Liquid-Crystalline Behavior in Fluorocarbon–Hydrocarbon Microblock Polymers. 2

T. Davidson, A. C. Griffin,† L. M. Wilson,* and A. H. Windle

Melville Laboratory for Polymer Synthesis, University of Cambridge, Pembroke Street, Cambridge CB2 3RA, U.K.

Received July 12, 1994®

ABSTRACT: A series of liquid-crystalline polymers has been synthesized in which the mesogenic perfluoroalkyl chains are directly linked to the hydrocarbon chains in an alternating sequence. Liquid-crystalline behavior was investigated by optical microscopy, DSC, and X-ray diffraction. The liquid-crystalline phase appears to be smectic B from X-ray data. Interesting differences in the mesophase transition temperatures are observed along the series, the polymers showing an odd–even effect in the isotropization temperatures as the length of the hydrocarbon is changed. Differences are also seen in layer spacing from X-ray data, which shows some alternation as the hydrocarbon content increases but is generally much smaller than the expected extended repeat unit length. We discuss these in relation to the lengths of the segments.

Introduction

It has previously been shown that the microblock polymers with alternating fluorocarbon and hydrocarbon segments show liquid-crystalline mesophases.[1] These materials are polymeric analogues of the diblock and triblock fluorocarbon–hydrocarbon small molecules which have been reported.[2–5] The small molecules show mesophases, usually of the smectic B type, although a smectic A phase has also been observed.[5]

We now report the synthesis of a series of these novel polymers, in which the lengths of the mesogenic perfluoroalkyl chains (n) and the hydrocarbon chains (m) were systematically varied to investigate the mesophase behavior and the polymer structure. A schematic representation of the polymer is shown below.

$$-[(CF_2)_n-(CH_2)_m-]_N-$$

The perfluoroalkyl segments in these polymers are directly linked to the hydrocarbon chains. The liquid-crystalline behavior was investigated by polarizing optical microscopy (POM), DSC, and X-ray diffraction. The analogous fluorocarbon–hydrocarbon polyesters, with perfluoroalkyl segments in the main chain, also show similar mesophases.[10]

Experimental Section

All polymers were synthesized as described in ref 1. All α,ω-dienes were obtained from Aldrich Chemical Co. except the following: Undecadiene and dodecadiene were synthesized from the bromodecene and dibromododecane by Hoffmann elimination using potassium *tert*-butoxide in DMSO.[11] Tridecadiene was synthesized from bromodecene and allyl Grignard by established procedures. The analyses corresponded to the proposed structures in all cases. The elemental analyses of the polymers all agreed with the calculated theoretical values to within 0.35% or better and they also showed the following: IR, 2830–3000 (broad), 1100–1230 cm^{-1}. Melting points, see Tables 1 and 2 and discussion. Note that two polymers, with $n = 6$ and $m = 6$ and 8, have higher melting points listed than found previously due to higher M_w. ^1H NMR in $CDCl_3$ (ppm vs TMS), all show 2.05–2.10 multiplet (2H), 1.60 multiplet (2H), and 1.28–1.45 multiplet ([m-4]H, where m is the number of methylene units in the polymer repeat unit). GPC (in $CHCl_3$, polystyrene standards) showed all polymers had M_w = 10000–26000 for the more soluble iodo-precursor polymers,[1] with $M_w/M_n = 1.2$.

Table 1. POM Thermal Transition Data for Polymers

m	solid–mesophase/°C	mesophase–isotropic/°C
	$n = 4$ Series	
7	112	152
8	118	155
9	133	148
10	124	144
11	125	135
12	119	131
13	112	128
14	121	129
	$n = 6$ Series	
6	147	183
7	137	155
8	125	165
9	110	148
10	100	151
11	105	134
12	120	145
13	117	139
14	114	141

Measurements were performed on the following instruments: IR, on a Nicolet 510M spectrometer, NMR, on a Bruker WM 250 MHz spectrometer; DSC, on a Perkin-Elmer Series 7; polarizing light microscopy, on a Leica Axioscope fitted with a Mettler FP82 microfurnace, GPC, on a Polymer Laboratories Knauer system with Viscotek viscosity, RI, and UV detectors (universal calibration). Elemental analyses were performed in the Department of Chemistry, University of Cambridge. The X-ray diffraction measurements were performed on a Philips PW 1710 diffraction system. The samples were measured at room temperature (crystalline) or at the mid-mesophase temperature on a hot stage.

Results and Discussion

The samples all show the same grainy mesophase texture[1] in the POM and usually exhibit a small change in the texture on heating from a more striated to a more grainy texture. The samples could all be sheared easily in the temperature ranges in Table 1, which lists the onset of a soft mesophase and the final loss of optical birefringence. These data are also plotted in Figure 1a,b for the two series of polymers with $n = 4$, containing

† Present address: Department of Chemistry and Biochemistry, University of Southern Mississippi, Box 5043 Southern Station, Hattiesburg, MS 39406.

® Abstract published in *Advance ACS Abstracts,* November 15, 1994.

0024-9297/95/2228-0354$09.00/0 © 1995 American Chemical Society

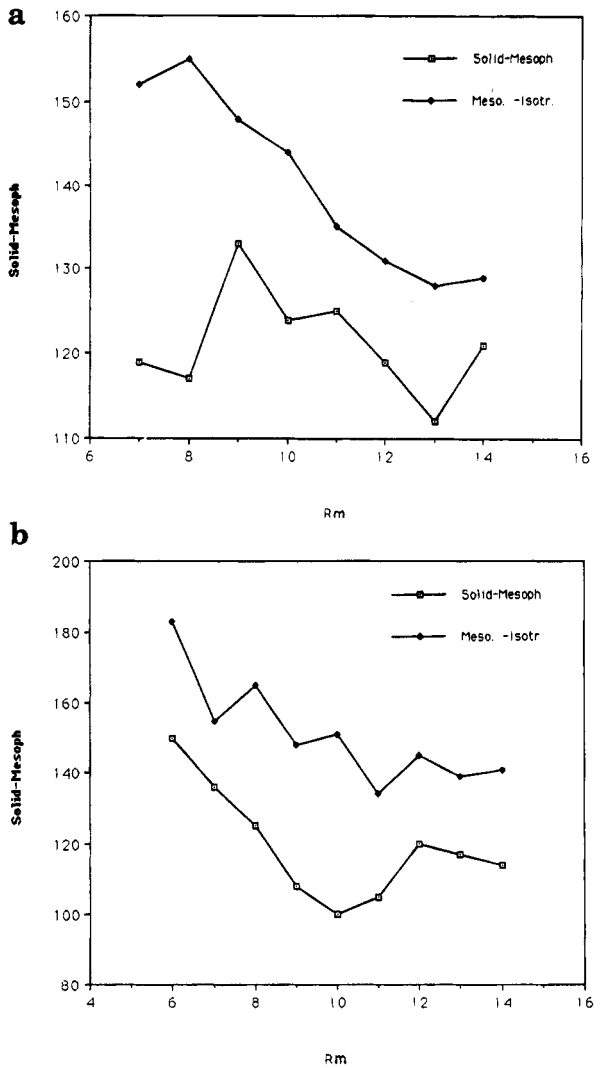

Figure 1. Graphs of solid to mesophase and mesophase to isotropic transition temperatures vs m: (a) $n = 4$; (b) $n = 6$.

$-(CF_2)_4-$ units, and $n = 6$, containing $-(CF_2)_6-$ units, respectively. The mesophase behavior in these polymers is due to the mesogenic perfluoroalkyl "rods", and therefore the similar appearance of the mesophase texture might be due to similar mesogen ordering in all the polymers. The onset of the mesophase was postulated to be due to the disordering of the hydrocarbon component, while the isotropization to the disordering of the perfluorocarbons.[1] This is discussed further below. The polymer with the shortest hydrocarbon segment, $m = 6$, and with $n = 6$ showed the widest mesophase temperature range and also the highest isotropization temperature.

In the DSC, however, the first transition that was observed above room temperature does not always correspond to the onset of the soft mesophase as observed in the POM. Therefore some solid–solid transitions presumably occur in these materials. This has previously been shown to be the case by dynamic mechanical analysis (DMA) as a function of temperature,[1] which showed a phase of high modulus in these materials corresponding to the DSC transitions below the temperature of the mesophase that could be sheared on the microscope slide in the POM. This phase could perhaps be described as a condis crystal, with the hydrocarbon in the "rotator" phase.[12] The DSC data are shown in Table 2 and two examples are given in Figure 2. Differences in the mesophase transition temperatures are observed along the series, as the length of the hydrocarbon chain (m) is changed. The final transition (on heating) in the DSC does correspond to the isotropization transition seen in the POM. This final transition was also the most sharp transition in the DSC in all cases (on second heating and was even sharper on cooling), which indicates it may be associated with the fluorocarbon component. However, this transition was usually overlapping other lower transitions, and it was therefore difficult to estimate its enthalpy.

Table 2. DSC Thermal Transition and Enthalpy Data for Polymers

m	solid–solid/ °C midpeak positions	total enthalpy [kJ/(mol of repeat unit)]	solid–mesophase/ °C midpeak positions (unless shldr)	mesophase–isotropic/ °C midpeak positions (unless shldr)
		$n = 4$ Series		
7	105	15.80	114	145
8	110	22.25	117	151
9	116	18.53	134 (shldr)	145
10	110	15.44	123 (shldr)	140
11		16.46	126 (shldr)	132
12		16.93	122	129
13	100	23.10	109 (shldr)	125
14		21.58	115 (shldr)	126
		$n = 6$ Series		
6		22.20	148	183
7	125	18.33	139	150
8		21.91	125	163
9		15.80	112	145
10		24.31	100 (shldr)	152
11		18.94	104	131
12		18.72	119	143
13	84	23.62	115	138
14	104	35.04	112	134

The isotropization temperature might be expected to be fairly constant if the disordering of the fluorocarbons was not affected by changes in the surrounding hydrocarbon. However, except for the first member of each series, in general, the mesophase to isotropic transition temperature declines as m increases (Figure 1), i.e., as the perfluorocarbon component is diluted with increasing m. This temperature would of course asymptotically approach the melting point of the pure hydrocarbon (polyethylene). This transition furthermore appears to show some odd–even effect in m, particularly for $n = 6$, being higher for even values of m and showing some odd–even effect superimposed on the general downward trend for $n = 4$. Therefore there is some ordering effect of the hydrocarbon chain in the mesophase. The origin of this effect may not be similar to the classic odd–even effect for two mesogenic units tied by a hydrocarbon spacer, since the effect of changing from an even to an odd number of methylenes in the hydrocarbon comonomer in these polymers is to displace the fluorocarbon segment by one methylene and to rotate it by 180° about its long axis rather than causing a kink in the chain. Thus every second fluoroalkyl segment is inverted with respect to the first although this is complicated by the normal helical ($^1/_{13}$) twist of the perfluoroalkyl. These effects may be sufficient to cause the observed odd–even variation. Note that an odd–even effect is also seen in the melting points of the homologous series of hydrocarbon paraffins.[13] A similar effect (but inverted with respect to m) was observed recently for a series of fluorinated side chain polyesters.[6]

The solid to mesophase transition temperatures vary for low m but then show some increase as m increases, the resulting mesophase temperature range therefore finally decreasing with m. Ultimately the mesophase stability temperature range would be expected to vanish

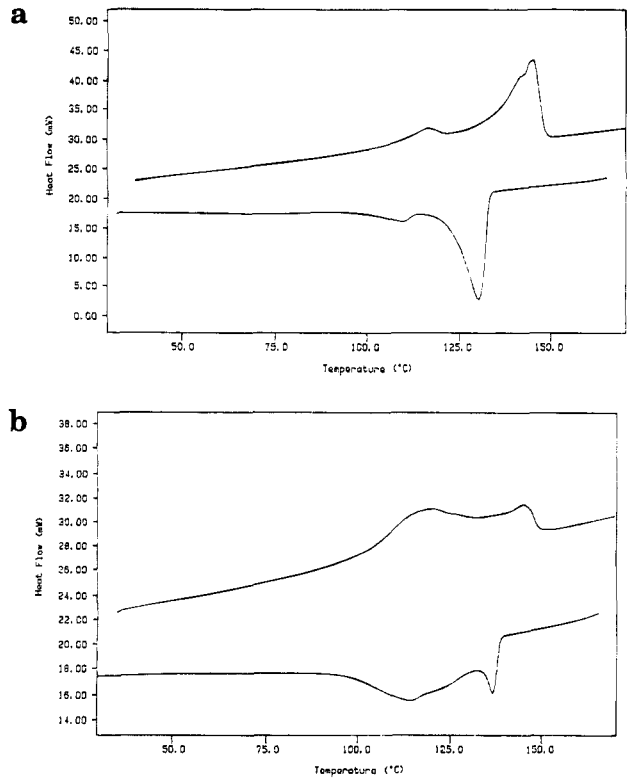

Figure 2. DSC plots for polymers with (a) $n = 4$ and (b) $n = 6$.

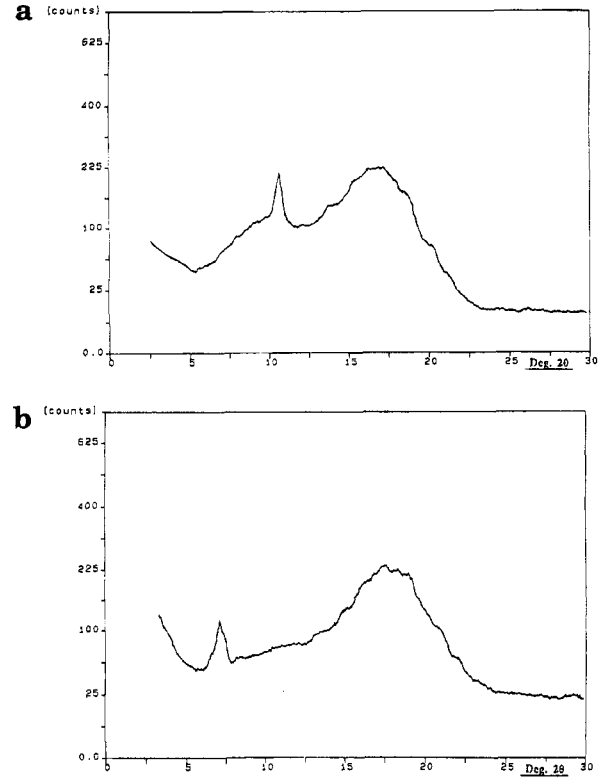

Figure 3. X-ray diffraction plots of intensity vs angle (2θ) for the polymers with (a) $n = 4$ and $m = 8$ and (b) $n = 4$ and $m = 14$ in the mesophase.

for very large m, and then both transitions would coincide with the melting point of polyethylene. The enthalpies from DSC data, calculated as kJ/(mol of repeat unit), for these polymers are also shown in Table 2. It is usually not possible to resolve the peaks and to calculate the enthalpy due to the final isotropization transition or the earlier transitions separately; however, the enthalpy of the sum of the preisotropic transitions appeared to be greater than for the final isotropization transition.

In the X-ray diffraction patterns, a layered lamellar structure is indicated by low-angle peaks, and the liquid-crystalline phase appears to be like a smectic A type, as the higher angle peak is broad and shows liquid-like order in the mesophase. Examples are shown in Figure 3, showing intensity vs angle 2θ. Differences are seen in the layer periodicity, which overall shows an upward trend as the hydrocarbon content, m, increases. These results are shown in Table 3 and plotted in Figure 5 vs m. Low-angle peaks, corresponding to layer lines, are observed for all the samples. These observed layer spacings are discussed below. The layer peaks are also seen in the crystalline solid at room temperature, together with intense and sharp higher angle peaks corresponding to d-spacings of about 4.8–4.6 and 4.4–4.1 Å. These show some variation, in general decreasing as (the hydrocarbon content) m increases. These peaks are similar in appearance to the (110) and (200) peaks seen in crystalline HDPE, but the d-values are greater (about 4.1 and 3.7 Å in HDPE). If the semifluorinated polymers have a similar structure, then by analogy a may be ~8.5 and $b \sim 5.8$Å for the unit cell (with $m \sim n$). Further work on oriented samples is being carried out to determine the structure and unit cell dimensions of these polymers. Above the isotropization temperature, two broad liquid-like peaks are observed, one centered at about 17° 2θ, corresponding to the average isotropic lateral spacing of about 5.2 Å, and the other at 8–10° 2θ, corresponding to an average unit length of about 9–11 Å.

Table 3. Low-Angle X-ray Diffraction Data for Polymers

	angle/(deg 2θ) (intensity)	d-value/Å
	$n = 4$ Series	
7	13.00 (m)	6.84
8	10.50 (m)	8.22
9	12.29 (m)	7.20
10	11.90 (m)	7.45
11	11.34 (m)	7.80
12	8.89 (m)	9.94
13	9.10 (m)	9.71
14	7.15 (m)	12.35
	$n = 6$ Series	
6	11.11 (m)	7.97
7	10.5 (m)	8.26
8	11.33 (m)	7.85
9	11.19 (s)	7.90
10	7.89 (m)	11.22
11	10.45 (m)	8.70
12	7.50 (m)	11.76
13	9.17 (m)	9.64
14	6.45 (s)	14.0

It might be expected that the layer spacing would increase isotonically and smoothly as the hydrocarbon length m increased. However, this is not observed, as shown in Figure 5. From molecular models it can be shown that the length of the $-(CF_2)_4-$ "rod" ($n = 4$) is about 5.2 Å, while the $-(CF_2)_6-$ "rod" is 7.8 Å. The distance taken up by the hydrocarbon spacer in the layers then depends on the packing of these units. Since the observed layer spacing of the $n = 4$ series increases from about 6.8 to 12.35 Å for m going from 7 to 14, the hydrocarbon takes up about 1.6–7.1 Å. Similarly, for the $n = 6$ series, the hydrocarbon takes up from about 0.2 to 6.2 Å in the layers for $m = 6$ to $m = 14$. This spacing is clearly too small to accommodate the hydrocarbon chains in an extended (or other) conformation

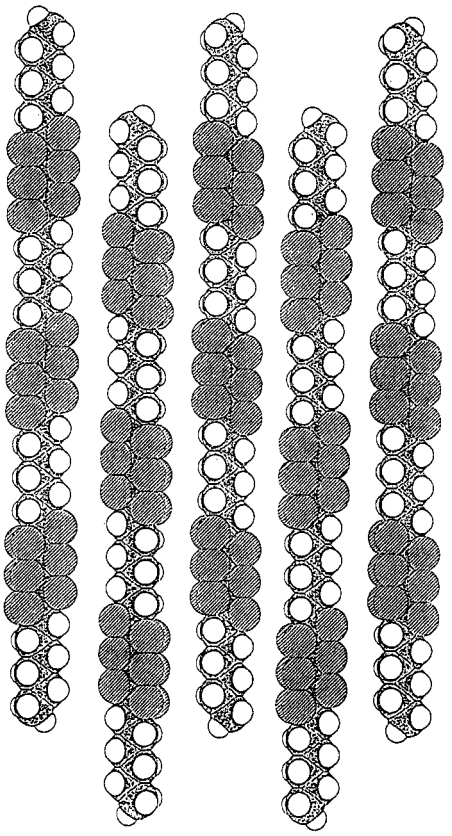

Figure 4. Schematic representation of polymer chain packing.

between layers of perfluorocarbon segments unless they are highly tilted. Some different layer structure is therefore indicated. In the alternating ethylene–tetrafluoroethylene copolymer, the structure has been found[9] to be orthorhombic or monoclinic, with the fluorocarbon next to the hydrocarbon in adjacent chains (rather than fluorocarbon on fluorocarbon). An arrangement of this type is indicated in these microblock polymers, as shown schematically in Figure 4. When the difference in the diameters of the perfluoroalkyl and the hydrocarbon units is considered, it can be seen that this hydrocarbon arrangement is in fact the likely packing because the perfluoroalkyl is much thicker.[7,8] The extended layer packing with only perfluorocarbon on perfluorocarbon is not possible as this would leave voids in the hydrocarbon layer. The smectic layers therefore probably consist of fairly closely packed fluorocarbon and hydrocarbon, and any voids due to the mismatch of microblock segment lengths (m being greater than n) could be filled by disordered or "melted" hydrocarbon.

The extended conformation of the hydrocarbon would give a polymer chain repeat unit length (L) of about 12.5–16.2 Å for $n = 4$ and 15–23.8 Å for $n = 6$, and a layer periodicity close to half of this value might be expected when m is comparable to n. However, in Figure 5, both series of polymers (with $n = 4$ and $n = 6$) show some alternation in the layer periodicity for higher m, most of the values for the $n = 6$ series being above the $L/2$ line when m is even (except $m = 8$) and below when m is odd. Thus it appears there may be some odd–even packing effect but in the case of some values of m, the situation seems to be quite complex; for example, for $n = 6$, the layer spacing is smaller with $m = 8$ than $m = 7$, and for the $n = 4$ series, the d-value for $m = 10$ is smaller than for $m = 8$. These polymers show interesting variations in their mesophase temperature transitions and unusual molecular ordering in the crystalline solid and in the mesophase along the series.

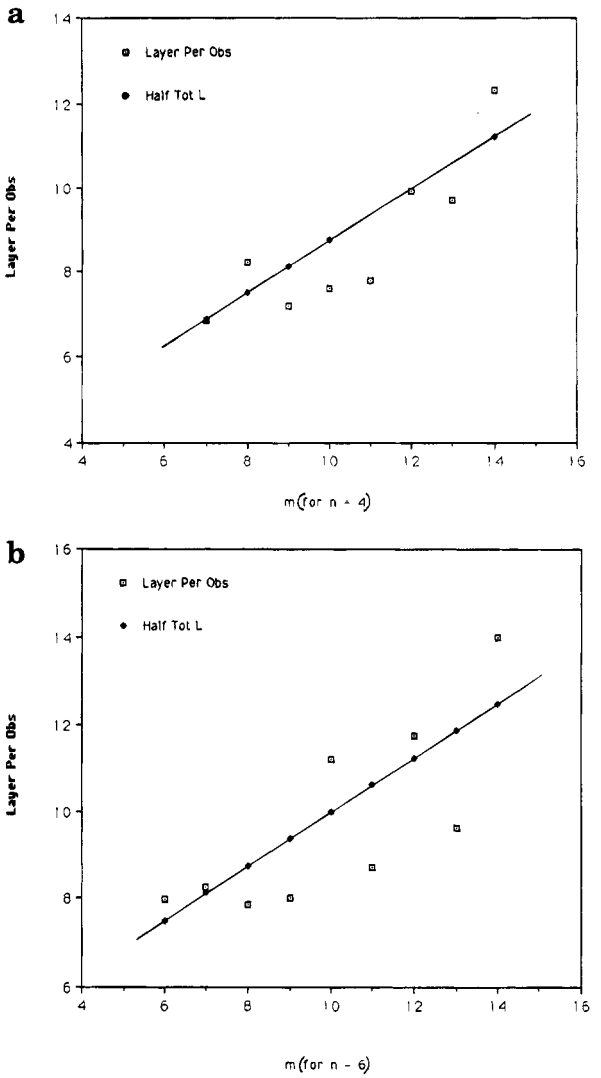

Figure 5. Plots of XRD observed layer spacing vs m and showing (calculated length)/2 for polymers with (a) $n = 4$ and (b) $n = 6$.

Acknowledgment. T.D. would like to thank the SERC for financial support. L.M.W. would like to thank the Melville Laboratory Consortium (ICI, Unilever, 3M, and the Isaac Newton Trust) for support of this work.

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MA941031F