SUMMARY OF RESEARCH

NASA Research Grant/Cooperative Agreement: NCC-1-376

"Low Dielectric Polymers"

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National Aeronautics and Space Administration Langley Research Center

Hampton, Virginia 23681-2199

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INTRODUCTION

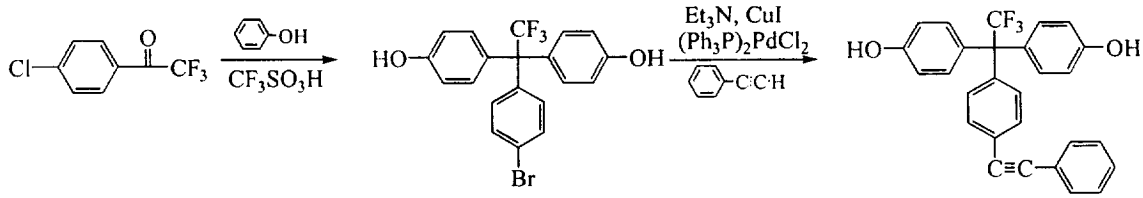
This report summarizes results obtained through our current research effort entitled "Low Dielectric Polymers". Results are reported in four areas [Tasks 1-4 in original proposal – Task 5 has been abandoned because of the difficulty involved in the preparation of the cardo-diphenol monomer (Compound 7 in the original proposal)]:

- Development of an alkyne – containing crosslinking agent for 12F-PEK and its analogues:
- Preparation and evaluation of new silicon-and/or fluorine-containing polymers for low temperature applications
- Polymers derived from a new highly fluorinated monomer.
- Continued evaluation of the scale-up of the preparation of 6FC11- and 6FC17-PEKs.

RESULTS

- **Development of an Alkyne-containing Crosslinking Agent for 12F-PEK and its Analogues**

Using established literature procedures, an alkynyl-substituted bisphenol, **1**, has been prepared.



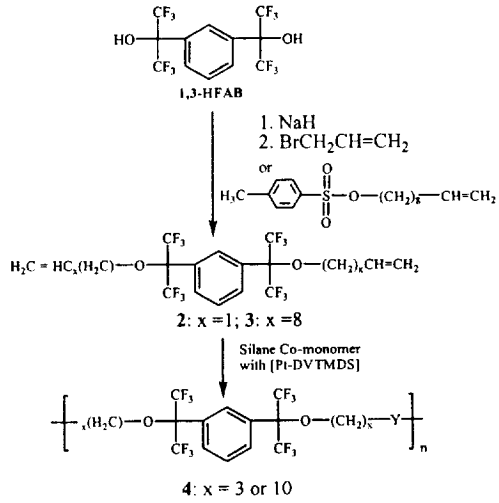
1

Preliminary results indicate that 12F-PEK can be modified by substituting **1** for part of the Bis-AF monomer in the preparation of the polymer. This soluble, modified 12F-PEK (at a 4% loading of the crosslinking monomer) was rendered insoluble by heating for one hour each at

100°, 200° and 350°C. It must be emphasized that this result is preliminary and will require additional study and replication.

- **Preparation and Evaluation of New Silicon and/or Fluorine-containing Polymers for Low Temperature Applications.**

Recently obtained results obtained in this area are promising. The diol, 1,3-HFAB, has been alkylated with allyl bromide and 10-bromo-1-decene to yield monomers **2** and **3** respectively, with varied distances between the HFAB moiety and the site of polymerization. The divinyl monomers were polymerized with the disilanes and siloxanes and karstedt's catalyst both in supercritical carbon dioxide (SC CO_2) (80°C, 5000 psi) and in benzene to form the polymers **4** as shown in Scheme 1.



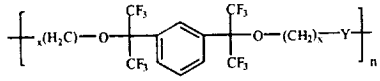
Scheme 1

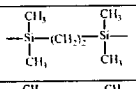
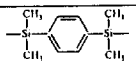
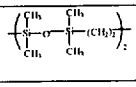
The molecular weights of these polymers are summarized in Table 1. Polymers obtained from SC CO_2 exhibited higher molecular weights compared with those obtained in benzene.

The thermal stability in air or argon and the glass transition temperatures (Tg) of these polymers are listed in Table 2. TGA data for these polymers showed that the short chain (x=3)

polymers started decomposing at 268°C, while long chain (x=10) polymers started at 289°C in air. Tgs ranged from –67 to -26°C.

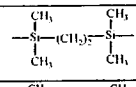
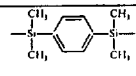
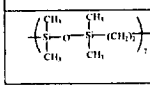
Table 1. Polymers Molecular Weights – Benzene vs SC CO_2



Y	x	Mn*		Mw*		Polydispersity	
		Benzene	SC CO_2	Benzene	SC CO_2	Benzene	SC CO_2
	3	5200	8000	6600	10900	1.29	1.35
	10	7600	10700	13000	13300	1.70	1.25
	3	3500	5300	5100	8600	1.45	1.60
	10	6400	24600	10000	41700	1.53	1.69
	3	2700	3600	3500	4800	1.34	1.28
	10	5900	10000	12400	18700	2.10	2.05
	3	4900	10000	6300	15000	1.28	1.50
	10	4800	5100	9700	16700	2.01	1.60
	3	2400	4000	3000	5600	1.24	1.38
	10	9400	10600	13300	24900	1.40	2.34

* by GPC

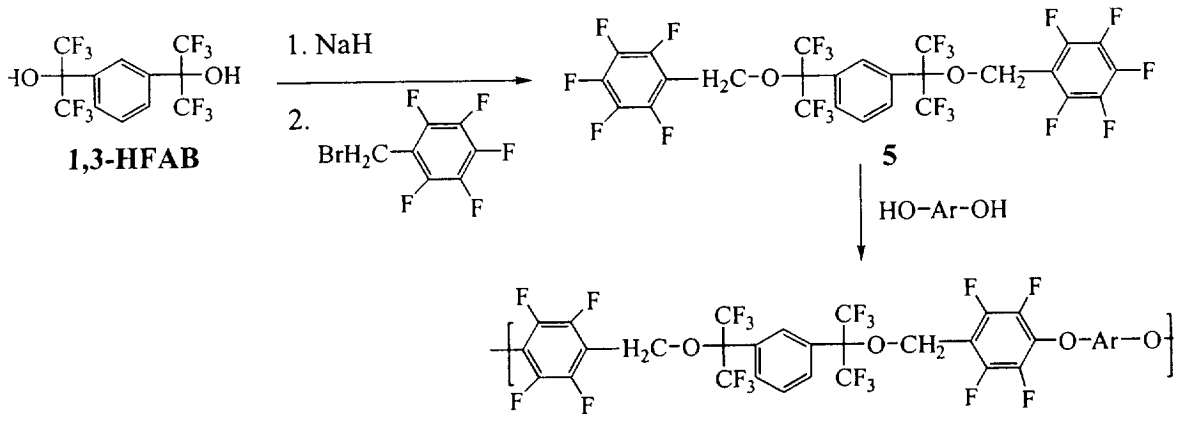
Table 2. Thermal Properties of Polymers

Y	x	Tg (°C)	TGA (10% wt loss)		% char Yields (600°C)	
			Air	Argon	Air	Argon
	3	-26	287	291	2	0
	10	-38	330	397	2	1
	3	-41	321	307	4	0
	10	-32	289	306	2	0
	3	-53	249	265	1	1
	10	-67	314	376	4	1
	3	-48	317	350	4	0
	10	-59	307	354	6	0
	3	-50	268	283	4	1
	10	-59	336	368	3	5

- **Polymers Derived from a New Highly Fluorinated Monomer**

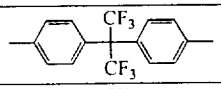
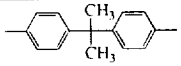
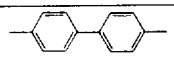
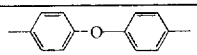
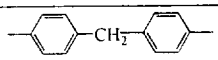
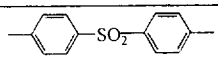
Work continues on the polymerization of our new highly fluorinated monomer **5** with bisphenols to give fluorinated polyethers (Scheme 2). The polymers are soluble in common organic solvents from which colorless films are readily formed. The properties of these

promising new materials are summarized in Table 3. The reason for the tremendous variations in molecular weights is not obvious, but might come about through hyper branching. It is known that reaction conditions must be carefully controlled to obtain soluble polymers because of the possibility of multiple fluoride displacement in the pentafluorophenyl group-containing monomer. The constant of the polymer derived from 4,4'-dihydroxydiphenyl ether has been determined to be 2.38 at 10GHz.



Scheme 2. Synthesis of Highly Fluorinated Polyethers

Table 3: Selected Properties of Highly Fluorinated Polyethers

Ar	η dL/g	Mw	PD	Tg (°C)	TGA (10% wt loss)		% Char Yields (800°C)	
					Air	Argon	Air	Argon
	0.41	43,000	2	111	424	456	2	12
	0.98	338,000	8	103	436	464	2	23
	0.57	215,000	3	112	420	451	0	18
	0.4	349,000	6	93		454		23
	0.41	25,000	2	83	438	445	29	27
	0.12	18,000	2	114	420	406		24

- **Continued Evaluation of the Scale-up of the Preparation of 6FC11 and 6FC17-PEKs.**

  Scale-ups of both of these preparations proceed without complication.

List of Publications/Presentations:

1. Welsch, R.; Blanda, M.T.; Venumbaka, S.R.; Cassidy, P.E.; Fitch, J.W., "Hydrosilation Polymerizations with Diallyl Monomer-Benzene solution Vs Supercritical Carbon Dioxide" *Polymer Preprints*, **2001**, 42(1), *159.*
2. Zhou, H.; Venumbaka, S.R.; Fitch, J.W.; Cassidy, P.E., "Synthesis of Crosslinkable Poly(carbosilane/siloxane)s by Hydrosilation in Toluene and Supercritical Carbon Dioxide" *Polymer Preprints*, **2001**, 42(2), *368.*
3. Gronewald, S.; Cassidy, P.E.; Fitch, J.W.; Arbaugh, J.; Herbold, H.; Jurek, D., "Poly(aryl ether ketones) bearing Alkyl side Chains" *High Perform. Polym.* **2001**, 13, *S117.*
4. Fitch, J.W.; Reddy, V.S.; Youngman, P.W.; Wohlfahrt, G.A.; Cassidy, P.E., "Polyether Ketones derived from bis[4-(4-fluorobenzyl)phenyl]phenylphosphine oxide" *Polymer Communication*, **2000**, 41, *2301.*