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Preliminary Communication

Novel fluorocarbon side-chain polyesters based on 3,5-dihydroxybenzoic acid

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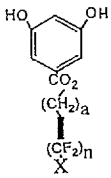
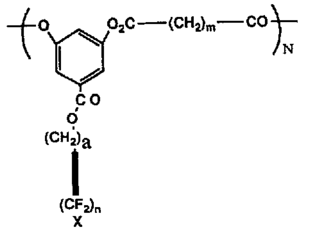
Perfluoroalkyl side-chain polyesters with aliphatic hydrocarbon backbone spacers of different chain lengths have been synthesized in high yield directly from the hydrocarbon diacid and perfluoroalkyl 3,5-dihydroxybenzoate. Molecular weights up to 22 000 $\bar{M}$n were obtained. The linear mesogenic perfluoroalkyl segment lengths $-(CF_2)_n-$ were varied, polyesters with $n = 10$ and 7 showing crystalline and liquid crystalline phases, while with $n = 6$ mainly amorphous polyesters were obtained. The mesophases were investigated by polarizing optical microscopy, DSC and X-ray diffraction. They have a grainy optical texture in the POM and give multiple transitions on DSC. In these polymers both the nature of the mesogenic group and the dilution of the mesogenic side-chains along the polymer backbone can be varied.

The perfluoroalkyl chain has been little studied as a mesogenic unit in small molecules or in polymers. The perfluoroalkyl side-chain polyacrylates [1–5] and polysiloxanes [6, 7] are the only well-documented polymers containing these units, and in the latter, rigid *para*-linked aromatic units are incorporated into the side chains. In order to study these systems, several polyesters containing perfluoroalkyl side chains as the only rigid mesogenic units and varying lengths of flexible alkyl backbone copolymerized in a regular repeating structure have been synthesized [8]. Here we describe polyesters based on perfluoroalkyl 3,5-dihydroxybenzoate monomers and aliphatic diacids, as shown below. The 3,5-dihydroxybenzoic acid system was chosen because it is possible to prepare monomers with a wide range of substituents.





Where $n = 6$ ($a = 1$ or $2, X = F$), $n = 7$ ($a = 1, X = F$) and $n = 10$ ($a = 1, X = H$ and $a = 2, X = F$).

The fluorinated monomers themselves are liquid crystalline [9]. The polymers are denoted as $F_n a PhR_m$, where n, a and m are as shown above. If a is 1, then it is omitted; m is 6, 12 or 20.

The dihydroxy monomers were prepared from the dibenzyl ether of 3,5-dihydroxybenzoic acid, and the corresponding 1H, 1H- or 1H, 1H, 2H, 2H-perfluoroalkanols using the carbodiimide procedure [10]. The 3,5-dibenzyl ether was made from 3,5-dihydroxybenzoic acid and benzyl bromide/K_2CO_3 (followed by hydrolysis of the benzyl ester), in the usual manner. The perfluoroalkyl 3,5-dihydroxybenzoates were obtained after debenzylation using palladium on carbon and ammonium formate [11]. The polymers were then obtained by polymerization with the aliphatic diacids using the carbodiimide procedure [10]. The final yields were 80–85 per cent. The results of elemental analyses were all within 0·1 per cent for C and H. Structures of the polymers were confirmed by IR (Nicolet 510M) and proton NMR (Bruker WM250 MHz) showing phenyl signals at 7·64(s, 2 H), 7·19(s, 1 H) and other signals at 4·6–4·8(t, 3 H), 2·55(t, 4 H), 1·70(m, 4 H) and 1·24–1·28(m, (2m-8) H), with the terminal H of the F_{10} unit giving a broad triplet at 6·05 (1 H). All the polymers had $\bar{M}$n values of 15–22 000 obtained by GPC (Polymer Laboratories Knauer System with RI and UV detectors using $CHCl_3$ as solvent, with M_w/M_n values of $\sim 1·5$.

All reagents were obtained from the Aldrich Chemical Co, except the fluorinated alcohols which were obtained from Fluorochem.

The preliminary results show that each of the solution crystallized polymers with perfluorohexyl and perfluoroheptyl (F_6 and F_7) units up to and including F_7PhR_{12} showed only a T_g with a very low enthalpy on the

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Table 1. DSC thermal transition data for polymers.

Polymer F_nPhR_m	Solid–mesophase/°C or T_g if observed (enthalpy/J g^{-1})	Mesophase–mesophase, if observed/°C	Mesophase–isotropic/°C (enthalpy/J g^{-1})
F_6PhR_{12}	$-10{\cdot}0\ T_g$		4·4 (1·76) (51 on 1st htg, 18)
F_62PhR_{12}	$1{\cdot}0\ T_g$		9 (3·0) (60 on 1st htg, 24)
F_7PhR_6	$8{\cdot}3\ T_g$		23·6 (0·25)
F_7PhR_{12}	$0{\cdot}0\ T_g$		10·2 (2·34)
F_7PhR_{20}	50 (22·7)	62sh., 73 (0·26, 0·27)	89 (0·21)
$F_{10}PhR_{12}$	64 (12·2)	85, 100 (2·1, 0·6)	135 (0·5)
$F_{10}PhR_{20}$	65 (22·0)	96·6 (6·0)	120 v.broad (1·1)
$F_{10}2PhR_{12}$	67·7 (8·9)		74 (2·1)

second heating and on cooling in the DSC (Perkin–Elmer Series 7), as shown in table 1. The first heating curves for the two F_6 polymers were however different, having a T_g and a clear melting endotherm of which the latter was totally absent on second or further heatings. These materials obtained from solution are therefore semi-crystalline, while the melt solidified materials are mainly amorphous. The F_7PhR_{20} polymer did show a reversible melting peak (at 50°C on second heating) and also a shoulder at 62°C and two very small peaks at 73 and 89°C, so this polymer did not cool to give a glassy material. The F_{10} polymers also had multiple peaks on heating and on cooling in the DSC, the first (melting) peak relating to a larger enthalpy than the other higher temperature peaks which were sometimes very broad (see figure 1) and sometimes quite sharp. On cooling, the peaks occurred again with supercooling to variable degrees. The T_g (where observed) and other transition values (giving the mesophase ranges) are given in table 1 together with the DSC enthalpies.

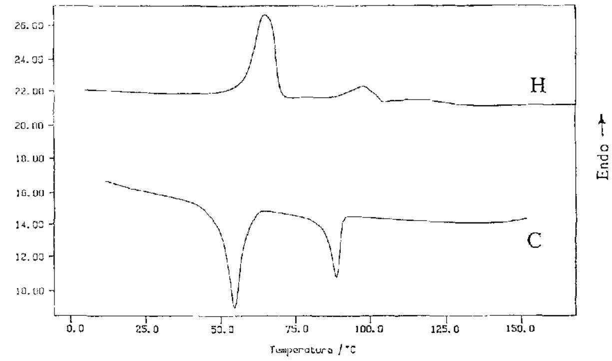
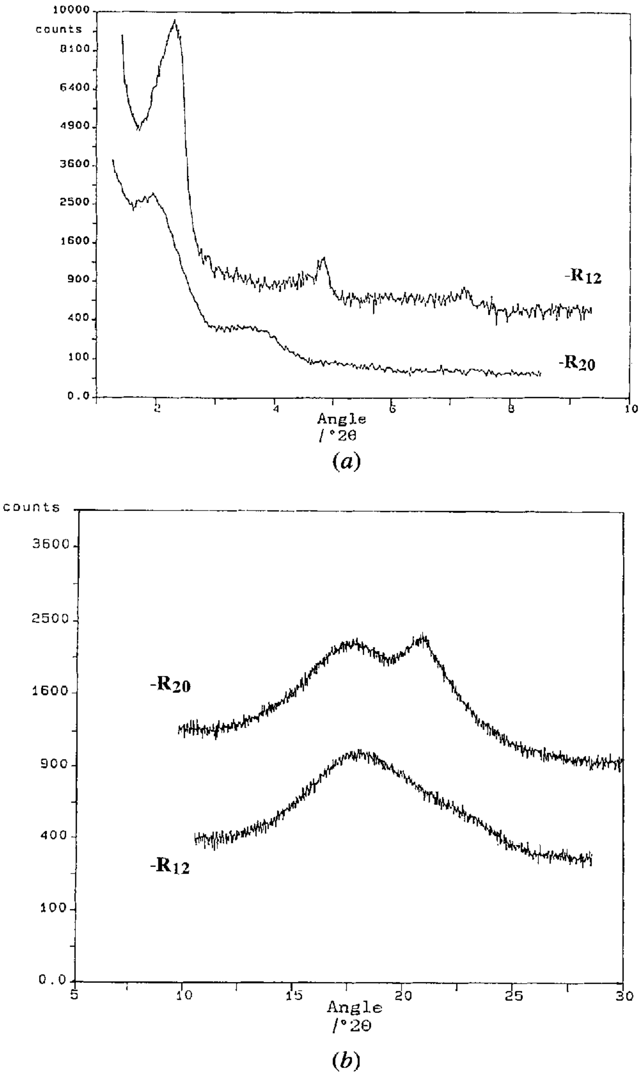


Figure 1. DSC scan for $F_{10}PhR_{20}$; second heating H and cooling C, at 7°C/min.

In the polarizing optical microscope (POM, using a Leica Axioscope fitted with a Mettler FP82 microfurnace), the F_6 and F_7 (up to and including F_7PhR_{12}) polymers showed texture only on shearing above the T_g, indicating some shear induced ordering in these materials up to about 40°C and up to 70°C for F_62PhR_{12}. All those polymers with a T_g and a higher melting transition were tacky and rubbery above the T_g, or, if melting occurred, became fluid and shearable in the POM above the melting transition, changing eventually to lower viscosity liquids above the final isotropization transition. This also applied to mesophases formed directly above T_g. F_7PhR_{20} showed a grainy texture above 50°C up to about 89°C, the mesophase being soft and fluid and the texture remaining grainy, but becoming weaker and more feint above 70°C; these transitions correspond to the transitions observed in the DSC. The F_{10} polymers also showed grainy textures up to about 120 or 130°C, or up to 74°C for the $F_{10}2PhR_{12}$ polymer.

Since the T_gs of some polymers were below room temperature, the structures of these were investigated by X-ray diffraction (XRD) at room temperature and the other polymers were first quenched. All the polymers showed small angle (001 index) peaks in the XRD (Philips PW 1710 diffraction system) which were very weak for the F_6 and F_7 polymers up to F_7PhR_{12} and were stronger for the other polymers, usually with a second weaker peak (002 index—figure 2(*a*)) and thus had layer structures. These results are given in table 2. The observed *d* layer spacings



(*a*)

(*b*)

Figure 2. XRD plots for polymers; (*a*) low angle for $F_{10}PhR_{12}$ and $-R_{20}$, (*b*) higher angle for F_7PhR_{12} and $-R_{20}$ (see text).

(001 index) are 13–25 per cent greater than the calculated extended lengths (*L*), as shown in table 2, which also gives the ratios (*d*/*L*) of the observed layer periodicity (*d*) to the calculated lengths (*L*). These suggest a bilayer type arrangement with almost overlapping perfluoroalkylphenyl units; *d*/*L* increased from 1·13 to 1·25 on going from R_6 to R_{20} as would be expected if the hydrocarbon takes up the space between the layers of perfluorocarbonphenyl units. The higher angle peaks were very broad and diffuse, suggesting S_A type mesophases with fairly liquid-like ordering (see figure 2 (*b*)) and showed a change on going from the polymers with comonomers of type R_6 to R_{20}, a shoulder to the higher angle peak becoming more prominent with R_{12}, and a second distinct, broad peak appearing for R_{20}. Such a double peak has been observed previously in the range 17–20°2*θ* for some liquid crystalline, semi-fluorinated small molecule systems [12]. The *d* spacings corresponding to these peaks were about 5·1 and 4·25 Å, probably the lateral spacings between the fluorocarbon and hydrocarbon segments of the polymers respectively, and similar to results for the analogous perfluoro-octyl sulphonamide polyester [8].

The results are consistent with the ordering found in some liquid crystalline, fluorinated side-chain polysiloxanes [5] and linear small molecule compounds consisting of 4-biphenyl-alkyl units with perfluoroalkyl tails [12]. These were found to have a smectic A phase consisting of parallel or antiparallel dimers of the mesogenic molecules and had a ratio (*d*/*L*) of 1·1–1·6 (1·1 for the small molecules), and the packing in these polymers may be similar [5]. The non-liquid crystalline, small molecule 3,5-dialkylbenzoates with fluoroalkyl tails corresponding to the monomers described here showed *d*/*L* very close to 1·0 in the crystalline phase, while the dihydroxy monomers [9] showed S_A (or S_B for F_{10}) mesophases having bilayers with *d*/*L* ~ 1·9. Finally it is interesting to note that there does not appear to be absolute microphase separation between hydrocarbon and perfluorinated segments; therefore the difference in molar volume between these segments seems to exert the dominant control over the molecular packing. A more complete series of these polymers is being investigated.

Table 2. X-ray diffraction data for polymers.

Polymer F_nPhR_m	Angle/deg-2*θ* (intensity)	*d* value/Å	Calculated repeat length (*d* observed/calculated value)
F_6PhR_{12}	2·95 (w)	30·0	26·25
	18·0 (m)	4·95	(1·13)
F_6PhR_{12}	2·62 (m)	33·7	27·5
	5·0 (v.w)	17·3	(1·20)
F_7PhR_6	3·24 (w)	27·2	24
	17·50 (m)	5·1	(1·13)
F_7PhR_{12}	2·75 (w)	32·0	27·5
	5·36 (v.w)	16·35	(1·16)
	17·60 (m)	5·03	
	21·5 (sh.w)	4·20	
F_7PhR_{20}	2·2 (m)	41·0	33
	4·65 (w)	19·30	(1·24)
	17·5 (m)	5·10	
	21·0 (m)	4·22	
$F_{10}PhR_{12}$	2·57 (m)	34·5	30·5
	5·23 (w)	16·9	(1·14)
	17·65 (m)	5·03	
$F_{10}PhR_{20}$	2·13 (m)	43·8	35
	4·0 (s)	22	(1·25)
	17·5 (m)	5·1	
	21·0 (m)	4·2	
$F_{10}2PhR_{12}$	2·45 (m)	36·0	31·5
	4·85 (w)	18·0	(1·14)
	7·30 (w)	12·0	
	17·9 (m)	4·96	

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