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Temperature dependent smectic mesophase ordering in fluorocarbon side chain polyesters

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Smectic mesophase behaviour in perfluorooctyl side chain polyesters with hydrocarbon comonomers has been investigated by DETA and X-ray diffraction at different temperatures. The polymers show clear transitions from the solid to the fluid mesophase and from the mesophase to the isotropic liquid.

Liquid crystalline polymers with all fluorocarbon mesogenic side chains are only known in the polyacrylate [1–3] series and have a single methylene between the pendant side chains. Polymers having longer spacer units along the main chain are known with polysiloxane backbones and pendant aromatic mesogenic groups [4] or with semi-fluorinated mesogenic side groups [5]. Here we describe perfluoroalkyl side chain polyesters with aliphatic hydrocarbon backbone spacers of two different chain lengths and of a regular repeating structure which have been synthesized in high yield directly from the hydrocarbon diacid and fluorinated sulphonamide diol [6, 7]. We believe that these polyesters are the first fluorinated polymers of this type to show liquid crystalline behaviour.

The polyesters have the structure

$$[\text{-O-CH}_2\text{CH}_2\text{-N(SO}_2\text{-(CF}_2)_8\text{F)-CH}_2\text{CH}_2\text{-O}_2\text{C-R}_m\text{-CO-}]_n$$

and those with $m = 8$ and 20 CH_2 units are discussed here.

Unlike the polyacrylate systems with perfluoroalkyl side chains, these polyesters show liquid crystalline mesophases without having flexible-(CH_2)- spacer linkages from the fluoroalkyl group to the polymer backbone. The polyacrylate systems having fluorocarbon–hydrocarbon side chains can show highly ordered smectic B mesophases [1–3], while the polysiloxanes [5] normally show smectic A mesophases. The polyesters [6, 7] described here also show a fluid smectic mesophase, which is investigated in more detail in this work, by X-ray diffraction (XRD) and dielectric thermal analysis (DETA).

All polymers were prepared and characterized as described in [6] and [7]. DETA was performed on a Polymer Laboratories dielectric thermal analyser and XRD on a Siemens D500 diffractometer with secondary monochromator and a Siemens Kristalloflex generator, using a Paar (Graz, Austria) hot stage with stability better than 0·1°C.

Previously, polarizing optical microscopy (POM) showed a transition to a fluid mesophase in both of these polyesters. This had a grainy texture and DSC showed two well-defined peaks corresponding to the solid to mesophase and the mesophase to isotropic liquid (at about 150°C) transitions which were reversible on cooling [6, 7].

XRD measurements were performed at different temperatures, from room temperature up to 160°C on the polyesters with $m = 8$ and 20, that is, from the solid phase to above the transition to the isotropic liquid. At the lower temperatures, in the solid and up to the solid to mesophase transition, they show strong sharp peaks at low angles and broad peaks at high angles. The ratios of the spacings corresponding to the sharp, low angle peaks are 1 : 1/2 : 1/3,

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indicating 001, 002 and 003 indexing due to periodic layer spacings in a smectic phase. From molecular models, the side chain length (with the hydrocarbon units in a folded hairpin arrangement to give smectic layers) can be calculated, and for the polyester with $m = 8$, the layer thickness is calculated to be approximately 22·5 Å. The X-ray data shows a layer periodicity of 36·2 Å giving a ratio (d/L) of 1·61 at the solid to mesophase transition. For $m = 20$, the layer thickness is calculated to be approximately 30 Å, while the X-ray data show a layer periodicity of 47·3 Å, again indicating a bilayer arrangement with a ratio (d/L) of 1·58. Since the polyesters described here have long hydrocarbon chains (from the m methylenes in the comonomer) between each side group along the backbone, the side groups in the bilayer could be tilted or quite interpenetrated. The greater chain length between side groups presumably would allow overlap of the perfluorocarbon chains giving a bilayer spacing which is less than twice the repeat length (L), as in antiparallel dimer packing of some smectics.

In the XRD measurements at higher temperatures, from the solid to mesophase transition temperature and above, it was found that the layer spacing, d, in the mesophase

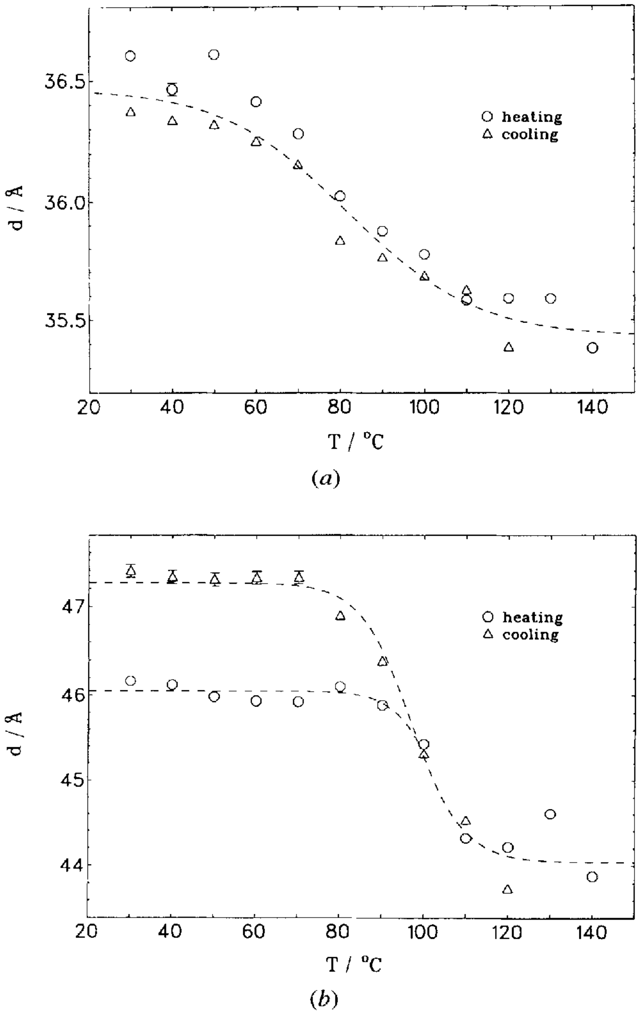

Figure 1. (a) Lower angle XRD d spacing versus temperature for the polymer with $m = 8$, showing heating and cooling. (b) Lower angle XRD d spacing versus temperature for the polymer with $m = 20$, showing heating and cooling.

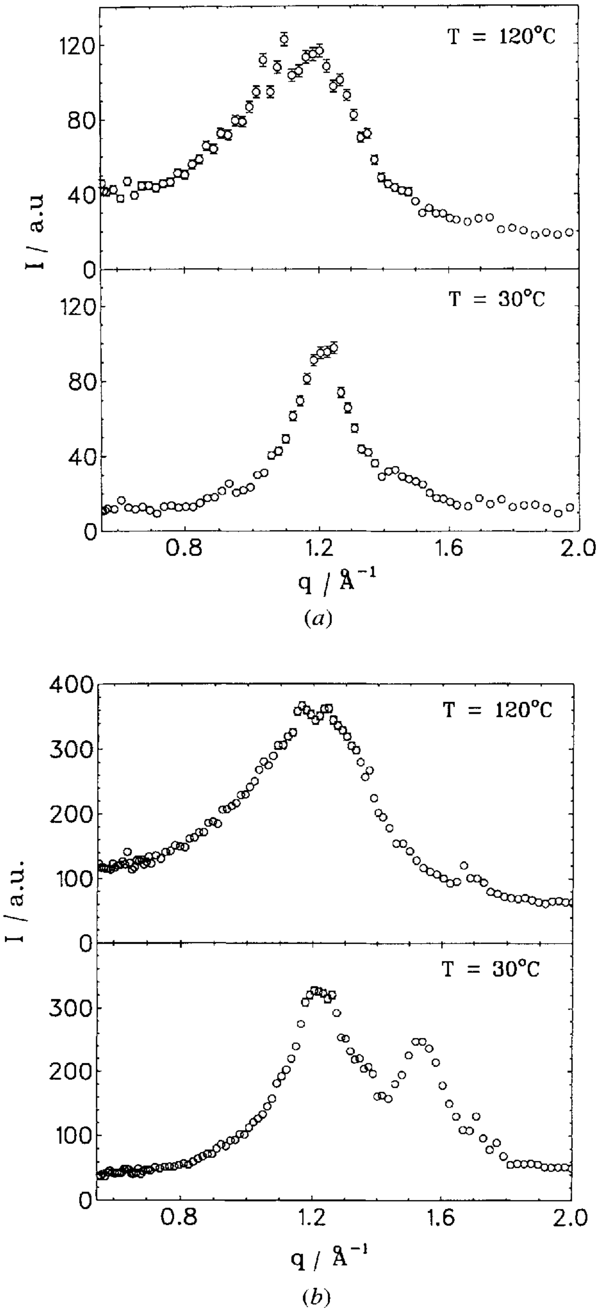

Figure 2. (a) Higher angle XRD intensity versus q plot for the polyer with $m = 8$ at 30 and 120°C. (b) Higher angle XRD intensity versus q plot for the polyer with $m = 20$ at 30 and 120°C.

decreased as the temperature was increased, from 36·3 to 35·3 for F8R8 and from 47·3 to 43·6 for F8R20, as shown in figure 1. This decrease in the layer spacing is consistent with smectic A type ordering and has been observed in both non-fluorinated and fluorinated side chain liquid crystalline polymers [5, 8, 9]. The solid to mesophase transition could clearly be observed as a rapid change in the low angle layer spacing versus temperature data, occurring at 81 and 95°C, respectively, for the F8R8 and F8R20 polyesters (see figure 1). The low angle peak width behaviour is different for the two polymers. For F8R20, the peak width increases slightly and the intensity decreases at the transition, while for F8R8, there is little observable change in the peak width and the intensity increases slightly. Below the solid to mesophase transition, the low angle peaks showed a fine splitting into two slightly different layer spacings (see DETA, below), but in both polyesters the higher d spacing peak of the two disappeared at the (solid–mesophase) transition. The mesophase to isotropic transition could be observed as a total disappearance of the low angle peaks at 150°C and 152°C for F8R8 and F8R20, respectively. The cause of this splitting is unknown, but may be due to two different solid phases, possibly caused by a small proportion (~ 10 per cent) of branched perfluoro-octyl isomer in the polymer [10] as shown by fluorine NMR. It was not possible to remove this isomer from the monomer by repeated purification.

At larger angles, there is a major peak corresponding to 5·1 Å in the polymers with $m = 8$ and 20; this occurs in the solid phase and the mesophase. This spacing corresponds to the expected lateral spacing between perfluoroalkyl chains. With $m = 20$, there is a second broad peak at 4·1 Å and the other polymer ($m = 8$) also had a small shoulder at this position in the solid. Since the textures in the microscope between crossed polarizers are similar, and this spacing is close to the usual lateral distance between hydrocarbon chains, this may be the lateral hydrocarbon chain spacing between nearest neighbours, growing in importance as the proportion of hydrocarbon in the polyester increases. The fact that both the perfluorocarbon and hydrocarbon lateral nearest neighbour spacings can be observed also supports the presence of a smectic A mesophase. However the peaks did not have the sharp appearance characteristic of a highly crystalline material even at room temperature. This may be due to a higher order mesophase or a micro-crystalline solid.

At higher temperatures, above the solid to mesophase transition, the major (5·1 Å) lateral fluorocarbon mesogen spacing peak was broad and showed liquid-like order in the mesophase temperature range, supporting a smectic A type ordering. The peak also showed a change on heating, becoming broader, while the 4·1 Å peak had declined and disappeared at the solid to mesophase transition. On isotropization, this broad peak remained essentially unchanged, showing the same liquid-like order within the layers. These changes are shown in figure 2. The disappearance of the peak or shoulder at $d = 4{\cdot}1$ Å may be due to the total melting/disordering of the hydrocarbon component of the polymer. A schematic representation of the possible packing in the polymer is shown in figure 3, with the hydrocarbon moiety in a folded arrangement. The alternative arrangement with the fluorocarbons groups on alternate sides of the unfolded hydrocarbon (in a bilayer type ordering) gives an equivalent layer thickness when the fluorocarbons groups are interpenetrated as above.

DETA for the polymer with $m = 8$ showed a double transition corresponding approximately to the lower temperature solid to mesophase transition observed above. At higher temperatures, the permittivity increased sharply, corresponding to the higher mesophase to isotropic transition. The double transition is shown in figure 4, and the first derivative curve shows increases at 76 and 81·5°C,

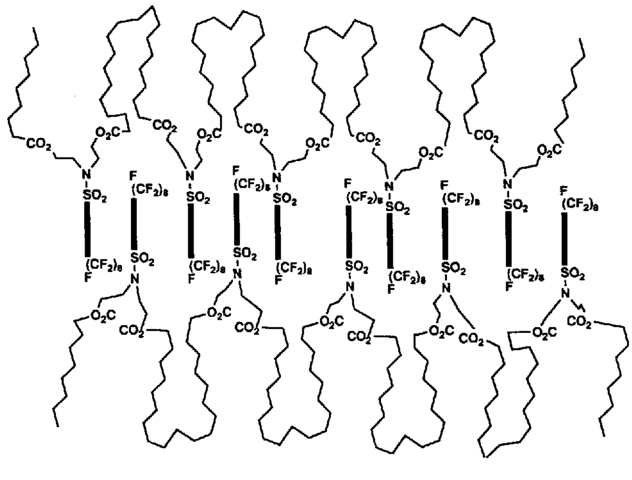

Figure 3. Schematic representation of the smectic bilayer packing of fluorinated sulphonamide polymer.

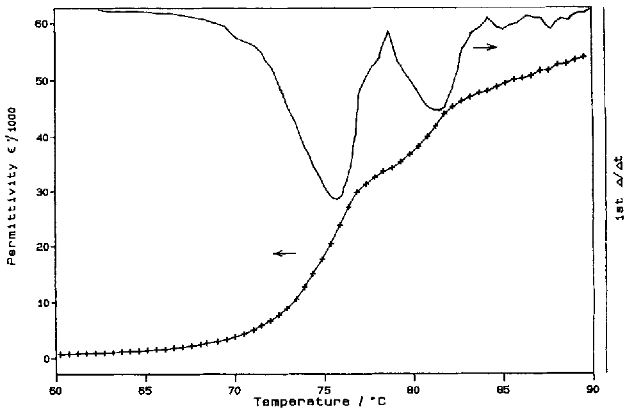

Figure 4. DETA permittivity versus temperature plot for the polymer with $m = 8$, showing the first derivative.

close to the 81°C transition observed by XRD, and the nature of this double transition may be connected with the fine splitting of the layer spacings seen in the XRD experiments at temperatures up to the solid to mesophase transition.

In conclusion, the mesophase in these polymers appears to be similar to a smectic A phase, while the solid to mesophase transition as observed by XRD and DETA is complex.

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