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Liquid-Crystalline Fluorocarbon-Hydrocarbon Microblock Polymers

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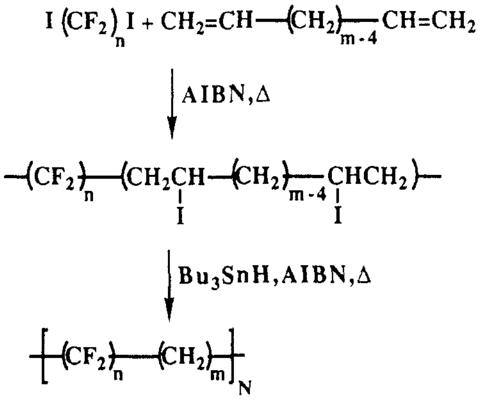
Introduction. The covalent linking of fluorocarbon and hydrocarbon segments leads to some extraordinary materials properties due to the strongly segregating tendencies of each component. Even in the small diblock molecules, $F(CF_2)_n-(CH_2)_mH$, novel solution behavior and lamellar solid-state structures arise from the incompatibility of the two segments. These compounds have been extensively studied[1-3] and show smectic liquid-crystalline phases corresponding to multiple transitions in differential scanning calorimetry. As expected the mesophase temperatures vary depending on the length and branching of each segment. The triblock molecules $F(CF_2)_n-(CH_2)_m-(CF_2)_nF$ are also known[4] but show only a single melting transition in the DSC although recently a smectic B phase has been optically detected.[5]

Because of the interesting properties arising from the incompatibility of these segments and the rigidity of the fluorocarbon chains, we wanted to examine their macromolecular analogues and several polymers of the type $(-(CF_2)_n-(CH_2)_m-)_N$ were made. It is believed that polymers of this type (containing $-(CF_2)_{n\geq 4}-$) with a regular repeating structure have not been made before. The polymerization method is also of interest because it opens up possibilities for various polymers that contain no linking groups (such as amide or ester functions) between the segments. The rigid fluorocarbon segment coupled with the flexible hydrocarbon segment should provide an excellent model for a wormlike polymer chain.

The fluorocarbon segments are, in fact, "rigid" linear rods in the melt, adopting a helical structure due to intramolecular steric repulsions of the fluorines along the carbon backbone. At higher temperatures defects such as helix reversal may occur, but the overall axial geometry is maintained.[4,6,7] By analogy with their small-molecule counterparts, it is expected that the R_F and R_H segments (longer than 6-8 carbons[3]) will tend to segregate, favoring ordering in the polymer to give either layered structures or some other ordered arrangement. Theoretical studies have shown that layered structures or "hockey pucks" are favored for incompatible diblock type compounds.[8,9] This shows the possibility of liquid-crystalline behavior in these polymers due to the fluorinated segments acting as the mesogenic units. Here we describe the synthesis, characterization, and some properties of these polymers.

Experimental Section. The syntheses of $(-(CF_2)_n-(CH_2)_m-)_N$ from the α,ω-diiodoperfluoroalkyl compounds and the relevant dienes were performed as follows. First, the iodo polymer is produced, which is then reduced to give the target polymers, as for the addition of perfluoroalkyl iodides to olefins.[10,11] Mechanistically the reaction is a free-radical addition of R_F–I across a terminal $CH_2{=}CHR$ double bond. This unambiguously places an iodo atom as shown in Scheme I. This secondary iodo thus formed is inert to the polymerization conditions. In our polymerizations it was found that side reactions were negligible and evidence of branching could not be detected by NMR in the purified polymers.

Scheme I



The reaction of 1,6-diiodoperfluorohexane with 1,9-decadiene was performed using method 1, while the other members of the series were made using method 2.

Method 1. In a small flask 1,6-diiodoperfluorohexane (2.50 g, 4.5 mmol) and 1,9-decadiene (0.62 g, 4.5 mmol) were added together under nitrogen equipped with a bubbler to prevent the entry of air. The mixture was heated to approximately 85 °C in an oil bath with stirring, while AIBN was added continuously in small portions of about 0.05 g every 10 min. The purple color of the mixture disappeared after about 20 min, and the solution became clear. Heating continued for 2 h while the solution became more and more viscous, and then the temperature was increased to 100 °C, 115 °C, and finally 145 °C over a period of about 1 h to enable stirring to continue and AIBN addition was then stopped. Finally, the solution was heated to 160 °C under vacuum to remove unreacted material and AIBN (sublimed). The product was cooled and after several hours had set to a pale yellow translucent solid. The yield was approximately 96%.

IR shows only a large C–H region and C–F at 2800-3000 and 1100-1210 (strong). ^{1}H NMR (in $CDCl_3$) shows CHI, CH_2 at 4.35 (m, 1), 2.84 (m, split, 2), 1.80 (m, 2), and 1.40 (m, 4). GPC in $CHCl_3$ shows a single distribution with MW 10 000-20 000 and $D = 1.66$. Elem anal. Calcd: H, 2.71; C, 28.30. Found: H, 2.81; C, 28.38.

Method 2. This is the same as above but using 10-15 mL of toluene as solvent and only heating at 90-95 °C for 3-4 h. As the reaction proceeds, the solution becomes more viscous. Solvent, AIBN, etc., can be removed by heating under vacuum as above. The yield was approximately 77%.

Synthesis of $(-(CF_2)_n-(CH_2)_m-)_N$ from Iodo Polymer. The iodo polymer can be reduced with AIBN and Bu_3SnH to replace iodine by hydrogen. The tin hydride can be added to the reaction mixture and the polymer reduced in situ using the same procedure as above but without heating to 160 °C in vacuo as the final step. Instead the mixture is cooled to 90 °C and 5-10 mL of toluene are added; then 2.4-3 g of Bu_3SnH is added slowly with stirring under nitrogen. Further small amounts of AIBN are added (0.35 g total) over 30 min, and the mixture is then heated for a further 3-4 h. On cooling the solution sets to a white opaque gel. The product was purified by recrystallization/precipitation from a mixture of chloroform with some methanol (approximately 2:1) three times to remove tin residues, etc. The yield after purification was approximately 75-91% (overall).

IR shows only a large C–H region and C–F at 2800-3000 and 1110-1230 (broad, strong). ^{1}H NMR (in $CDCl_3$) shows CH_2 at 2.11 (m), 1.67 (m), 1.39 (m, with shoulder at 1.45). Fluorine NMR shows the following peaks of equal intensity

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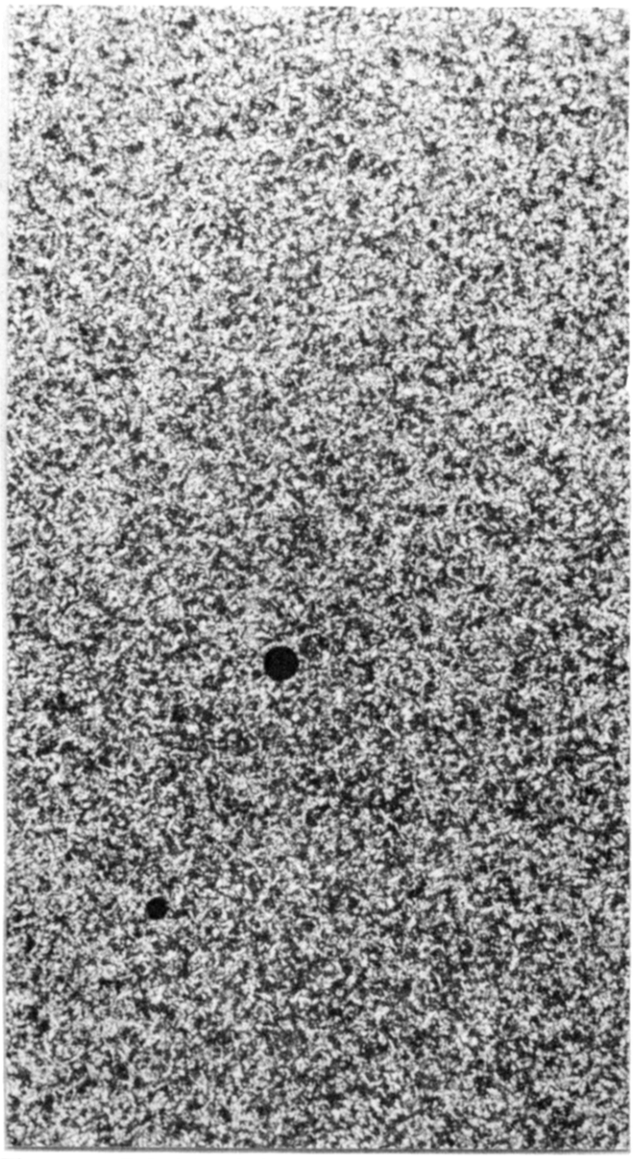

Figure 1. Polarizing light photomicrograph of microblock polymers $(-(CF_2)_6-(CH_2)_6-)_N$ at 100× in the high-temperature mesophase (M_2).

relative to CCl_3F: $-R_H-\mathit{CF}_2-R_F$, −114.94; $R_H-CF_2-\mathit{CF}_2-R_F$, −122.41; $R_H-CF_2-CF_2-\mathit{CF}_2-\mathit{CF}_2-CF_2-CF_2-R_H$, −124.25. Elem anal. Calcd for $(-(CF_2)_6-(CH_2)_{10}-)_N$: H, 5.88; C, 49.40. Found: H, 5.98; C, 49.61.

All fluorinated chemicals were obtained from Fluorochem; AIBN was obtained from BDH; all others were obtained from Aldrich. Analyses were performed using the following instruments: IR on a Nicolet 510M; NMR on a Bruker WM 250 MHz; DSC on a Du Pont 2100 (heating rate, 10 °C/min); viscosity on a Rheometrics RDS II dynamic spectrometer.

Results and Discussion. This polymerization method opens up interesting possibilities for unbranched, linear polymers, which do not contain the conventional linking functions (e.g., ester, amide, etc.) between monomer units. The mechanism of polymerization is free-radical addition, yet it is a step–growth process. It was found that a higher degree of polymerization was obtained by raising the temperature in stages and performing the reaction without solvent (method 1).

Table I. Thermal Behavior (°C) of Microblock Polymers[a]

polymer	K–M_1	M_1–M_2	M_2–I
$(-(CF_2)_6-(CH_2)_6-)_N$	88	99	107
$(-(CF_2)_6-(CH_2)_8-)_N$	86	107	118
$(-(CF_2)_6-(CH_2)_{10}-)_N$	100	140	150
$(-(CF_2)_4-(CH_2)_{10}-)_N$	95	110	120

[a] K = crystal or solid phase. M_1 = mesophase 1 (or soft solid). M_2 = mesophase 2. I = isotropic phase.

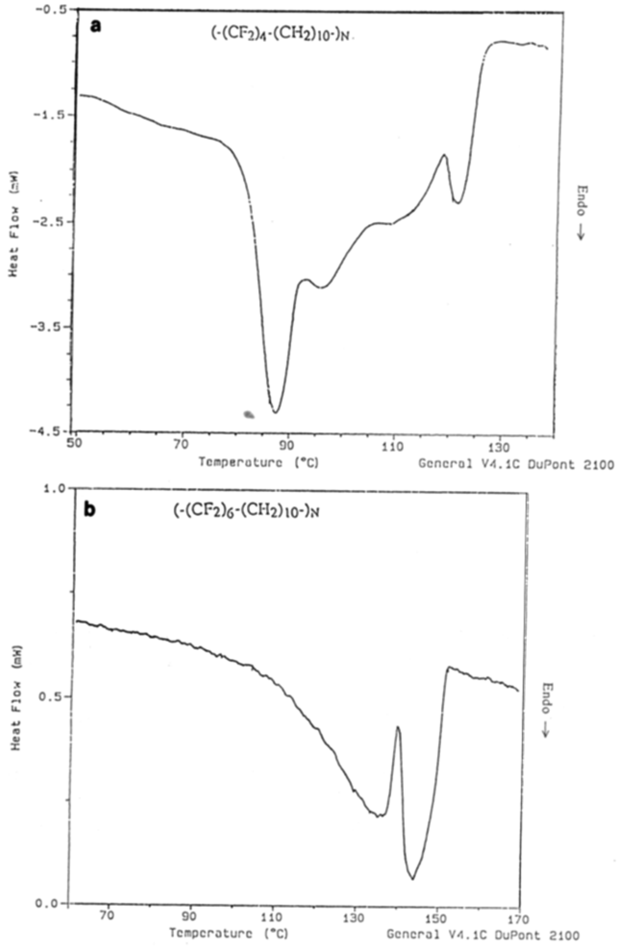

Figure 2. DSC heating curves (second) for (a) $(-(CF_2)_4-(CH_2)_{10}-)_N$ polymer and (b) $(-(CF_2)_6-(CH_2)_{10}-)_N$ polymer.

The high-temperature mesophase texture (M_2) under the polarizing microscope is shown in Figure 1 and appears grainy under low magnification (100×), yet mosaic with irregular boundaries at higher magnification (320×). The polymers all showed this optical texture upon cooling from the melt, with only small differences or changes on subsequent heating or cooling, i.e., thermotropic behavior, as reported for the $F(CF_2)_n-(CH_2)_mH$ compounds.[3] The transition temperatures are given in Table I. However, the viscosity in the mesophase changed on heating, from high to low, while still retaining these optical textures. Parts a and b of Figure 2 show typical second heating DSC curves for the polymers $(-(CF_2)_4-(CH_2)_{10}-)_N$ and $(-(CF_2)_6-(CH_2)_{10}-)_N$. All of the polymers show multiple thermal transitions before the final isotropic clearing point. The relative sizes of these high-temperature peaks may reflect the different enthalpies of disordering in the hydrocarbon and fluorocarbon segments on heating. It is assumed that the fluorocarbon segments disorder at the clearing point, preceded at lower temperature by disordering of the hydrocarbon segments. Disordering of fluorocarbon chains is usually indicated by a sharp endothermic peak but this is not seen here. The rheological curves in Figure 3a,b show the viscosity changes in the polymers as the temperature increases and reflect the thermal transitions seen in the DSC curves. For the polymer $(-(CF_2)_4-(CH_2)_{10}-)_N$ it can be clearly seen optically that the sample softens at

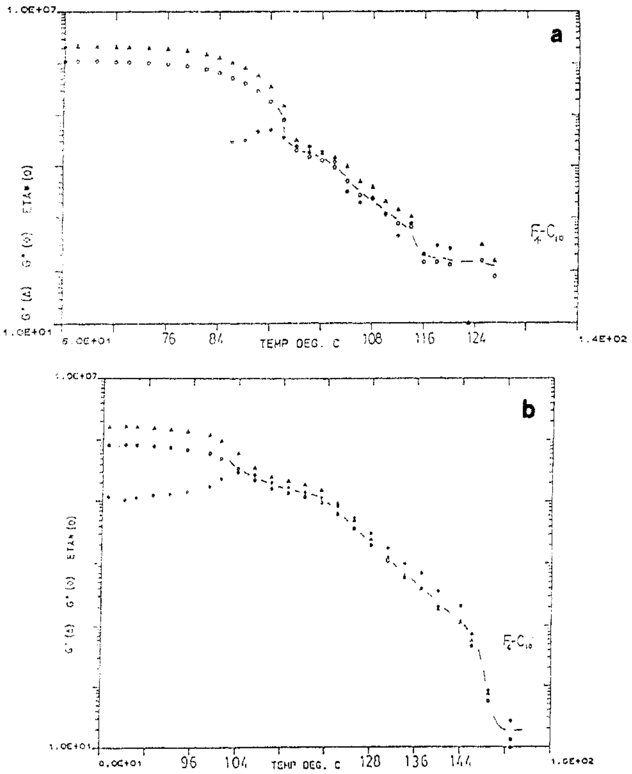

Figure 3. Rheology data (heating) for (a) ($-(CF_2)_4-(CH_2)_{10}-)_N$ polymer and (b) ($-(CF_2)_6-(CH_2)_{10}-)_N$ polymer. G' = storage modulus; G'' = loss modulus; ETA = complex viscosity.

95 °C. The material can be deformed above this temperature, but its viscosity is very high (Figure 3a) and the polymer could not be sheared easily on a microscope slide. Whether this reflects a mesophase or a soft solid is not clear. The transition to a low-viscosity, birefringent liquid phase begins at 108–110 °C, i.e., thermotropic mesophase behavior between 110 and 120 °C, as shown by the DSC (Figure 2a). The sample clearly shows two rheological regimes (on heating), the first of high viscosity and the second of a lower and decreasing viscosity which could be sheared easily. One or both of these may be highly ordered smectic phases, by analogy with similar fluorinated systems. This is again consistent with the DSC data and the optical textures. The data for $-(CF_2)_6-(CH_2)_{10}-$ show similar changes, but this is less complicated with two main peaks. The rheological curve again corresponds to the onset of the first peak in the DSC at 100 °C. Clearing of the lower and decreasing viscosity mesophase corresponds to the final transition in the DSC, and the sample could be sheared easily in this temperature range, showing a fluid mesophase between 140 and 150 °C. X-ray diffraction experiments are in progress to further examine the mesophase structure. The liquid-crystalline properties of these polymers, together with the established oil and water repelling properties of fluoropolymers, may give them useful practical applications.

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