1928 *Macromolecules* **1994,** *27,* 1928–1931

Liquid Crystalline Fluorocarbon Side-Chain Polyesters

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Received September 23, 1993[⊛]

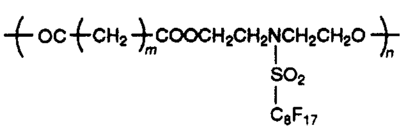
ABSTRACT: Perfluoroalkyl side-chain polyesters of the type $-[O(CH_2)_2N\{SO_2(CF_2)_8F\}(CH_2)_2O_2C(CH_2)_mCO]_n-$, with $m = 2$–4, 8, 12, and 20, have been synthesized in high yield directly from the diacid and the diol, using a coupling agent. Molecular weights up to 40 000 were obtained. The polyesters with $m > 3$ showed enantiotropic mesophases, although they have no flexible spacer between the main chain and the side-group mesogen. The rigid perfluoroalkylsulfonamide group and the segregating tendency of fluorocarbons and hydrocarbons give these polyesters their liquid crystalline behavior. The mesophases were investigated by polarizing optical microscopy, DSC, and rheological DMA. They have a grainy optical texture in the POM, multiple transitions in the DSC and a low-viscosity mesophase regime in mechanical analysis.

Introduction

Polymers in which liquid crystalline properties are due to perfluoroalkyl segments are an unusual and interesting class of materials. Previously, polymers from acrylate and methacrylate esters of the partially fluorinated alcohol $H(CF_2)_nCH_2OH$, giving a hydrocarbon backbone with $-COOCH_2(CF_2)_nH$ side chains, have been reported[1] and are claimed to show a liquid crystalline phase for $n = 10$. Similar polymers with $-COO(CH_2)_m(CF_2)_nF$ side chains having $n = 8$, 10, 12 and $m = 4$, 6, 10 also exhibit mesophases.[2]

The liquid crystalline behavior in these materials is presumably due to the strongly segregating tendency of fluorocarbons (R_f) with hydrocarbons (R_h) and also to the rigid-rod-like nature of the fluorocarbon segments[3] which adopt a helical structure along their length due to intramolecular steric repulsions between the fluorines along the carbon backbone.[4-6] While the hydrocarbon segments are "flexible" aliphatic chains, the fluorocarbon segments are therefore actually rodlike in the melt. There is also a strong tendency to segregation for R_f and R_h segments which are longer than 6–8 carbons[7] which would favor some ordering in the polymer leading to either layered structures or some other ordered assembly. This allows the possibility of liquid crystalline (mesomorphic) behavior in these materials. Recently, we have reported mesophases in a series of main-chain fluorocarbon–hydrocarbon microblock copolymers,[8] which do not contain any rigid aromatic or ring system or heteroatom linking unit. This is in contrast to the usual situation in which the majority of nonfluorinated liquid crystalline polymers contain ringed structures to produce molecular rigidity.

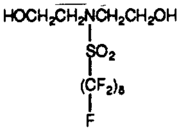
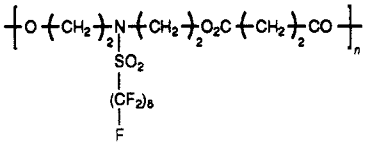
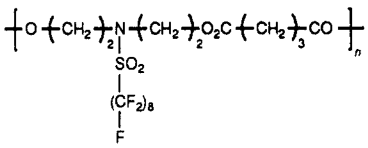
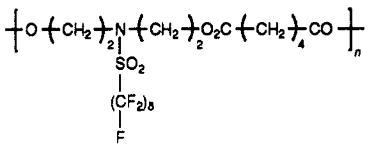
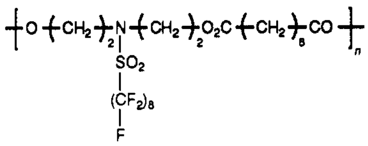
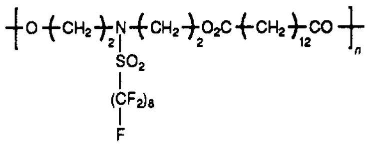
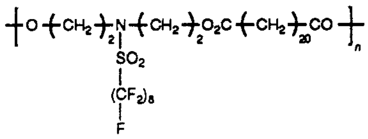
Here we describe the synthesis, characterization, and some properties of aliphatic hydrocarbon polyesters with $-SO_2(CF_2)_8F$ side chains. Several polymers of the type



$$-[OC(CH_2)_mCOOCH_2CH_2N(SO_2C_8F_{17})CH_2CH_2O]_n-$$

were prepared (with $m = 2$–4, 8, 12, and 20), and all having $m > 3$ show a liquid crystalline phase. We believe that this type of liquid crystalline polymer having fluoroalkyl side chains bonded to the hydrocarbon backbone without any hydrocarbon segment or decoupling spacer has not previously been known. These polyesters have hydrocarbon linkages between the pendant side chains that are longer than those for polyacrylate systems. One other system having longer spacing along the polymer backbone between the pendant mesogens is known, based on polysiloxane,[9] and it was found to be liquid crystalline. The pendant species was however conventional, having flexible spacer groups to the mesogens which were themselves based on rigid *p*-phenylene rings.

Table 1. Chemical Analysis Data for a Fluorinated Monomer and Polyesters

compound	elem anal. (%)			¹H NMR (δ) (vs TMS)
		calcd	found	
 $HOCH_2CH_2N(SO_2(CF_2)_8F)CH_2CH_2OH$	H C N	1.70 24.50 2.39	1.64 24.54 2.43	in $(CD_3)_2CO$ 4.35t, 2H 3.83m, 4H 3.75m, 2H 3.64m, 2H
 $-[O(CH_2)_2N(SO_2(CF_2)_8F)(CH_2)_2O_2C(CH_2)_2CO]_n-$	H C N	1.79 28.70 2.09	1.90 29.02 2.13	in $CDCl_3$ 4.42m, 4H 3.94m, 2H 3.74m, 2H 3.77s, 4H
 $-[O(CH_2)_2N(SO_2(CF_2)_8F)(CH_2)_2O_2C(CH_2)_3CO]_n-$	H C N	2.05 29.87 2.05	2.11 30.02 2.04	in $CDCl_3$ 4.30m, 4H 3.84m, 2H 3.61m, 2H 2.41t, 4H 1.97m, 2H
 $-[O(CH_2)_2N(SO_2(CF_2)_8F)(CH_2)_2O_2C(CH_2)_4CO]_n-$	H C N	2.29 31.00 2.01	2.26 31.24 1.94	in $CDCl_3$ 4.28t, 4H 3.83m, 2H 3.62m, 2H 2.36t, 4H 1.65m, 4H
 $-[O(CH_2)_2N(SO_2(CF_2)_8F)(CH_2)_2O_2C(CH_2)_8CO]_n-$	H C N	3.19 35.06 1.86	3.20 35.28 1.83	in $CDCl_3$ 4.31t, 4H 3.84m, 2H 3.65m, 2H 2.35t, 4H 1.62m, 4H 1.32m, 8H
 $-[O(CH_2)_2N(SO_2(CF_2)_8F)(CH_2)_2O_2C(CH_2)_{12}CO]_n-$	H C N	3.95 38.60 1.73	3.96 38.65 1.70	in $CDCl_3$ 4.26t, 4H 3.85m, 2H 3.66m, 2H 2.33t, 4H 1.61m, 4H 1.25m, 16H
 $-[O(CH_2)_2N(SO_2(CF_2)_8F)(CH_2)_2O_2C(CH_2)_{20}CO]_n-$	H C N	5.21 44.30 1.52	5.24 44.20 1.56	in $CDCl_3$ 4.28t, 4H 3.83m, 2H 3.64m, 2H 2.31t, 4H 1.60m, 4H 1.23m, 32H

[⊛] Abstract published in *Advance ACS Abstracts,* February 15, 1994.

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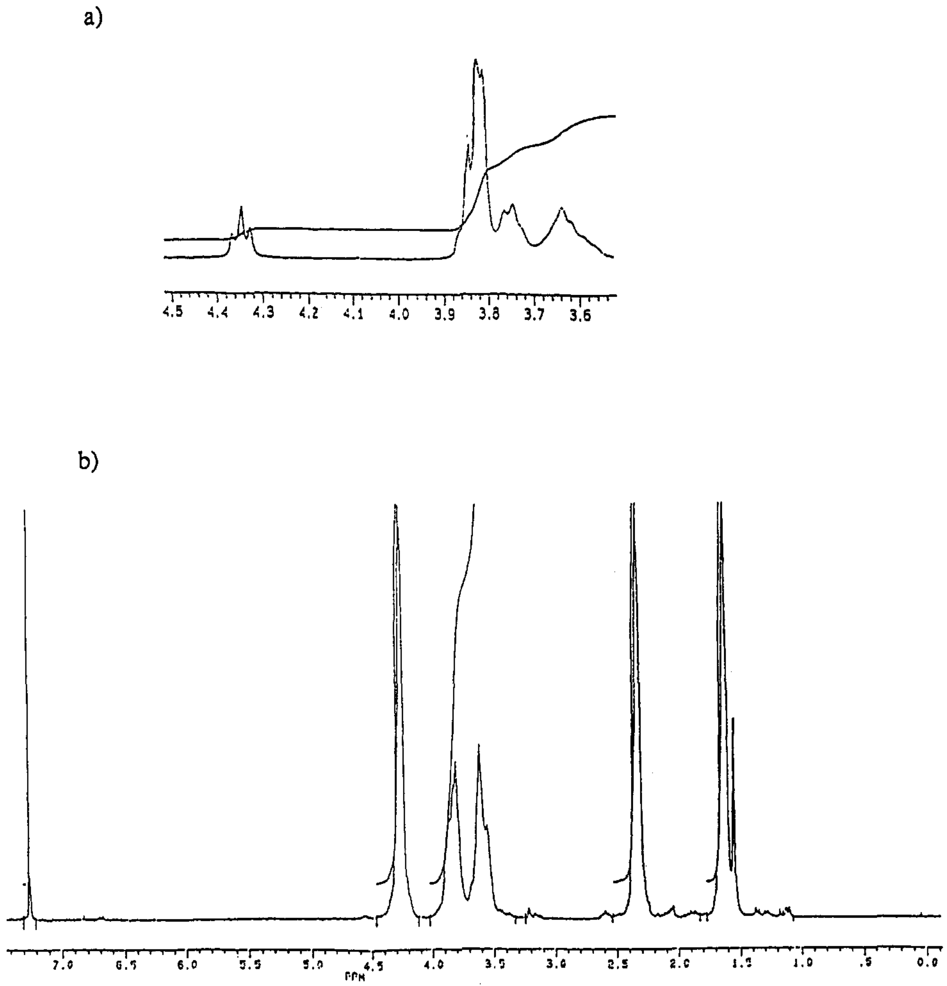

Figure 1. (a) ^{1}H NMR (δ) in $(CD_3)_2CO$ of perfluorooctylsulfonamide diol monomer, $F(CF_2)_8SO_2N(CH_2CH_2OH)_2$. (b) ^{1}H NMR ($\delta$) in $CDCl_3$ of a fluorocarbon side-chain polyester, with $m = 4$.

A very small number of nonfluorinated side-group liquid crystalline polymers without $-CH_2-$ spacer groups are known, the so-called rigid side-group polymers, which have mesogens based on *p*-phenyls connected to a polyacrylate backbone via the ester group.[12-14]

Experimental Section

Polymerization of a perfluoroalkylsulfonamide diol ($F(CF_2)_8SO_2N(CH_2CH_2OH)_2$, **A**) with the dicarboxylic acids $HO_2C(CH_2)_mCO_2H$, **B**, with $m \geq 2$) was carried out using the Stupp method of polyester formation.[10] Both the diol and diacids were purified by recrystallization before use. For polymerization, 0.587 g (1.0 mM) of the fluorinated diol **A** was stirred with a stoichiometric equivalent of the dried diacid **B** in approximately 50 mL of dry CH_2Cl_2 and 10 mL of THF (all reagents were dried). Then 0.19 g of *p*-toluenesulfonic acid (PTSA) and 0.122 g of 4-(*N*,*N*-dimethylamino)pyridine (DMAP) were added together to this solution at which point 0.8–1.2 mL of diisopropylcarbodiimide was added to the stirred solution. After a few hours at room temperature a white precipitate formed. After 1 day the product was precipitated by pouring the solution into a larger volume of methanol (approximately 150–200 mL) and the polymer collected by filtration. The product was precipitated twice from chloroform/methanol, washed several times with methanol to remove PTSA/DMAP and diisopropylurea (byproduct from the coupling agent), and then dried in a vacuum oven at 50 °C.

IR (KBr) shows ester, –CF, and –CH. Main peaks are at approximately 1730, 1100–1250, and 2800–3000 cm^{-1}. ^{1}H NMR shows NCH_2CH_2O at: one multiplet, δ 4.30, 2H; two multiplets δ 3.85, 1H; 3.65δ, 1H; aliphatic diester between δ 2.8 and 1.2. Final yield, typically 80–90%. White solid. GPC showed M_n typically of 20 000–40 000. See tables for details including elemental analyses.

The diacids, DMAP, PTSA, and diisopropylcarbodiimide were obtained from Aldrich Chemical Co. The fluorinated diol was obtained as a gift from 3M.

Measurements were performed on the following instruments: IR, on a Nicolet 510M spectrometer; NMR, on a Bruker WM250 MHz spectrometer; GPC, on a Polymer Laboratories Knauer system with RI and UV detectors; DSC, on Du Pont 2100 and Perkin-Elmer Series 7; polarizing light microscopy, on a Leica Axioscope fitted with a Mettler FP82 microfurnace; viscosity measurement, on a Rheometrics RDS II dynamic spectrometer.

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

Results and Discussion

As discussed in the Introduction, these fluorinated side-chain polymers show liquid crystalline properties without having any rigid hydrocarbon (aromatic or other) segments in the side group or in the main chain. One polymer, however, was made containing biphenyl-4,4′-dicarboxylate units instead of an aliphatic dicarboxylate, and it shows a liquid crystalline phase, similar optically to the aliphatic polyesters although this behavior is found at higher temperatures (mesophase between 220 and 257 °C on heating) than for the aliphatic polymers. In these polymers the perfluoroalkyl segments act as rigid rods and are strongly segregating, giving rise to crystalline or, as reported here, liquid crystalline behavior. Liquid crystalline mesophases have almost without exception only been observed in acrylates or methacrylates with a flexible hydrocarbon spacer, between the polymer backbone and the mesogen, to decouple[15] the mesogen from the backbone. Our polyesters however do not have any flexible side-chain spacer group but do have flexible polymer backbone

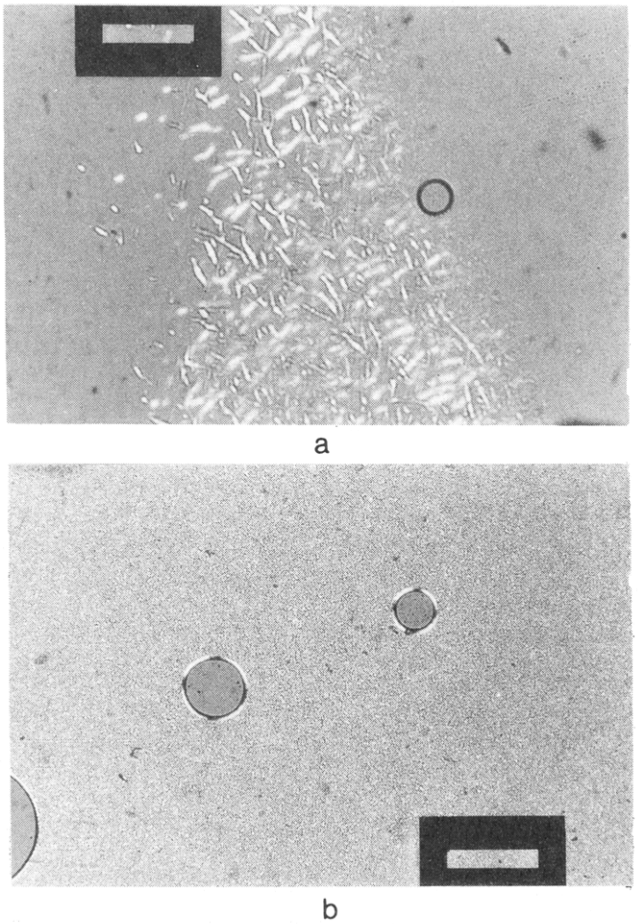

Figure 2. (a) Polarizing optical micrograph of perfluorooctylsulfonamide diol at 100× in the transition from isotropic to the high-temperature smectic phase. (b) Polarizing optical micrograph of a fluorocarbon side-chain polyester with $m = 4$, at 100× in the mesophase.

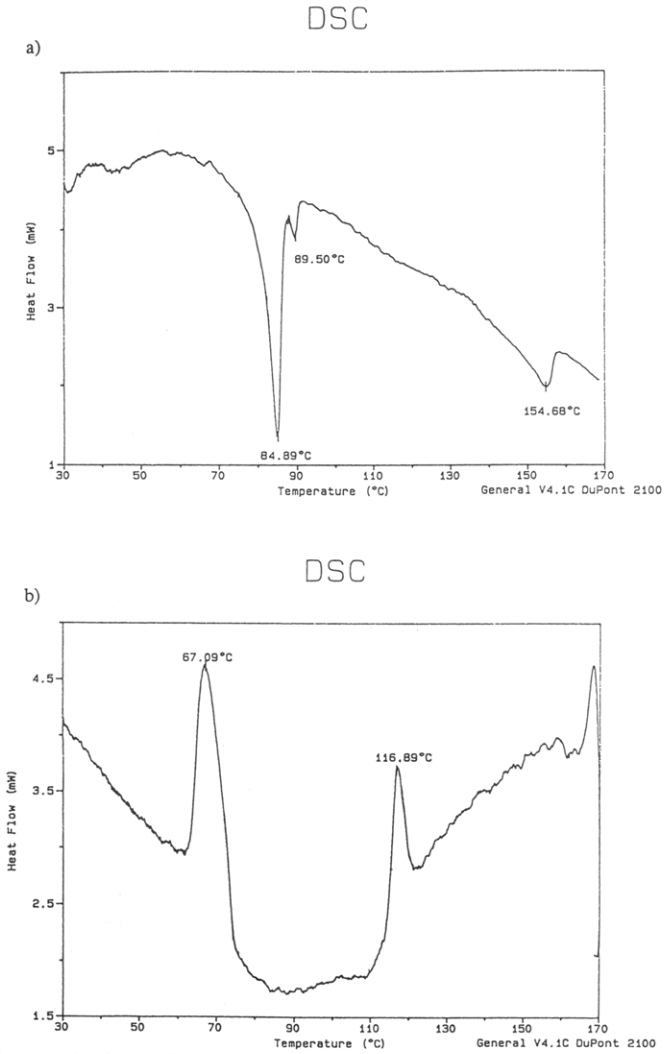

Figure 3. (a) DSC second heating thermograph of a fluorocarbon side-chain polyester with $m = 8$. (b) DSC cooling thermograph of a fluorocarbon side-chain polyester with $m = 8$.

Table 2. Thermal Transition Data (°C) for Mesomorphic Polyesters Having Different *m*

m	solid–mesophase	mesophase–isotropic
4	75	145
8	87	150
12	91	148
20	97	152

segments ($m > 3$ and the CH_2CH_2–units from the fluorinated monomer), which presumably can microphase separate from the aggregating fluorocarbon units, giving rise to an ordered structure. It is interesting to observe that in polyacrylate (or substituted acrylate) systems[1,2,11] a mesophase is observed when the fluorocarbon side-chain spacer ($-COO[CH_2]_n-$) length is $n \geq 1$ or 2, and in this polyester system a mesophase is observed when $m > 3$. This would indicate that there is not enough flexibility with $m = 2$ or 3 to permit effective microphase separation (with anisotropic ordering) leading to mesophase formation and/or to lower the melting point sufficiently to give a liquid crystalline mesophase.

In support of this idea, a comparison can be made with the melting points of classical aliphatic hydrocarbon polyesters similar to the backbone polyesters in these fluorinated compounds. The melting point of poly(1,4-butylene adipate), $-[O(CH_2)_4O_2C(CH_2)_4CO]_n-$, is 56–60 °C, which is similar to the solid–mesophase melting transition in the liquid crystalline fluorinated polymers and indicates that this transition is a melting of the polyester backbone. The melting point of poly(ethylene succinate), $-[OCH_2CH_2O_2CCH_2CH_2CO]_n-$, is rather higher at 108–112 °C, which is perhaps whey the mesophase behavior is thermally masked in the fluorinated side-chain polyesters with $m = 2$ and 3.

The results of chemical characterization are shown in Table 1. All IR spectra show a fluorinated alkyl (1060–1290 cm^{-1}), ester (1737 cm^{-1}) (except the diol monomer which shows OH groups at 3200–3400 cm^{-1}), and hydrocarbon (3000–2850 cm^{-1}). Proton NMR for one polymer is shown in Figure 1b. In all the polymers the NCH_2- is split, probably due to steric restriction of rotation caused by the large sulfonamide group. This is also found in the diol monomer (Figure 1a).

The textures under the optical microscope are shown in Figure 2a and typically appear as grainy. The polymers with $-OCR_mCO-$ ($m > 3$) all showed these "liquid-crystalline" textures in the melt at a temperature between the crystal melting point and the isotropic clearing point (the last two major peaks in the DSC, see below). The sample was homogeneous, could be sheared easily, and was fluid in this temperature range. The sample was therefore enantiotropic. The diol monomer itself showed a similar liquid crystalline texture at lower temperature and also a homeotropic smectic phase at higher temperature. The higher temperature phase of the diol showed a wave of batonnets sweeping across the field of view on cooling from the isotropic phase. This is captured in Figure 2b and is thought to be a smectic A phase. The polymers with $m = 2$ and 3 were not fluid and could not be sheared

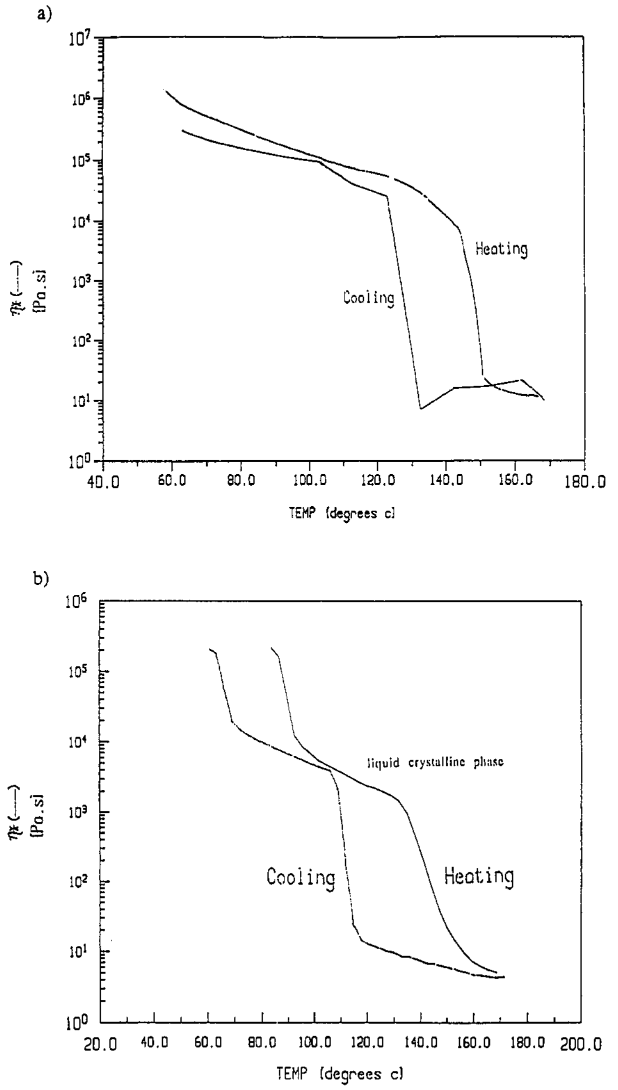

Figure 4. (a) DMA plot measured on heating and on cooling for a fluorocarbon side-chain polyester with $m = 3$. (b) DMA plot measured on heating and on cooling for a fluorocarbon side-chain polyester with $m = 8$.

below the clearing point. These two polymers are therefore not liquid crystalline (see DMA analysis, below).

Figure 3 shows a typical second heating DSC curve for the polymer with $m = 8$. All the polymers in fact show more than one thermal transition, with mesophase transitions for $m > 3$ before the isotropic clearing point. We feel the relative sizes of these peaks reflect the different enthalpies of disordering in the hydrocarbon and fluorocarbon segments. The DSC cooling curve shows considerable (~38 °C at 5 °C/min) undercooling for the highest transition but not for the lower one (~18 °C). Thermal disordering of fluorocarbon chains is usually indicated by a sharp endotherm although in these polymers it is usually quite broad. It may be for these materials that disordering of the fluorocarbon segments is quite sluggish, as is the reverse process on cooling. This must reflect the lack here of typical cooperativity in fluorocarbon order–disorder transitions. The transition temperatures are given in Table 2.

The dynamic mechanical analysis (DMA; complex viscosity) curves in Figure 4 reveal the physical changes in the polymer as the temperature increases and reflect the thermal transitions seen in the DSC curves. For the polymer with $m = 8$ it can be seen clearly that the softening or onset of the fluid mesophase on heating is at 82 °C, while the clearing to a lower viscosity liquid phase begins at 128 °C; i.e., the thermotropic liquid crystalline phase is the plateau of intermediate viscosity between 82 and 128 °C, as shown in the DSC (Figure 3) and optical microscopy. The cooling curve shows some "hysteresis" because of undercooling. In the case of the polymer with $m = 3$, the viscosity does not show a plateau and there is therefore no mesophase on heating or on cooling. Only a single melting transition is observed. This polymer also did not show a fluid mesophase optically.

It was found that the first two members of the series, $m = 2$ and 3, did not show liquid crystalline phases although they do show several thermal transitions in the DSC which are similar in appearance to those of the other polymers. With $m = 4$ and the higher members of the series ($m = 8$, 12, and 20) fluid liquid crystalline mesophases were observed. The first transitions are thought to be due to disordering of the hydrocarbon segments, and the final transition is thought to be due to a disordering of the fluorocarbon segments. We feel that the mesophase is smectic, and X-ray diffraction experiments are in progress to determine this issue.

The ease of synthesis and availability of the fluorinated diol surfactant starting materials, together with the liquid crystalline properties of these polymers, their oil- and water-repelling properties, and well-known chemical and thermal stability, may render them useful for practical applications.

Acknowledgment. This work was supported by the Melville Laboratory Consortium (3M, Davy Corp., ICI, Unilever, and the Isaac Newton Trust).

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