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Melt condensation and solution polymerization of highly fluorinated aliphatic polyesters

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Abstract

Highly fluorinated aliphatic polyesters were synthesized from a fluorodiol [$HOCH_2CH_2(CF_2)_8CH_2CH_2OH$] and both sebacoyl chloride and adipoyl chloride. Melt condensation polymerization followed by fractionation resulted in polymer samples with number average molecular weights in excess of 10 000. The use of solution polymerization yielded inferior results — with sebacoyl chloride the resultant polymers were of lower molecular weight, and with adipoyl chloride no polymer was formed. The fluoropolyesters have been characterized by ^1H NMR and FT-IR spectroscopies, solubility, water contact angle, DSC and TGA. Crosslinking via peroxide of the polyester derived from sebacoyl chloride was successful; however, the resultant elastomeric-type material possessed residual crystallinity (from the parent polymer) and a low melting point.

Keywords: Aliphatic polyesters; Melt condensation polymerization; Solution polymerization; NMR spectroscopy; IR spectroscopy

1. Introduction

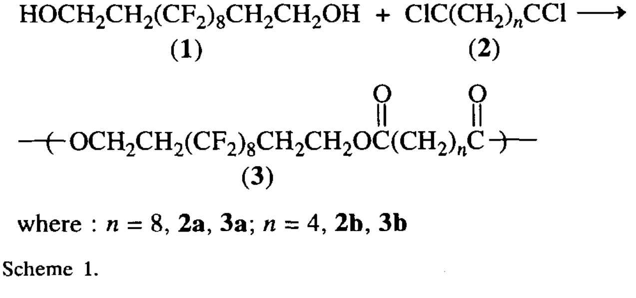
Fluoroaliphatic polyesters which contain a large amount of fluorine have a potential for yielding new and interesting materials. One can anticipate that these types of polymers would possess some of the 'desirable' properties of Teflon, such as low water absorption, good chemical resistance, low surface energies and low coefficients of friction.

Previous attempts to synthesize fluoroaliphatic polyesters have met with limited success [1–3]. The use of fluorinated aliphatic dicarboxylic acid derivatives with either aliphatic or fluoroaliphatic diols leads to polymers that are hydrolytically unstable. The fluorinated diols used are generally of the structure $HOCH_2(CF_2)_x$-CH_2OH, where $x=3$ or 4. One disadvantage of using diols such as these is the relatively low amount of fluorine they and the polyesters derived from them possess. Another disadvantage is their higher acidity, and thus lower reactivity, relative to nonfluorinated diols due to the inductive effect of the fluorine atoms [4].

We have obtained a long-chain fluorinated diol (**1**) which contains two $-CH_2-$ units between the fluorinated portion of the molecule and the hydroxy functionality. Initial results on synthesizing fluoroaliphatic polyesters from **1** appeared promising [5]. In this paper we report the polymerization of **1** with diacid chlorides by both melt condensation and solution polymerization, the characterization of the new fluoropolysters and the results of crosslinking studies in an attempt to synthesize a fluoroelastomer from one of the fluoroaliphatic polyesters.

2. Results and discussion

The fluoroaliphatic polyesters were synthesized from the fluorinated diol **1** and both sebacoyl chloride (**2a**, $n=8$) and adipoyl chloride (**2b**, $n=4$), as shown in Scheme 1. The results of polymer syntheses by melt condensation polymerization are given in Table 1.



$$\underset{(1)}{HOCH_2CH_2(CF_2)_8CH_2CH_2OH} + \underset{(2)}{Cl\overset{\overset{O}{\|}}{C}(CH_2)_n\overset{\overset{O}{\|}}{C}Cl} \longrightarrow$$

$$\underset{(3)}{-\!\!\left(OCH_2CH_2(CF_2)_8CH_2CH_2O\overset{\overset{O}{\|}}{C}(CH_2)_n\overset{\overset{O}{\|}}{C} \right)\!\!-}$$

where : $n = 8$, **2a**, **3a**; $n = 4$, **2b**, **3b**

Scheme 1.

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Table 1
Results of condensation polymerizations

(a) Polymer **3a** (using sebacoyl chloride)

Run No	Reaction conditions	As-made M_n (from VPO)	Weight % lost upon fractionation	Fractionated M_n (from VPO)
1	$T=120–135$ °C $t=30$ h	5700	10	10300
2	$T=130–145$ °C $t=30$ h	6800	6	8600
3	$T=120–135$ °C $t=48$ h	7000	11	10600
4	$T=130–145$ °C $t=48$ h	7900	9	8900

(b) Polymer **3b** (using adipoyl chloride)

Run No.	Reaction conditions	As-made M_n (from VPO)	Weight % lost upon fractionation	Fractionated M_n (from VPO)
1	$T=120–130$ °C $t=24$ h	4500	12 32[a]	8100 10200[a]
2	$T=130–140$ °C $t=24$ h	4300	17	6600
3	$T=120–130$ °C $t=44$ h	4200	21	5900

[a] Fractionated using three times the amount of solvent and one-third the amount of nonsolvent.

For the synthesis of polymer **3a** (using sebacoyl chloride), the molecular weight of the as-made polymer increased as the polymerization time and/or temperature increased. The amount of material lost upon fractionation varied; however, the results were consistent in that more material lost upon fractionation translated into a higher fractionated molecular weight. It can be seen that fractionated samples of **3a** with number average molecular weights in excess of 10 000 can be obtained without invoking unduly long or severe reaction conditions.

The results for the synthesis of polymer **3b** (using adipoyl chloride) were not as promising. In this case the molecular weight did not increase with increasing polymerization time and/or temperature, but remained relatively low. Large amounts of material were lost upon fractionation and yet, in some instances, the fractionated molecular weights remained lower than expected.

The most probable explanation for this anomalous behaviour in synthesizing **3b** is the thermal instability of adipoyl chloride [6, 7]. Upon heating above 150 °C or upon prolonged heating, adipoyl chloride can decompose, producing a black char. Even a small amount of decomposition will disrupt the stoichiometry of the reaction, making it impossible to synthesize high molecular weight polymer. The polymer samples became increasingly darker in color with increasing reaction time and temperature, indicating that some form of decomposition was taking place.

Due to the thermal decomposition of adipoyl chloride, it does not appear that good quality high molecular weight polymer (**3b**) can be synthesized in high yield using melt condensation polymerization. If one is willing to sacrifice high yield, then higher molecular weight material can be obtained by synthesizing **3b** via polymerization in the melt, using the mildest reaction conditions possible (to minimize decomposition) and then fractionating the polymer differently. This experiment has been performed and the results are included in Table 1. The use of three times the amount of solvent and one-third the amount of nonsolvent in the fractionation process resulted in a polymer sample with a number average molecular weight in excess of 10 000, but at a sacrifice of approximately one-third the yield.

Another approach to synthesizing these fluoropolyesters that avoids the use of high heat which leads to adipoyl chloride decomposition is the use of solution polymerization. Solution polymerization was first attempted using sebacoyl chloride to give polymer **3a**, to see how the results would compare to those for melt condensation polymerization. Various solvents, reaction times and reaction temperatures were used to optimize polymerization conditions; these results are given in Table 2. Note that the as-made molecular weights in this case refer to initially isolated polymer samples, after precipitation in methanol (see Experimental section). Some very low molecular weight material is surely lost during this process; thus, one cannot directly compare these values to the as-made molecular weights from melt condensation polymerization, which are measured on the true initial polymer samples. Comparison of the fractionated molecular weights shows that, in all cases, the solution polymerization method gave samples with somewhat lower values than obtained after melt condensation polymerization. One must keep in mind, however, that the reaction conditions (time and temperature) needed to obtain these values for solution polymerization were considerably milder than those employed for melt condensation polymerization. Also, the total yields of fractionated polymer after solution polymerization, 74%–80%, are lower than those obtained after melt condensation polymerization (89%–94%).

Attempted solution polymerization with adipoyl chloride to give polymer **3b** led to no isolatable polymer formation, i.e., upon pouring the reaction solution into methanol nothing precipitated. From all of the solution polymerization results, it can be concluded that there is some other type of reaction taking place which is consuming one of the monomers, thus leading to no or low molecular weight polymer formation. A probable side reaction is the dehydrohalogenation of acid halides by aliphatic tertiary amines to form ketenes [8,9]. Under certain conditions this reaction can occur with both sebacoyl chloride [10–12] and adipoyl chloride [11], leading to diketene formation. In this solution polymerization method, ketenes can potentially be formed if the acid chloride is in contact with the tertiary amine long enough for the reaction to take place — this can occur if the polymerization reaction (reaction of acid chloride with alcohol) is not fast enough. The inductive effect of the fluorine atoms on the diol has the potential to lower the reactivity of the alcohol functionality enough to slow the polymerization rate such that ketene formation becomes appreciable. This disrupts the 1:1 stoichiometry necessary for high molecular weight polymer formation. The data indicate that adipoyl chloride is more susceptible to this side reaction, since no isolatable polymer was found. Thus, the method of solution polymerization was inferior to melt condensation polymerization for the synthesis of high molecular weight fluoropolyesters **3a** and **3b**.

Fluoropolyester **3a** was soluble at room temperature in chloroform, methylene chloride, tetrahydrofuran and *m*-cresol. It was also soluble in acetone, ethyl acetate, *N*,*N*-dimethylformamide, benzene and toluene when heated. It was insoluble in diethyl ether, methanol and petroleum ether. (See Experimental section for ^{1}H NMR, FT-IR and DSC data.) The fluorine content of this polyester was 46 wt.% based on the structure of the repeat unit. As a consequence, the water contact angle of this material was $95 \pm 2°$, which implies that the surface is very hydrophobic. For comparison (no data on other aliphatic polyesters could be found), water contact angles for polyethylene terephthalate, polyethylene and Teflon are 81°, 94° and 108°, respectively [13]. Fluoropolyester **3a** is a highly crystalline material and difficulty was encountered in measuring T_g values by DSC. A very weak T_g inflection could be obtained only by heating a sample above T_m and then quenching in liquid nitrogen; however, this procedure yielded irreproducible results. Also, under these conditions, the polymer exhibited no recrystallization exotherms but did exhibit a large melting endotherm,

Table 2
Results of solution polymerizations of polymer **3a** (using sebacoyl chloride)

Solvent	Reaction conditions	As-made polymer yield (%)	As-made M_n (from VPO)	Weight % lost upon fractionation	Fractionated M_n (from VPO)
1,2-Dichloroethane	$T=50$ °C $t=2$ h	84	7100	6	7100
Acetone	$T=50$ °C $t=2$ h	85	7200	5	7800
Acetone	$T=50$ °C $t=6$ h	87	7200	7	8200
Toluene	$T=50$ °C $t=2$ h	83	5700	9	6900
Toluene	$T=85$ °C $t=2$ h	82	6600	6	6900

which implies that the polymer is highly crystallizable. TGA analysis showed that this polymer exhibited 5% and 10% weight losses at 385 °C and 398 °C, respectively; the total weight loss at 500 °C was 93.4%.

Fluoropolyester **3b** exhibited the same solubilities as **3a**. (See Experimental section for ^{1}H NMR, FT-IR and DSC data.) The fluorine content of this polyester was 51 wt.%, based on the structure of the repeat unit. The water contact angle of this material was 96 ± 2 °C, which was the same as that of **3a**. The DSC results were similar to those of **3a**, except that the T_g value was slightly more pronounced and was reproducible. TGA analysis of this polymer showed 5% and 10% weight losses at 389 °C and 400 °C, respectively; the total weight loss at 500 °C was 95.1%.

In an attempt to synthesize a new fluoroelastomer, crosslinking experiments using benzoyl peroxide and fluoropolyester **3a** were carried out. The free-radical crosslinking reaction in solution (refluxing benzene) was unsuccessful. The use of 1 wt.% benzoyl peroxide in the polymer melt resulted in mostly unreacted polymer with a small amount of insoluble (presumably crosslinked) particles. However, 5 wt.% benzoyl peroxide intimately mixed in the polymer melt caused gelation at 110 °C after 40 min. The resultant insoluble, slightly rubbery material was shown by DSC to possess residual crystallinity (approximately 30% of the original crystallinity was still present) with a melting point of 85 °C. Thus, it is possible to crosslink this type of fluoropolyester; however, the material is too highly crystalline and has too low a melting point to make a useful elastomer.

3. Experimental

3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,-Hexadecafluoro-1,12-dodecanediol (**1**) (obtained from Fluorochem, Inc.) was recrystallized twice from benzene and stored in a vacuum desiccator over P_2O_5 prior to use. Gold label sebacoyl chloride (**2a**) (obtained from Aldrich) was used as received; adipoyl chloride (**2b**) (98%, obtained from Aldrich) was distilled under reduced pressure and used immediately. Solvents used for solution polymerization (acetone, toluene and 1,2-dichloroethane) along with triethylamine were dried and purified by refluxing for 1 h under nitrogen over 4 Å molecular sieves, then distilling and storing under nitrogen over fresh 4 Å molecular sieves; they were used within a day of purification. All other solvents were used as received.

^{1}H NMR spectra were recorded on a Varian EMS 390 spectrometer at 90 MHz; chemical shifts are reported in parts per million (ppm) downfield from tetramethylsilane (TMS). IR spectra were obtained on a Perkin-Elmer 1800 Fourier Transform IR spectrophotometer; samples were prepared by solution casting thin films directly onto KBr plates. Polymer number average molecular weights (M_n) were measured by vapour pressure osmometry (VPO) using a Corona Wescan model 232A molecular weight apparatus; measurements were made at 30 °C using chloroform as the solvent. Water contact angle measurements were made using an NRL C.A. goniometer, model A-100; samples were melt-cast (45 mil film) onto Teflon. Polymer thermal transitions were measured using a Perkin-Elmer differential scanning calorimeter (DSC 2) controlled by a Perkin-Elmer Thermal Analysis Data Station (TADS) and thermogravimetric analyses were performed using a Dupont 951 thermogravimetric analyzer (TGA) controlled by a Dupont Thermal Analyst 2100 System. Both DSC and TGA experiments were performed under a nitrogen atmosphere at a heating rate of 20 °C min^{-1}. Polymer property measurements (solubility, NMR, FT-IR, water contact angle, DSC and TGA) were performed on samples which had M_n values greater than 10 000.

3.1. General procedure for the condensation polymerization of fluoropolyesters 3

In a clean flame-dried reaction vessel was placed a quantity of the diol. The flask was stoppered with a rubber sleeve septum and, via inlet and outlet needles, flushed thoroughly with nitrogen. The nitrogen flow was decreased to a low flow rate (approximately 1 bubble s^{-1}) and an equimolar quantity of the diacid chloride was added via a syringe. The reaction vessel was placed in a preheated oil bath set at the low end of the polymerization temperature range. The reaction was allowed to proceed for the desired time with a constant low nitrogen flow maintained and the temperature gradually increased to the high end of the range. Upon completion, the polymer was isolated in virtually quantitative yield.

3.2. General procedure for the solution polymerization of fluoropolyesters 3

In a clean flame-dried round-bottom flask equipped with a stir bar and an addition funnel was placed a quantity of the diol. The system was stoppered with a rubber sleeve septum and flushed with nitrogen. Solvent (5 ml per mmol of diol) and 2 equiv. of triethylamine were added to the flask via a syringe and the flask was placed in an oil bath preset to the desired temperature with commencement of stirring. An equimolar quantity of the diacid chloride and additional solvent (5 ml per mmol of diacid chloride) were introduced into the addition funnel via a syringe and mixed. This solution was allowed to drip into the reaction flask over 30 min with continued stirring. The reaction was allowed to proceed under nitrogen with stirring for the desired length of time. The polymer was isolated by pouring the reaction solution into methanol (1:8.5 v/v solvent/methanol), stirring for 30 min, collecting the precipitated polymer by filtration, washing with methanol and drying thoroughly under vacuum.

Fluoropolyester 3a

For polymerization details, see Tables 1 and 2. Samples of *3a* were light tan waxy solids: T_g, −24 °C, −36 °C (irreproducible); T_m, 102 °C. ^{1}H NMR (in $CDCl_3$) δ: 4.4 (tr, 4H); 2.5 (br m, 4H); 2.3 (tr, 4H); 1.6 (m, 4H); 1.3 (m, 8H) ppm. IR (cm^{-1}) 2930, 2854 (CH_2); 1735 (C=O); 1213, 1145, 1107 (CF_2).

Fluoropolyester 3b

For polymerization details, see Table 1. Samples of **3b** were light to dark brown waxy solids: T_g, −43 °C; T_m, 112 °C. ^{1}H NMR (in $CDCl_3$) δ: 4.4 (tr, 4H); 2.5 (br m, 4H); 2.3 (tr, 4H); 1.6 (m, 4H) ppm. IR (cm^{-1}) 2950, 2877 (CH_2); 1740 (C=O); 1205, 1148, 1108 (CF_2).

3.3. General procedure for the fractionation of fluoropolyesters 3

Polymer (1.0 g) was dissolved in 30 ml chloroform with stirring. The solution was poured into 250 ml of methanol and stirred for 30 min to ensure complete polymer precipitation. The polymer was collected via filtration and thoroughly dried under vacuum. For data on individual polymer samples, see Tables 1 and 2.

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