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Polymerization of reactive fluoroaliphatic diamines with sebacoyl chloride to give fluorinated aliphatic polyamides (Nylons)

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Abstract

Both aminoacylated fluoroaliphatic diamines ('reactive' diamines) [$H_2N(CH_2)_3C(=O)NHCH_2CH_2(CF_2)_nCH_2CH_2NHC(=O)(CH_2)_3NH_2$; $n=4,8$] and their tetrahydrobromide salts have been polymerized interfacially with sebacoyl chloride to give fluoroaliphatic polyamides. The polymers have been characterized by solution viscometry, DSC, TGA, water contact angle measurements, equilibrium water absorption and solubility, and compared to Nylon 6,10. The effects of using free diamine versus diamine salt as the monomer and of amount of fluorine in the monomer on polymer molecular weight are discussed. Also, the synthesis of the tetrahydrobromide salts is included since previous preliminary reports had identified the products as dihydrobromide salts.

Introduction

The incorporation of fluorine into a polyamide (Nylon) has the potential for improving certain polymer properties. Among these are increases in hydrophobicity, heat resistance and flame retardancy, and decreases in the coefficient of friction and refractive index.

Many examples exist in the literature of fluorinated aromatic polyamides (where the fluorine is directly attached to a benzene ring) [1–3], but examples of useful fluorinated aliphatic polyamides are not so numerous. Both aliphatic and aromatic copolyamides with fluoroacrylate grafts have been synthesized [4]. Aliphatic fluorinated Nylons have been made where the fluorine is incorporated within the diacid portion of the polymer [5–7]; however, these materials are subject to hydrolytic degradation due to the inductive effect of the fluorine atoms weakening the amide linkages. A few attempts have been made to synthesize fluorinated polyamides where the fluorine is incorporated within the diamine portion of the polymer [5, 6]. The materials obtained were of low molecular weight due to the inductive effect of the fluorine atoms lowering the basicity, and thus the reactivity, of the diamines.

We have used peptide blocking group and coupling techniques to synthesize 'reactive' diamines (**2**), which are fluoroaliphatic diamines in an aminoacylated form, from the di-*N*-carbobenzoxy-blocked precursors (**1**) [8]. In this paper, we report the synthesis and characterization of high molecular

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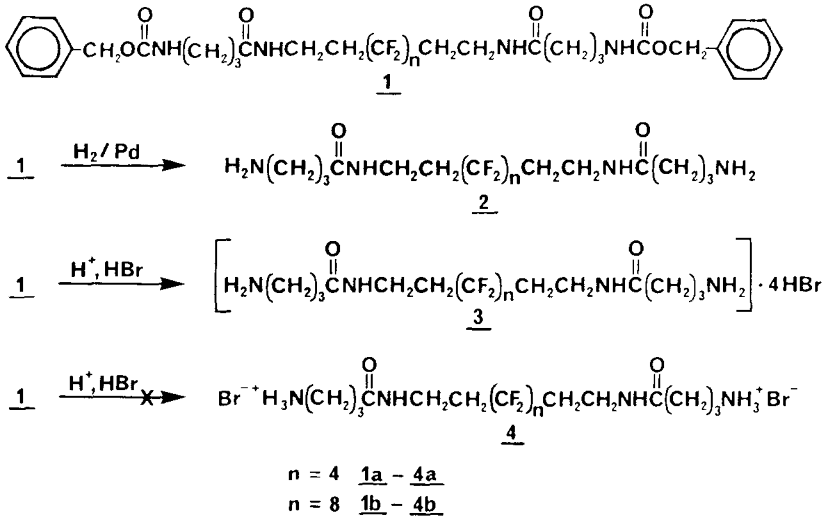
weight, hydrolytically stable fluorinated aliphatic polyamides from these diamines as well as from their hydrobromide salts.

Results and discussion

The synthesis of the aminoacylated fluoroaliphatic diamines **2** via hydrogenation of the di-*N*-carbobenzoxy-blocked precursors **1**, as shown in Scheme 1, has been reported previously [8]. Preliminary reports of the synthesis of the salt forms of the aminoacylated diamines **3** obtained via acidic hydrobromination of the precursors have been made [8, 9]; however, it was stated that dihydrobromide salts **4** were isolated. In peptide chemistry, the use of this technique to remove *N*-carbobenzoxy-blocking groups results in high yields of pure amine hydrobromide salts [10], thus the assumption that the products isolated here were dihydrobromide salts of structure **4**. An attempt at making a polyamide assuming a dihydrobromide salt structure **4b** resulted in a polymer which did not have as high a molecular weight as expected [9], leading to the conclusion that something else present was interfering with the polymerization.

Upon closer examination of the products by ^1H NMR spectroscopy and NaOH titrations coupled with pH measurements, it was determined that there were four molecules of HBr present for every one molecule of aminoacylated diamine. (An example of an NaOH titration using **3a** is as follows: first a pH measurement of a known quantity of the diamine **2a** in water was obtained (11.4). Next the same molar amount of the salt **3a** was dissolved in water and a standardized 1 N NaOH solution titrated until the pH reached 11.4, which required four equivalents of NaOH.) Two HBr molecules are definitively

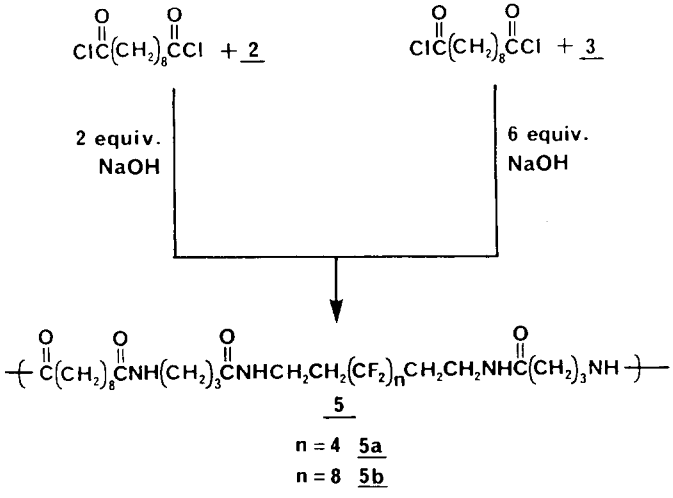


Scheme 1.

associated with the end amine functionalities, as evidenced by ^{1}H NMR spectroscopy (brs, 7.9 ppm, 6H). The other two HBr molecules are most probably associated with the amide functionalities. In acidic solutions it is possible to form amide salts; the most probable site for protonation is the carbonyl oxygen [11]. ^{1}H NMR spectroscopy appears to confirm this configuration since the amide peaks (br tr, 8.3 ppm, 2H) and the *H*Br peaks (s, 8.9 ppm, 2H) are not coupled; however, it may be that the amide salt association is weak enough to fall apart in DMSO-d$_6$, giving rise to two separate peaks. In either case the result is that, upon precipitation, the products are isolated as tetrahydrobromide salts (**3**) and not as dihydrobromide salts (**4**).

The polymerization of the aminoacylated diamines and their tetrahydrobromide salts with sebacoyl chloride was carried out via standard interfacial polymerization. In this method the diamine moiety and an acid acceptor (in this case NaOH) were dissolved in water and the diacid moiety dissolved in an organic solvent immiscible with water; the polymerization reaction took place on the organic solvent side of the water/organic solvent interface. The advantages of using this method to synthesize polyamides are short reaction times (in the order of minutes), room-temperature reaction conditions, tolerance to deviations in stoichiometry (did not need exactly 1:1 ratio of diamine to diacid chloride), and tolerance to some impurities (such as the excess NaBr formed when using the tetrahydrobromide salt) [12]. The synthesis of the fluoroaliphatic polyamides is shown in Scheme 2. In all cases using this polymerization method, the reaction proceeded smoothly to give very good yields of moderate to high molecular weight polymers.

The properties of polymers **5a** and **5b** as compared to Nylon 6,10 are listed in Table 1. The samples of **5a** and **5b** used were those that had the



$$-\!\!\left[\overset{O}{\overset{\|}{C}}(CH_2)_8\overset{O}{\overset{\|}{C}}NH(CH_2)_3\overset{O}{\overset{\|}{C}}NHCH_2CH_2(CF_2)_nCH_2CH_2NH\overset{O}{\overset{\|}{C}}(CH_2)_3NH\right]\!\!-$$

Scheme 2.

TABLE 1

Properties of fluoroaliphatic polyamides **5a** and **5b** compared with Nylon 6,10

Property	**5a**	**5b**	Nylon 6,10
Glass transition temperature (T_g) (°C)	56	51	(50) [13]
melting point (T_m) (°C)	194	196	(216) [13]
Water contact angle (°)	86±3	88±2	76±2 (77) [14]
Equilibrium water absorption (%)	4.0	2.6	3.5
TGA 5% weight loss at	322 °C	318 °C	422 °C
10% weight loss at	335 °C	332 °C	443 °C
weight loss at 500 °C	72%	73%	97%

highest inherent viscosities — these were the polymers made via standard interfacial polymerization from the tetrahydrobromide salts of the diamines. The values for Nylon 6,10 in parentheses were obtained from the literature.

Both **5a** and **5b** were semicrystalline materials with T_m values slightly lower than that for Nylon 6,10. Water contact angle measurements showed that the surfaces of films of **5a** and **5b** were more hydrophobic than Nylon 6,10; however, equilibrium water absorption measurements did not show the same results for the bulk films. Polymer **5a** absorbed more water than Nylon 6,10 despite the presence of fluorine in the polymer. A possible explanation, for long-term tests such as this, is that the effects of hydrogen bonding and of the fluorine are competing forces. The fluoroaliphatic polyamides have a less regular structure than that of Nylon 6,10 which should lead to less interchain hydrogen bonding and more 'unassociated' amide groups which can then hydrogen bond to water, leading to larger water absorption values. The fluorine, being hydrophobic, helps repel water and should lead to lower water absorption values. For polymer **5a** (which has less fluorine than **5b**) it appears the hydrogen-bonding effects are predominant, giving rise to a larger water absorption value than for Nylon 6,10; for polymer **5b** the effect of fluorine is predominant leading to a smaller value than for Nylon 6,10. It is interesting to note that the aminoacylated diamines themselves exhibit a similar phenomenon in their solubilities in water — **2a** was totally water-soluble whereas **2b** was only partly water-soluble [8].

Thermogravimetric analysis (TGA) results showed that the fluoroaliphatic polyamides were less thermally stable than Nylon 6,10, with the onset of decomposition occuring approximately 100 °C lower. Preliminary mass spectral analysis of the volatiles given off in the initial stages of thermal decomposition for both **5a** and **5b** detected 2-pyrrolidinone (cyclized and dehydrated 4-aminobutyric acid) as the major component, indicating breakdown of the polymer backbone. The less regular structure of the fluorinated polymers is the most probable cause, leading to lower thermal stability. It can be seen that char yields at 500 °C for **5a** (28%) and **5b** (27%), whilst not being very substantial, were much higher than that of Nylon 6,10 (3%). This effect is almost certainly due to the presence of fluorine in polymers **5a** and **5b**.

Solubility results for the fluoroaliphatic polyamides (same samples of **5a** and **5b** used as for property evaluation in Table 1) and Nylon 6,10 are given in Table 2. All were tested as 2% solutions stirred at room temperature overnight. For most solvents the solubilities for all three polymers were the same. In a few cases, the trend was towards decreasing solubility with increasing fluorine content in the polymer.

It was stated earlier that the fluoroaliphatic polyamides synthesized via standard interfacial polymerization were all obtained in moderate to high molecular weight. Upon examination of the inherent viscosities obtained for these four polymer syntheses (see Experimental Section), it can be seen the values for **5a** were higher than those for **5b**, and the values for the polymers made from the aminoacylated diamines **2** were lower than those made from the corresponding tetrahydrobromide salts **3**.

One possible explanation for **5a** having a greater inherent viscosity (and thus higher molecular weight) than **5b** is that the corresponding aminoacylated diamine (**2a**) is totally water-soluble whereas **2b** is only partly water-soluble, leading to much more efficient polymer formation in synthesizing polymer **5a**. If this is true, then the use of nonaqueous interfacial polymerization (substitution of a solvent for water which is immiscible with tetrachloroethylene and in which **2b** and an acid acceptor are totally soluble) should lead to higher inherent viscosities (molecular weights) for **5b**. A solvent which fits this description is ethylene glycol; it has been successfully used before in other nonaqueous interfacial polymerizations [12]. Due to solubility considerations with ethylene glycol, KOH (instead of NaOH) was used as the acid acceptor.

The results of nonaqueous polymerizations using **2b** and **3b** (see Experimental Section) were not very good. Yields were lower than those obtained using the standard interfacial method, and inherent viscosities were disappointingly low, indicating formation of rather low molecular weight polymer. Thus, either ethylene glycol was not a good choice as a solvent, nonaqueous

TABLE 2

Solubility of fluoroaliphatic polyamides and Nylon 6,10[a]

Solvent	**5a**	**5b**	Nylon 6,10
Water	I	I	I
Tetrachloroethylene	I	I	I
Chloroform	I	I	I
N,*N*-Dimethylformamide	I	I	I
Methanol	I	I	I
m-Cresol	S	S	S
Conc. sulfuric acid	S	S	S
Formic acid	S	MS	S
Trifluoroacetic acid	MS	PS	S
Hexafluoroisopropanol	MS	PS	S

[a] S = soluble; MS = mostly soluble; PS = partly soluble; I = insoluble.

interfacial polymerization was not a good choice as a method, or there is some explanation for this effect other than monomer solubility. It is an area worthy of future considerations.

There are a few possible explanations for the fluoroaliphatic polyamides made from the aminoacylated diamines having lower molecular weights than those made from the corresponding tetrahydrobromide salts. One could be a purity effect. The diamines synthesized via hydrogenation were isolated, characterized and stored for a few days under vacuum prior to use in polymerization, leading to the possibility of a small amount of carbonate formation. This could serve as a chain terminator (nonreactive end-group) in polymerization, leading to lower than expected molecular weights. When using the tetrahydrobromide salts, the amine functionalities were generated *in situ* via addition of NaOH, leading to a higher purity monomer and thus higher polymer molecular weight. Another explanation could be the effect of additional salt (NaBr) in the aqueous phase derived from the neutralization of the four HBr molecules. Neutral salts have an undetermined effect on the polycondensation process; both beneficial and harmful effects can occur, depending on the system studied [12]. Further experiments are in progress to determine what effect, if any, this additional salt has on the polymerization of these fluoroaliphatic polyamides.

Experimental

Gold label sebacoyl chloride (obtained from Aldrich) was used as received. All other reagents and solvents were either used as received or dried (where noted) by standard methods [15].

^{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 infrared spectrophotometer. Elemental analyses were performed by E+R Microanalytical Laboratory, Inc. Polymer inherent viscosities were measured using an Ubbelohde viscometer (size 1B) suspended in a 25.0 °C water bath; solutions were made in *m*-cresol with a concentration of 0.5 g dl^{-1}. Water contact angle measurements were made using a NRL C.A. Goniometer, model A-100. Polymer thermal transitions were measured using a Perkin-Elmer differential scanning calorimeter (DSC 7) and thermogravimetric analyses (TGA) were performed using a Perkin-Elmer thermogravimetric analyzer (TGA 7). Both were controlled by a Perkin-Elmer thermal analysis data station (TADS). All thermal analyses were performed under a nitrogen atmosphere at a heating rate of 20 °C min^{-1}.

The sample of Nylon 6,10 used for comparing polymer properties was obtained from Scientific Polymer Products, Inc. It had a measured inherent viscosity of 1.2 dl g^{-1}. Using the equation derived for estimating intrinsic viscosity [16], a calculated value of 1.3 dl g^{-1} was obtained. From this a viscosity average molecular weight was calculated as 14 000 g mol^{-1} using the Mark–Houwink–Sakurada equation with the appropriate constants [17]. Samples of all polymers were melt-pressed into films approximately 10 mil thick; 1 in. diameter circles were cut from the films for use in water contact angle and equilibrium water absorption measurements.

*Tetrahydrobromide salt of 1,8-bis(4-aminobutyryl)-3,3,4,4,5,5,6,6-octafluorooctanediamine (**3a**) (nc)*

A solution of 2.26 g (3.1 mmol) **1a** in 40 ml dry glacial acetic acid (heated to 60 °C until homogeneity was achieved) was added to a solution of 20 ml dry glacial acetic acid saturated with HBr. The reaction was stirred for 1 h at 60 °C with a drying tube on the flask. After cooling, the reaction mixture was added to 150 ml dry ether with stirring. The product precipitated and the supernatant liquid was decanted. The salt was washed twice with a total of 100 ml dry ether, each time decanting off the liquid. After addition of another 50 ml dry ether the salt was collected via filtration, washed with dry ether, and dried to give 2.32 g (95% recovered yield) of **3a**. NMR (in DMSO-d_6) δ: 8.9 (s, 2H); 8.3 (br, tr, 2H); 7.9 (br s, 6H); 3.4 (q, 4H); 2.8 (m, 4H); 2.5 (br m, 4H); 2.2 (tr, 4H); 1.8 (m, 4H) ppm. IR (KBr pellet): 3308 (amide NH); 3005 (broad, NH_3^+); 2924 (CH_2); 1651 (C=O amide I); 1547 (NH amide II); 1251, 1213, 1168, 1120, 1013 (CF_2) cm^{-1}.

*Tetrahydrobromide salt of 1,12-bis(4-aminobutyryl-3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10-hexadecafluorododecanediamine (**3b**) (nc)*

This compound was synthesized in the same manner as **3a**, using 1.64 g (1.8 mmol) **1b** in 20 ml dry glacial acetic acid and 13 ml dry glacial acetic acid saturated with HBr, to give 1.70 g (98% recovered yield) of **3b**. NMR (in DMSO-d_6) δ: 8.9 (s, 2H); 8.3 (br tr, 2H); 7.9 (br s, 6H); 3.4 (q, 4H); 2.8 (m, 4H); 2.5 (br m, 4H); 2.2 (tr, 4H); 1.8 (m, 4H) ppm. IR (KBr pellet): 3308 (amide NH); 2997 (broad, NH_3^+); 2922 (CH_2); 1653 (C=O amide I); 1542 (NH amide II); 1251, 1208, 1182, 1143, 1107, 1015 (CF_2) cm^{-1}.

Polymer syntheses via standard interfacial polymerization

*(a) Polyamide **5a** from diamine **2a***

In a seven-speed commercial Waring blender was placed a solution of 0.61 g (1.33 mmol) **2a**, 0.11 g (2.75 mmol) NaOH and 100 ml water. The solution was stirred at low speed, then all at once a solution of 0.28 ml (1.31 mmol) sebacoyl chloride in 100 ml tetrachloroethylene was added with the stirring increased to high. After addition of the organic solution, the reaction mixture was stirred on high for an additional 3–5 min. The polymer was isolated by filtration and washed with water, water/ethanol (3:1, 2:1) and then water. After air drying overnight, the polymer was collected, placed in 50 ml water and stirred for 24 h (to extract any residual salt). The polymer was again isolated by filtration, washed with water and dried. Final drying (to remove residual tetrachloroethylene) was accomplished by heating the polymer under vacuum to 70–80 °C for 3–4 h. The resultant polymer, 0.82 g (99% recovered yield), had an inherent viscosity of 1.0 dl g^{-1}.

*(b) Polyamide **5a** from the tetrahydrobromide salt of diamine **3a***
The polymer was synthesized in the same manner as **5a** (a), using 3.24 g (4.15 mmol) **3a**, 1.01 g (25.25 mmol) NaOH, 180 ml water, 0.92 ml (4.32 mmol) sebacoyl chloride and 180 ml tetrachloroethylene. The resultant polymer [obtained after washing and drying as in **5a** (a)], 2.43 g (94% recovered yield), had an inherent viscosity of 1.6 dl g^{-1}. Analysis: Found: C, 48.3; H, 6.3; N, 8.6; F, 25.4%. $C_{26}H_{40}N_4F_8O_4$ requires: C, 50.0; H, 6.5; N, 9.0; F, 24.3%.

*(c) Polyamide **5b** from diamine **2b***
The polymer was synthesized in the same manner as **5a** (a), using 1.00 g (1.52 mmol) **2b**, 0.12 g (3.00 mmol) NaOH, 110 ml water, 0.32 ml (1.50 mmol) sebacoyl chloride and 100 ml tetrachloroethylene. The resultant polymer [obtained after washing and drying as in **5a** (a)], 1.02 g (82% recovered yield), had an inherent viscosity of 0.6 dl g^{-1}.

*(d) Polyamide **5b** from the tetrahydrobromide salt of diamine **3b***
The polymer was synthesized in the same manner as **5a** (a), using 1.40 g (1.43 mmol) **3b**, 0.36 g (9.00 mmol) NaOH, 100 ml water, 0.29 ml (1.36 mmol) sebacoyl chloride and 100 ml tetrachloroethylene. The resultant polymer [obtained after washing and drying as in **5a** (a)], 1.12 g (98% recovered yield), had an inherent viscosity of 0.9 dl g^{-1}. Analysis: Found: C, 43.8; H, 4.9; N, 6.6; F, 36.8%. $C_{30}H_{40}N_4F_{16}O_4$ requires: C, 43.7; H, 4.9; N, 6.6; F, 36.8%.

Polymer syntheses via nonaqueous interfacial polymerization
*(e) Polyamide **5b** from diamine **2b***
The polymer was synthesized in the same manner as **5a** (a), using 0.95 g (1.44 mmol) **2b**, 0.18 g (2.83 mmol) 88% KOH, 110 ml ethylene glycol, 0.30 ml (1.41 mmol) sebacoyl chloride and 100 ml tetrachloroethylene. The resultant polymer [obtained after washing and drying as in **5a** (a)], 0.77 g (65% recovered yield), had an inherent viscosity of 0.2 dl g^{-1}.

*(f) Polyamide **5b** from the tetrahydrobromide salt of diamine **3b***
The polymer was synthesized in the same manner as **5a** (a), using 1.22 g (1.24 mmol) **3b**, 0.52 g (8.17 mmol) 88% KOH, 110 ml ethylene glycol, 0.24 ml (1.13 mmol) sebacoyl chloride and 100 ml tetrachloroethylene. The resultant polymer [obtained after washing and drying as in **5a** (a)], 0.71 g (76% recovered yield), had an inherent viscosity of 0.2 dl g^{-1}.

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