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# Mesophase behaviour in fluorocarbon-hydrocarbon polyesters

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**To cite this Article** Wilson, L. M.(1994) 'Mesophase behaviour in fluorocarbon-hydrocarbon polyesters', Liquid Crystals, 17: 2, 277 — 282
**To link to this Article: DOI:** 10.1080/02678299408036566
**URL:** http://dx.doi.org/10.1080/02678299408036566

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LIQUID CRYSTALS, 1994, VOL. 17, NO. 2, 277–282

# Mesophase behaviour in fluorocarbon–hydrocarbon polyesters

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(*Received 21 December 1993; accepted 1 February 1994*)

A series of liquid crystalline main chain polyesters has been synthesized in which mesogenic, linear perfluoroalkyl groups are linked to aliphatic hydrocarbon chains. The liquid crystalline phase appears to be smectic B from X-ray diffraction data. Interesting differences in the mesophase transition temperatures and enthalpies are observed along the series, as the hydrocarbon and perfluoroalkyl contents are changed. These are discussed in relation to the length of the segments. One polymer was also synthesized from biphenyl-4,4′-dicarboxyic acid for comparison with the polyesters prepared using aliphatic dicarboxylic acids.

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## 1. Introduction

To date, mesophase behaviour in fluorinated alkyl compounds has been relatively little studied compared with that in classical non-fluorinated calamitic compounds [1]. Interest lies here in examining the limits of structure in partially fluorinated polymers that are compatible with liquid crystallinity, where the perfluoroalkyl segments or ‘rods’ act as the mesogenic units.

In previous studies, it has been found that perfluoroalkyl side chain polyacrylates with hydrocarbon spacers have liquid crystalline mesophases [2, 3]. It has also been observed by us that fluorocarbon side chain polyesters without spacer groups from the perfluoroalkyl group to the backbone show mesophases [4] and that mesophases are observed in main chain polymers composed of short alternating fluorocarbon and hydrocarbon blocks, ‘microblock polymers’, even when the fluorocarbon ‘rod’ is very short (four carbons in length) [5]. The axial ratio of such a unit is of course much less than that for a biphenyl unit. It appears that there is a greater driving force for segregation into an ordered (layered) mesophase than in other non-fluorinated (for example, phenyl ring) compounds, because of the strong incompatibility of fluorocarbon with hydrocarbon blocks in these materials. Diblock and triblock carbon–carbon linked small molecule compounds, usually with longer fluorinated segments, have also been investigated [6, 7, 8] and found to show smectic B or smectic A mesophases.

Here we describe the synthesis and characterization of ester-linked polymers containing linear perfluoroalkyl units of 4 or 6 carbons linked to aliphatic hydrocarbon chains. The materials show liquid crystalline mesophases which have been investigated

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using DSC, polarizing optical microscopy and X-ray diffraction. Schematic representations of the polymers are shown below.

$$[-O-CH_2-(CF_2)_4-CH_2-O_2C-(CH_2)_6-CO-]_N$$

Polymer **1**

$$[-O-(CH_2)_3-(CF_2)_6-(CH_2)_3-O_2C-Ph-Ph-CO-]_N$$

Polymer **2**

$$[-O-(CH_2)_n-(CF_2)_6-(CH_2)_n-O_2C-(CH_2)_m-CO-]_N$$

Polymers **3–5**

**3**, $n = 3, m = 6$; **4**, $n = 11, m = 6$; **5**, $n = 11, m = 20$

## 2. Experimental

All partially fluorinated diols, except that for polymer **1**, were prepared from $\alpha,\omega$-diiodoperfluorohexane and the corresponding prop-2-en-1-ol or undec-10-en-1-ol as described previously [9]. All the polymers were prepared from $HOOC-(CH_2)_m-COOH$, where $m = 6$ or 20, or biphenyl-4,4′-dicarboxylic acid and the corresponding partially fluorinated alcohol, using the carbodiimide activated ester forming procedure described previously [10]. Polymer **1** was synthesized from the commercially available octafluorohexan-1,6-diol.

Elemental analysis, polymer **1**: Calculated C 42·00, H 4·00 per cent; found C 42·13, H 4·07 per cent. Yield, approximately 90 per cent. IR: Main peaks at 1740, 1250–1100, 2800–3000 cm$^{-1}$. Proton NMR($CDCl_3$) shows 4·56 t 1 H, 2·40 t 1 H, 1·65 m 1 H, 1·33 m 1 H. Melting point C 47·07°C smectic 53°C I.

Elemental analysis, polymer **2**: Calculated C 50·00, H 3·20 per cent; found C 49·89, H 3·30 per cent. Yield, approximately 90 per cent. IR. Main peaks at 1716, 1090–1239, 2800–3000, 3060, 1609 cm$^{-1}$. Proton NMR($CDCl_3$) shows 8·11 d 1 H, 7·69 d 1 H, 4·42 t 1 H, 2·28 m 1 H, 2·14 m 1 H. Melting point C 145·5°C smectic 161°C I.

Elemental analysis, polymer **3**: Calculated C 43·16, H 4·32 per cent; found C 43·22, H 4·37 per cent. Yield, approximately 90 per cent. IR. Main peaks at 1730, 1250–1100, 2800–3000 cm$^{-1}$. Proton NMR($CDCl_3$) shows 4·12 t 1 H, 2·32 t 1 H, 2·15 m 1 H, 1·93 m 1 H, 1·61 m 1 H, 1·31 m 1 H. Melting point C 89°C smectic 96°C I.

Elemental analysis, polymer **4**: Calculated C 55·38, H 7·18 per cent; found C 55·46, H 7·25 per cent. Yield, approximately 90 per cent. IR. Main peaks at 1732, 1250–1100, 2800–3000 cm$^{-1}$. Proton NMR($CDCl_3$) shows 4·04 t 1 H, 2·28 t 1 H, 2·02 m 1 H, 1·59 m 3 H, 1·28 m 8 H. Melting point C 80°C smectic 94·1°C I.

Elemental analysis, polymer **5**: Calculated C 61·47, H 8·61 per cent; found C 61·52, H 8·74 per cent. Yield, approximately 90 per cent. IR. Main peaks at 1731, 1250–1100, 2800–3000 cm$^{-1}$. Proton NMR($CDCl_3$) shows 4·07 t 1 H, 2·27 t 1 H, 2·03 m 1 H, 1·57 m 3 H, 1·24 m 15 H. Melting point C 84°C smectic 95°C I.

All reagents were obtained from the Aldrich Chemical Co, except for the fluorinated hexane-1,6-diol and diiodoperfluorohexane which were obtained from Fluorochem.

Measurements were performed using the following instruments: IR: Nicolet 510M spectrometer; NMR: Bruker WM250 MHz spectrometer; DSC: Perkin–Elmer Series 7; polarizing optical microscopy: Leica Axioscope fitted with a Mettler FP 82 microfurnace.

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The X-ray diffraction measurements were performed using a Philips PW 1710 diffraction system. The sample was prepared by heating to the isotropic liquid and then cooling it down into the mesophase. The sample was then quenched in liquid nitrogen and ground to a powder for the X-ray measurements.

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

## 3. Results and discussion

The results of chemical characterization are shown in the experimental section above.

In the polarizing optical microscope (POM), the mesophase showed a grainy blue and orange coloured texture, very similar to that previously observed for fluorocarbon polymers [4, 5]. A typical texture is shown in figure 1. This is not clearly similar in appearance to any standard smectic (or nematic) phase [11], but perhaps resembles a small scale mosaic (smectic B) type. In each case it was possible to shear the material in the mesophase temperature range.

Thermal (DSC) transition temperatures are shown in table 1 for the polymers **1–5** which all show a mesophase. Two examples are given in figure 2 of the cooling and second heating curves for polymers **3** and **5**. In each of the polymers multiple peaks were observed and the endotherm indicating the onset of the shearable mesophase observed in the POM is given in table 1, as is the peak indicating the transition to the isotropic liquid on second heating. In polymers **2**, **4** and **5** the peaks were not well separated, having broad multiple (more than 2) endotherms that could not easily be resolved. The enthalpies given in table 1 are therefore only approximate. Polymers **2**, **4** and **5** showed reversibility, with multiple peaks (or a shoulder on the peak) on cooling. Polymers **1** and **3** do not appear to show this reversibility, having only one peak on cooling. However the cooling (exotherm) peak observed for polymer **1** was quite broad.

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Figure 1. Polarizing optical micrograph of polymer **5** ( × 100 magnification) in the smectic phase at 92°C.

Table 1. Thermal (DSC) transition data for polymers **1–5**.

| Polymer | Solid–mesophase/°C (enthalpy/J g$^{-1}$) | Mesophase–isotropic/°C (enthalpy/J g$^{-1}$) |
|---|---|---|
| **1** | 47<br>(8) | 53<br>(5) |
| **2** | 145·5<br>( ~ 12 broad) | 161<br>( ~ 5 shldr) |
| **3** | 89<br>(20) | 96<br>(36) |
| **4** | 80<br>(shldr) | 94·1<br>( ~ 38·5) |
| **5** | ~ 84<br>(shldr) | 95<br>( ~ 26) |

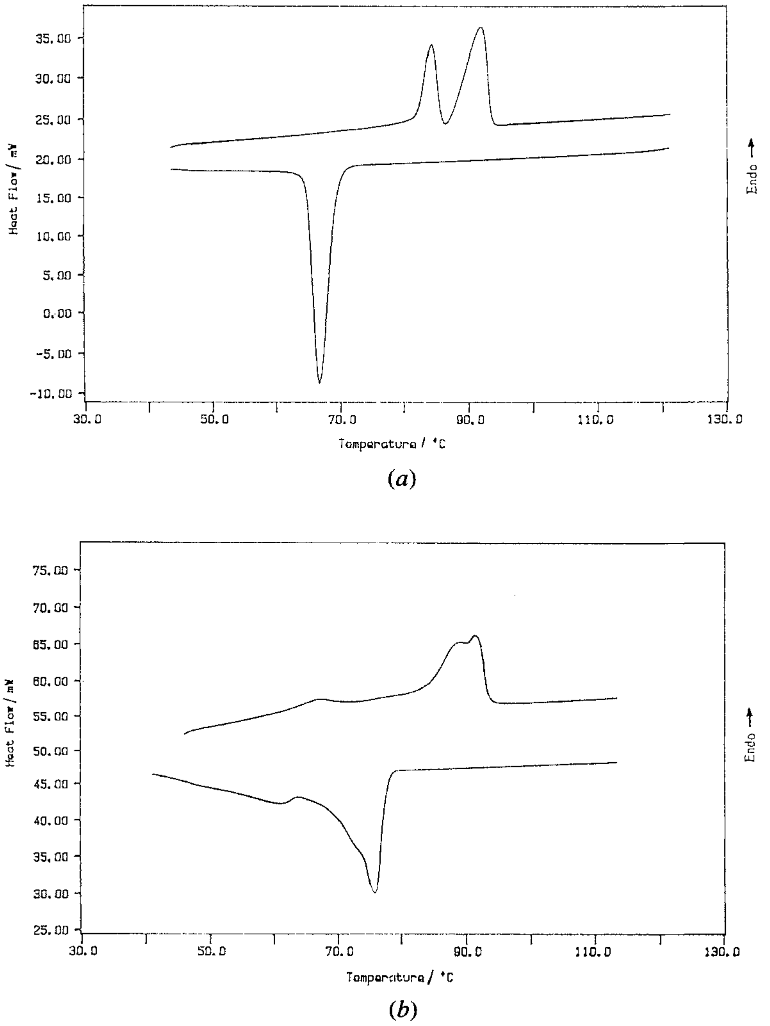

Figure 2. (*a*) Cooling and second heating DSC traces for polymer **3** at 10°C min$^{-1}$. (*b*) Cooling and second heating DSC traces for polymer **5** at 5°C min$^{-1}$.

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Polymer **5** also showed a small endotherm at 65°C, which is presumably a solid–solid transition since the polymer could not be sheared easily at this temperature.

The mesophase temperature ranges were about 6 to 14°C for the polymers with aliphatic segments. Polymer **1** has a clearing point significantly lower than the comparable polymers **3**, **4** and **5** which have longer mesogenic perfluoroalkyl segments. Where they are observable as simple peaks, the enthalpies of these transitions—see table 1—and those of solid to mesophase transitions are of about the same order of magnitude for polymers **1**, **2** and **3**. Polymer **2**, containing the biphenyl ring system had a larger mesophase temperature range and also higher transition temperatures, as would be expected with the mesogenic biphenyl ester unit. However for polymers **4** and **5**, the enthalpies for the solid to mesophase transition appear to be larger than for the mesophase to isotropic transition, although they could not be measured accurately since the peaks are not resolved. In the analogous carbon–carbon linked polymers [5, 13] and in the fluorinated side chain polyesters [4] it has been observed that the isotropization transition is determined by the fluorocarbon and is usually sharp, while the preisotropization and solid to mesophase transitions are broad and usually show an increasing ethalpy as the polymer hydrocarbon content is increased. The polymers described here seem to show a similar trend.

X-ray diffraction was performed on polymer **4** to verify its liquid crystallinity and

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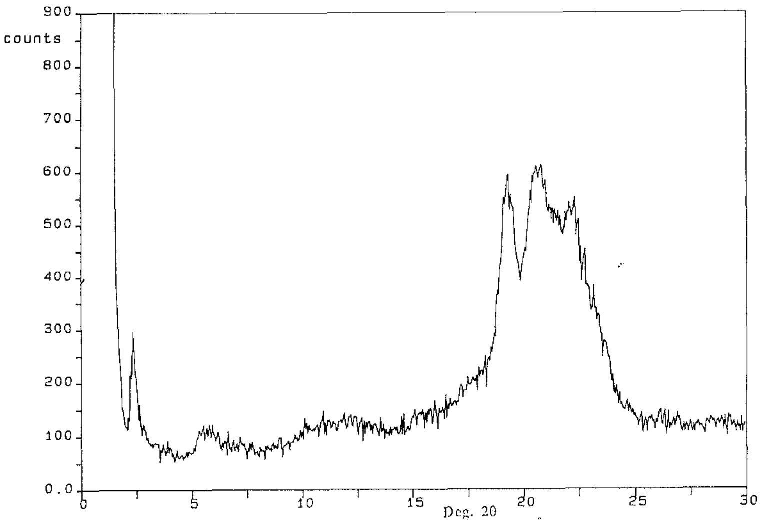

Figure 3. X-ray diffraction scan (intensity versus angle) of polymer **4**.

Table 2. X-ray diffraction data for polymer **4**.

| Polymer | Angle/degrees 2$\theta$ (intensity) | $d$-value/Å |
|---|---|---|
| 4 | 2·45 (m) | 35·8 |
| | 5·40 (vw) | 16·75 |
| | 19·0 (m) | 4·75 |
| | 20·56 (s) | 4·3 |
| | 22·26 (w shldr) | 4·0 |

if possible to determine its nature. The intensity versus diffraction angle plot is shown in figure 3 and the data are listed in table 2. A sharp peak is seen at low angle with a weaker second order peak, indicating a smectic layer ordering. The spacings corresponding to these low angle peaks are in the ratio of 1 : 1/2, indicating 001 and 002 indexing. At high angles there is a fairly broad, but not diffuse peak, indicating fairly close smectic B type ordering. This peak corresponds to 4·3 Å, with a fairly sharp shoulder at 4·75 Å (and a small shoulder at 4 Å). These are the lateral spacings within the layers and correspond to the spacings between the hydrocarbon and the perfluorocarbon units. These are similar to the peaks in (high density) polyethylene but the spacings are different. The perfluorocarbon chain is 20 per cent 'thicker' than the aliphatic chain and similar spacings have been seen previously [12, 13]. The layer periodicity, at about 36 Å, is approximately 25 per cent smaller than that expected for the fully extended conformation of the (quite long) hydrocarbon–ester chain between perfluoroalkyl units. However, because of the large difference between the diameters of the perfluorocarbon and the hydrocarbon chains (see above), the fully extended conformation of the hydrocarbon chains would lead to severe packing problems and the smaller value of the layer periodicity is thus expected. The hydrocarbon may therefore be quite coiled, folded, melted and otherwise 'disordered' in this material. The chains may also be overlapping or tilted, but some disordering of the hydrocarbon is expected in the mesophase [4, 5].

It is interesting to note that polyester **1** with only a 4 carbon perfluoroalkyl segment which has a very low axial ratio also showed a mesophase, as noted above. The mesophase transition temperatures and the isotropization temperatures are generally lower than for the analogous carbon–carbon linked microblock polymers [5], although the mesophases appear to be similar. Further work to determine the structure of smectic phases is planned.

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This work was supported in part by the Melville Laboratory Consortium (3M, Davy Corp., ICI, Unilever, and the Isaac Newton Trust). I also wish to thank A. C. Griffin for his help and useful discussions.

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