions are also given in Table 2. Because the solid to mesophase transition enthalpies are much smaller than the mesophase to isotropic transition enthalpies, it suggests quite highly ordered mesophases. Compounds $\mathbf{F_6R_{20}F_6}$, $\mathbf{F_7R_{20}F_7}$ (**9**), and $\mathbf{HF_{10}R_{20}HF_{10}}$ (**10**) had mesophase temperature ranges of 7.5, 16, and 11 °C, while $\mathbf{F_7R_{12}F_7}$ (**8**) had a smaller range of 4 °C. As the perfluoroalkyls become longer (compounds **7**, (**9**), and **10**) the clearing points increase. Compound **1**, $\mathbf{HF_{10}R_8}$, had the largest liquid-crystalline temperature range of the linear compounds, 29.1 °C. It also showed two fairly small endotherm peaks (at −2 and 8.5 °C), with a shallow exotherm between them on heating, which was reproducible on second heating. This indicates typical melting–crystallization–remelting behavior between −2 and 8.5 °C. The corresponding compound **2**, $\mathbf{HF_{10}R_{12}}$, had a very narrow smectic B phase, which appeared just before crystallization on cooling from the isotropic phase. In fact, this phase was not detected by DSC, only a single unresolved peak being obtained on heating and on cooling, and the phase was only seen optically. However, compound **3**, $\mathbf{HF_{10}R_{17}}$, with a longer aliphatic tail did not show any mesophase.

The phenyl and *trans*-cyclohexyl compounds **4** and **5** (Figure 1b) had textures very similar to those of the diblocks **1** and **2** in Figure 1a, showing a smectic B phase. The phenyl compound was monotropic, and again for these compounds the isotropic transition ethalpy is larger than the solid to mesophase transition enthalpy in **4** (but quite small) and nearly equal in **5**. The cyclohexyl compound also showed a small transition at 13 °C on heating (enthalpy 2.0 J/g), which is probably a solid–solid transition.

For the nonlinear diol compounds, all of which showed thermotropic mesophases, a typical texture observed for all the compounds except $\mathbf{HF_{10}Ph(OH)_2}$ (**16**) is shown in Figure 1e. This shows smectic A type batonnets and fans on cooling the isotropic liquid, although this texture

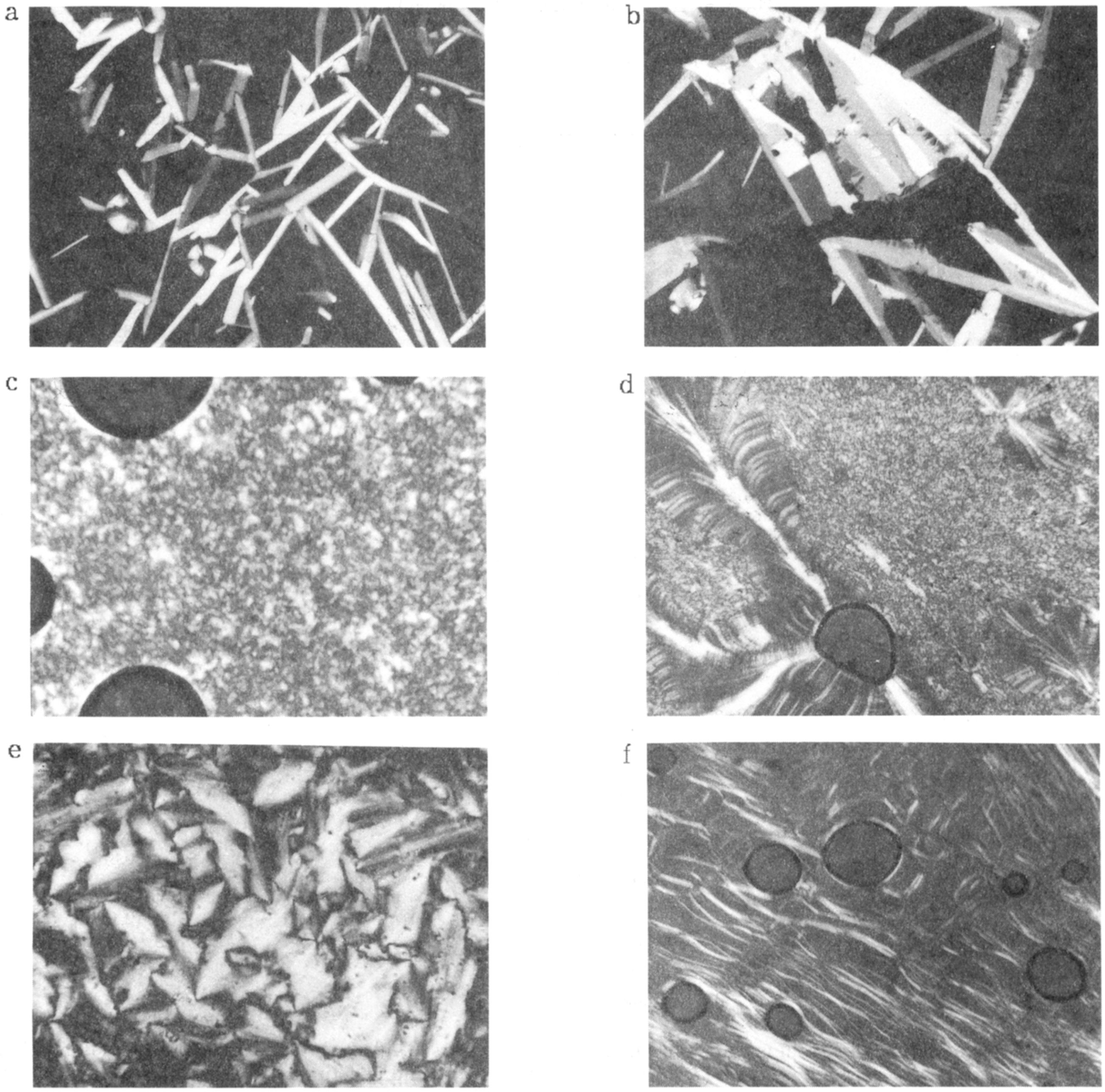

Figure 1. Polarizing optical micrographs of (a) **$HF_{10}R_8$** (100×, 34.5 °C) and (b) **$HF_{10}CyR_5$** (100×, 56 °C) in the smectic phase, (c) **$F_6R_{20}F_6$** (320×, 66 °C) in the smectic phase, (d) **F_6-2Ph(OH)$_2$** (100×, 133 °C) in the thermotropic smectic phase, (e) **F_7Ph(OH)$_2$** (320×, 120 °C) in the thermotropic smectic phase, and (f) **F_6Ph(OH)$_2$** (100×) in the aqueous lyotropic phase.

was usually poorly resolved and looked grainy (Figure 1d) before annealing (similar to Figure 1c). In all of these compounds the isotropic transition enthalpy was smaller than the solid to mesophase transition enthalpy, indicating a mesophase that is less highly ordered, except for compound **16**. This had a different texture in the POM, very similar to that in Figure 1b, indicating a smectic B phase, and also had an isotropic transition enthalpy that was larger than the solid to mesophase transition enthalpy (see Table 2). This change in phase type along this series of compounds is interesting and is a consequence of the increasing perfluoroalkyl segment length. Possibly, with a longer perfluoroalkyl segment, the series with $m = 2$ would also change to a smectic B phase. It should be noted that in **F_6Ph(OH)$_2$** and **F_7Ph(OH)$_2$** the solid to mesophase peak in the DSC is split, as it is also on cooling in the other compounds, **F_6-2Ph(OH)$_2$** and **F_{10}-2Ph(OH)$_2$**. Therefore there is also a possible higher order phase in these compounds. Second heating and cooling DSC scans for these diol compounds are shown in Figure 2. All the diol compounds also appear to have lyotropic phases. Typical myelin type textures were observed in water below their thermotropic transition temperatures for the compounds with perfluorohexyl and -heptyl units, as shown in Figure 1f. The longer perfluorodecyl compounds showed more marble-like textures.

Powder X-ray diffraction measurements were made to investigate the liquid-crystalline mesophase structure on quenched samples. The X-ray diffraction data are shown in Table 2 for all the mesomorphic compounds. These data show sharp low-angle peaks giving the observed long period (*d*) for each compound. In addition, the calculated fully extended molecule length (*L*) is given, with the ratio (*d*/*L*) of the observed layer periodicity to the calculated molecular length, which helps to determine the type of packing, e.g., monolayer or bilayer. For compound **1**, the X-ray diffraction (XRD)

Table 1. Thermal Transition Data for Mesomorphic Compounds

compd	solid–mesophase/°C (enthalpy/(J/g)) LC phase by POM and X-ray	mesophase–mesophase/°C (enthalpy/(J/g))	mesophase–isotropic/°C (enthalpy/(J/g))
$\mathbf{HF_{10}R_8}$ (**1**)	−2, 8.5 (15.6, 12) S_B		37.6 (26.8)
$\mathbf{HF_{10}R_{12}}$ (**2**)	monotropic [40] S_B		46.9 (27) [40.5]
$\mathbf{HF_{10}PhOR_4}$ (**4**)	monotropic [31] (30.3) S_B		64.5 (58.3) [54.8] (28.8)
$\mathbf{HF_{10}CyR_5}$ (**5**)	51, 54, 56 (6) S_B		61 (8.6)
$\mathbf{F_6R_{20}F_6}$ (**7**)	62.5 (6) S_B?		70 (31.5)
$\mathbf{F_7R_{12}F_7}$ (**8**)	52.7 (4.4)		56.5 (36)
$\mathbf{F_7R_{20}F_7}$ (**9**)	59 (6.85)		75 (34.6)
$\mathbf{HF_{10}R_{20}HF_{10}}$ (**10**)	(77); 88.7, 90.8 (2.7); (6.85) S_B?		100 (51.5)
$\mathbf{F_6Ph(OH)_2}$ (**13**)	55 (2.6) S_B?, also lyotropic	85.5, 89.5 (20.8) S_A	120 (3.04)
$\mathbf{F_6\text{-}2Ph(OH)_2}$ (**14**)	123.3 (47.8) S_A, also lyotropic		142.1 (3.18)
$\mathbf{F_7Ph(OH)_2}$ (**15**)	108 (26.9) S_B?, also lyotropic	113 (2) S_A	134.0 (1.79)
$\mathbf{HF_{10}Ph(OH)_2}$ (**16**)	134.7 (10.1) S_B, also lyotropic		144.2 (30.8)
$\mathbf{F_{10}\text{-}2Ph(OH)_2}$ (**17**)	160.5 (58) S_A, also lyotropic		189.65 (2.15)
$\mathbf{F_8(OH)_2}$ (**18**)	112 (23) S_A, also lyotropic		158 (14.5)

intensity versus angle (2θ) diagram is shown in Figure 3. A fairly sharp low-angle peak is seen together with the second and third orders, indicating smectic layers with a layer periodicity of 25 Å. At high angles only one peak is seen, which is fairly narrow. This indicates smectic B type ordering and the spacing corresponds to 4.92 Å, which is the lateral spacing between the fluorocarbons. Since there is no observed long-range order in these compounds and the mesophase is quite fluid, a hexatic B phase is indicated. No separate peak is seen for the hydrocarbon segment at lower d spacing. Similar peaks are seen for compounds **2**, **4**, **5**, and **7–10** (**3** and **6** not showing a mesophase). However, compound **10** also had a transition at 77 °C in the DSC, and a solid–solid transition or another (e.g., crystal B) phase is indicated (see below also for the diol compounds). For these compounds the ratio of the observed to the calculated layer spacing is 0.76–0.90 (which is similar to that found for the corresponding polyesters[7]) and for **4** and **5** it is 0.92 and 0.89. This indicates monolayer packing for all of these compounds except **2**, which had a ratio of 1.73 showing bilayer ordering (as for the non-liquid-crystalline compound **3**). Compound **2** however only showed a vary narrow monotropic S_B phase of 0.5 °C and the XRD shows too many crystalline type peaks (Table 2) for a mesophase, so it is likely that this compound is actually in a crystalline phase which has bilayer packing. The ratios of observed to calculated molecular length were in fact a little lower for the compounds with the longest hydrocarbon spacer (m = 20) than for the others, as might be expected if there is relatively more shortening due to disordering or tilting for longer m. In fact, since the fluorocarbon has about a 50% larger cross section area than the hydrocarbon chains, the hydrocarbon in the layers can take up about 2/3 of its fully extended length. This appears to be the case for the layer spacing in most of these compounds with aliphatic chains. In general, the smectic diblock (and triblock) esters showed monolayer ordering, while the non-liquid-crystalline compounds showed bilayers. On going from the diblock to the triblock compounds, the molecules become rather more like polymers, and as noted above, the texture becomes grainy as found for all the polyesters and the ratio of d/L (repeat unit length) for the polyesters is also a little less than 1. Because the diameter of the phenyl unit is a little closer to that of the perfluorocarbon compared to the aliphatic hydrocarbon chain, the phenyl compounds **11** and **12**, and all the diols (**13–17**) should be able to fit more easily into layers without tilting or disordering etc., and

Table 2. X-ray Diffraction Data for Mesomorphic Compounds

compd	angle / deg 2θ (intensity)	d-layer value/Å	diffract peak width/ deg 2θ	calcd mol length/Å (ratio d/L)
HF$_{10}$R$_8$ (1)	3.60 (s)	24.8	0.20	27.5
	6.84 (w)	12.94	0.15	(0.90)
	10.13 (w)	8.72	0.14	
	18.04 (m)	4.92	0.62	
HF$_{10}$R$_{12}$ (2)	1.56 (s)	56.54	0.10	32.5
	3.14 (m)	28.15	0.10	(1.73)
	4.71 (m)	18.75	0.12	
	6.29 (m)	14.04	0.10	
	7.87 (w)	11.23	0.14	
	9.55 (w)	9.25	0.12	
	18.1 (m)	4.90	0.50	
	18.95 (m)	4.67	0.20	
	22.6 (vw)	3.93	0.65	
	23.8 (vw)	3.74	0.45	
	25.38 (w)	3.51	0.25	
HF$_{10}$PhOR$_4$ (4)	3.27 (s)	27.0	0.15	29
	3.62 (s)	24.0	0.12	(0.92)
	6.91 (w)	13.0	0.14	
HF$_{10}$CyR$_5$ (5)	3.405 (s)	25.92	0.18	29.25
	6.76 (w)	13.05	0.14	(0.89)
F$_6$R$_{20}$F$_6$ (7)	2.54 (s)	34.90	0.15	46
	5.00 (w)	17.35	0.15	(0.76)
	18.60 (s)	4.77	0.80	
	19.79 (s)	4.48	0.65	
F$_7$R$_{12}$F$_7$ (8)	2.60 (s)	33.3	0.35	38.2
	5.01 (m)	17.3	0.20	(0.89)
	7.60 (w)	11.60	0.30	
	18.40 (s)	4.83	1.25	
	19.55 (sh m)	4.50	1.50	
F$_7$R$_{20}$F$_7$ (9)	2.33 (s)	38.0	0.30	48.5
	4.43 (w)	19.8	0.40	(0.80)
	6.41 (w)	13.5	0.35	
	18.45 (s)	4.80	1.40	
	19.52 (s)	4.51	1.25	
HF$_{10}$R$_{20}$HF$_{10}$ (10)	1.73 (s)	51	0.15	60
	3.50 (m)	25.2	0.24	(0.85)
	5.24 (m)	16.8	0.20	
	18.18 (m)	4.90	0.48	
	19.11 (m)	4.65	0.33	
	25.11 (w)	3.55	0.26	
F$_6$Ph(OH)$_2$ (13)	2.64 (s)	33.50	0.25	17.5
	5.21 (w)	16.90	0.25	(1.91)
	8.0 (w)	11.0	0.26	
	10.72 (vw)	8.25	0.26	
	17.7 (s)	5.00	1.0	
	18.25 (s)	4.84	1.0	
F$_6$-2Ph(OH)$_2$ (14)	2.74 (s)	32.25	0.35	18.7
	5.44 (m)	16.25	0.20	(1.72)
	8.16 (w)	10.80	0.30	
	17.50 (s)			
	18.1 (m)			
F$_7$Ph(OH)$_2$ (15)	2.51 (s)	34.9	0.25	18.8
	5.02 (m)	17.6	0.40	(1.86)
	7.53 (w)	11.75	0.35	
	9.90 (vw)	8.90	0.35	
	17.89 (m)	5.00	1.7	
	26.0 (w)	3.35	1.8	
HF$_{10}$Ph(OH)$_2$ (16)	2.08 (s)	42.4	0.15	22.5
	4.14 (m)	21.33	0.25	(1.88)
	6.23 (w)	14.20	0.20	
	17.82 (s)	4.98	1.0	
	18.2 (s)	4.88	1.05	
F$_{10}$-2Ph(OH)$_2$ (17)	2.00 (s)	44.20	0.18	23.8
	4.03 (m)	21.90	0.20	(1.85)
	6.08 (w)	14.54	0.30	
	8.01 (vw)	11.04	0.35	
F$_8$(OH)$_2$ (18)	3.40 (s)	26.10	0.30	19.5
	6.75 (w)	13.14	0.40	(1.36)
	10.02 (w)	8.80	0.35	
	17.0 (s)	5.30	1.30	
	18.0 (s)	4.90	1.20	

the XRD data show that the observed long period for compounds **11** and **12**, was very close to the calculated molecular length (ratio 0.97−0.98). However, while **11** and **12** were not liquid crystalline, all of the diol compounds were. Here we have the possibility of hydrogen bonding between the hydroxyl groups. Therefore the most likely arrangement is in fact a bilayer packing with the hydroxyls together. The XRD results for the diol compounds all show bilayer type ordering, with all (except the non-phenyl diol **18**) showing a long period close to twice the molecular length, the ratios being 1.72−1.91. The sulfonamide diol (**18**) had a ratio of 1.36 and the corresponding perfluoroalkyl side-chain polyesters all show bilayer ordering, with a ratio d/L (repeat unit length) of about 1.6−1.8.

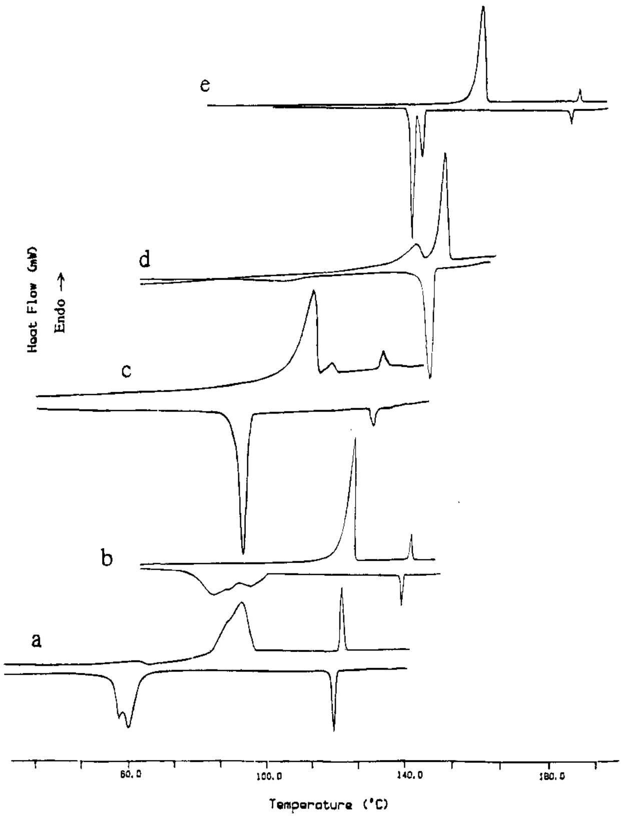

Figure 2. DSC plots of diol compounds: (a) **F$_6$PH(OH)$_2$**, (b) **F$_6$-2PH(OH)$_2$**; (c) **F$_7$Ph(OH)$_2$**; (d) HF$_{10}$**Ph**(OH)$_2$; (e) **F$_{10}$-2Ph(OH)$_2$** (all run at 8 °C/min).

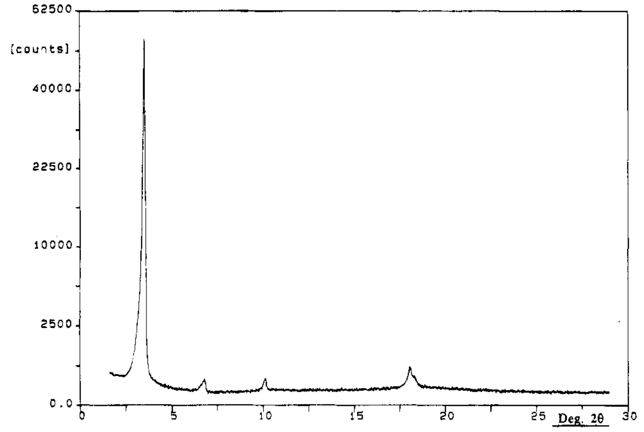

Figure 3. X-ray diffraction intensity versus angle (2θ) plot for **1**.

The di- and triblock compounds are small-molecule models of the linear fluorocarbon−hydrocarbon polyesters,[8] ands the triblock compounds show similar optical textures and XRD layer spacings but lower mesophase transition temperatures. In this series of materials, the ones having sufficiently long linear perfluorocarbon groups and sufficient hydrocarbon spacer showed a mesophase. It is also interesting to note that the overall

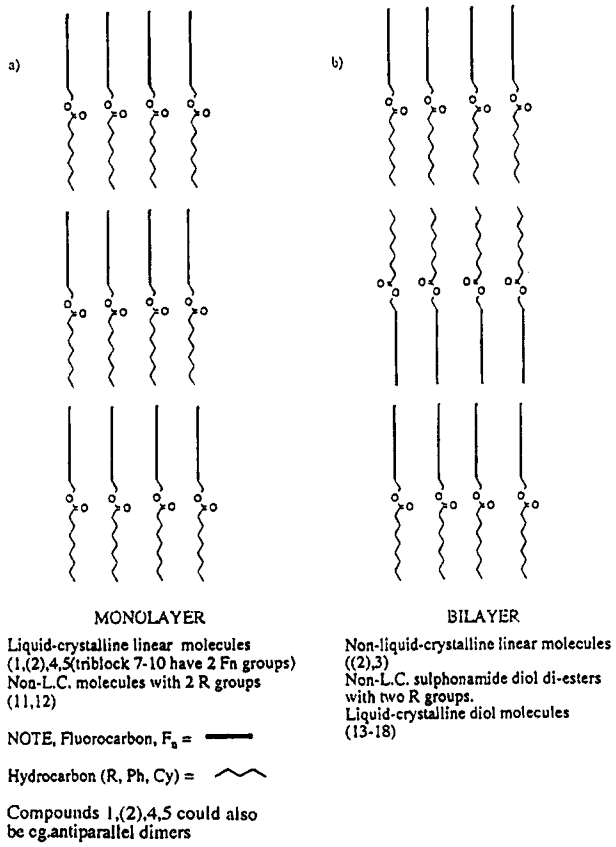

Figure 4. Schematic representation of mesophase layer arrangement in semifluorinated compounds.

tendency to form mesophases in these small molecules appears to be less than in the corresponding polymers,[7,8] presumably due to a lower mesogenic field ordering effect and/or a high crystallinity, as several compounds with linear perfluorohexyl, -heptyl, and -decyl units showed only a small mesophase or did not show one at all. The XRD data showed that all these linear compounds having a mesophase had a monolayer structure (except 2, which had an extremely narrow S_B phase just before crystallization). This is similar to the situation found for the analogous polyesters, where the ratios of d/L were all a little less than 1. However, the linear polymers cannot easily adopt a bilayer arrangement, while the small molecules can. A schematic summary of the monolayer/bilayer mesophase ordering is shown in Figure 4, but note that antiparallel packing is also possible.

The phenyl compounds with hydroxyl groups showed smectic thermotropic as well as aqueous lyotropic phases. The XRD data for all the nonlinear (3,5-substituted) phenyl compounds except **11** and **12** indicate bilayer formation, and unlike the linear molecules, no thermotropic behavior in the non-hydroxy "side-chain" model compounds was observed. These non-hydroxy compounds (**11** and **12**) showed monolayer spacings, and presumably the mesogenic field ordering of the polymer backbone stabilizes the mesophase, as observed in the corresponding polyesters.[12] These fluorinated side-chain polyesters all show bilayer ordering in the mesophase, as found for the liquid-crystalline side-chain model compounds. Therefore the small molecules again appear to favor the same mono- or bilayer arrangement as the polymers.

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