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Highly Fluorinated Polymers

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1.0 Introduction

Current work sponsored by the grant at Southwest Texas State University is directed toward the synthesis and characterization of: (1) polyesters derived from 2-hydroxyhexafluoro-2-propyl-substituted arenes and/or 2,5-difluoroterephthalic acid, (2) N-alkylated polyamides derived from o-fluorinated diacids, (3) Highly fluorinated polyethers, and (4) silicon-containing fluoropolymers. The current status of each of these projects is reported below.

2.0 Highly Fluorinated Polyesters

2.1 Polyesters Derived from 1,3- or 1,4-bis-2-Hydroxyhexafluoro-2-propyl Benzene

As noted in the July-December, 1992, Semiannual Report (refer to Table 1 in cited report), polyesters derived from 1,3- or 1,4-*bis*-2-hydroxyhexafluoro-2-propyl benzene (1,3- or 1,4- HFAB) and isophthalic acid, terephthalic acid or *bis*- 2,2-(4-carboxyphenyl)hexafluoropropane are poorly soluble, moderately thermally stable (10% wt. loss by TGA in N₂ = *ca.* 375-400 °C.) materials. Inherent viscosities range from about 0.2 to 0.85 dL/g for these apparently highly crystalline materials. All reactions were effected by solution polymerization of the acid chlorides and diols in THF using 4-dimethylaminopyridine (DMAP) as catalyst, triethylamine (TEA) as HCl acceptor. It is thought that the degree of polymerization in these systems is limited by two factors, the poor nucleophilicity of the diols and the low solubility of the polyesters in most solvents (*e.g.*, THF) which causes their precipitation before a high molecular weight material can be obtained.

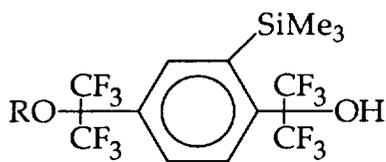
In order to address these problems we have prepared 2,5-difluoroterephthalic acid which is much more soluble in all solvents than terephthalic acid itself. As anticipated, it reacts readily with 1,3- or 1,4-HFAB in the THF/DMAP/TEA mixture, but, so far has not yielded materials with significantly better properties than the terephthalates themselves. The use of alternate synthetic routes to these polyesters has also been extensively investigated but none have been found which give substantially higher molecular weight polyesters with these two diols.

2.2 Polyarylates Derived from 2,5-Difluoroterephthalic Acid

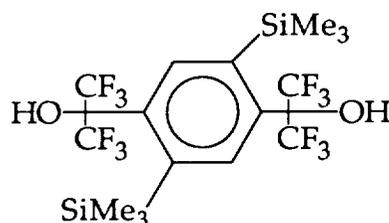
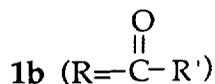
Work has been initiated on the reaction of 2,5-difluoroterephthalic acid with several diphenols (bisphenol A, bisphenol AF, 4,4'-oxydiphenol and 4,4'-sulphonyldiphenol). Two standard procedures are being evaluated for use in these reactions. One procedure involves reaction of the diacid with the diphenol in chlorobenzene in the presence of oxalyl chloride, pyridine and triphenylphosphine oxide; the other method is an interfacial synthesis using the acid chloride, CHCl_3 , aq. KOH, diphenol and decyltrimethylammonium bromide as phase transfer agent. Both procedures show promise in preliminary studies.

2.3 Polyesters Derived from Trimethylsilylated 1,3- or 1,4- HFAB

The proposed series of polyesters derived from **1a** or **2** below will not be synthesized. Simple esters of **1a** have been prepared and found to



1a (R=H)



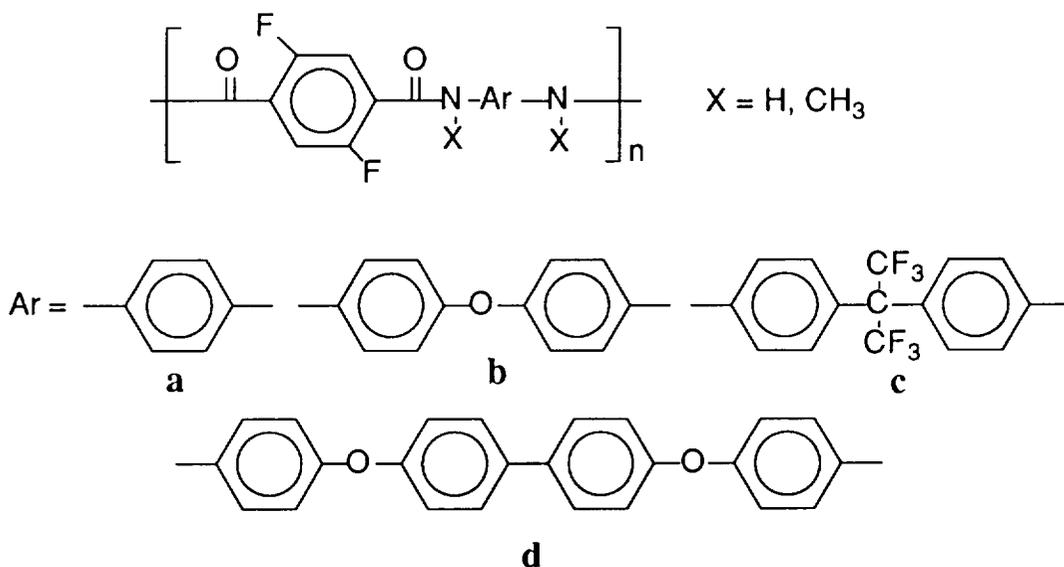
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be extraordinarily sensitive to water. For example, the diacetate or diacrylate of **1a** can be readily synthesized by standard procedures, but they are both rapidly and quantitatively hydrolyzed to monoesters, **1b**, upon exposure to water. Because of this new and unexpected reaction, polyesters of silyl-substituted HFAB's will not be investigated further under this grant.

3.0 N-Alkylated Polyamides

The objective of this research is to determine the structure *versus* property relationship of an analogous series of fluorine-containing co-polyamides, with nitrogen pendant hydrogen and methyl groups.

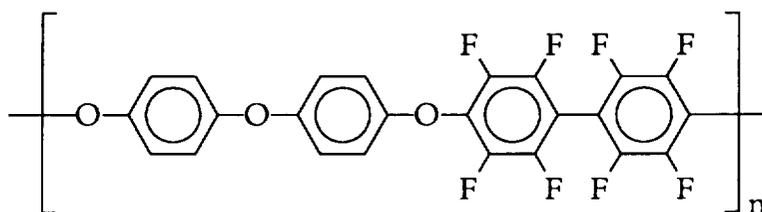
We have initiated work on the synthesis of a series of N-alkylated, fluorine-containing polyamides. This study represents an extension of our previously reported work on N-methylated poly(imide-amides). Previous work [Oishi *et al.*, *J. of Poly. Sci.: Part A: Poly Chem.*, **27**, 3393 (1989)] has indicated that aromatic polyamides derived from o-fluorinated acids undergo thermal decomposition (10% wt. loss at 360-400 °C.) by elimination of HF with the hydrogen atom coming from the amide nitrogen. By using monoalkylated diamines we hope to prepare fluorinated polyamides with both improved thermal stability and enhanced solubility. Polymers of structures shown below have been targeted for synthesis and characterization.



At this time we report the preparation of the polyamides derived from the N-methylated diamines **c** and **d**. Although molecular weights are not yet high enough for good film formation, the polymers are soluble in THF. More importantly TGA data suggest considerable improvement in thermal stability (Polymer from methylated diamine **c** - 10% wt. loss by TGA at 460° in air, at 480° in N₂; polymer from methylated diamine **d** - 10% wt. loss by TGA at 470° in air, at 505° in N₂).

4.0 Highly Fluorinated Polyethers

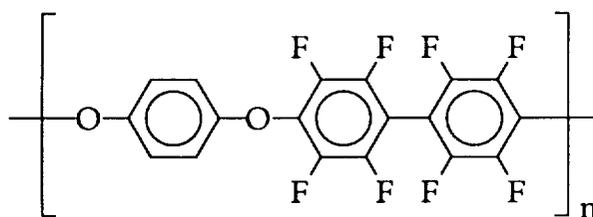
The object of this work is the synthesis of polyethers derived from decafluorobiphenyl (DFBP). The polymer from oxydiphenol and DFBP (8HO8F APE, 3), reported previously, was found to be highly thermally stable.



8HO8F APE, 3

Thermogravimetric analysis (TGA) revealed 10% weight loss at 600 °C in N₂; isothermal gravimetric analysis (IGA) showed only 10% weight loss after 300 h at 350 °C in air. More of this polymer is currently being prepared for further analysis at NASA-Langley. X-ray analysis at NASA-LRC shows a very low crystallinity.

The polymer from hydroquinone and DFBP, also reported previously, was further analyzed. While the material was initially prepared using standard solution polycondensation, oxidation of the hydroquinone often occurred with heating in DMAc; phase transfer-catalyzed polymerization in diglyme (with 18-crown-6 as the catalyst) was successful in eliminating this problem. The resulting polymer (4H8F APE, 4) was insoluble (but swelled slightly in DMAc), possibly due to the rigidity of the polymer chain.

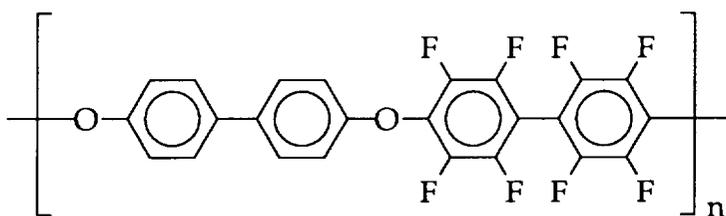


4H8F APE, 4

Elemental analysis of the 4H8F APE deviated somewhat from calculated values (C, -1.65%; H, -0.21%; F, -3.15%). This is probably due to impurities (such as K₂CO₃) in the sample; the sample could not be completely purified due to its insolubility. While insolubility made purification and most analyses impossible,

a sample was sent for solid state NMR; results are pending. Thermal analysis of the polymer revealed temperature at 10% weight loss of 600 °C in N₂; while no glass transition temperature was detected by DSC, the polymer underwent a melt transition at 275 °C.

A polymer was also prepared from the reaction of 4,4'-biphenol with DFBP. The rigid polymer (8H8F APE, 5) was insoluble; elemental analysis deviated from theoretical values (C, -1.57%; H, +0.14%; F, -4.76%); solid state NMR is pending.



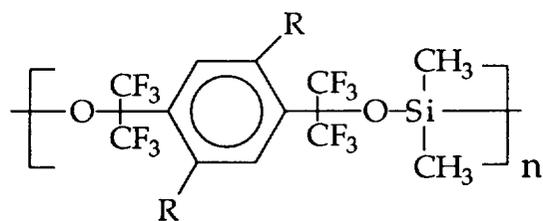
8H8F APE, 5

Thermal stability of 8H8F APE was good, with 10% weight loss after break occurring at 600 °C in N₂; no phase transitions were detected by DSC below 300 °C.

5.0 Silicon-containing Fluoropolymers

5.1 Polysilicates Derived from 1,4- HFAB

Work continues on the effort to develop routes to high molecular weight polysilicates from 1,4-HFAB, 6. We now report that 6 has been



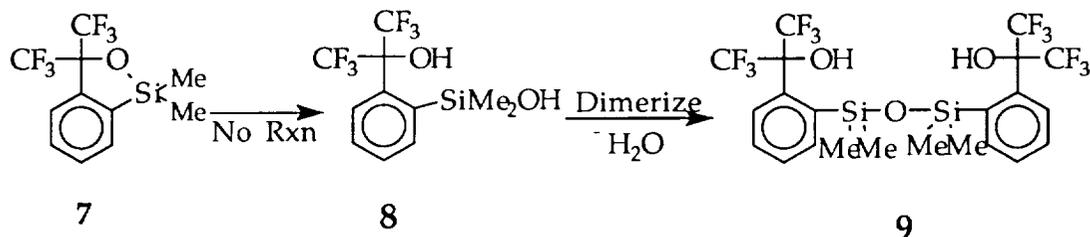
6 R = H, -SiMe₃

prepared as a gummy solid ($\eta_{inh} = 0.29$ dL/g in THF at 25°) by reaction of 1,4- HFAB with *bis*-dimethylaminodimethyl silane in THF. GPC suggests a rather broad MW distribution ranging from about 1800 to 17,000 (DP = 4 to *ca.* 35). Hydrolysis studies are in progress as is an effort to narrow the MW distribution. Work with the trimethylsilyl-substituted

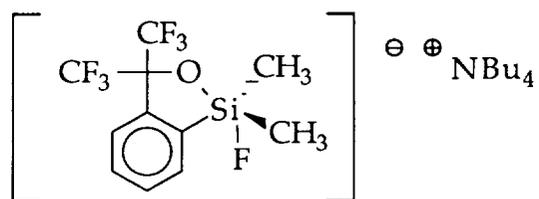
system **6** (R = SiMe₃) which is expected to be resistant to hydrolysis will commence when synthetic details have been worked out with unsilylated **6** (R = H).

5.2 Poly(silphenylene-siloxanes) - Model Compound Studies

A series of model compound studies are being carried out to determine possible synthetic routes to hexafluoroisopropylidene-containing poly(silphenylene)siloxanes using various derivatives of HFAB.

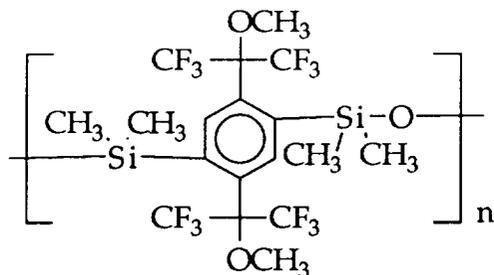


One of the synthetic routes proposed was a ring-opening reaction of **7** to **8** which would dimerize to yield **9**. If this had proven successful, difunctional dicyclic analogues of **7** would have been used for ring-opening polymerization. Various ring-opening protocols have been tried on **7** including reaction with acids (HCl, CH₃COOH), bases (aq. OH⁻, RO⁻ in ROH), acetic anhydride, acetyl chloride, and (C₄H₉)₄N⁺ F⁻. All of these reagents failed to cleave the ring to **8**. The F⁻ ion is considered one of the most effective reagents for cleaving siloxanes due to the high bond energy of the Si-F bond formed during cleavage, but it yielded only the pentacoordinate silicate **10**.



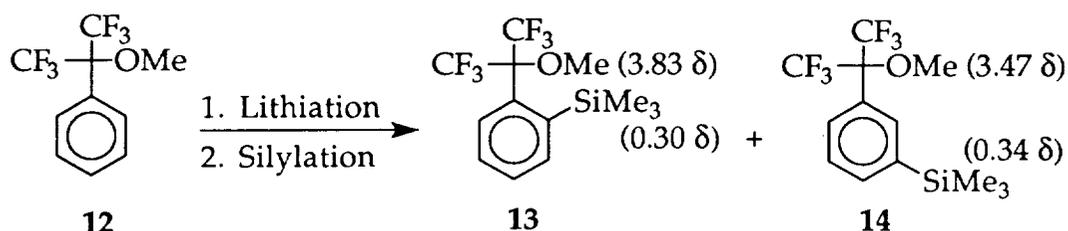
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Because attempts to open the ring of **7** have failed, an alternate synthetic route that could ultimately lead to a polymer of type **11**, in which the pendant -OH groups are blocked as methyl ethers, is under development.

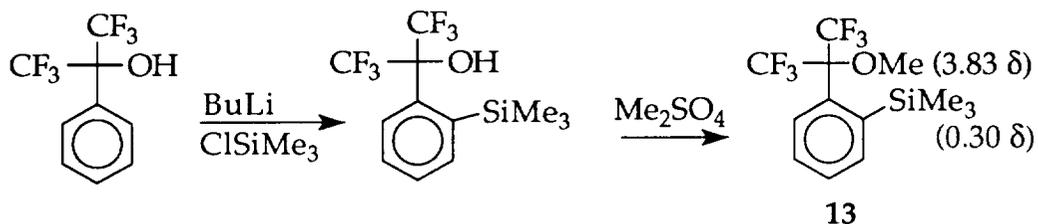


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To this end model compound **12** was prepared, lithiated and then silylated. It was discovered that lithiation occurs in both the ortho and meta positions leading to two silylated isomers in an equimolar ratio. This



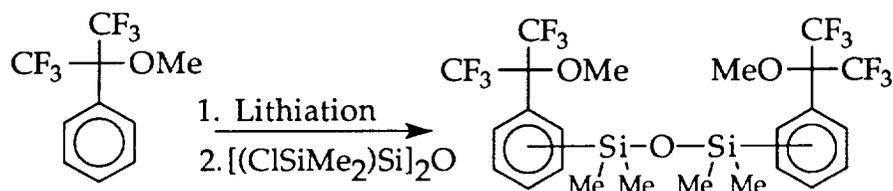
is unlike the free alcohol, HFAB, which lithiates solely in the ortho position. It is believed that the difference in the acidities of the ortho and meta protons (ortho > meta) coupled with the steric hindrance created by the methoxy group on the ortho position explain the formation of the isomers in an equimolar ratio. The mixture thus far has not been separated. However, compound **13** was synthesized by an alternate method to determine peak assignment for the ¹H NMR spectrum of the mixture.



The ¹H NMR spectrum of the mixture show significantly different methoxy methyl shifts for both the ortho and meta isomer at 3.83 δ and 3.47 δ respectively. Interestingly, the fluorine coupling of the methoxy

methyl group of **13** is greater than that of **14**, being 1.6 Hz and 1.0 Hz respectively. The reasons for these differences are currently being investigated.

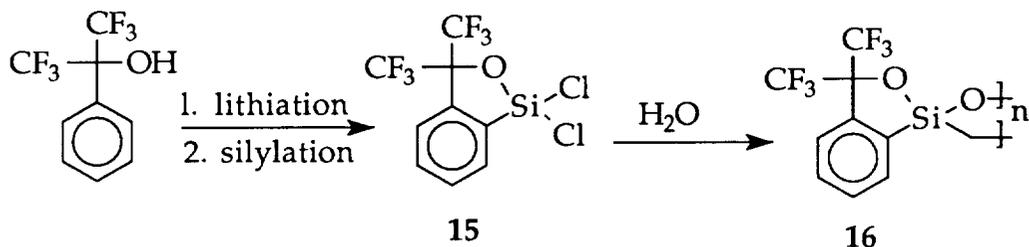
Now that the lithiation and silylation reactions of **12** are more clearly understood, its conversion to a disiloxane are currently underway.



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Preliminary results indicate the disiloxane has been synthesized leading to a (o-o, o-m, m-m) substituted disiloxane. Purification of **14** is in progress at this time. The final step in polymer preparation will involve dilithiating 1,4-HFAB followed by reaction with 1,3-dichlorotetra-methylidisiloxane.

Another interesting development in our laboratories involves the synthesis of a new monomer **15** derived from HFAB using SiCl_4 . The polymer synthesized from this monomer shows promise for various



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16

applications. This monomer has been synthesized and subsequently hydrolyzed to form **16**. The NMR, IR, and elemental analyses are in agreement with the structure. GPC results indicate that **16** is a mixture of a high polymer (low yield) and, primarily, the cyclic trimer ($n = 3$). We hope to develop methods for opening the cyclic system to give linear polysiloxanes. These polysiloxanes represent an entirely new type of silicone polymer and are anticipated to possess interesting (highly nucleophilic but hydrophobic) properties.

6.0 Conclusions and Plans

Based on the above technical results to date most tasks will continue. These include some of the highly fluorinated polyesters (except the silylated versions) for higher molecular weights, N-alkylate polyamides and silicon-containing fluoropolymers. The polyether work will be brought to a close pending further direction from the sponsor. The poly (imide-amide) will also be completed; a patent application is recommended for consideration here due to the significant advantages of alkylation of the amide.

A visit with the sponsor is anticipated during September, 1993, to discuss progress and plans.