

SUMMARY OF RESEARCH
(ANNUAL STATUS REPORT)

NASA Research Cooperative agreement: NCC-1-01033

“Low dielectric Polymers”

Termination Date: 05/09/02

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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 from research funded through Research Cooperative Agreement No. NCC-1-01033-“Low Dielectric Polymers” (from 5/10/01 through 5/09/02).

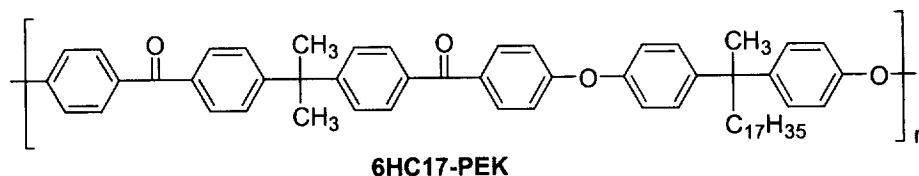
Results are reported in three of the proposed research areas (Tasks 1-3 in the original proposal):

- **Repeat and confirm the preparation and properties of the new alkyl-substituted PEK, 6HC17-PEK**
- **Prepare and evaluate polymers derived from a highly fluorinated monomer**
- **Prepare and evaluate new silicon and/or fluorine-containing polymers expected to retain useful properties at low temperature**

RESULTS

- **Repeat and Confirm the Preparation and Properties of the New Alkyl-substituted PEK, 6HC17-PEK**

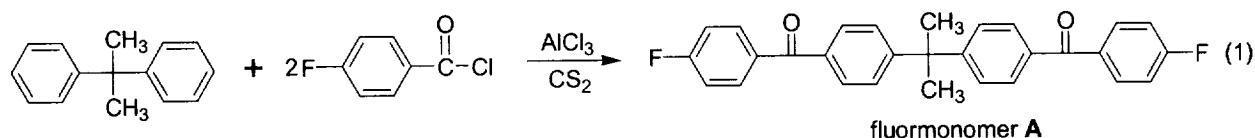
As indicated in the proposal, the non-fluorinated PEK, 6HC17-PEK, is of interest to NASA because a film of this material prepared some time ago exhibited unusual and potentially useful



properties. This first sample of this material produced a tough, white, opaque film (looking very much like Teflon[®]) which had a dielectric constant of 1.74. The C&H analysis of this material was low; C₆₀H₆₈O₄ (Found: %C = 79.16, 80.79; %H = 7.36, 7.97. calc.: %C = 84.51; %H = 7.98), and GPC analysis of this material indicated M_n=10,260, M_w = 22,950 and a polydispersity

of 2.24. The 6HC17-PEK was resynthesized (the standard synthetic protocol used was very labor intensive and time consuming) to yield a second sample of the polymer, 6HC17-PEK-2. This polymer is virtually identical to the first sample. However, the film of 6HC17-PEK-2 was translucent, rather than opaque, and has a dielectric constant of 2.54. Clearly these contradictory results must be reconciled.

In order to address the difficulty in the preparation of the activated fluoro-monomer precursor, **A**, a new synthesis of this material was developed (eq.1).



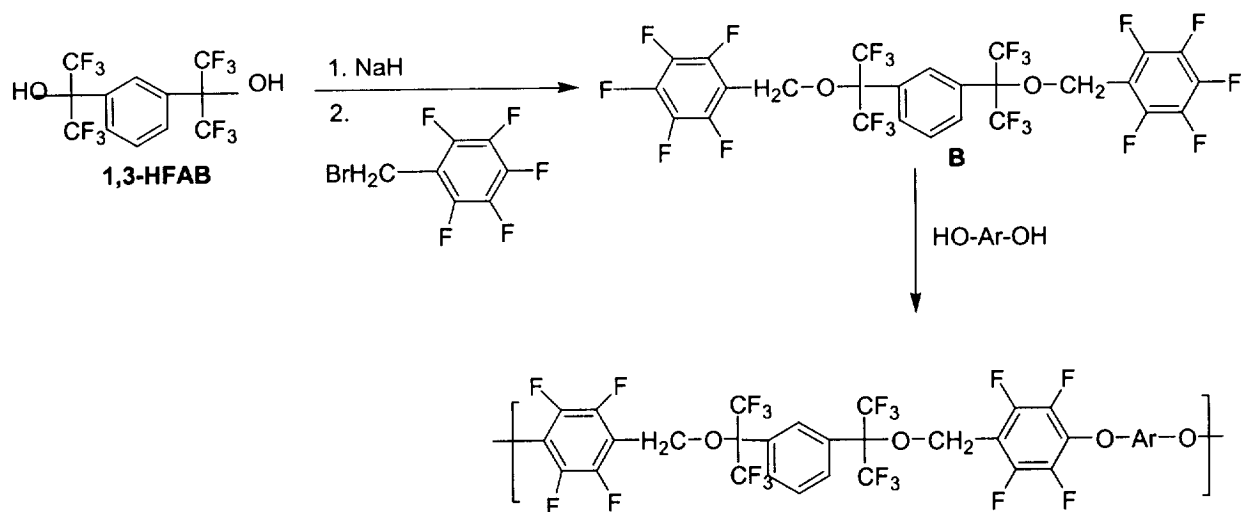
Yields of **A** as high as 70% have been obtained in CS₂ after reaction for three to five days at 46°. This new synthesis allows for a much simplified procedure for the preparation of **A**, and ultimately of 6HC17-PEK.

A recent report by M. Srinivasarao, *et al.* (*Science*, **2001**, 292, 79), which has been forwarded to us by our NASA-LRC technical director, may have direct bearing on the variability of the dielectric properties of 6HC17-PEK. The report suggests that microporous films are formed when the humidity, solvent and evaporation rates are properly controlled. This possible phenomenon is under active investigation and preliminary results look very promising. Consideration is being given to a possible patent for this technique.

- **Prepare and Evaluate Polymers Derived from a Highly Fluorinated Monomer.**

Work continued on the polymerization of our new highly fluorinated monomer, **B**, with bisphenols to give fluorinated polyethers (Scheme 1). As noted in the proposal, rather large variations in molecular weight and polydispersities, which were suggested to be due to possible

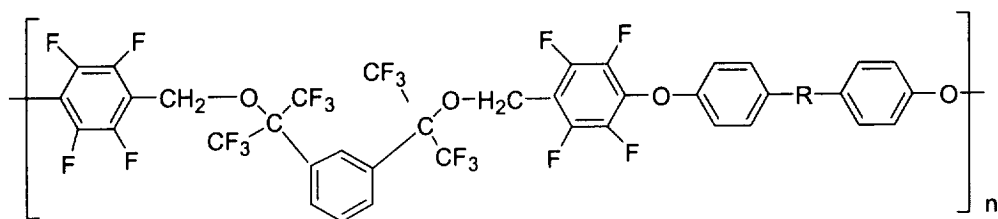
hyper-branching, were observed for these polymers. Additionally, good film forming polymer samples have been difficult to obtain reproducibly. When the polymerization reaction is conducted at elevated temperatures insoluble gels are obtained which are presumed to be

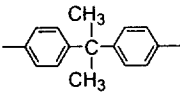
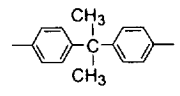
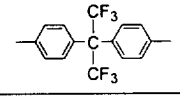
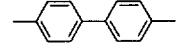
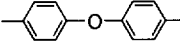
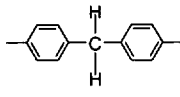


Scheme 1. Synthesis of Highly Fluorinated Polyethers

crosslinked through multiple nucleophilic substitution of the aromatic fluorines. On the other hand, if the reactions are performed at room temperature, low molecular weight materials are formed. For these reasons an extensive study directed toward optimization of reaction conditions for the reproducible production of these polymers in reasonable yield with good molecular weights and polydispersities has been conducted. The results of this study are summarized in Table 1. Film forming polymers are obtained in 85-90% yield when the polycondensation is conducted in DMAC at 40° for 24 hours. Molecular weights are acceptable and polydispersities range from 1.8 to 3.4. The dielectric properties of films of these polymers are under investigation at NASA-Langley Research Center. The earlier value of 2.38 which was obtained at NASA-LCR for the polymer derived from 4,4'-dihydroxydiphenylether suggests that the entire series of polyethers should have excellent dielectric properties.

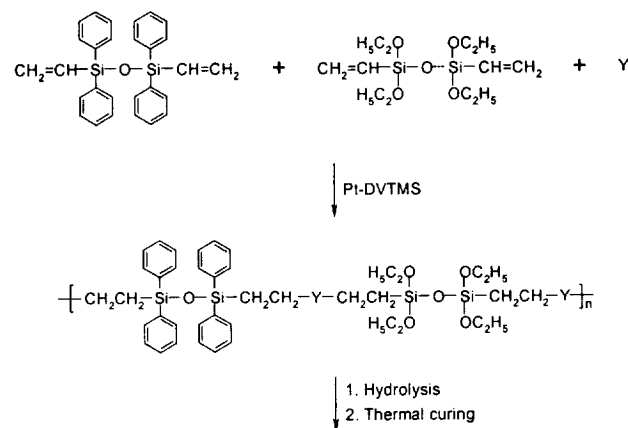
Table 1. Highly Fluorinated Polyethers



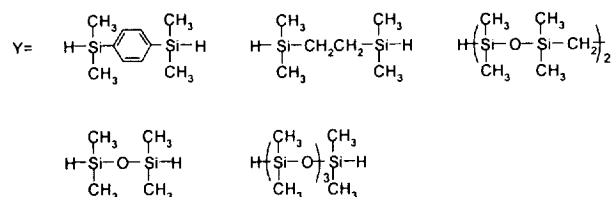
Diphenol	Mn (GPC)	Mw (GPC)	PD	TGA (10%wt loss) Argon	%Char Yield (800°C) Argon	Tg (°C) (DSC)	Water Contract Angle (23°C)
 Room Temperature	58,700	140,000	2.4	464	23	103	90 ± 1
	75,300	247,300	3.2	464	23	102	93 ± 1
	84,300	224,200	2.6	456	12	108	91 ± 1
	66,300	226,400	3.4	451	18	110	90 ± 2
	77,600	200,200	2.6	454	23	92	90 ± 2
	34,600	64,100	1.8	445	27	89	92 ± 2

- Prepare and Evaluate New Silicon- and/or Fluorine-containing Polymer Expected to Retain Useful Properties at Low Temperature.**

The feasibility of obtaining crosslinkable polymers in which Tg does not increase appreciably upon crosslinking has been demonstrated using the reaction of a mixture of 1,1,3,3-tetraphenyl-1,3-divinyldisiloxane (95mol%) and 1,1,3,3-tetraethoxy-1,3-divinyldisiloxane (5mol-%) with selected silicon-containing disilanes (Scheme 2, Tables 2 and 3).

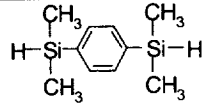
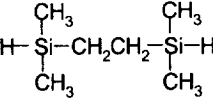
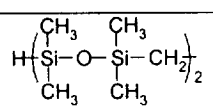
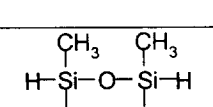
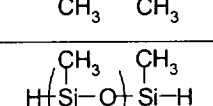


Crosslinked Polymer



Scheme 2. Synthesis of polymers

Table 2. Properties of Crosslinkable Polymers

Y	Mw ^a x10 ⁻³	PD	Tg ^b (°C)	TGA (°C 10% wt loss)		% Char Yield (@ 600°C)	
				Air	Argon	Air	Argon
	11	3.1	24	427	454	50	51
	15	1.5	0	392	421	40	22
	39	2.3	-26	393	398	35	23
	6	1.6	-12	347	350	36	35
	28	1.9	-32	421	426	33	24

a: measured by GPC; b: measured by DSC

Table 3. Properties of Polymers After Hydrolysis^d and Thermal Curing^e

Y	Mw ^a x10 ⁻³	PD	Tg ^b (°C)	TGA (°C 10% wt loss)		% Char Yield (@ 600°C)	
				Air	Argon	Air	Argon
	38	9.3	29	435	481	51	37
	115	11.8	9	351	454	26	16
	49	2.8	-25	371	377	15	8
	10	2.1	1	357	373	19	10
	-- ^c	-- ^c	-26	371	488	37	23

a: measured by GPC; b: measured by DSC; c: partially soluble in THF; d: hydrolysis in wet (2% H₂O) diglyme at 80 °C for 24 h; e: thermal cure *in vacuo* at 135 °C for 48 h.

The molecular weights of the crosslinkable silicon-containing polymers ranged from 6,000 to 39,000. After hydrolysis and thermal curing, the molecular weights of the polymers increased and ranged from 10,000 to 115,000. The relationship between the molecular weight and the curing time was studied by varying the curing time (Figure 1). The results indicated that higher molecular weight polymers could be obtained by increasing the curing time; however, in most cases they become partially insoluble.

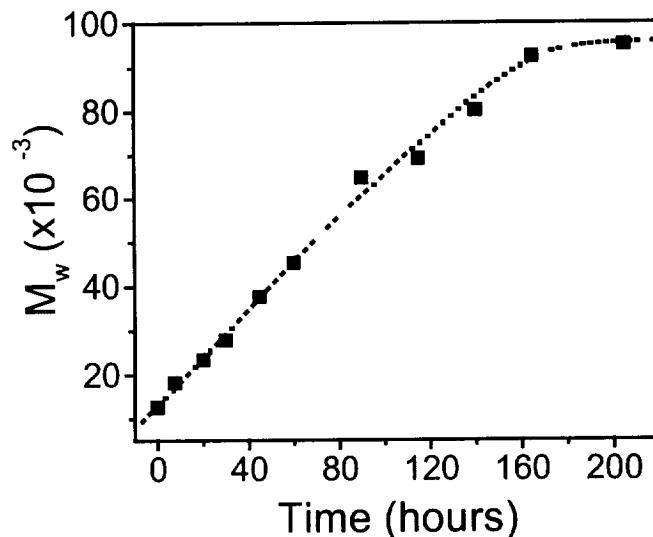
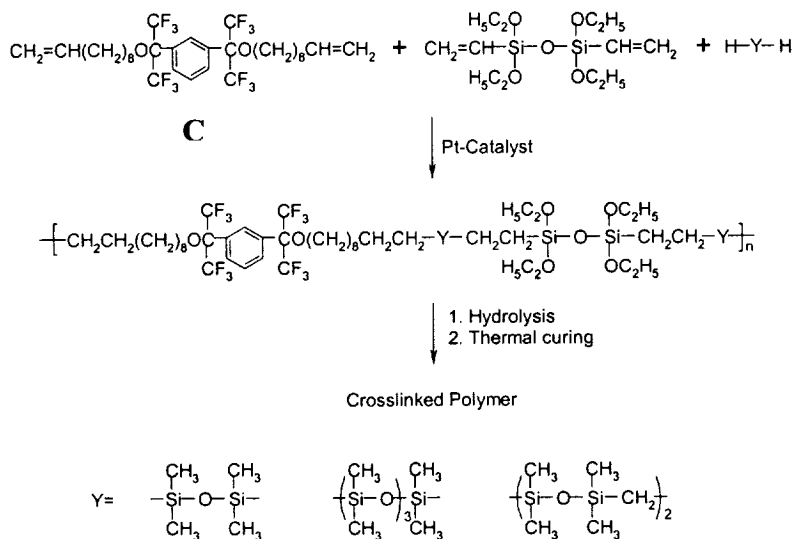


Figure 1. Molecular weight as function of thermal curing

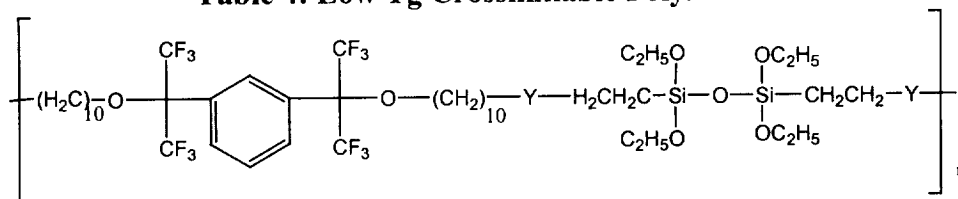
Finally, we have prepared a series of crosslinkable siloxane-containing polymers derived from the monomer labeled **C** in Scheme 3. These polymers were then hydrolyzed and thermally cured



Scheme 3. Synthesis of polymers

as described above (see footnotes in Table 3). As anticipated, the T_g s of the hydrolyzed and thermally cured polymers remains essentially unchanged (Table 4).

Table 4: Low Tg Crosslinkable Polymers



Y	Ethoxy-containing (5%) Polymers			Hyper Branched Polymers		
	Mw	PD	Tg(C°)	Mw	PD	Tg(C°)
$\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\ \quad \\ -\text{Si}-\text{O}-\text{Si}- \\ \quad \\ \text{CH}_3 \quad \text{CH}_3 \end{array}$	14,000	2	-49	56,000	5	-46
$\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\ \quad \\ (\text{Si}-\text{O})-\text{Si}- \\ \quad \\ \text{CH}_3 \quad \text{CH}_3 \end{array}$	41,000	3	-63	402,000	6	-60
$\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\ \quad \\ (\text{Si}-\text{O}-\text{Si}-\text{CH}_2)_2 \\ \quad \\ \text{CH}_3 \quad \text{CH}_3 \end{array}$	35,000	3	-56	156,000	8	-55

In summary, this research supports the conclusion that the degree of crosslinking and/or hyperbranching in these systems can be controlled by changing the initial mol-% of the ethoxysilane monomer and by varying the cure time (during which we suggest that Si-OH groups formed by hydrolysis crosslink through dehydration to form disiloxane bonds). The curing protocol could yield either a crosslinked or a hyperbranched system. Because the polymers increase their molecular weights after hydrolysis and curing, but remain soluble, they are either very lightly crosslinked or, more probably hyper-branched. Insolubility, however, can easily be achieved by increasing the percent of the hydrolyzable monomer in the original polymer and/or extending the cure time. Probably the most significant observation for these polymers is the relative insensitivity of Tg to this light crosslinking protocol. Our working hypothesis toward achieving the goal of a material retaining good flexibility from -40°F to +200°F has been to target low Tg materials which eventually can give lightly crosslinked (or hyper-branched) products retaining a low Tg. It should be mentioned at this point that other potentially

crosslinkable silicon functionalities, such as acetoxy, may eventually be more practical than the ethoxysilane chosen for this initial work. They can be readily substituted in the future if required without changing reaction protocols. One potential difficulty with these and all of the polymers prepared by hydrosilation polymerization is their dark color. It is thought that the color originates from small amounts of residual platinum compounds remaining in the materials.

PUBLICATIONS/PRESENTATIONS:

1. K. Kimura, Y. Yamashita, V. S. Reddy, J. W. Fitch, III and P.E. Cassidy, "(2,3,4,5,6-Pentafluorobenzoyl) Diphenyl Ether Compound, Method for Production Thereof, Fluorine-Containing Aryl Ether Ketone Polymer, and Method for Production Thereof" (in press).
2. H. Zhou, S. R. Venumbaka, J. W. Fitch and P. E. Cassidy, "Novel Synthesis of Crosslinkable Fluorinated Polysiloxanes by Hydrosilation in Toluene and Supercritical Carbon Dioxide" *Polymer Preprints*, **43(1)**, 617 2002.
3. H. Zhou, S. R. Venumbaka, J. W. Fitch and P. E. Cassidy, "Synthesis of Crosslinkable Poly(Carbosilane/siloxane)s by Hydrosilation in Toluene and Supercritical Carbon Dioxide" *Polymer Preprints*, **42(2)**, 368 2001.
4. R. Welsch, M. T. Blanda, S. R. Venumbaka, P. E. Cassidy and J. W. Fitch, "Hydrosilation Polymerizations with Diallyl Monomer – Benzene Solution Vs Supercritical Carbon Dioxide", *Polymer Preprints*, **42(1)**, 159 2001.
5. X. Hu, M. T. Blanda, S. R. Venumbaka and P. E. Cassidy, "Ring-Opening Metathesis Polymerization of Norbornene in Supercritical Carbon Dioxide", *Polymer Preprints*, **42(1)**, 518 2001.