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TRIFLUOROMETHYL-SUBSTITUTED POLYMERS

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Semiannual Status Report

January 1, 1990 to June 30, 1990

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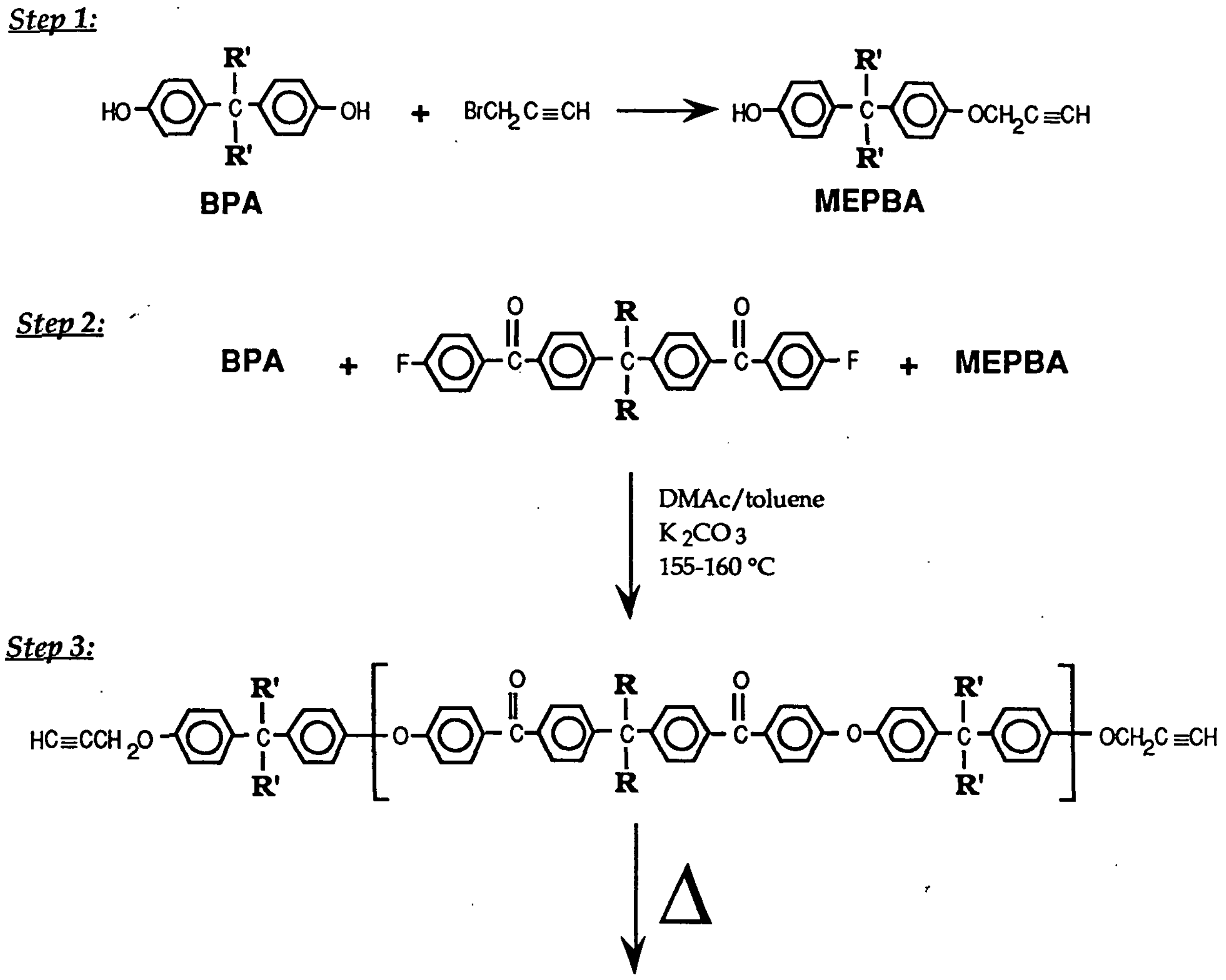
INTRODUCTION

Our current research efforts at Southwest Texas State University concern: 1) the synthesis of fluorine-containing crosslinked poly(ether ketones), 2) the synthesis and characterization of poly(imide amides) and their *N*-methylated analogues, 3) the synthesis of fluorine-containing aromatic polyethers, 4) the synthesis of novel fluorine-containing aromatic polysiloxanes, and 5) the conversion of 6F-containing polythioethers to polysulfones. It is hoped that these polymers will find use as low dielectric materials in electronic applications, function as thermal control coatings, or be suitable elastomeric sealants for extreme service conditions. The following is a brief summary of the research results obtained from January 1, 1990 to June 30, 1990.

1.0 Crosslinked poly(ether ketones)

Recently, a series of new aromatic poly(ether ketones) or PEKs were synthesized in these laboratories. Due to the extreme solubility of these polymers in common organic solvents, a project was begun to synthesize thermally- crosslinkable PEKs in order to render them insoluble. The propargyl group was chosen as the crosslinking functionality for this effort because of its low curing temperature, low price, and absence of off-gas evolution during cure.

The first attempt at synthesizing crosslinkable PEKs involved end-capping PEK oligomers with a monofunctional propargyl compound, as is shown in reaction **Scheme I**. The stoichiometry was adjusted to give an average of 20 repeat units. A product was obtained which could be cast into a brittle film. Upon curing at 280 °C for 1 hour, the film became brown and creasable. The film sample swelled greatly in common organic solvents and lost all mechanical strength. From these results it was determined that end capping would not give the desired degree of crosslinking and the precured polymer would be too low of a molecular weight to utilize as a tough coating even after curing.

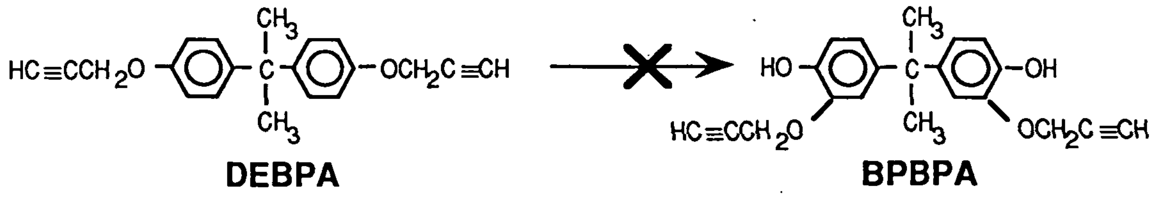


CROSSLINKED POLY(ETHER KETONE)

where: R and R' are CH_3 or CF_3

Scheme I- Possible Synthetic Route to Crosslinked PEKs.

The current attempt at producing crosslinked PEKs involves the incorporation of the propargyl moiety on the polymer backbone. Reaction of the disodium salt of bisphenol A (BPA) with propargyl bromide in ethanol gave the propargyl diether of BPA (DEBPA) in almost quantitative yield. A Claisen rearrangement of the diether to the dipropargyl bisphenol A (BPBPA) was attempted by heating (**Scheme II**).



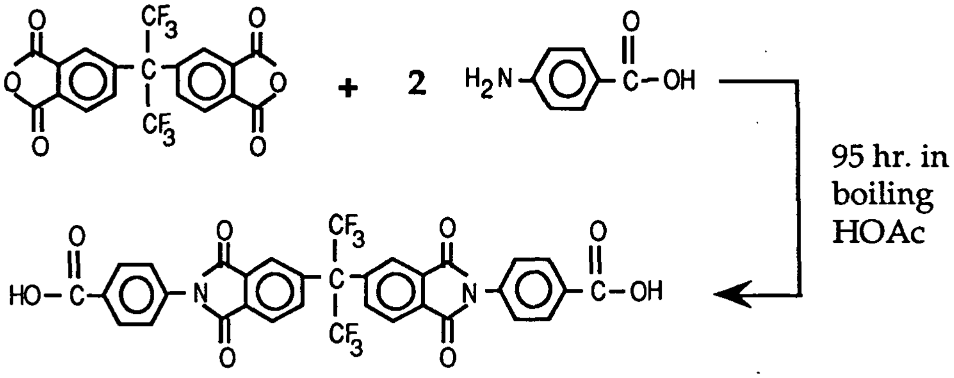
Scheme II- Claisen Rearrangement Attempt

It appears that the temperature required for rearrangement is above the B-staging temperature of this bisacetylene.[1] The products isolated were extremely viscous, brown, and probably partially crosslinked.

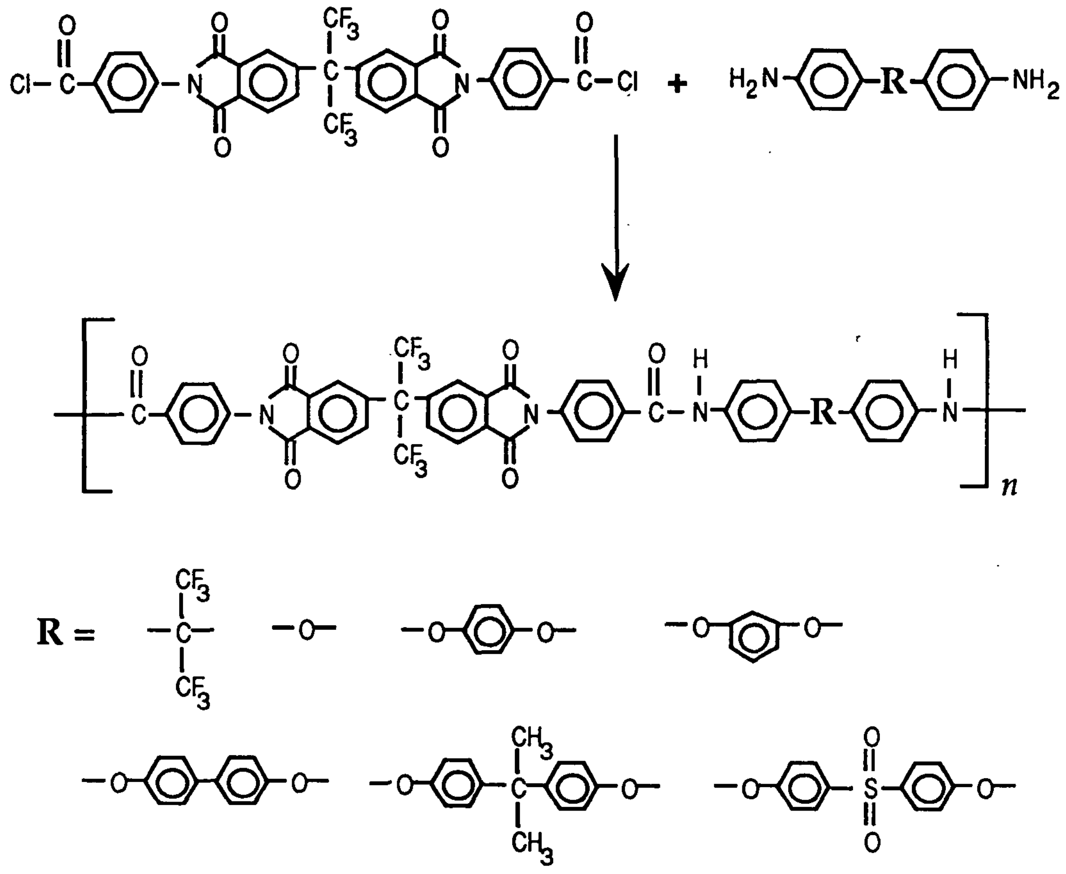
Closely related research indicated that an alternate route to the synthesis of the dipropargyl ether of BPA would also yield a rearranged byproduct of BPBPA and the mono-rearranged product.[2] Reaction of BPA with propargyl bromide in aqueous sodium hydroxide at reflux was attempted. This yielded an alkaline-soluble product and the expected DEBPA. Further characterization by NMR indicated that the base-soluble material is not the desired BPBPA but is MEBPA, the end-capping agent described earlier. Research is continuing on this project and other approaches are being designed.

2.0 Poly(imide amides)

Consistent with our research into novel low-dielectric and thermally stable materials, we have recently synthesized a series of hexafluoroisopropylidene-containing (6F) poly(imide amides). Preparation of the imide-containing monomer (**Scheme III**) is accomplished in a single-



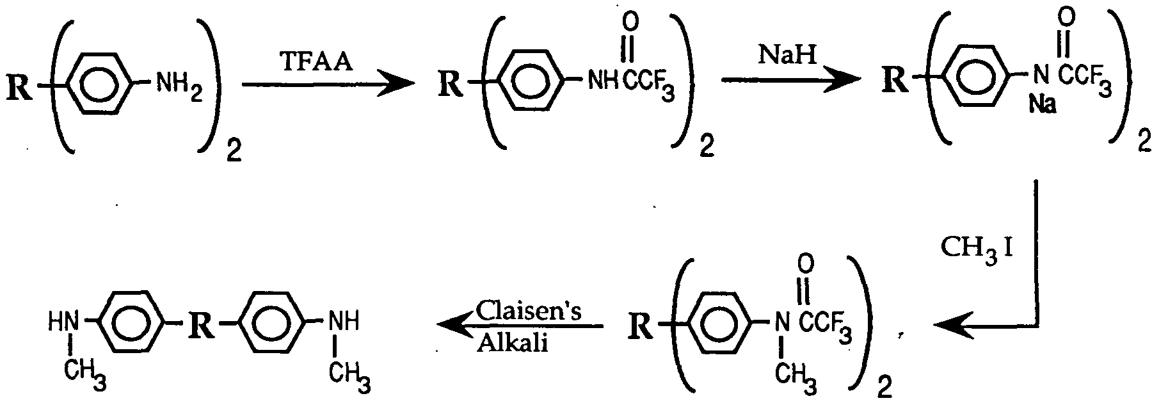
Scheme III- Synthesis of 6F-Diimide acid step imidization reaction of *p*-aminobenzoic acid with 6F-dianhydride (6FDA) in boiling glacial acetic acid. The diacid , obtained in 94% yield, is then converted to the acid chloride by reaction with thionyl chloride. Polymerization of this monomer is accomplished by low temperature (0 °C) condensation with various diamines in DMAc (**Scheme IV**). All polymers were obtained in 85%-95% yields with intrinsic viscosities ranging from 0.90 to 2.26 dL/g at room temperature in DMAc. These polymers all give clear, creasable films that are readily cast from solution and are colorless to slightly yellow in color. Thermal analysis of these materials shows thermal stabilities above 500 °C in air and above 515 °C in nitrogen.



Scheme IV- Polyamides Derived from 6F-Diimide Acid Chloride

In order to improve the thermo-oxidative and UV resistance of these poly(imide amides), research is under way to replace the *N*-hydrogen of the amide linkage by synthesizing the *N*-methylated analogues of the diamines used.

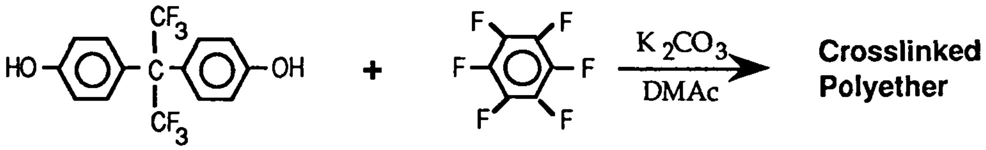
As shown in **Scheme V**, the *N*-methylated diamines was obtained by first producing the trifluoroacetamide analogue, followed by the synthesis of the *N*-sodium salt of the diamide. Reaction of this sodium salt with methyl iodide and subsequent cleavage of the thifluoroacetyl group yielded the desired *N*-methylated diamine. At this time, methylated analogues of 6F-diamine and 4,4'-*bis*-(4-aminophenoxy)biphenyl have been synthesized in overall yields of ~50%. Research is continuing on these and other *N*-methylated diamines in the areas of monomer synthesis and subsequent polymerization with diacid chlorides.



Scheme V- Synthetic Route to *N*-Methylated Diamines

3.0 Fluorine-containing aromatic polyethers

This research project concerns the synthesis of fluorine-containing polyethers for use as thermal control coatings. Previous researchers have demonstrated that bisphenates will react with hexafluorobenzene to yield aromatic polyethers.[3] In our research, we attempted the polymerization of bisphenol AF (BPAF) with hexafluorobenzene according to reaction **Scheme VI**.

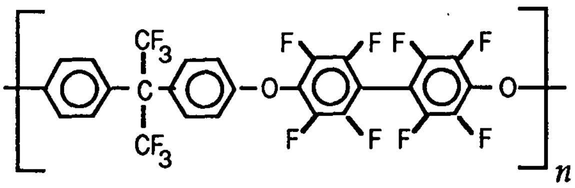


Scheme VI- Attempted Reaction of BPAF with Hexafluorobenzene

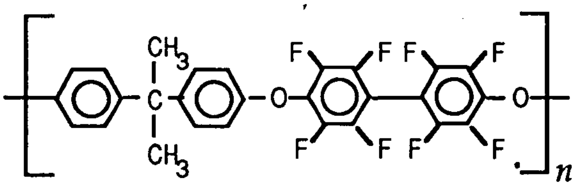
The polymerization proceeded at room temperature for one day to yield a crosslinked product which was only very slightly soluble in chloroform. Creasable films could be cast from unfilterable solutions of this swelled product. The results indicate that hexafluorobenzene undergoes a sufficient degree of substitution to render it unusable. Variance of the reaction times and conditions did not decrease the degree of crosslinking significantly.

The polymerization of BPAF with 1,2,4,5-tetrafluorobenzene failed to yield a polymer. Evidently, the tetrafluorobenzene is not activated enough towards nucleophilic substitution to yield high molecular weight polymer. This low reactivity and low boiling point (90 °C) made the monomer difficult to work with.

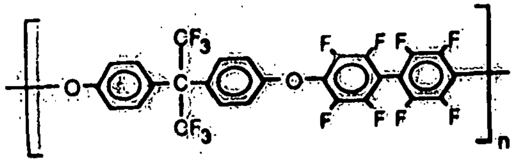
Polymerization of BPAF with decafluorobenzene for 1 day at room temperature yielded a high molecular weight linear polyether. Since no crosslinking was evident, the reaction temperature was increased to 60 °C for shorter reaction times. again, high molecular weight polymer, **14F-poly(ether ether)**, was obtained, an indication of decafluorobenzene's difunctionality towards nucleophilic substitutions. Films of material cast from chloroform solutions were clear, colorless, tough, and creasable. A UV-visible spectrum of the polymer showed optical transparency or >90% transmittance from 300-900 nm as seen in **Figure 1**. Polymerization of BPA with decafluorobenzene yielded a polyether, **6H8F-poly(ether ether)**, which formed clear, colorless and tough films when cast from chloroform solutions. The UV-visible spectrum of this polymer was virtually identical the BPAF-derived polyether. These results show that the 6F group located between the bisphenol portion of the polyether does not improve UV-visible transmittance as compared to the 6H moiety in this series of polymers. However, the 6F group will most likely be more resistant than the 6H group



14F-Poly(ether ether)



6H8F-Poly(ether ether)



Operator: Jennifer Ash
Date: 5/14/90
Trace: 1
Sample identity:
Percentage Transmission mode
Ordinate Maximum 100.0
Ordinate Minimum 0.0
Upper Wavelength 600.0 nm.
Lower Wavelength 200.0 nm.
Scan Speed 100.0 nm/min.
Bandwidth 1.0 nm.
Time Constant 0.5 sec
0 Peak(s) detected

Film thickness 1.0 mil
cast from chloroform.

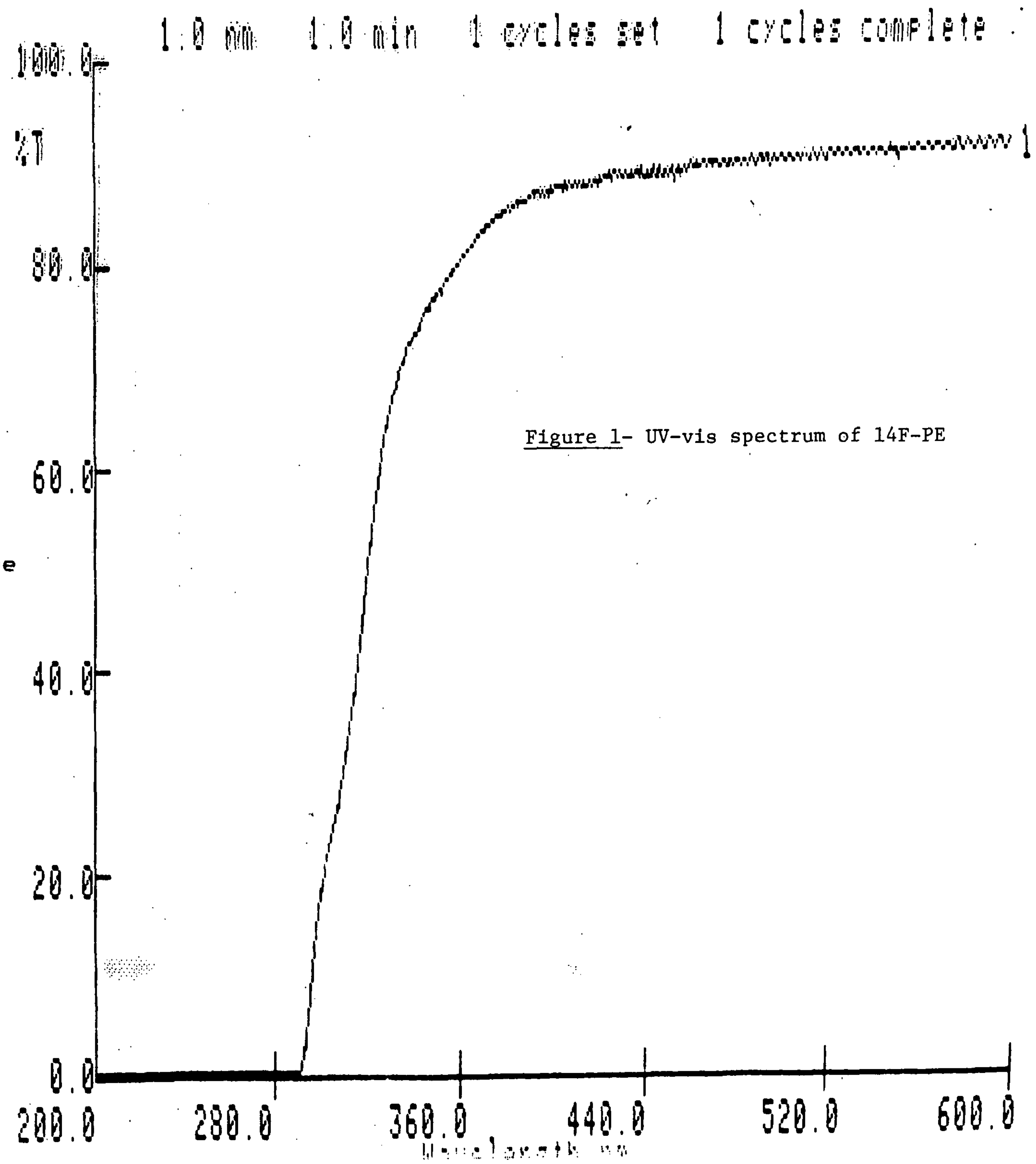


Figure 1- UV-vis spectrum of 14F-PE

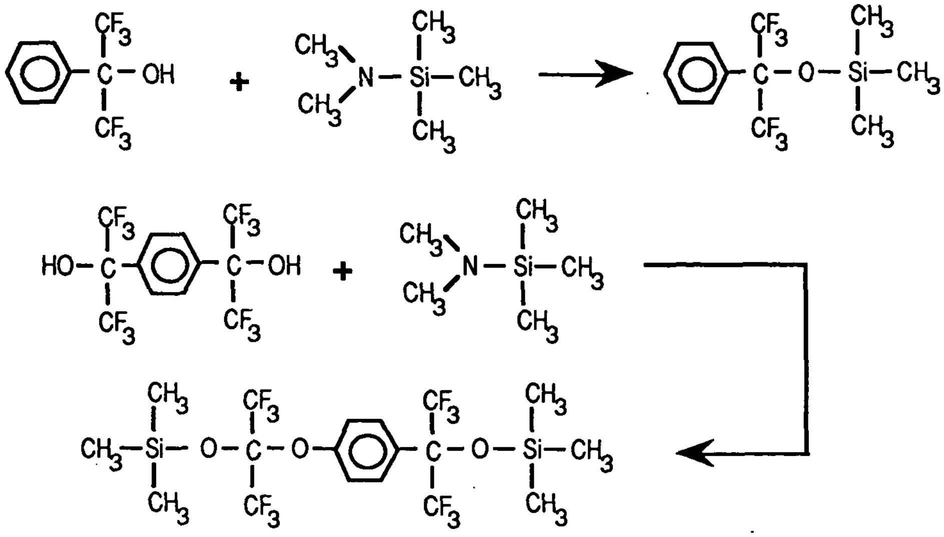
to intense UV radiation and thus present a gradual loss in UV transmittance under harsh conditions.

4.0 Novel fluorine-containing aromatic polysiloxanes

Our research efforts in this area involve synthesizing polymers containing the [C$(CF_3)_2$-O-SiR_2-O] function in backbones. We are very excited about the potential for these new backbones because we anticipate outstanding properties. A related compound, 2,2-dimethyl-4,4,5,5-*tetrakis* (trifluoromethyl)-2-sila-1,3-dioxolane, is known[4] and gives some indication of the properties to be anticipated in the new polymers. It is stable in boiling water, dilute acids and concentrated H_2SO_4, and it is unaffected when heated in a sealed tube at 350°c for one day.

We expect our new polymers to be highly flexible, thermally stable, high temperature elastomers. They will also be transparent, non-adherent, and resistant to most solvents. In addition we anticipate resistance to atomic oxygen as well as U.V. radiation. Crosslinking *via* siloxane linkages should be relatively simple using well known silicone technology, and property fine-tuning will be easily accomplished by varying the R-groups attached to silicon and the length of the siloxane block.

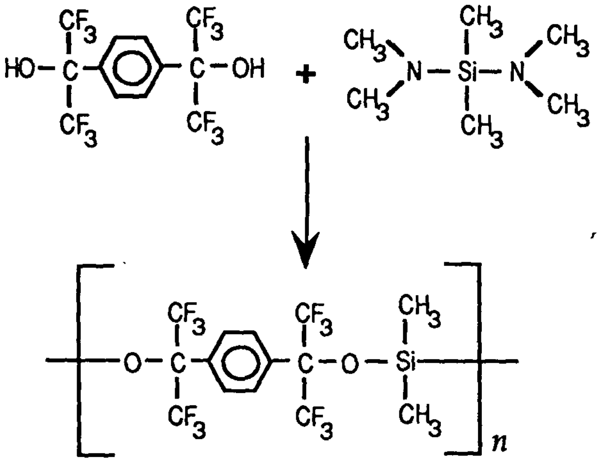
The progress that has been made thus far on this polymer system has been to study the reactivity of aromatic hexafluoropropanols by condensing the mono- and diols with a monoaminosilane, as shown in **Scheme VII**.



Scheme VII- Reactions of 6F-carbinols with Aminosilanes

The 6F- and 12F-carbinols appear to be highly reactive with the aminosilanes and the reaction may be complete in less than one hour. To ensure completion, however, reactions have been run for at least 8 hours at reflux. The model reactions gave quantitative yields of the siloxanes. Spectral analysis (IR and NMR) and elemental analysis confirm the structures of products to be the desired compounds.

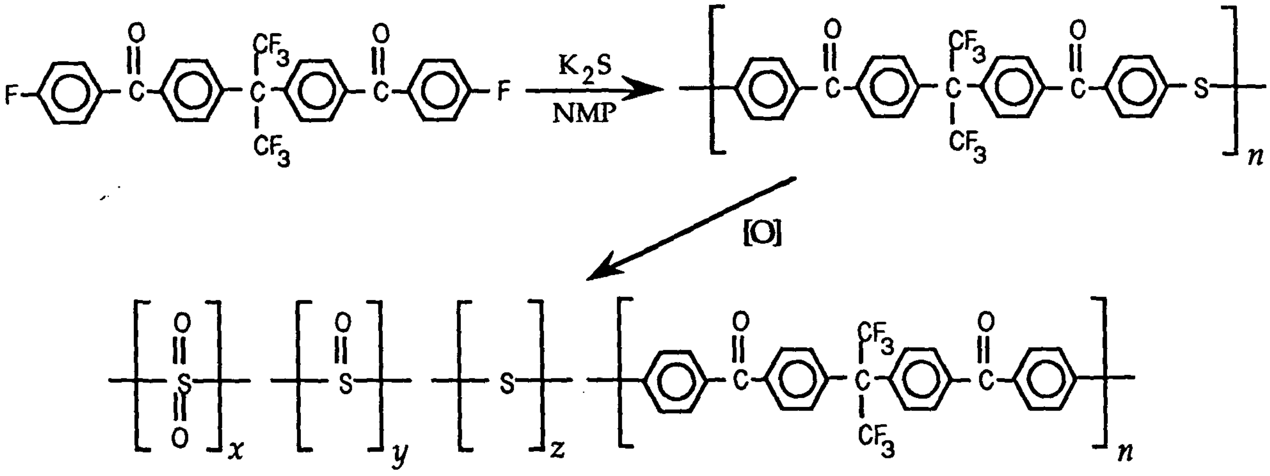
Several attempts have been made to polymerize 1,4-*bis*-(2-hydroxyhexafluoropropyl)benzene with *bis*-(*N,N*-dimethylamino) dimethylsilane (**Scheme VIII**). The first reaction yielded a polymeric material with an inherent viscosity of 0.14 dL/g in THF. The material swells in chloroform and DMAc and is slightly soluble in these solvents. Recent polymerization attempts have not met with success. Research on these polysiloxanes is continuing with great interest.



Scheme VIII- 6F-Containing Polysiloxane

5.0 Oxidation of Poly(ketone thioethers) to Poly(ketone sulfones).

We have recently synthesized a new aromatic 6F-poly(ketone thioether) [6F-PKT] from K_2S and the 6F-bisfluoride monomer shown in **Scheme IX**. This PKT was shown to be superior to Ryton® polysulfide in solubility and glass transition temperature, and comparable in thermal stability. 6F-PKT also presented a unique opportunity to study the chemical oxidation of polysulfides owing to PKT's excellent solubility in common organic solvents. Oxidation of 6F-PKT was carried out under a variety of conditions using several different types of reagents.



Scheme IX- Synthesis and Subsequent Oxidation of 6F-PKT

A single batch of 6F-PKT was prepared and then samples were oxidized in solution, as films, or as powders. Oxidation was conducted under acidic, basic, phase-transfer conditions in homogeneous and heterogeneous systems. All oxidation methods yielded to some extent the conversion of thioether to sulfone but the most successful oxidation occurred using tetrabutylammonium permanganate in a water/methylene chloride solvent system.

In most cases, the reaction product was a nearly colorless material, soluble in chloroform and readily cast into films, and still retained the high thermal stability of the brown polysulfide (>505 °C in air). Interestingly, any reaction conducted under basic conditions resulted in the formation of phenolic endgroups. This is suggestive of nucleophilic attack by hydroxide on the polysulfide linkage. Work on this study in continuing and is near completion.

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2. S. Dirkilov and Y. Feng, Proceedings of the 3rd International SAMPE Electronics Conference, Vol. **34**, pp. 169-180, June 20-22,1990.

3. R. Kellman, D. Gerbi, R. Williams, and J. Morgan, ACS Polymer Preprints, **21** (2), 164-165, (1980).

4. R.A. Braun, U.S. Pat. 3,433,819 (1969).)

PRESENTATIONS AND PUBLICATIONS

The following publications were issued and presentations made on the research work at SWT conducted under the auspices of the NASA grant #NAG-1-631.

P. E. Cassidy, A. K. St. Clair, and G. L. Tullos, "Low Dielectric Fluorinated Poly(ether-ketone) Film and Coating", U. S. Patent No. 4,902,769, February 20, 1990.

D. W. Reynolds, P. E. Cassidy, C. G. Johnson, and M. L Cameron, "Exploring the Chemistry of the 2-Aryl-hexafluoro-2-propanol Group: Synthesis and Reactions of a New, Highly Fluorinated Monomer Intermediate and Its Derivatives", Journal of Organic Chemistry, **55**, 4448-4454, (1990).

M. L. Cameron, K. M. Kane, P. E. Cassidy, and G. L. Tullos, "Film-forming Polymers Derived from Hexafluoroacetone" a poster presented at the ACS Symposium on Polyimides and Other High Performance Polymers Conference, January 21-24, 1990, in San Diego, CA.

M. L. Cameron, P. E. Cassidy, and K. N. Ludwig, "Polymers Derived from Hexafluoroacetone: 6F Poly(ketone thioether) [6F-PKT]", a poster presented at the April 1990 ACS National Meeting, Boston, MA. Polymer Preprints, **31** (1), 297, 1990.

D. W. Reynolds, P. E. Cassidy, C. G. Johnson, and M. L. Cameron, "Exploring the 2-Arylhexafluoroisopropanol Group: Synthesis and Reaction of a New Highly Fluorinated Monomer Intermediate and Its Derivatives", a poster presented at the April 1990 ACS National Meeting, Boston, MA. Polymer Preprints, **31** (1), 299, 1990.

D. J. Irvin, P. E. Cassidy, and M. L. Cameron, "Copoly(imide amides) Containing Hexafluoroisopropylidene", presented at the 4th International SAMPE Electronics Conference, June 12-14, 1990, Albuquerque, NM.