Available online at www.sciencedirect.com
ScienceDirect
Journal of Fluorine Chemistry 129 (2008) 193–203
JOURNAL OF FLUORINE CHEMISTRY
www.elsevier.com/locate/fluor

Understanding the influence of hydrocarbon insulators in fluorinated amines: Reactivity of poly(hexafluoropropylene oxide) amine containing methylene spacers

Chadron M. Friesen [a,*], Jon L. Howell [b,*], Ashley Jamieson [a,c], Daryl A. Nyvall [c]

[a] *Trinity Western University, Department of Chemistry, 7600 Glover Road, Langley, BC V2Y 1Y1, Canada*
[b] *E. I. du Pont de Nemours, Experimental Station, Building 402, Room 4332C, Rt 141 Henry & Clay Works, Wilmington, DE 19880-0402, USA*
[c] *E. I. du Pont de Nemours, Jackson Laboratory, Chambers Works, Deepwater, NJ 08023, USA*

Received 2 August 2007; received in revised form 26 October 2007; accepted 28 October 2007
Available online 17 November 2007

Abstract

Although reactions involving hydrocarbon amines have been thoroughly investigated, very little is currently known about reactions of corresponding fluorinated amines containing a methylene spacer group. Furthermore, such reactions involving the poly(hexafluoropropylene oxide) (herein, polyHFPO) amine have been completely unexplored. The addition of acyl, sulfonyl and alkyl halides, isocyanates, aldehydes, anhydrides and esters to polyHFPO amine has been accomplished. The results of these reactions, including reaction mechanisms, yields, byproducts, etc. are discussed.

Keywords: Poly(hexafluoropropylene oxide); Amines; Perfluoropolyalkylethers

1. Introduction

Amines are one of the most common moieties found in organic chemistry. The uses of amino containing compounds are widespread, ranging from epoxies [1] and anti-cancer drugs [2] to cosmetics [3] and corrosion inhibitors [4]. Although fluorinated amines containing methylene spacers were reported as early as 1943, there has been little additional work, regarding the preparation of their derivatives, since then [5]. Poly(hexafluoropropylene oxide) [polyHFPO] materials have seen wide use since 1964 as lubricants [6]. This is due to their high thermal stability and excellent chemical inertness as compared to conventional hydrocarbon lubricants [7]. Also, there is a wide range of patent art that deals with functional perfluoropolyethers but the recent preparation of polyHFPO amine clearly warrants additional study. Thus, a few typical reactions of alkyl amines were attempted with polyHFPO amine to better understand reactivity, yields, mechanisms, etc. in fluorinated amine reactions. With the polyHFPO methylene amine being similar in electronic properties to 2,2,2-trifluoroethyl amine (the simplest fluorinated equivalent), the reactions of the two can be compared. The primary differences being the sterics and the somewhat different electronic effects of the terminal –OCF(CF_3)– moiety.

2. Results and discussion

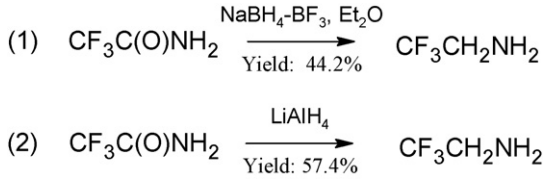
2.1. The preparation of polyHFPO methylene amine, an overview

2.1.1. Introduction

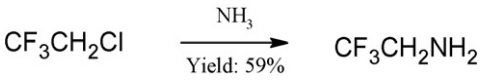
Although there have been a few papers and patents written for the preparation of 1H,1H-perfluorinated alkylamines, the chemistry employed by 3M in the 1940's and 50's seems to be the most efficient and economical [8]. Their research studied the reduction of 2,2,2-trifluoroethylamide to 2,2,2-trifluoroethylamine. As an extension of their work, in 1959 Bissel and Finger studied these reductions in more depth. In order to determine the most appropriate reducing agent for the reduction of substituted 2,2,2-trifluoroethylamides, Bissel and Finger

* Corresponding authors.
E-mail addresses: chad.friesen@twu.ca (C.M. Friesen), jon.l.howell@usa.dupont.com (J.L. Howell).

0022-1139/$ – see front matter © 2008 Published by Elsevier B.V.
doi:10.1016/j.jfluchem.2007.10.009



Schemes 1 and 2. Reduction of 2,2,2-trifluoroethylamide using sodium borohydride or lithium aluminum hydride.



Scheme 3. Amination of 2,2,2-trifluoroethyl chloride using ammonia.

concluded that the use of sodium borohydride alone was insufficient for the reduction of full substituted amides [9]. Consequently, the reaction required the addition of either boron trifluoride etherate or aluminum chloride (see Scheme 1). Lithium aluminum hydride alone, however, proved to be a most effective reducing agent (see Scheme 2).

Aside from the formation of an amine by carbonyl reduction, there are two other methods that have been reported. Firstly, Elliot and Astrologes describe the preparation of 2,2,2-trifluoroethylamine from the amination of 2,2,2-trifluoroethyl chloride using ammonia [10,11] (see Scheme 3).

While this reaction has the advantage of requiring just one step, the extreme reaction conditions make this reaction far from ideal (240 °C, 300 psig for 24 h).

The second preparation of 2,2,2-trifluoroethylamine takes advantage of a [1,3]-proton transfer [12]. Beginning with a perfluorinated alkyl carboxylic acid, Soloshonok et al. describe the reduction to an amine hydrochloride salt by a seven-step reaction that, remarkably, avoids the use of a conventional reducing agent. This procedure is quite enticing as a result of the elimination of a hazardous reducing agent, but the method described is far too complex. The extensive reaction steps are outlined in Scheme 4. In addition, yields from this reaction have been found to be, at best, 70%.

The method employed in the synthesis of polyHFPO methylene amine is a multi-step synthesis that follows the method reminiscent of that of Bissel and Finger [9]. In this method, polyHFPO methyl ester ($F[CF(CF_3)CF_2O]_nCF(CF_3)$-$C(O)OCH_3$) is first synthesized by the methanolysis of polyHFPO acid fluoride (caution: hydrofluoric acid is produced). The polyHFPO methyl ester is then converted to the amide using ammonia gas. An attempt was made to reduce the amide to the amine directly; however, this was unsuccessful. It is, therefore, necessary to convert the amide to the nitrile followed by its reduction with sodium borohydride or even lithium aluminum hydride (LAH). Overall yields resulting from the conversion of polyHFPO acid fluoride to polyHFPO amine are approximately 82%. The advantage of this synthetic pathway is its high conversion rate and relative purity. Each step will be discussed in detail below.

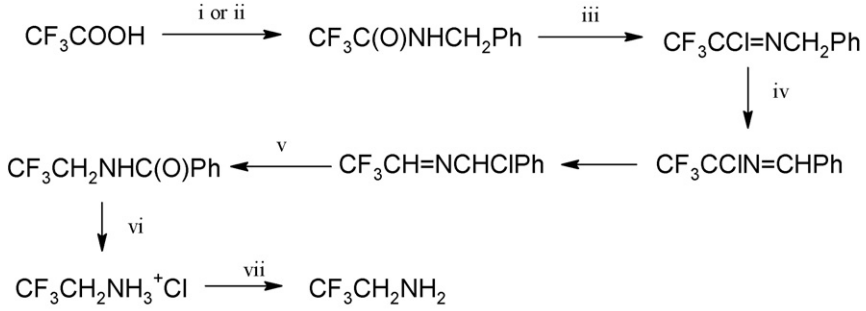
2.2. The preparation of polyHFPO methyl ester

The formation of polyHFPO methyl ester from polyHFPO acid fluoride is a simple reaction resulting in the creation of the ester via the S_N2 attack of methanol on the carbonyl carbon. This reaction occurs in quantitative yield (Scheme 5).

GC/MS and ^1H NMR spectroscopy confirm reaction completion. The sole peak in the ^1H NMR is the singlet resulting from the three methyl protons. In electron impact mass spectrometry the peaks indicative of the methyl ester are 59 *m/z* ($+C(O)OCH_3$), 159 *m/z* ($+CF(CF_3)C(O)OCH_3$), and 325 *m/z* ($+C_3F_6OCF(CF_3)C(O)OCH_3$).

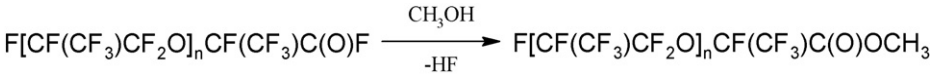
2.3. The preparation of polyHFPO amide

PolyHFPO amide is synthesized by the addition of a two fold molar excess of gaseous ammonia to a chilled (0–10 °C)

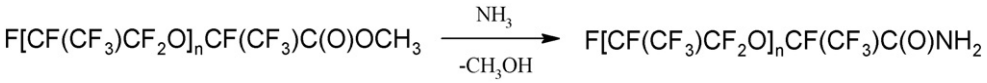


i) $(CF_3CO)_2O$, $PhCH_2NH_2$, $CHCl_3$, 0 °C ;ii) Ph_3P/CCl_4, $PhCH_2NH_2$, $CHCl_3$, Reflux for 40 min; iii) Ph_3P/CCl_4, $CHCl_3$, Reflux for 40 min; iv) Ph_3P/TEA (cat.), $CHCl_3$, Reflux for 40 min; v) TEA/H_2O, $CHCl_3$, Reflux overnight; vi) CH_3OH/HCl(conc.), Reflux for 24 h; vii) Neutralize with base

Scheme 4. Synthesis of 2,2,2-trifluoroethyl amine starting with 2,2,2-trifluoroacetic acid.



Scheme 5. Formation of polyHFPO methyl ester.



Scheme 6. Synthesis of polyHFPO amide from the methyl ester.

round-bottomed flask containing polyHFPO methyl ester. The excess ammonia is used to ensure reaction completion. This addition is conducted over the course of 1 h followed by an additional hour of stirring. The flask is then allowed to warm to room temperature, thus facilitating the evaporation of the excess ammonia. The mixture is degassed by applying vacuum to the flask. Once complete, the methanol byproduct is removed by a reduced pressure distillation at 70 °C. The reaction completion was confirmed by GC/MS. The prominent 44 *m/z* and 144 *m/z* peaks represent, respectively, the $+C(O)NH_2$ and $+CF(CF_3)C(O)NH_2$ ions. The absence of the 59 *m/z* and 159 *m/z* peaks (characterizing the methyl ester), verify the complete conversion. Yields have been as high as 99+% [13] (Scheme 6).

Likewise, the product has been confirmed by ^1H NMR spectroscopy. As is typical of amides, the limited rotation of the carbonyl causes two peaks, which are found between 7.0 and 8.0 ppm in this spectrum [13].

2.4. The direct reduction of polyHFPO amide to polyHFPO methylene amine

Since the direct reduction of 2,2,2-trifluoroethylamide to 2,2,2-trifluoroethylamine had been successfully reported in the literature, it was hypothesized that polyHFPO amide could undergo the same reduction [14]. PolyHFPO amide was added to a 1 M lithium aluminum hydride in THF solution in a 1.05:1 ratio at 0 °C. The reaction was stirred for several hours and allowed to warm to room temperature. GC/MS analysis showed that none of the polyHFPO amide was converted to the amine. The reaction mixture was then heated to reflux (66.2 °C) for several hours in an effort to force the reaction to occur. After several hours of heating, the solution had changed from a pale yellow colour to a dark brown; therefore, it was hoped that the desired reaction had occurred. Unfortunately, the GC/MS showed that formation of the amine had not occurred. Therefore, it was decided that it would be necessary to reduce the polyHFPO amide to the nitrile and then to the amine via a two-step method.

2.5. The preparation of polyHFPO nitrile

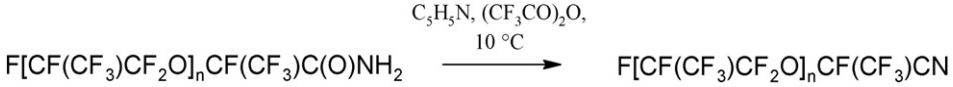
PolyHFPO amide was reduced to the nitrile by mixing it with trifluoroacetic anhydride and pyridine with stirring at reduced temperature (about 0 °C). The reaction was heated to reflux overnight. The trifluoroacetic acid pyridine salt byproduct is removed by water wash. The crude yield of the reaction was 101% [13]. The conversion is confirmed by the presence of a high abundance 126 *m/z* $[+CF(CF_3)CN]$ peak along with the disappearance of the characteristic 44 *m/z* $(+C(O)NH_2)$ peak (Scheme 7).

2.6. The preparation of polyHFPO methylene amine from the nitrile

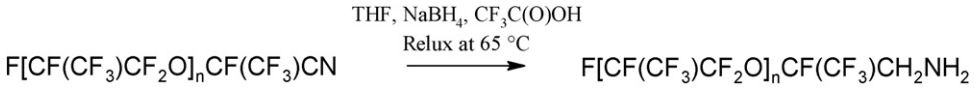
Normally, polyHFPO derivatives will undergo the same reactions as those seen in short-chain perfluorinated alkanes; consequently, these reactions can often be used as models for the polymer to mimic. As was previously noted, however, reduction of polyHFPO amide with lithium aluminum hydride, a very powerful reducing agent, was unsuccessful. As a result of the successes seen in the reduction of 2,2,2-trifluoroacylamide with sodium borohydride, the reduction of polyHFPO nitrile was also attempted using sodium borohydride in the presence of trifluoroacetic acid. In comparison to the poor yields observed in the reduction of 2,2,2-trifluoroacylamide by Bissell and Finger ($LiAlH_4$ = 57.4%; $NaBH_4$ = 44.2%) [9], the reduction of the polyHFPO nitrile using sodium borohydride was much more effective, resulting in an 83% yield [13] with >99% conversion (Scheme 8).

Characterization of polyHFPO amine was completed by GC/MS and ^1H NMR spectroscopy. By GC/MS, the amine can easily be confirmed by the abundant 130 *m/z* $(+CF(CF_3)CH_2NH_2)$ peak and the absence of the 126 *m/z* $(+CF(CF_3)CN)$ peak (see Fig. 1).

The ^1H NMR spectrum of the amine contains two primary peaks as expected. The amino protons produce a broad singlet spanning from approximately 2.6–3.4 ppm. This peak is seen to vary greatly in definition and location throughout the ^1H NMRs of each amino derivative. The methylene proton chemical shift appears at 3.29 ppm. It is split as a doublet due to the fluorine atom on the adjacent carbon. As is usual, splitting does not occur between the methylene and amino protons; furthermore, integration of these peaks displays a 1:1 ratio (see Fig. 2).



Scheme 7. Reduction of polyHFPO amide to the nitrile.



Scheme 8. Conversion of polyHFPO nitrile to the methylene amine.

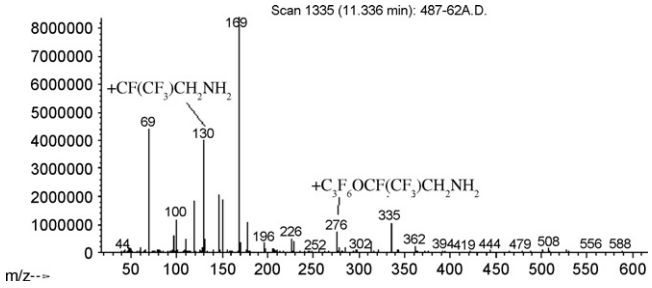


Fig. 1. The mass spectrum of polyHFPO methylene amine.

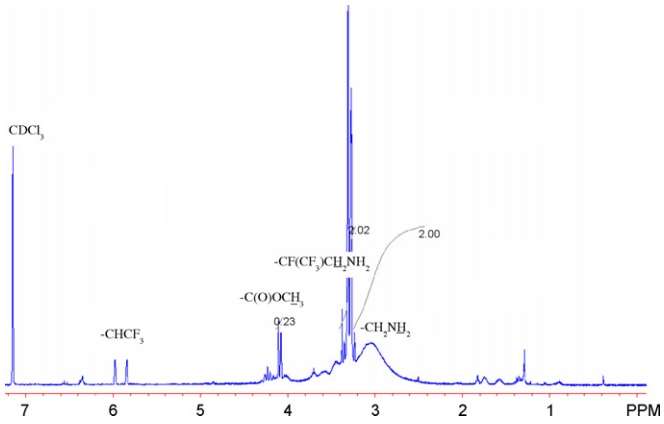


Fig. 2. The ^{1}H NMR of polyHFPO methylene amine.

2.7. The preparation of polyHFPO amide derivatives

Amides via acylation, imines, ureas and sulfonamides can all be prepared from polyHFPO methylene amine. These are all important reactions of hydrocarbon amines.

2.7.1. The preparation of polyHFPO amides via acyl halides

These reactions were run by the mixing the acyl halide with the amine and stirring overnight at 50 °C. The reaction was monitored by GC/MS which shows the reaction was complete. The disappearance of the 130 *m/z* amine peak and the appearance of the 43 *m/z* ($+C(O)CH_3$) and 105 *m/z* ($+C(O)C_6H_5$) peaks for the acetyl and benzoyl groups, respectively, indicate the presence of the new compounds. In ^{1}H NMR spectra the methylene protons are split into a doublet of multiplets, implying that, in both compounds, the methine fluorine and the amino proton are splitting the methylene peak (Scheme 9).

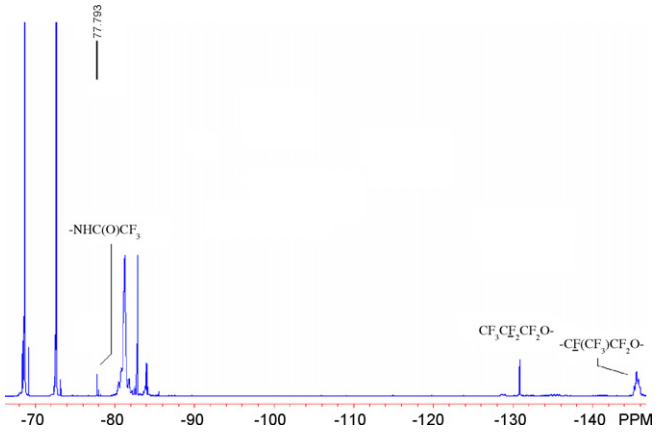


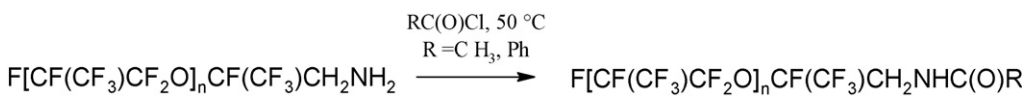
Fig. 3. The ^{19}F NMR of polyHFPO trifluoroacylamide.

2.7.2. The preparation of polyHFPO amides from anhydrides

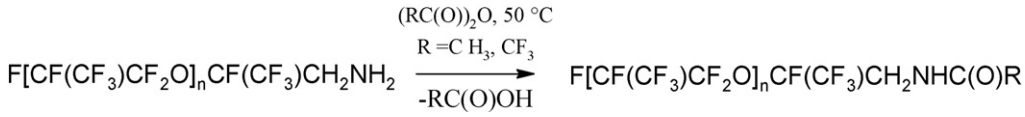
In addition to acyl halides, anhydrides may also be used in the preparation of hydrocarbon amide derivatives. The result is the formation of an alkylamide derivative, while the acid of the original anhydride is lost. Trifluoroacetic anhydride and acetic anhydride were used to produce the trifluoroacylamide and the acylamide polyHFPO derivatives (Scheme 10).

These reactions were run in much the same manner as the acyl halides. Once again, the anhydride was dripped into the amine and stirred at 50 °C overnight. Preliminary monitoring was completed by GC/MS by the disappearance of the 130 *m/z* amine peak and the appearance of the 43 *m/z* and 97 *m/z* peaks for the acetyl and trifluoroacetyl groups, respectively.

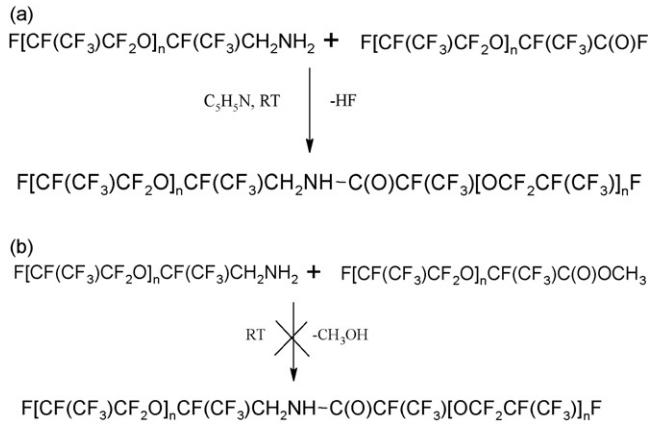
In addition to GC/MS analysis, confirmation of the product was done by ^{1}H NMR, ^{19}F NMR and infrared spectroscopy. The spectra obtained from acetic anhydride were consistent with those previously seen for the method using acetyl chloride; consequently, polyHFPO trifluoroacylamide was also successfully prepared by this method. By comparing the ^{19}F NMR spectra of this product (see Fig. 3) to that of the amine, a new peak appears at approximately −78 ppm. Due to the low intensity of the peak and the lack of splitting, it is thought that it is representative of the new CF_3 group found in the product. Furthermore, the literature value of the fluorine atoms found in 1,1,1-trifluoroacetone ($CF_3C(O)CH_3$) is −82.6 ppm, thus reinforcing the likelihood that this peak corresponds to the new trifluoromethyl group [15]. It is clear from the yields of both amide reaction types that either acyl halides or anhydrides



Scheme 9. Reaction of polyHFPO methylene amine with acyl halides.



Scheme 10. Reaction of polyHFPO methylene amine with anhydrides.



Scheme 11. (a) Synthesis of 1H, 1H-polyHFPO-methamidyl-polyHFPO using the methylene amine and the acyl fluoride of polyHFPO. (b) Synthetic attempt to make 1H, 1H-polyHFPO-methamidyl-polyHFPO from the methylene amine and the methyl ester of PolyHFPO.

may be used in the formation of the substituted amides from polyHFPO methylene amines.

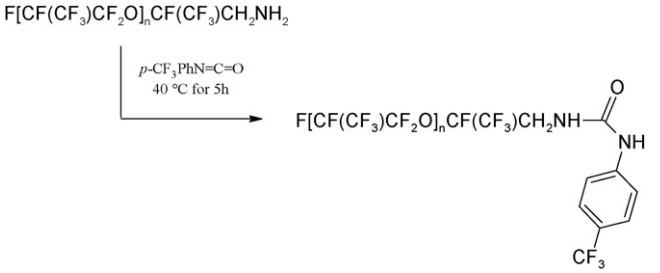
2.7.3. The preparation of 1H,1H-polyHFPO-methamidyl-polyHFPO

PolyHFPO methylene amine was observed to readily undergo reactions with acyl halides and anhydrides to form the corresponding amides; consequently, it was questioned whether polyHFPO acid fluoride would react with the polyHFPO methylene amine due to the bulkiness of the acyl fluoride. It was already known that polyHFPO acid fluoride is a highly reactive compound that is readily available, as it is the precursor to all polyHFPO materials. It was expected that it would undergo the same reaction as the smaller acyl halides to form a substituted amide (Scheme 11a).

After allowing the methylene amine and the acyl fluoride derivatives to stir at room temperature for several hours, the reaction was complete. Preliminary characterization of the reaction was done by removing an aliquot and quenching it with methanol to create the polyHFPO methyl ester derivative of any remaining polyHFPO acid fluoride. Upon GC/MS analysis, it was determined that a reaction did occur, but the actual product did not elute from the column. Thus, in order to confirm the structure of the newly formed compound, a ^{1}H NMR was performed.

The spectrum shows only two peaks in the spectrum representing methylene and amido protons in a 2:1 ratio (Scheme 11b).

In previous research [16], it has been found that polyHFPO methyl ester will readily react with primary alkyl amines to form primary amides. Consequently, an obvious reaction to attempt in order to determine the reactivity of polyHFPO amine was the addition of polyHFPO methyl ester to polyHFPO amine. Initially, this reaction was attempted at 50 °C with stirring for several hours. GC/MS analysis of the mixture showed that no reaction had occurred between the two polymers. The mixture was then heated to 120 °C overnight and, once again, the GC/MS analysis showed no reaction had occurred. This lack of reactivity, between polyHFPO fluorinated amine and polyHFPO methyl ester, shows that the fluorinated amine has very poor nucleophilicity [17].



Scheme 13. Formation of a polyHFPO urea.

2.8. The preparation of a polyHFPO Schiff base

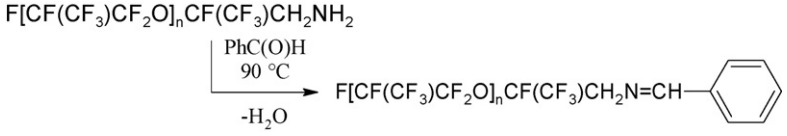
A Schiff base (also known as an imine) is created by the condensation of a primary amine with a ketone or aldehyde [18]. Due to the primary substitution of polyHFPO methylene amine, this was another obvious derivative to prepare. Synthesis of the derivative was successful as shown by the characterization of the products by mass spectrometry. GC/MS showed an ion of 118 *m/z* corresponding to the desired ($+CH_2N{=}CH{-}C_6H_5$) imine product (Scheme 12).

2.9. The preparation of polyHFPO urea

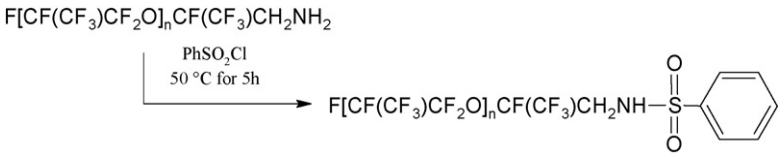
By the addition of *para*-trifluoromethylphenyl isocyanate to polyHFPO methylene amine at 40 °C, a urea derivative of the polymer was also synthesized. After stirring for 5 h, GC/MS analysis of the mixture showed the complete disappearance of the amine peaks in the gas chromatogram. Following the work-up of the product, a ^{1}H NMR spectrum was obtained and it confirmed the desired product. The low yield was due to an emulsion during product work-up (Scheme 13).

2.10. The preparation of a polyHFPO sulfonamide

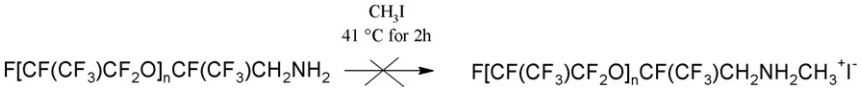
The reaction of polyHFPO amine and benzene sulfonyl chloride proceeded as expected at 50 °C to produce the benzene sulfonamide derivative. The product was confirmed by ^{1} NMR spectroscopy (Scheme 14).



Scheme 12. Condensation reaction with polyHFPO methylene amine and benzaldehyde.



Scheme 14. Formation of a polyHFPO sulfonamide.



Scheme 15. Attempted alkylation of polyHFPO methylene amine.

2.11. The alkylation of polyHFPO methylene amine

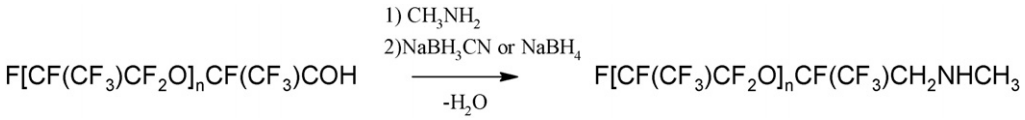
Due to the strong nucleophilic nature of amines, they consistently are seen attacking the halogenated carbon of alkyl halides in order to produce an amine of higher substitution [19]. Consequently, it was expected that poly(hexafluoropropylene oxide) amine would undergo the same reaction. Methyl iodide was added in a 1:1 ratio with the amine and stirred at room temperature. Due to the high reactivity associated with this reaction, no additional heat was believed to be required. Characterization by GC/MS after several hours, however, showed that no reaction had occurred. Due to the incredibly quick kinetics associated with this reaction, it was necessary to look for not only the secondary, but also tertiary and quaternary amine compounds in the ^{1}H-NMR spectrum [20]. However, these were not present in the spectrum, which showed only the primary amine. The mixture was then heated to reflux (41 °C) for several hours to force the reaction; however, once again, none of the alkylated amine formed. Until now, there have been no scholarly references to the alkylation of perfluorinated amines containing a methylene spacer. Consequently, this reaction was either attempted by others and seen to fail, and therefore never reported, or has never previously been attempted. Thus, there is no framework to compare these results (Scheme 15).

Due to the strongly electron withdrawing polyHFPO chain, the amine end-group of polyHFPO amine is considered to be very weakly basic [17]. For example, the ammonium salt of 2,2,2-trifluoroethylamine was determined to have a pK_a of just 5.7; whereas ethylamine, the corresponding alkylamine, has a pK_a of 10.81. Thus, the electron withdrawing nature of polyHFPO could cause the amine to be about as basic as 2,2,2-trifluoroethylamine. As a result, it is a poor nucleophile and it has similar reactivity as its weakly nucleophilic amide counterparts [21]. Thus, it is not surprising that no product has been seen in the reaction between polyHFPO amine and methyl iodide. Amides have been seen to react so slowly with alkyl halides that the formation of the substituted amine is usually carried out via reductive amination [22] (see Scheme 16).

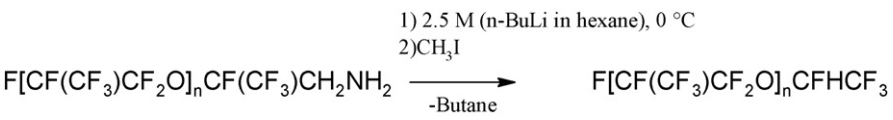
Although such a method would likely work for such an electronegative R group as polyHFPO, the aldehyde derivative of the polymer has not yet been successfully produced.

As an alternative method for the formation of a substituted amine, *n*-butyl lithium was used to cause the loss of one of the amino protons and form the lithium-stabilized ion. Methyl iodide was then added to the reaction to alkylate the amine (see Scheme 17).

The amino protons of polyHFPO amine were expected to react with butyl lithium without any difficulty. Once the polyHFPO amine anion formed, the displacement of the iodine ion from methyl iodide should easily occur. Consequently, 2.5 M *n*-butyl lithium in hexanes was added dropwise to polyHFPO amine (chilled to 0 °C) in a 1:1 molar ratio and allowed to stir for several hours. Methyl iodide was dripped into the solution (also in a 1:1 molar ratio) and the mixture was allowed to warm to room temperature. GC/MS characterization of the product showed the complete disappearance of the polyHFPO amine starting material; however, none of the substituted product was seen in the spectrum. Instead, only polyHFPO-CFHCF$_3$ was seen to be present. ^{1}H NMR characterization confirms near complete conversion of the polyHFPO amine to polyHFPO–CFHCF$_3$. This has also been seen when reducing polyHFPO methyl ester with sodium



Scheme 16. Postulated synthesis of an alkylated amine.



Scheme 17. Degradation of the polyHFPO methylene amine with a strong base.

borohydride [7]. This is the second time we have observed a strong base attacking the secondary position of the fluorinated terminus of polyHFPO. It is this case instead of the methyl ester group, the methylene amino group has been replaced with hydrogen.

3. Experimental

3.1. Equipment

The primary form of instrumental analysis used for preliminary product characterization was GC/MS. Gas chromatography/mass spectrometry data was obtained using an Agilent 6890N gas chromatograph with a 5973 N electron-impact mass-selective detector. The GC was equipped with a 30 m × 0.250 mm capillary column with a 1 μm stationary film thickness (DB-5). The programmed temperature for the method employed began with the injection at 60 °C. The temperature was maintained at 60 °C for 2 min and then was increased at a rate of 10 °C per minute until 200 °C was reached. The temperature was held at 200 °C for 20 min before increasing at 30 °C per minute to 260 °C. The 43-min run was completed by the maintaining the temperature at 260 °C for 5 min. The products containing one polyHFPO chain were seen to completely come off the column within the first 25–30 min; whereas, none of the two polyHFPO chain compounds were seen to come off the column at all. The scanning of the MS was performed over the range of 30–600 *m/z*. Noteworthy fragments are provided in the EI/MS sections.

As a secondary confirmation of the product structure, ^{1}H NMR spectroscopy was employed. Samples were diluted in Freon 113 with a $CDCl_3$ reference. Each sample also underwent ^{19}F NMR spectroscopy for confirmation of structure and average molecular weight. All spectra were recorded on a Bruker DRX 400 MHz spectrometer.

3.2. The preparation of polyHFPO methyl ester

A 5 L 4-neck round bottomed flask was set up equipped with a nitrogen purge, condenser, thermocouple, mechanical stirrer and addition funnel. A silver HF smock, butyl elbow-length gloves and faceshield were used while transferring 3470 g (2.49 mol, 1390 g/mol) polyHFPO acid fluoride to the flask. The flask was then chilled with wet ice to 10 °C. 799 g (24.96 mol) of anhydrous methanol was slowly added by dropping funnel at a rate to maintain the temperature below 45 °C. The mixture was then stirred for 30 min, followed by the addition of 1500 g deionized water and 15 min of additional stirring. After allowing the layers to separate, the top aqueous layer was then drawn off by vacuum aspirator. The product was washed two additional times with water. Methanol was added, as needed, to break any emulsions. The wash water was, once again, drawn off and the product distilled at 60 °C with oil pump vacuum. Yield (≥99%).

NMR spectroscopy data: 1H NMR (400 MHz; $CDCl_3$) δ: 3.928 (s, 1H, C(O)CH_3). ^{13}C-NMR (90.5 MHz, C_6D_6, δ): 161.3 [d, –C(O)OCH$_3$, $^{2}J_{CF}$ = 31.9 Hz, 1C]; *EI/MS Characterization (70 eV) m/z (fragment)*: 59 *m/z* (+C(O)OCH$_3$), 69 *m/z* (+CF$_3$), 147 *m/z* (+C$_3$F$_5$O), 159 *m/z* (+CF(CF$_3$)C(O)OCH$_3$), 169 *m/z* (+C$_3$F$_7$), 325 *m/z* (+C$_3$F$_6$OCF(CF$_3$)C(O)OCH$_3$).

3.3. The preparation of polyHFPO amide

An ammonia tank was placed on a balance and connected to a suck back trap. This trap was connected to a second suck back trap in parallel. A gas inlet tube was connected to the second suck back trap and to a 250 mL 4-neck round bottomed flask equipped with mechanical stirrer, condenser, nitrogen purge and thermocouple. 102.1 g (0.073 mol, 1400 g/mol) polyHFPO methyl ester was placed in flask and chilled to 0–10 °C with wet ice. 3.77 g (0.22 mol 3:1 molar excess) ammonia was added to the flask over a period of 1 h. The flask contents are allowed to stir for an additional hour once all ammonia has been added. The reaction mixture was then allowed to warm to room temperature as the excess ammonia was evaporated. All necks of the flask were stoppered except for one containing a dry ice trap connected to the house vacuum. The flask remained under vacuum while a magnetic stir bar stirred until no more degassing occurred. Lastly, the flask contents were heated to 65 °C to remove the methanol byproduct. Yield (≥99%).

NMR spectroscopy data: 1H NMR (400 MHz; $CDCl_3$) δ: 6.80 & 7.60 (bs, 2H, –C(O)ONH_2) ^{13}C-NMR (90.5 MHz, C_6D_6, δ): 164.15 [–C(O)NH$_2$, $^{2}J_{CF}$ = 28.0 Hz, 1C]; *EI/MS Characterization (70 eV) m/z (fragment)*: 44 *m/z* (+C(O)NH$_2$), 69 *m/z* (+CF$_3$), 144 *m/z* (+CF(CF$_3$)C(O)NH$_2$), 147 *m/z* (+C$_3$F$_5$O), 169 *m/z* (+C$_3$F$_7$); 210 *m/z* (+CF$_2$OCF(CF$_3$)C(O)NH$_2$), 310 *m/z* (+C$_3$F$_6$OCF(CF$_3$)C(O)NH$_2$); IR (NaCl) υ_{max} (cm^{-1}): 3510(N–H stretch) 1745 (C=O stretch, Amide I band) 1610(N–H bend, Amide II band), 1250 (s, CF$_3$ and CF$_2$ stretching), 1150 (s, C–O–C stretching), 980 (m, CF$_3$ stretch) [23].

3.4. The preparation of polyHFPO nitrile

101.3 g (0.073 mol) 1387 amu polyHFPO amide was placed in a 250 mL 4-neck round bottomed flask equipped with mechanical stirrer, nitrogen purge, condenser, addition funnel and thermocouple. The flask was then cooled to 0–10 °C with wet ice. 11.6 g (0.15 mol; 2:1 molar ratio) of pyridine and 61.4 g (0.29 mol; 3:1 molar ratio) of trifluoroacetic anhydride were placed in the addition funnel and added dropwise to flask while maintaining the reaction temperature below 10 °C. The contents were then stirred for an additional hour below 10 °C before heating to 40 °C and refluxing overnight. The product was then washed two times with 5% HCl and two times with water. Any remaining water was removed by distillation at 60 °C with oil pump vacuum. Product characterization was performed by GC/MS. Yield (≥99%).

NMR spectroscopy data: ^{13}C-NMR (90.5 MHz, C_6D_6, δ): 164.3 (d, –C(O)NH$_2$, $^{2}J_{CF}$ = 30.3 Hz); *EI/MS Characterization(70 eV) m/z (fragment):* 69 *m/z* (+CF$_3$), 126 *m/z* (+CF(CF$_3$)CN), 142 *m/z* (+OCF(CF$_3$)CN), 147 *m/z* (+C$_3$F$_5$O), 169 *m/z* (+C$_3$F$_7$), 192 *m/z* (+CF$_2$OCF(CF$_3$)CN), 292 *m/z* (+C$_3$F$_6$OCF(CF$_3$)CN); *IR spectroscopy data:* IR

(NaCl) υ_{max} (cm^{-1}): 2260 (CN stretch), 1250 (s, CF_3 and CF_2 stretching), 1150 (s, C–O–C stretching), 980 (m, CF_3 stretch) [23].

3.5. The preparation of polyHFPO amine

A 4.14 g (0.109 mol; 1.9:1 molar ratio) portion of sodium borohydride was placed in a 500 mL 4-neck round bottomed flask equipped with mechanical stirrer, nitrogen purge, condenser, addition funnel and thermocouple. A 101.9 g (1.41 mol; 19.37:1 molar ratio) portion of THF was added to the flask and cooled to 10 °C with wet ice. 0.98 g (0.547 mol; 0.75:1 molar ratio) of deionized water and 11.49 g (0.547 mol; 0.75:1 molar ratio) of trifluoroacetic anhydride were added to a beaker. Trifluoroacetic anhydride was added dropwise to the water in beaker. The trifluoroacetic acid solution was slowly added to the flask at a rate to maintain the temperature below 20 °C followed by the addition of 99.7 g (0.073 mol) of 1369 amu polyHFPO nitrile using an addition funnel. The contents of the flask were refluxed at 65 °C overnight. In the morning, the reaction was cooled to room temperature and 50 mL of 20% ammonium chloride (aq) was slowly added to flask. The product was then washed with methanol and a 5% NaCl aqueous solution three times and then distilled at 70 °C under oil pump vacuum. Yield (83%).

NMR spectroscopy data: ^{1}H NMR (400 MHz; $CDCl_3$) δ: 3.035 (broad s, 2H, $CH_2\mathit{NH_2}$); 3.290 (d, –$CF(CF_3)\mathit{CH_2}NH_2$); ^{13}C-NMR (90.5 MHz, C_6D_6, δ): 43.53 (d, –$CF(CF_3)\mathit{C}H_2NH_2$, $^2J_{CF}$ = 25.35 Hz, 1C); *EI/MS Characterization (70 eV) m/z (fragment):* 30 *m/z* (+CH_2NH_2); 69 *m/z* (+CF_3); 130 *m/z* (+$CF(CF_3)CH_2NH_2$); 146 *m/z* (+$OCF(CF_3)CH_2NH_2$); 147 *m/z* (+C_3F_5O); 169 *m/z* (+C_3F_7); 196 *m/z* (+$CF_2OCF(CF_3)CH_2NH_2$); 296 *m/z* (+$C_3F_6OCF(CF_3)CH_2NH_2$); *IR spectroscopy data:* IR (NaCl) υ_{max} (cm^{-1}): 1710 (w, N–H bend (scissoring), 1250 (s, CF_3 and CF_2 stretching), 1150 (s, C–O–C stretching), 980 (m, CF_3 stretch) [23].

3.6. The preparation of polyHFPO–$CH_2NHC(O)CH_3$

3.6.1. Method A: acetyl chloride

A 100 mL 3-neck round bottomed flask was equipped with a mechanical stirrer, thermocouple, addition funnel, nitrogen purge and condenser. A 72.8 g (0.052 mol,1400 g/mol) portion of polyHFPO amine and 4.52 g (0.057 mol; 1.1:1 molar ratio) of pyridine were placed in the flask. Then, 4.28 g (0.055 mol; 1.05:1 molar ratio) of acetyl chloride were added dropwise by addition funnel. The reaction was then heated with stirring to 50 °C overnight. Monitoring was completed by GC/MS. The product was then washed three times with a mixture of acetone and 5% (aq) NaCl and vacuum stripped at 65 °C with an oil pump vacuum. Thorough washing is required to ensure the removal of the pyridine hydrochloride salt. Final product characterization was done by GC/MS, ^{1}H NMR and ^{19}F NMR. Yield (98.2%).

3.6.2. Method B: acetic anhydride

A 100 mL 3-neck round bottomed flask was equipped with a mechanical stirrer, thermocouple, addition funnel, nitrogen purge and condenser. A 71.6 g (0.051 mol) portion of 1400 amu polyHFPO amine and 4.45 g (0.056 mol; 1.1:1 molar ratio) of pyridine were placed in flask. Then, 5.48 g (0.054 mol; 1.05 molar ratio) acetic anhydride were added dropwise by addition funnel. Reaction was then heated with stirring to 50 °C overnight. Monitoring was completed by GC/MS. The product was then washed three times with a mixture of acetone and 5% (aq) NaCl and then vacuum stripped 65 °C with an oil pump vacuum. Thorough washing is required to ensure the removal of the pyridine hydrochloride salt. Final product characterization was done by GC/MS and ^{1}H spectroscopy and the yield was 98%.

NMR spectroscopy data: ^{1}H NMR (400 MHz; $CDCl_3$): 1.920 (s, 3H, –$CF(CF_3)CH_2NHC(O)\mathit{CH_3}$); 4.042 (m, 2H, $CF(CF_3)\mathit{CH_2}NHC(O)CH_3$); 5.792 (s, 1H, $CF(CF_3)CH_2$ $\mathit{NH}C(O)CH_3$); *EI/MS Characterization (70 eV) m/z (fragment):* 43 *m/z* (+$C(O)CH_3$); 69 *m/z* (+CF_3); 72 *m/z* (+CH_2 $NHC(O)CH_3$); 147 *m/z* (+C_3F_5O); 169 *m/z* (+C_3F_7) 172 *m/z* (+$CF(CF_3)CH_2NHC(O)CH_3$).

3.7. The preparation of polyHFPO–$CH_2NHC(O)CF_3$

A 50 mL 3-neck round bottomed flask was equipped with a stir bar, thermocouple, addition funnel, nitrogen purge and condenser. A 48.5 g (0.035 mol, 1400 g/mol) portion of polyHFPO amine and 3.01 g (0.038 mol; 1.1:1 molar ratio) of pyridine were placed in flask. Then, 2.86 g (0.036 mol; 1.05:1 molar ratio) of trifluoroacetic anhydride were added to flask dropwise by addition funnel. The reaction mixture was heated to 38.5 °C overnight. Preliminary monitoring was performed by GC/MS. The product was washed three times with a mixture of acetone and water and then vacuum stripped at 65 °C with an oil pump vacuum. Final characterization was performed using ^{1}H and ^{19}F NMR spectroscopy and GC/MS and the yield was 97.7%.

NMR spectroscopy data: ^{1}H NMR (400 MHz; $CDCl_3$) δ: 4.127 (m, 2H, $CF(CF_3)\mathit{CH_2}NHC(O)CF_3$); 6.300 (s, 1H, $CF(CF_3)CH_2\mathit{NH}C(O)CF_3$); *EI/MS Characterization (70 eV) m/z (fragment):* 69 *m/z* (+CF_3); 97 *m/z* (+$C(O)CF_3$); 126 *m/z* (+$CH_2NHC(O)CF_3$); 147 *m/z* (+C_3F_5O); 169 *m/z* (+C_3F_7); 206 *m/z* (+$CF(CF_3)CH_2NHC(O)CF_3$—loss of HF); 226 *m/z* (+$CF(CF_3)CH_2NHC(O)CF_3$); 392 *m/z* (+$C_3F_6OCF(CF_3)CH_2$ $NHC(O)CF_3$).

3.8. The preparation of polyHFPO–$CH_2NHC(O)–C_6H_5$

A 50 mL 3-neck round bottomed flask was equipped with a stir bar, thermocouple, addition funnel, nitrogen purge and condenser. 46.5 g (0.033 mol, 1400 g/mol) of polyHFPO amine and 2.9 g (0.037 mol; 1.1:1 molar ratio) of pyridine were added to flask. Benzoyl chloride (4.9 g, 0.035 mol; 1.05:1 molar ratio) was added dropwise to flask via addition funnel. The reaction was heated to 50 °C with stirring overnight. Preliminary monitoring was performed by GC/MS. Product was then washed three times with an acetone/water mixture and vacuum stripped 65 °C. Final characterization was performed by ^{1}H and ^{19}F NMR spectroscopy and GC/MS and the yield was 79%.

NMR spectroscopy data: 1H NMR(400 MHz; $CDCl_3$): 4.282 (m, 2, $CH_2NHC(O)C_6H_5$), 6.215 (s, 1H, $CH_2NHC(O)C_6H_5$), 7.378 (t, 2H, $CH_2NHC(O)C_6H_5$—*meta* protons) 7.487 (t, 1H, $CH_2NHC(O)C_6H_5$—*para*-proton); 7.700 (d, 1H, $CH_2NHC(O)C_6H_5$—*ortho* protons); *EI/MS Characterization(70 eV) m/z (fragment):* 69 *m/z* ($+CF_3$); 77 *m/z* ($+C_6H_5$); 105 *m/z* ($+C(O)C_6H_5$); 134 *m/z* ($+CH_2NHC(O)C_6H_5$); 147 *m/z* ($+C_3F_5O$); 169 *m/z* ($+C_3F_7$); 234 *m/z* ($+CF(CF_3)CH_2NHC(O)C_6H_5$); 300 *m/z* ($+C_3F_6OCF(CF_3)CH_2NHC(O)C_6H_5$).

3.9. The preparation of polyHFPO–$CH_2NHC(O)$–polyHFPO

A 250 mL 4-neck round-bottomed flask was equipped with nitrogen purge, condenser, thermocouple, addition funnel and mechanical stirrer. A 66.3 g (0.043 mol, 1559 g/mol) portion of polyHFPO acid fluoride were placed in the flask. Then 3.7 g (0.047 mol; 1.1:1 molar ratio) of pyridine were placed in an addition funnel and slowly added to the flask. An exotherm was not expected by the addition of pyridine; consequently, any exotherm indicates moisture in the pyridine resulting in the formation of polyHFPO acid and hydrofluoric acid. If an exotherm is seen, the reaction should be restarted with fresh pyridine. Then 59.7 g (0.043 mol 1:1 molar ratio to polyHFPO acid fluoride, 1400 g/mol) of polyHFPO amine were placed in an addition funnel and added dropwise to flask with stirring. The reaction was allowed to stir at room temperature for several hours. After 1 h, the conversion was incomplete and the reactions was allowed to stir at 60 °C overnight yielding 74.3% of poly(HFPO) amide product.

Aliquots were regularly taken and mixed with methanol prior to GC/MS analysis in order to form the polyHFPO methyl ester of any unreacted polyHFPO acid fluoride. GC/MS provided the preliminary analysis of completion by the disappearance of the polyHFPO amine and polyHFPO methyl ester peaks since the product was too heavy to come off the column. Once complete, the product was washed several times with acetone and water until the pH was neutral. Finally, the product was vacuum stripped at 65 °C with an oil pump vacuum. Characterization of the final product was done with ^{1}H NMR spectroscopy.

NMR spectroscopy data: 1H NMR (400 MHz; $CDCl_3$): 4.147 (m, 2H, –$CF(CF_3)CH_2NHCF(CF_3)$–); 6.458 (s, 1H, –$CF(CF_3)CH_2NHCF(CF_3)$–).

3.10. The preparation of the polyHFPO Schiff base

A 100 mL 3-neck round bottomed flask was set up and equipped with a mechanical stirrer, thermocouple, condenser and nitrogen purge. Then 47.0 g (0.034 mol, 1400 g/mol) polyHFPO amine and 3.74 g (0.035 mol; 1.03:1 molar ratio) benzaldehyde were placed in the flask, heated to 90 °C and stirred for 1.5 h. Preliminary product analysis was performed by GC/MS. Product was then washed with 5% (aq) NaCl solution, acetone and perfluorobutyl-methyl ether (HFE 7100; available through 3M) and vacuum stripped at 65 °C. Characterization of the final product by ^{1}H and ^{19}F NMR spectroscopy and GC/MS, showed a yield of 93.4%.

NMR spectroscopy data: 1H NMR (400 MHz; $CDCl_3$): 4.229 (d, 2H, $CF(CF_3)CH_2N{=}CH{-}C_6H_5$); 7.28 (*ortho*), 7.75 (*meta*, *para*) (m, 5H, $CF(CF_3)CH_2N{=}CH{-}C_6H_5$); 8.232 (s, 1H, $CF(CF_3)CH_2N{=}CH{-}C_6H_5$); *EI/MS Characterization (70 eV) m/z (fragment):* 69 *m/z* ($+CF_3$); 77 *m/z* ($+C_6H_5$); 91 *m/z* ($+CH_2C_6H_5$); 118 *m/z* ($+CH_2N{=}CHC_6H_5$); 147 *m/z* (C_3F_5O); 169 *m/z* ($+C_3F_7$); 218 *m/z* ($+CF(CF_3)CH_2N{=}CHC_6H_5$).

3.11. The preparation of polyHFPO urea

A 50 mL 3-neck round bottomed flask was set up and equipped with stir bar, nitrogen purge, condenser, addition funnel, and thermocouple. A 35.7 g (0.025 mol, 1400 g/mol) portion of polyHFPO amine were placed in the flask. Then 5.0 g (0.027 mol; 1.05:1 molar ratio) of *p*-trifluoromethylphenyl isocyanate were placed in the addition funnel and added to the flask dropwise. The mixture was then stirred at 40 °C for 5 h. Preliminary monitoring was done by the disappearance of the polyHFPO amine peaks from the gas chromatogram, as the product did not come off of the column. Once complete, the product was washed three times with acetone, 5% (aq) NaCl and perfluorobutyl-methyl ether (HFE 7100) and vacuum stripped at 65 °C. Final product characterization was done by ^{1}H and ^{19}F NMR spectroscopy showed a 36.2% yield.

NMR spectroscopy data: 1H NMR (400 MHz; $CDCl_3$): 4.006 (m, 2H, $CH_2NHC(O)NH\text{-}C_6H_4CF_3$), 5.293 (s, 1H, $CH_2NHC(O)NHC_6H_4CF_3$), 5.642 (s, 1H, $CH_2NHC(O)NHC_6H_4CF_3$) 7.305 (d, 2H, $CH_2NHC(O)NHC_6H_4CF_3$—protons *meta* to polyHFPO substitution), 7.455 (d, 2H,$CH_2NHC(O)NHC_6H_4CF_3$—protons *ortho* to polyHFPO substitution).

3.12. The preparation of the polyHFPO sulfonamide

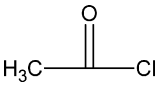
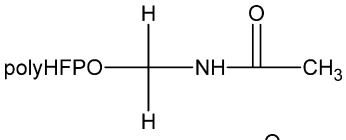
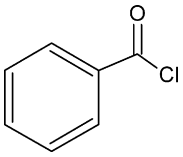
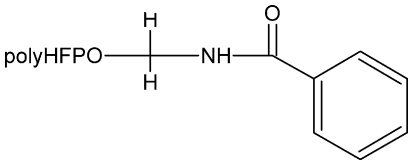
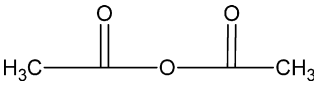
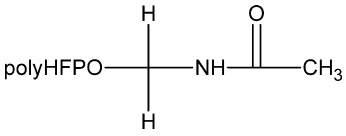
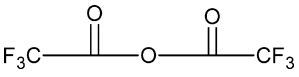
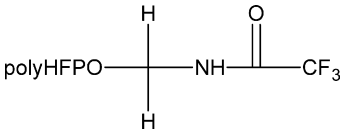
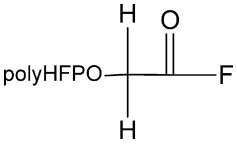
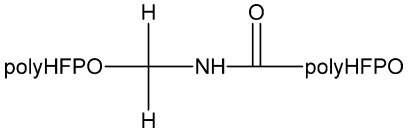
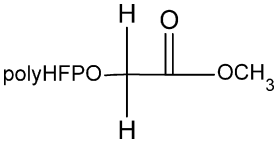
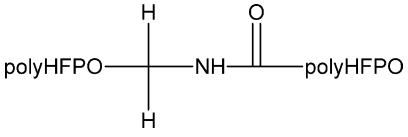
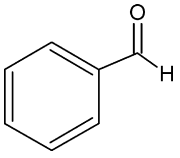
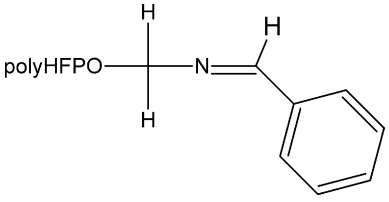
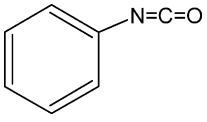
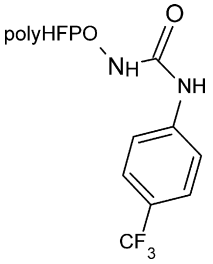
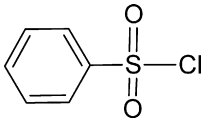
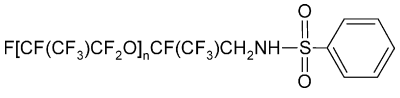
A 50 mL 3-neck round bottomed flask was set up and equipped with nitrogen purge, condenser, thermocouple, stir bar and addition funnel. A 45.5 g (0.032 mol, 1400 g/mol) portion of polyHFPO amine were placed in the flask. Benzenesulfonyl chloride (6.02 g, 0.034 mol; 1.05:1 molar ratio) was added dropwise to the flask via addition funnel and the mixture was stirred at 50 °C overnight. Preliminary monitoring was done by the disappearance of the polyHFPO amine peaks in the gas chromatogram, as the product did not come off the column. The product was then washed three times with acetone, 5% (aq) NaCl and perfluorobutyl-methyl ether (HFE 7100) and vacuum stripped at 65 °C. Final product characterization by ^{1}H NMR spectroscopy showed a 20% yield.

NMR spectroscopy data: 1H NMR (400 MHz; $CDCl_3$): 3.749 (m, 2H, –$CF(CF_3)CH_2NHS(O)_2C_6H_5$), 7.265 (s, 1H, –$CF(CF_3)CH_2NHS(O)_2C_6H_5$), 7.459 (t, 2H, –$CF(CF_3)CH_2NHS(O)_2C_6H_5$—*meta* protons), 7.538 (t, 1H, –$CF(CF_3)CH_2NHS(O)_2C_6H_5$—*para* proton), 7.834 (d, 2H, –$CF(CF_3)CH_2NHS(O)_2C_6H_5$—*ortho* protons).

4. Conclusions

The first perfluorinated amine containing a methylene spacer, 2,2,2-trifluoroethylamine, was prepared in 1943. The

Table 1
Product yields using polyHFPO amines and acyl halides

Reagent	Product	Yield (%)
		98.2
		79.0
		98.0
		97.7
		74.3
		0
		93.4
		36.2[a]
		20
CH_3I	$F[CF(CF_3)CF_2O]_nCF(CF_3)CH_2NH–CH_3$	0
Butyl lithium, CH_3I	$F[CF(CF_3)CF_2O]_nCF(CF_3)CH_2NH–CH_3$	0

[a] Difficulty in emulsion formation.

reactivity of such amines, however, has remained relatively unknown. Consequently, a series of reactions were carried out with polyHFPO amine ($CF_3CF_2CF_2O[CF(CF_3)CF_2O]_n$-$CF(CF_3)CH_2NH_2$ to provide a greater understanding for the reactions of all fluorinated amines with methylene spacers.

Several different types of reactions were carried out on the polyHFPO amine including the addition of acyl, sulfonyl and alkyl halides, anhydrides, aldehydes, isocyanates, and esters. The expected products were obtained for most reactions in moderately high yields (>70%).

Benzoyl chloride, acetyl chloride, acetic anhydride, trifluoroacetic anhydride, and polyHFPO acid fluoride were all used in reactions to form the benzylamide, acylamide, trifluoroacylamide, and polyHFPO methanamide derivatives of polyHFPO amine, respectively. The corresponding yields of these products are listed in Table 1. In addition to amide formation, other reactions of polyHFPO amine were also explored. The addition of benzaldehyde to the amine gave, as hoped, a Schiff base (PolyHFPO–CH_2N=CH–C_6H_5) in 93.4% yield. The addition of *p*-trifluoromethylphenyl isocyanate to the amine produced the expected urea (polyHFPO–$CH_2NHC(O)NHC_6H_4CF_3$), with a yield of 36.2%. The low yield is due to an emulsion. Characterization of these compounds and the amides previously named, were performed by GC/MS and ^{1}H NMR spectroscopy.

Benzenesulfonyl chloride was also added to the amine in order to form the sulfonamide derivative (polyHFPO-$CH_2NHS(O)_2C_6H_5$). While the product was obtained from this reaction, ^{1}H NMR spectroscopy showed that only a small portion of the product was the sulfonamide showing a yield of 20.0%.

PolyHFPO amine was seen to readily undergo many of the typical reactions of amines; however, not all of the reactions occurred as planned. The expected reaction of polyHFPO amine with polyHFPO methyl ester failed, even when heated to high temperatures. This is undoubtedly due to the weak nucleophilic character of the polyHFPO amino group. This product could, nevertheless, be synthesized through the addition of polyHFPO acid fluoride to polyHFPO amine.

The weak nucleophilic character of polyHFPO amine was, once again, observed through its attempted alkylation using methyl iodide. Even with excess methyl iodide, none of the secondary, tertiary or quaternary amine products were observed. Therefore, we believe that the weakly nucleophilic nature of the amine is like that of amides. One alternate route to the alklylated amine was attempted. *n*-Butyl lithium was added to the amine to form an anion and methyl iodide subsequently added. Characterization of the product by GC/MS showed the near-complete conversion of polyHFPO amine to poly-$HFPOCFHCF_3$. As we have observed before, a group attached to the secondary carbon atom of the terminal group on polyHFPO can be removed under certain circumstances.

Overall, a number of new poly(hexafluoropropylene oxide) derivatives have been prepared: simple amide, nitrile, methylene amine, alkyl and poly(HFPO) amides, Schiff base, urea, and a sulfonamide. The amine was reactive with electrophiles, carbonyls and isocyanates. The weak nucleophilicity of the compound prevented it from reacting with alkyl halides and polyHFPO methyl ester.

References

[1] H.D. Tarlas, Mater. Protect. 9 (5) (1970) 37.
[2] G.A. Rabinovich, A. Cumashi, G.A. Bianco, D. Ciarvadelli, I. Lurisci, M. D'Egidio, E. Piccolo, N. Tinari, N. Nifantiev, S. Iacobelli, Glycobiology 16 (3) (2006) 210.
[3] H. Nagasawa, Jpn. Kokai Tokkyo Koho (2006) 7.
[4] N.M. Agayev, K.A. Maksimov, G.S. Sharifov, Azarbaycan Neft Tasarrufati 11 (2005) 46.
[5] H. Gilman, R.G. Jones, J. Am. Chem. Soc. 65 (1943) 1458.
[6] J.T. Hill, J. Macromol. Sci. Chem. A8 (3) (1974) 499.
[7] J.L. Howell, N. Lu, C.M. Friesen, J. Fluorine Chem. 126 (2005) 281.
[8] 3M Co., Br. Patent 689,425 (1953).
[9] E.R. Bissell, M. Finger, J. Org. Chem. 24 (1959) 1256.
[10] A.J. Elliot, G.W. Astrologes, US Patent 4,618,718 (1986).
[11] N. Kondo, K. Kawada, S. Arai, JP Patent 332,078 (2001).
[12] V.A. Soloshonok, H. Ohkura, K. Uneyama, Tetrahedron Lett. 43 (2002) 5449.
[13] C.M. Friesen, J.L. Howell, DuPont Tech. Report DCSE-JL-2001-13 (2001).
[14] E.J. Bourne, S.H. Henry, C.E.M. Tatlow, J.C. Tatlow, J. Chem. Soc. (1952) 4014.
[15] C.H. Dungan, J.R. Van Wazer, Compilation of Reported F19 NMR Chemical Shifts, Wiley Interscience, New York, 1970, p. 2146.
[16] S.J. Falcone, US Patent 6,187,954 (2001).
[17] V. Badescu, A. Nemchik, O. Phanstiel, Tetrahedron 59 (2003) 4315.
[18] P.W. Hickmott, Tetrahedron 38 (23) (1982) 3363.
[19] M.S. Gibson, R.W. Bradshaw, Angew. Chem. Int. Ed. Engl. 7 (1968) 919.
[20] F.A. Carey, R.J. Sundberg, Advanced Organic Chemistry. Part B: Reactions and Synthesis, fourth ed., Kluwer Academic/Plenum Publishers, New York, 2001.
[21] E.N. Gate, M.D. Threadgill, M.F.G. Stevens, D. Chubb, L.M. Vickers, S.P. Langdon, J.A. Hickman, A. Gescher, J. Med. Chem. 29 (1986) 1046.
[22] P.L. Salzberg, J.V. Supniewski, Org. Synth. 1 (1932) 119.
[23] C.M. Friesen, Perfluoropolyalkylethers: the synthesis and characterization of lubricant derivatives for new industrial applications, including improvements in thermal oxidative environments. Dissertation, The University of Alabama (2000) 124.