FINAL REPORT
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NEW RTM/RI RESINS FOR THE HSCT

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INTRODUCTION

The initial objective of this research was to utilize the chemistry of perfluorovinyl ethers in the development of RTM/RI resins and in the development of elastomers that could be used in high temperature fuel tank sealants. This research was carried out as part of the NASA funded High Speed Research (HSR) Program. The principal objective of the HSR Program was to develop technology to permit the Boeing Company to proceed with the development of a high speed civil treansport (HSCT). The HSCT in this program was a commercial passenger airplane for transoceanic flights that could fly at speeds approaching Mach 2.4. The requirements for a fuel tank sealant for this airplane included high elongation, moderate peel strength, fuel resistance, and stability at 177^0C for 60,000 h. The high temperature requirement was because aerodynamic heating while in flight at Mach 2.4 was projected to cause the fuel tank sealant (when the tank was empty) to reach temperatures approaching 177^0C.[1] **Since no commercial sealant met the requirements of the HSCT, our work was concentrated in this area.**

The most popular commercially available fuel tank sealant that can be used near 177^0C is based upon poly(3,3,3-trifluoropropylmethylsiloxane) (fluorosilicone). Continued exposure of this polysiloxane to high temperatures, however, results in nearly 80 % conversion to cyclic degradation products.[2] The depolymerization is thought to proceed through an intramolecular four-centered transition state that leads to the formation of predominantly six and eight-membered siloxane rings.[3] It has been postulated that if a rigid repeat unit were placed between no more than two siloxane repeat units (an alternating copolymer), the primary degradation process would not occur.[4]

Several researchers have prepared silanol-functionalized monomers that were copolymerized with siloxane monomers to form alternating copolymers.[4-6] For example, silalkarylene-siloxane and silarylene-siloxane copolymers have been synthesized that display increased thermal stability. However, the incorporation of the rigid repeat units also significantly increased the glass transition temperature (Tg), which prevented the use of the copolymers as sealants. Recent work has suggested that perfect alternation of the monomers is not necessary due to a thermal isomerization process that randomizes silphenylene-siloxane copolymers at temperatures below their degradation temperature.[7] This is consistent with other studies that have shown that polysiloxanes undergo both intramolecular and intermolecular exchange reactions at temperatures below their degradation temperature.[8] In fact, Grassie found that incorporation of as little as 15 mol % silphenylene repeat units imparts considerable thermal stability to polydimethylsiloxane.[9]

This work was divided into three main parts. The objective of the first portion of this work was the preparation of a series of random fluorosilicone copolymers containing 1,2-catenated perfluorocyclobutane repeat units. The perfluorocyclobutane repeat unit has been shown to display excellent thermal stability.[10] The 1,2-catenation was expected to aid in the maintenance of a low Tg. The additional fluorine in the backbone of the polymer was also expected to result in enhanced fuel (hydrocarbon) resistance, relative to the silphenylene repeat unit. The approach selected involved the condensation of silanol-terminated fluorosilicone oligomers with silanol-terminated perfluorocyclobutanes. The effects of the incorporation of the cyclobutane repeat units on the copolymer Tgs, thermal stabilities, and resistance to hydrocarbons were then to be determined.

The objective of the second portion of this work was the preparation of trifluorovinyl-terminated siloxane monomers that could be polymerized and crosslinked via cyclodimerization. Specifically, two monomers 1,3-bis[4-trifluorovinyl(oxy) phenyl]1,3-(3,3,3-trifluoropropyl)dimethyldisiloxane and 1,3-bis[3-trifluorovinyl (oxy)phenyl]1,3-(3,3,3-trifluoropropyl)dimethyldisiloxane, were to be prepared and polymerized via the thermal cyclodimerization of terminal trifluorovinylether moieties. Crosslinked polymers were also to be prepared via the use of a tetrafunctional trifluorovinylether compound. All of the polymers were to be thoroughly characterized.

The objective of the final part of this work was the preparation and polymerization of a trifluorovinylether-terminated perfluoropolyether oligomer. The commerically available α,ω-hydroxy-terminated perfluoropolyether oligomer Fluorolink D^{R} was to be treated with two equivalents of 4-[trifluorovinyl(oxy)]benzoylchloride to afford the desired oligomer. The oligomer was then to be converted to a crosslinked network. The properties of the resulting elastomer were to be determined.

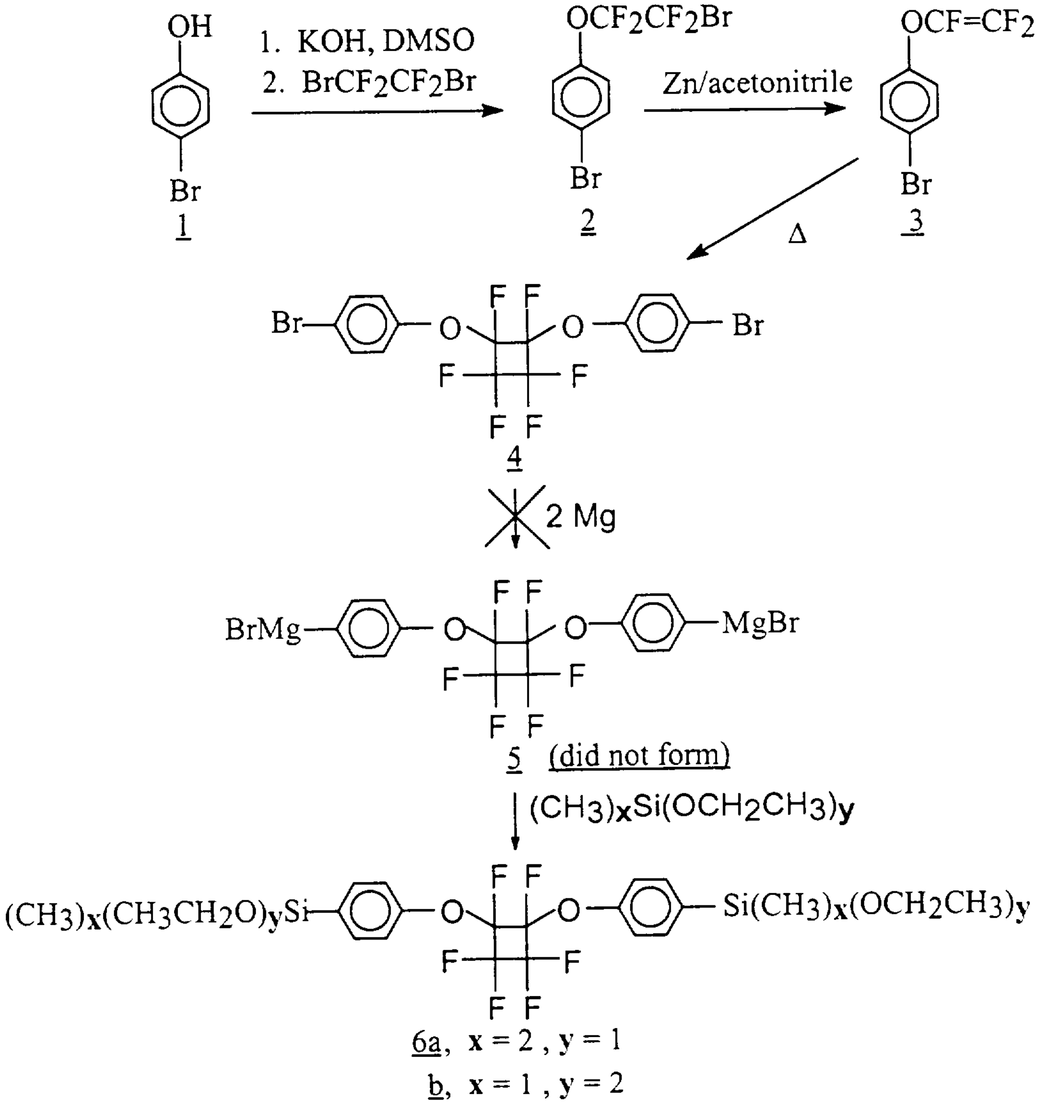
RESULTS AND DISCUSSION

1. ATTEMPTED POLYMERIZATION OF ALKOXY-TERMINATED PFCB-CONTAINING SILANES

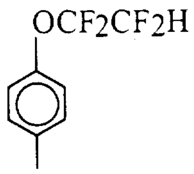
Synthesis of 1,2,3,3,4,4-hexafluoro-1,2-bis[4-(dimethylsilylethoxy)phenoxy] cyclobutane (6a) and of 1,2,3,3,4,4-hexafluoro-1,2-bis[4-(diethoxymethylsilyl) phenoxy]cyclobutane (6b)

The initial objective was to prepare ethoxysilane-functionalized PFCB-containing monomers (6a,b) and to copolymerize these monomers with silanol-terminated fluorosilicone oligomers. The first approach involved the preparation of compound 4 (Scheme 1). From 4, it was postulated that compounds 6a,b could be prepared using a Grignard reaction.

The sequence was begun with the preparation of compound 2 (Scheme 1). Treatment of 4-bromophenol with 1 equivalent of potassium hydroxide generated potassium 4-bromophenoxide. To the potassium salt was then added 1,2-dibromotetrafluoroethane. The water by-product in the first step had to be removed by azeotropic distillation over 3 days to prevent formation of the undesired byproduct 7. The presence of 7 (Figure 1) was easily detected by the absorption (triplet) at 5.5 ppm in the ^{1}H-NMR spectrum. An unusual mechanism involving the generation of tetrafluoroethylene has been invoked to account for the products of this reaction.[11,12] The yield of 2 was as high as 90% when the reaction was carried out in a small vessel where azeotropic removal of water under reduced pressure was very efficient. Compound 2 was then added to a suspension of zinc and acetonitrile over 4 h to effect dehalogenation. The fluoride ion elimination, which most likely proceeds via an organozinc intermediate, is promoted by the use of a polar solvent and slightly elevated temperatures (reflux temperature of acetonitrile). Rigorously dried solvents are again required in this reaction to prevent formation of compound 7, which can be generated by the reaction of the organozinc intermediate with water or any other protic source.


OH
1. KOH, DMSO
2. BrCF2CF2Br
OCF2CF2Br
Zn/acetonitrile
OCF=CF2
Br
1
2
3
Δ
Br
F F
O
F
4
2 Mg
BrMg
MgBr
5 (did not form)
(CH3)xSi(OCH2CH3)y
(CH3)x(CH3CH2O)ySi
Si(CH3)x(OCH2CH3)y
6a, x = 2 , y = 1
b, x = 1 , y = 2

Scheme 1



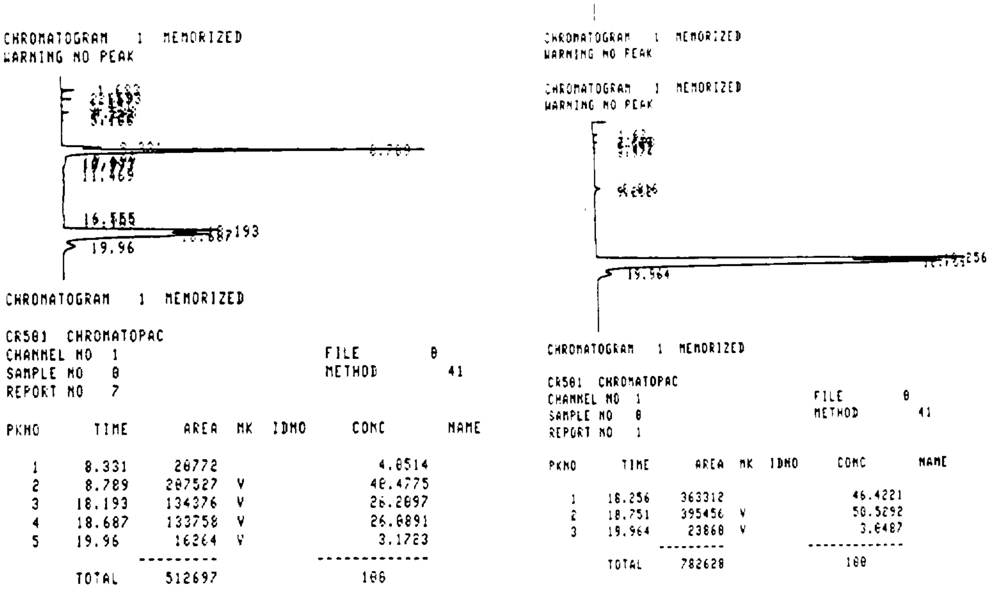
7

Figure 1. Structure of 4-[tetrafluoroethoxy]bromobenzene.

In addition, to maximize the yield of 3, it is important to slowly add 2 to the vigorously stirred refluxing reaction mixture. In order to prevent formation of a brown tar, oxygen had to be excluded by thoroughly flushing the reaction mixture with either argon or nitrogen before the addition of compound 2.

Cyclodimerization of compound 3 was carried out by heating at temperatures above 140^0C. HPLC revealed that when compound 3 was heated at higher temperatures (approximately 200^0C for 10 h), a significant amount of a byproduct formed that distilled at temperatures very close to the boiling point of 4 (Figure 2). In fact, the amount of this byproduct increased with longer reaction times and higher temperatures. Therefore, most of the preparative cyclodimerization reactions involving trifluorovinylether-containing atoms with homolytically weak bonds were carried out at temperatures below 175^0C to prevent undesired side reactions. Closer examination of the HPLC chromatogram revealed the presence of the two 1,2-disubstituted isomers (*cis* and *trans*) and a small shoulder peak, which was postulated to be the 1,3-disubstituted isomers.[13]

All attempts to form a Grignard reagent from 4 and magnesium in THF failed. Rigorous drying of the solvent, activation of the magnesium, and the use of entrainment agents such as 1,2-dibromoethane did not enable formation of the di-Grignard reagent 5. The same lack of reactivity was also observed in diethyl ether. Thus, a new approach was needed to prepare compounds 6a,b.



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WARNING NO PEAK

CHROMATOGRAM   1  MEMORIZED

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SAMPLE NO   0                          METHOD        41
REPORT NO   7

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   2      8.709      207527  V                   40.4775
   3     10.193      134376  V                   26.2097
   4     10.687      133758  V                   26.0891
   5     19.96        16264  V                    3.1723
                  ---------              --------------
          TOTAL      512697                    100
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A

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WARNING NO PEAK

CHROMATOGRAM   1  MEMORIZED
WARNING NO PEAK

CHROMATOGRAM   1  MEMORIZED

CR501  CHROMATOPAC
CHANNEL NO  1                          FILE        0
SAMPLE NO   0                          METHOD        41
REPORT NO   1

PKNO       TIME        AREA  MK  IDNO        CONC          NAME

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   2     10.751      395456  V                   50.5292
   3     19.964       23860  V                    3.0487
                  ---------              --------------
          TOTAL      782628                    100
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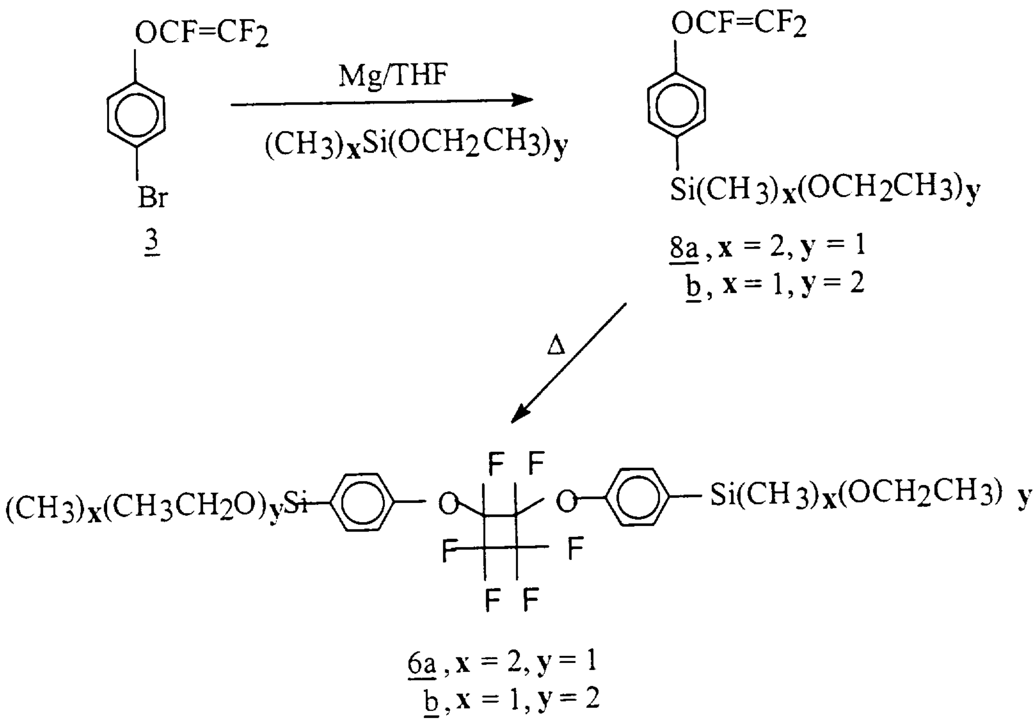
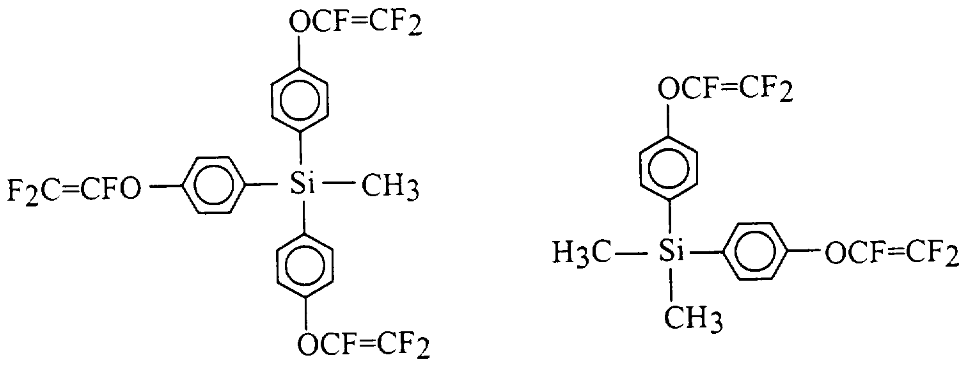
B

Figure 2. HPLC chromatograms of product(s) obtained after heating 3 at 200°C for 8 h (A) and 150°C for 8 h (B) to afford 4.

Smith and Babb had shown that 4-[trifluorovinyl(oxy)]bromobenzene (3) will react with magnesium to form a Grignard reagent.[10] Subsequent work by these authors showed that 3 will also react with organolithium compounds if the temperature is kept below -20°C.[14] Compounds 8a,b had been prepared by Wang in her attempt to prepare cyclic siloxanes with pendant trifluorovinylether moieties (Scheme 2).[15] Thus, the syntheses of 6a,b by the route shown in Scheme 2 were carried out. Compounds 8a,b were prepared by an *in situ* Grignard reaction. Compound 3 was added to a suspension of magnesium, THF, and either diethoxydimethylsilane or methyltriethoxysilane at reflux. Upon formation of the Grignard reagent of 3, the 5 equivalent excess of the ethoxysilane compound promoted formation of the mono-substituted product (8a or b).[16] In addition to 8a,b, a significant amount of the multi-functional compounds 9 and 10 most likely formed (Figure 3). However, these compounds were not isolated. Compounds 8a and b were separated by reduced pressure distillation. Reaction times longer than 4 h at reflux were necessary in order to ensure complete reaction of 3. The yield of this reaction was generally about 35-40 %.



Scheme 2



9

10

Figure 3. Structure of by-products of 9 and 10.

Compounds 8a and b were converted from 6a and b, respectively, by heating at elevated temperatures. The very large difference in boiling points between the trifluorovinylether compounds and the perfluorocyclobutane compounds allowed for an almost quantitative separation with one simple distillation. The yields of the cyclodimerization reactions were generally about 60-70 % after one heating cycle. The unreacted trifluorovinylether-containing starting materials were reheated to give additional product.

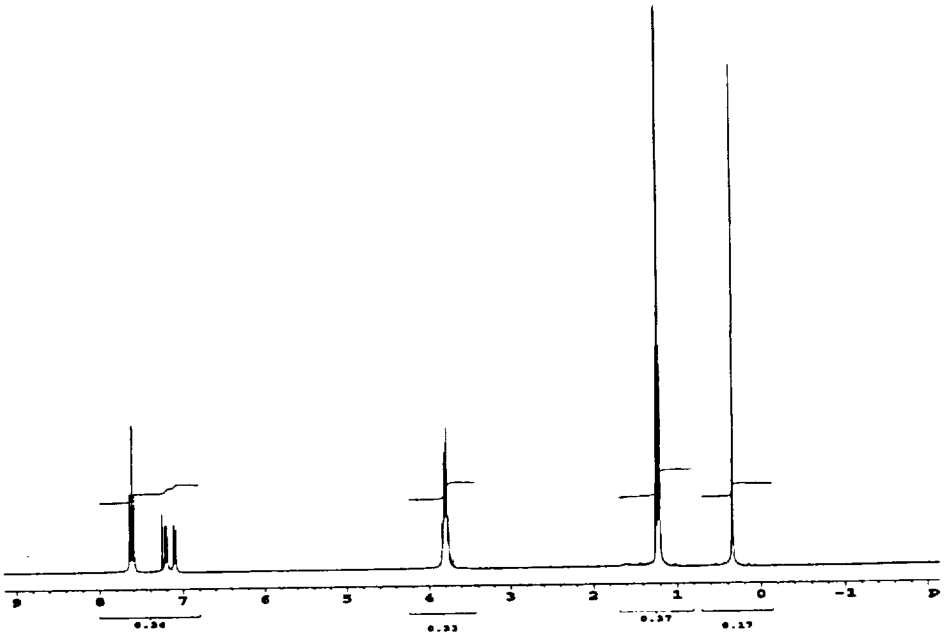
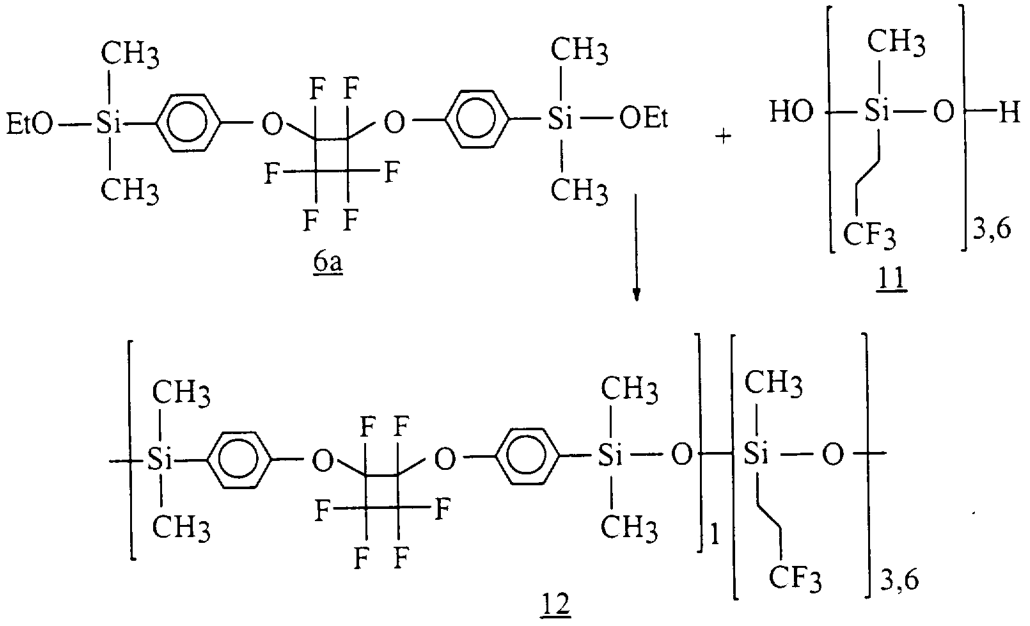


Figure 4. ^{1}H-NMR spectrum of compound 6b.

Attempted polymerization of compound 6a

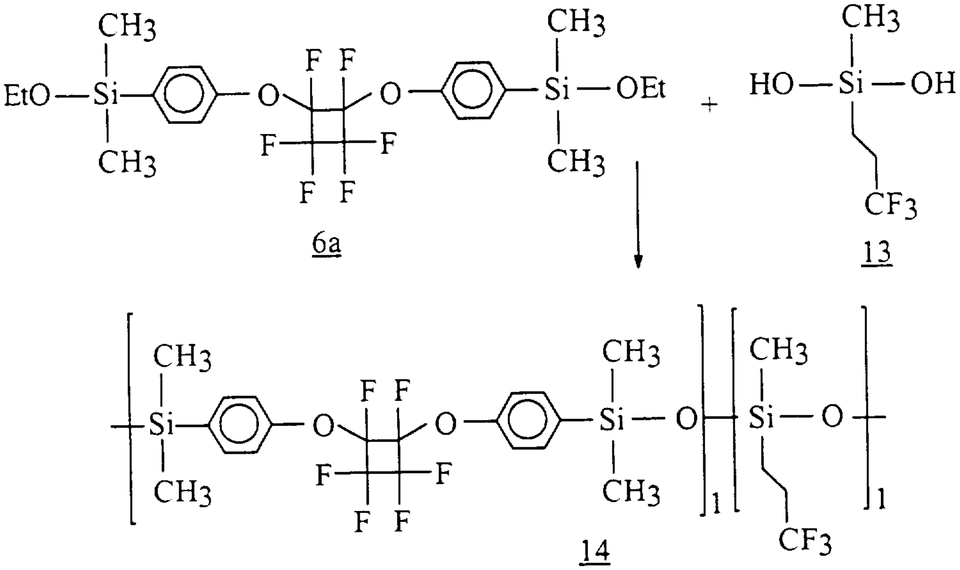
The initial objective was to copolymerize compound 6a with the oligomeric silanol-terminated fluorosilicone fluid 11 (Scheme 3). Several attempts at polymerizing stoichiometric quantities of compounds 6a and 11 at temperatures from 25- 80^{0}C in solvents such as DMSO, DMF, and diglyme gave products with Mns less than 4,000 as determined by GPC. The fluorosilicone fluid 11, which was obtained from General Electric, was a mixture containing approximately 70 % of an oligomer with a degree of polymerization of 3, and 30 % of an oligomer with a degree of polymerization of 6. In addition, the mixture also reportedly contained up to 5 % (w/w) of cyclics.



Scheme 3

Thus, an average Mn of 626 g/mol was calculated and used for stoichiometry purposes. A significant amount of error was possible in determining the average Mn due to an amount of cyclic material that could not quantified with GPC or with HPLC. Therefore, a different fluorosilicone material was used for polymerization.

3,3,3-Trifluoropropylmethylsilanediol (13), was prepared by controlled hydrolysis of 3,3,3-trifluoropropylmethyldichlorosilane.[17] Repeated recrystallization of this compound from toluene afforded a very pure monomer. Several attempts were then made at polymerizing stoichiometric quantities of compound 6a with compound 13 (Scheme 4). Similar to 11, however, very little molecular weight build-up was observed even after several days at elevated temperatures. The lack of reactivity between the silanol moiety and an alkoxysilane had been noted previously.[18,19] Thus, a different mode of polymerization was necessary to prepare high molecular weight copolymers.



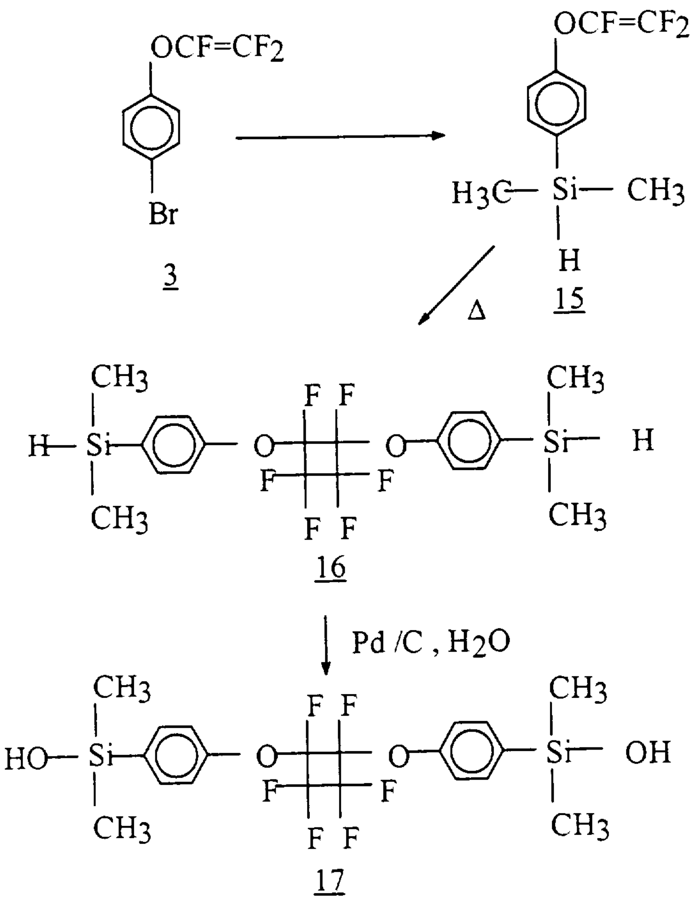
Scheme 4

2. SYNTHESIS AND POLYMERIZATION OF SILANOL-TERMINATED PERFLUOROCYCLOBUTANE-CONTAINING MONOMERS

Synthesis of 1,2,3,3,4,4-hexafluoro-1,2-bis[4-(dimethylhydroxysilyl) phenoxy]cyclobutane (17)

Compound 17 could have been prepared by the hydrolysis of compound 6a. However, a higher yield route was developed using the silane intermediate (3) that Babb[10] had prepared (Scheme 5). Thus, compound 3 was coupled with chlorodimethylsilane using an *in situ* Grignard reaction to form compound 15. Independent formation of the Grignard reagent of 3, followed by addition to chlorodimethylsilane, failed to give significantly greater yields than those obtained by the *in situ* technique. In fact, the *in situ* technique allows the use of solvents that are not as rigorously dried because the chlorosilane effectively scavenges any water present in the THF. Direct reaction of the chlorodimethylsilane with magnesium is effectively suppressed if the temperature does not exceed room temperature. Compound 16 was prepared by heating 15 at 150^0C for 6-8 h. The relatively weak Si-H bond is not attacked by the diradical intermediate if the temperature is kept below approximately 180^0C. Compound 16 could be easily separated from 15 by distillation under reduced pressure.

Compound 17 was prepared by the hydrolysis of 16 using a 5 % Pd / C catalyst. Preliminary attempts at using the sodium meditated reaction developed by Breed and coworkers produced oligomers with Mns of about 2000-4000.[20] The use of the Pd / C catalyst and low temperatures resulted in high yields of the disilanol 17. However, a small amount of oligomers still formed. Compound 17 was separated from these oligomers by recrystallization from hexane.

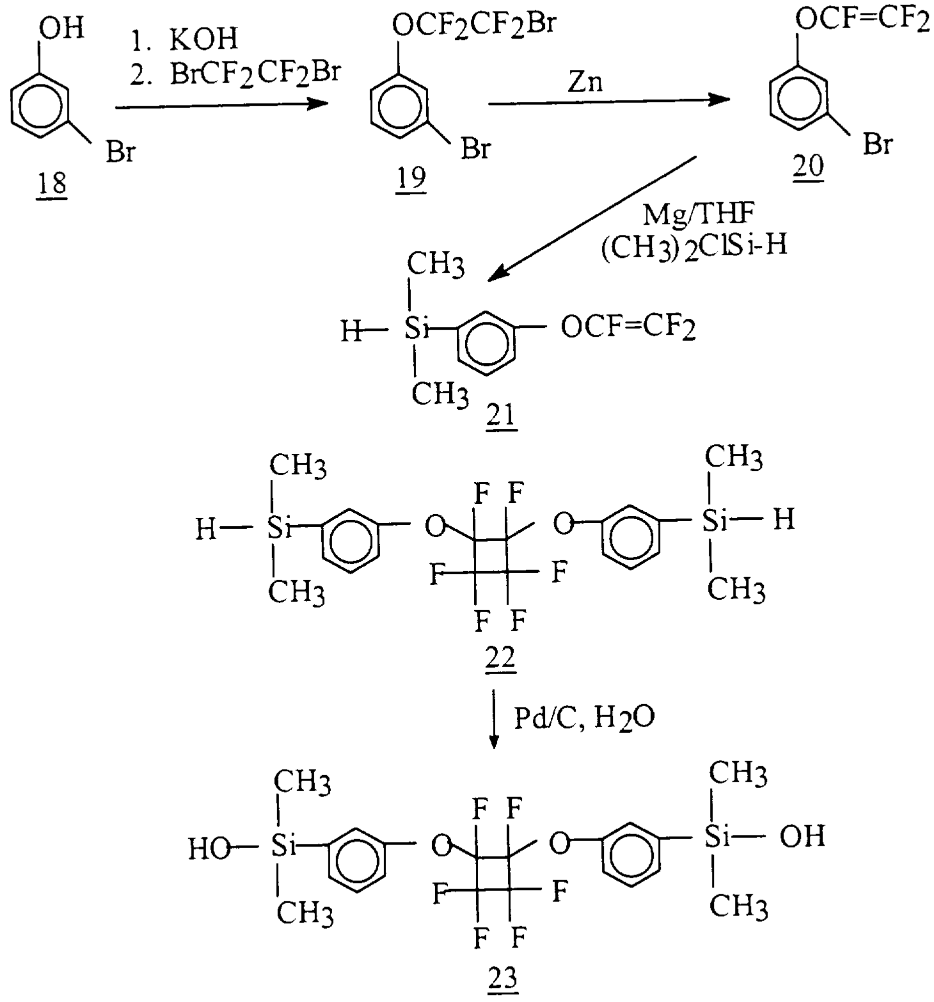


Scheme 5

Several attempts were made to prepare *para*-catenated disilanol monomers (similar to 17) with functional groups pendant to the aromatic ring. For example, 4-bromo-2,6-dimethylphenol and 4-bromo-2-fluorophenol, which are commercially available, were converted in high yield to the corresponding saturated ether intermediates. However, subsequent dehalogenations gave very low yields (5-10 %). It appears that substituents in the *ortho* position (electron donating or withdrawing) retard the dehalogenation reaction.

Synthesis of 1,2,3,3,4,4-hexafluoro-1,2-bis[3-(dimethylhydroxysilyl)phenoxy]cyclobutane (23)

The *meta*-catenated isomers 19-23 were prepared from 3-bromophenol using the same procedures used for the *para*-catenated compounds (Scheme 6). Compound 20 formed a Grignard reagent with magnesium at about the same rate as compound 3. Only slight physical property differences were displayed by the *meta* and *para*-catenated isomers. Compound 23 was a viscous oil that resisted crystallization. GPC analysis showed that 23 was a mixture containing approximately 90-95 % disilanol and 5-10 % higher oligomers. IR and ^{1}H-NMR clearly showed

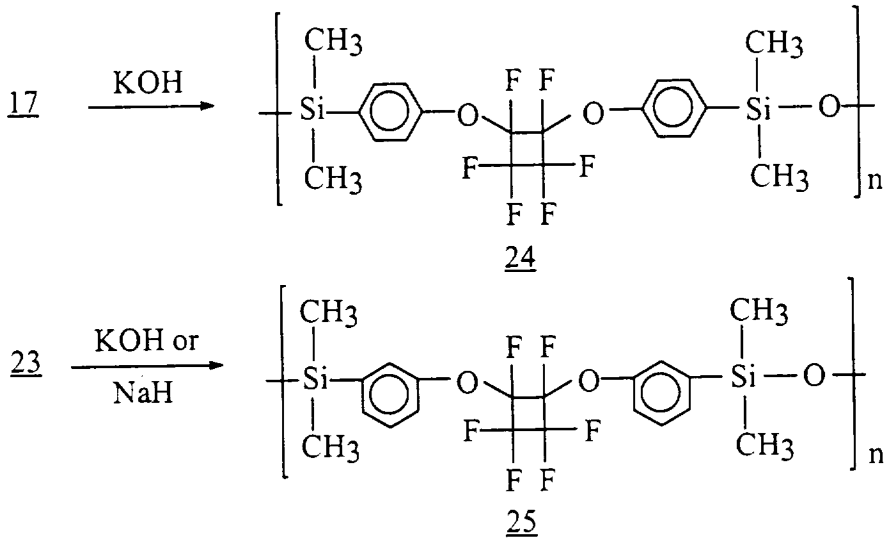


Scheme 6

the presence of the O-H bond and the complete disappearance of the Si-H bond. All attempts to isolate the disilanol from the oligomers were unsuccessful. The small amount of oligomer did not interfere with the polymerizations.

Homopolymerization of 17 and 23

There are two primary ways that arylene disilanol compounds similar to 17 and 23 have been polymerized.[21] These two techniques include base-catalyzed polymerization (e.g. sodium hydroxide, ammonium hydroxide etc.) and polymerization by the use of amine salt catalysts (e.g. tetramethylguanidine di-2-ethylhexanoate). The amine salt catalysts, which do not catalyze rearrangement of the backbone repeat units, are generally used to form block copolymers with oligomeric α,ω-silanol-terminated siloxanes. In this study, higher molecular weight products were obtained when base catalysis was used. Polymerization was accomplished by heating a 50 % (w/w) solution of 17 or 23 in toluene containing from 0.2 to 0.01 % of KOH for 1-3 h at 100^0C. After removal of toluene, the residue was heated at approximately $130\text{-}150^0$C for 1-2 h (Scheme 7). Consistent with the work of Sveda, the molecular weight of the product increased with decreasing amounts of base catalyst.[22] This has been postulated to be due to termination of the polymer chains with hydroxide ions. The acidity of the silanol moiety ensures that almost complete conversion to the silanolate ion is the first step.[23] This step is followed by silanol self-condensation and displacement of the hydroxide ion by the silanolate ion. There was no evidence of any by-products in polymers 24 and 25 as determined by ^{29}Si-NMR and ^{1}H-NMR (Figures 5-8). Polymer 24 had been prepared previously by Smith and Babb who utilized the thermal cyclodimerization of 1,3-bis{4-[(trifluorovinyl)oxy] phenyl]}-1,1,3,3-tetramethyldisiloxane.[10] However, the cyclodimerization route provided a considerably lower molecular weight than obtained in this study (Table 1).



Scheme 7

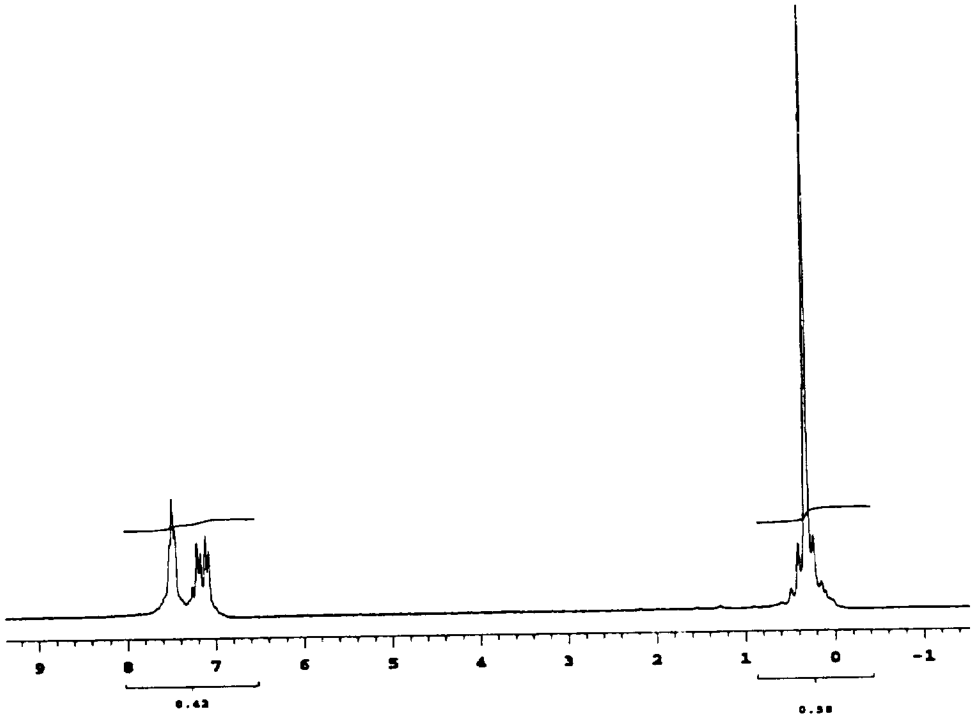


Figure 5 . ¹H-NMR spectrum of 24.

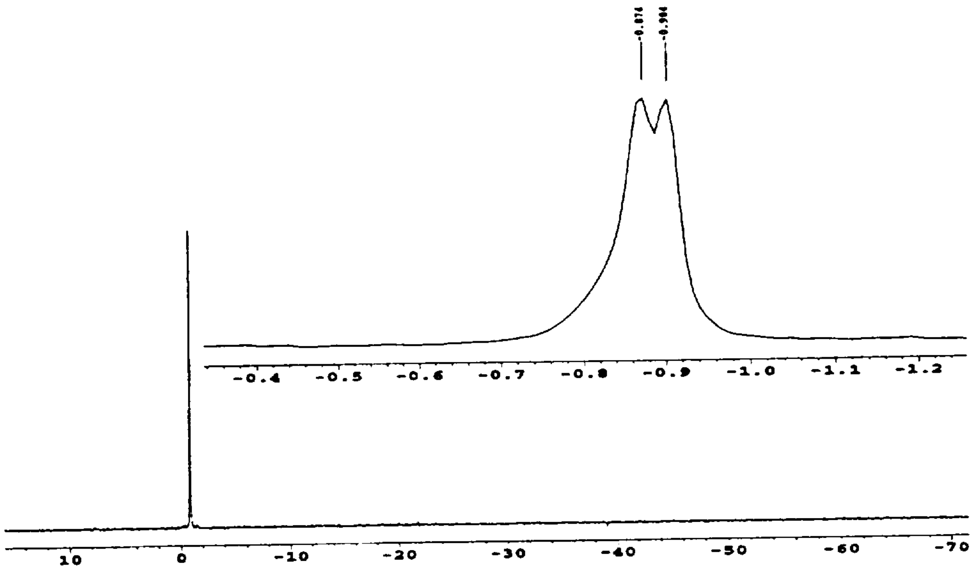


Figure 6. ^{29}Si-NMR spectrum of 24.

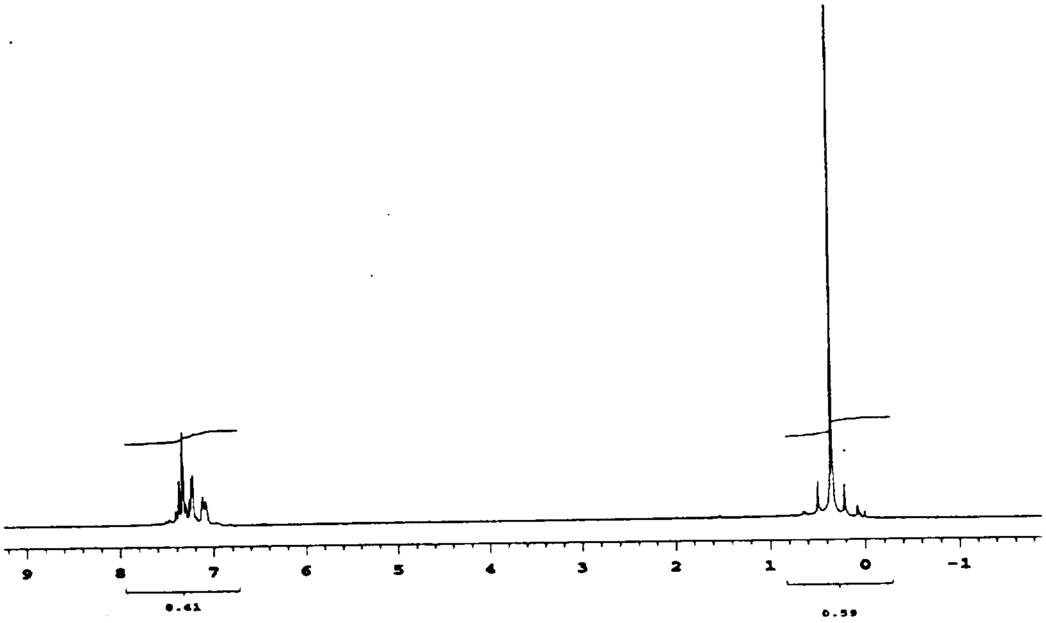


Figure 7. ^{1}H-NMR spectrum of 25.

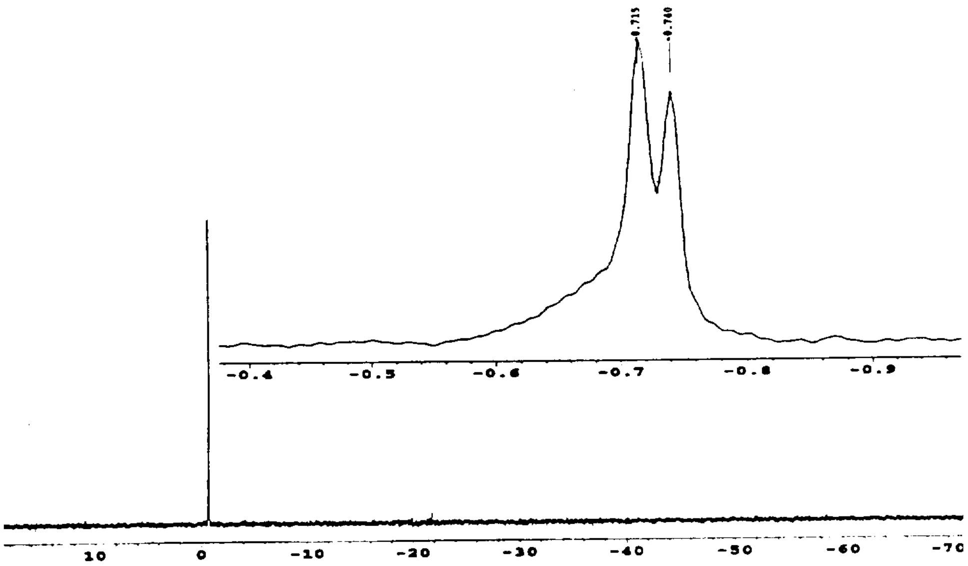


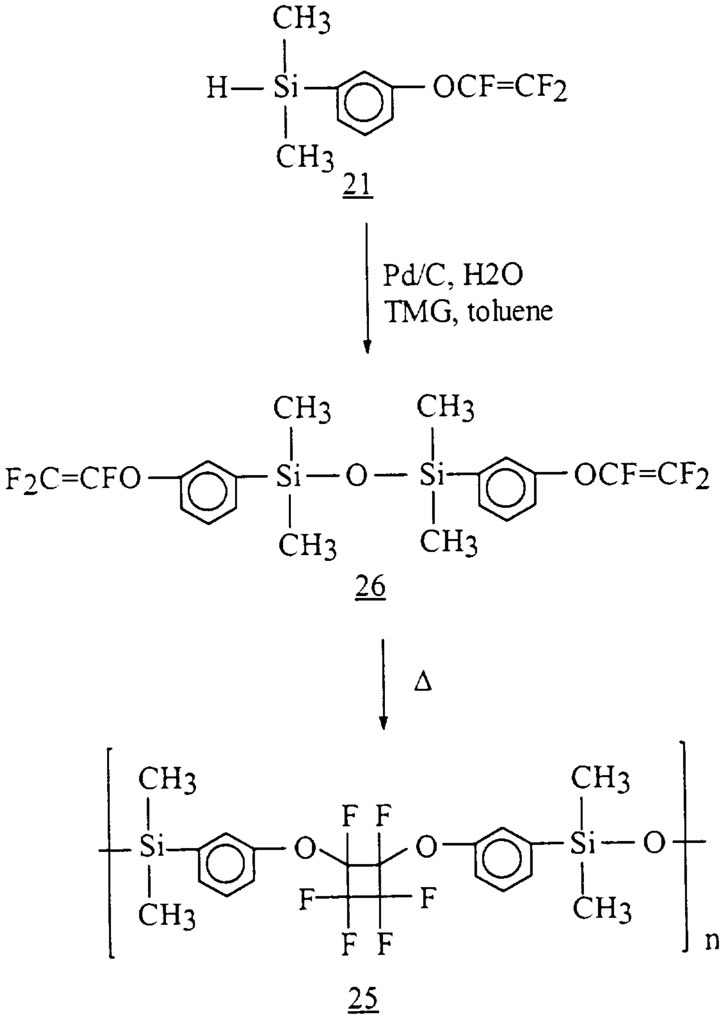
Figure 8. ^{29}Si-NMR spectrum of 25.

Although the first attempt to prepare polymer 25 from monomer 23 using KOH was successful, the polymer initially displayed poor thermal stability. This was evidently due to the presence of residual base or to incomplete neutralization of the chain ends, as several washings with dilute acetic acid resulted in a dramatic improvement in thermal stability. Since this procedure was extremely time consuming, the catalyst was replaced with 0.1 % sodium hydride, which was as effective as KOH and gave polymers that displayed excellent thermal stability after one washing with dilute acetic acid. It is speculated that the *meta*-catenated polymer may have formed a complex with unreacted KOH.

To verify the structure of polymer 25, it was prepared by another independent route. Thus, compound 26 was prepared by hydrolysis of the Si-H bond with Pd / C, followed by condensation to the siloxane in the presence of the amine salt catalyst tetramethylguanidine di-2-ethylhexanoate (TMG). Polymerization was accomplished by heating compound 26 for 8 h at

200^{0}C. The spectra and properties of polymer 25 prepared via this route were nearly identical to the properties of the polymer prepared from monomer 23 (Table 1).

The crosslinking of homopolymers 24 and 25 was accomplished by first chain-extending using KOH. When an Mn of approximately 10,000 g/mol was reached, the reaction mixture was cooled, and the chain terminated by the addition of dilute acetic acid. The oligomer was then crosslinked with 66 in a 50/50 (v/v) mixture of chloroform and toluene in the presence of dibutlytindilaurate. The solvent was allowed to evaporate over 1 d, and then the sample was heated at 50^{0}C in 100 % relative humidity for 5 d.



Scheme 8

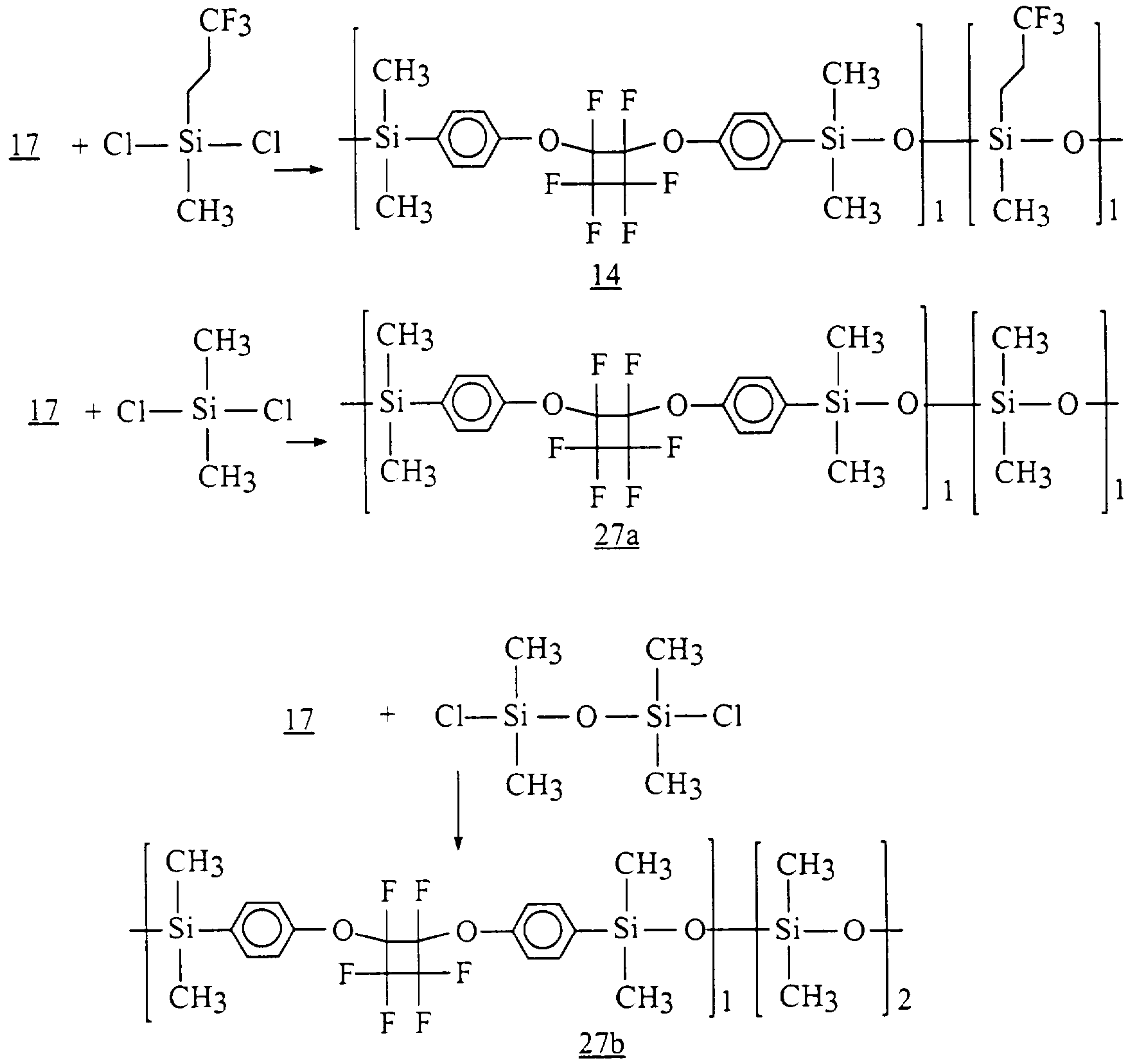
Table 1. Properties of polymers <u>24</u> and <u>25</u>.

Polymer	Catalyst	Conc. (w/w)	Time (h)	Temp (^{0}C)	Mw[a]	Mn[a]	PDI	Tg[b] (^{0}C)
<u>24</u>[c]	---------	-------	---	------	34,000	10,000	3.4	16
<u>24</u>	KOH	0.1 %	2	135	33,000	19,000	1.8	18
<u>24</u>	TMG	0.1 %	2	140	82,000	32,000	2.6	22
<u>24</u>	KOH	0.05 %	2	140	113,000	58,000	2.0	27
<u>24</u>	KOH	0.01 %	2	140	687,000	300,000	2.3	27
<u>25</u>[d]	---------	-------	8	195	110,000	47,000	2.3	-12
<u>25</u>	NaH	0.08 %	2	135	66,000	29,000	2.3	-14

a. Determined by GPC using THF as the eluent at 30^{0}C, relative to polystyrene standards.
b. Mid-point in the change in slope of a DSC thermogram obtained using a heating rate of 10^{0}C / min.
c. Data taken from reference 10.
d. Prepared via cyclodimerization of compound <u>26</u>.

Copolymers prepared by dichlorosilane / disilanol condensation (<u>14</u>, <u>27a</u>, and <u>27b</u>)

Copolymers <u>14</u>, <u>27a</u>, and <u>27b</u> were prepared by the room temperature condensation of <u>17</u> with the commercially available dichlorosilanes, 3,3,3-trifluoropropylmethyldichlorosilane, dimethyldichlorosilane, and 1,3-dichlorotetramethyl disiloxane, respectively (Scheme 9). This type of copolymerization has been shown to produce copolymers with significant blockiness.[24-26] This is because even with controlled monomer addition and a strong inert gas flow, the hydrogen chloride by-product can react with the siloxane bonds in the polymer backbone leading to redistribution of the repeat units. The dependence of Mn on the dichlorosilane used is likely due to steric factors (Table 2). The less sterically hindered monomers gave higher molecular weights. Desilylation does not appear to be a significant side reaction in these polymerizations as evidenced by the relatively high molecular weights obtained. In fact, only in one instance, where several aromatic groups were attached to silicon, has desilylation been postulated to be a significant side reaction during polymerization.[27]



Scheme 9

Table 2. Properties of polymers prepared by dichlorosilane / disilanol condensation.

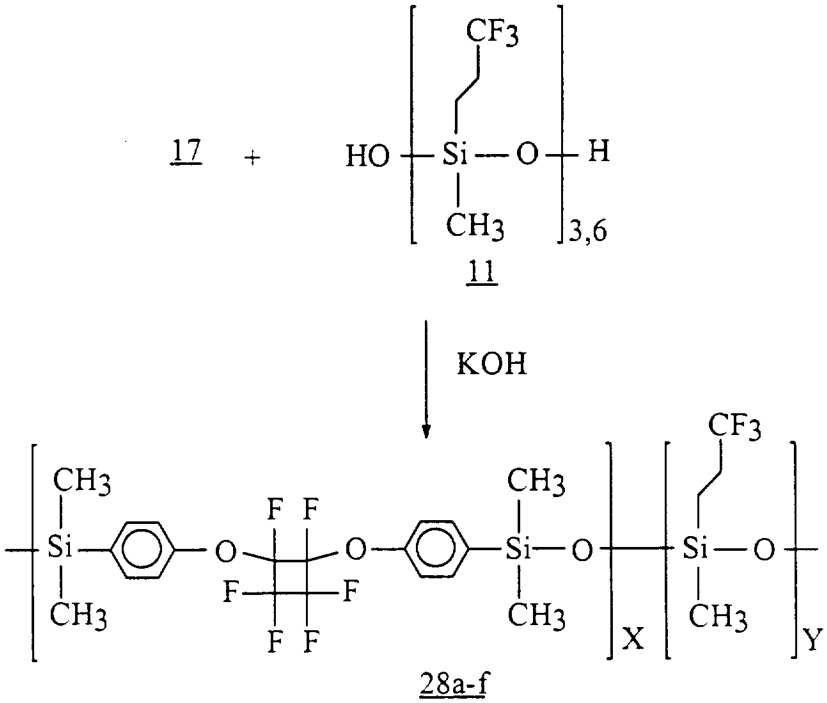
Polymer	Mw[a]	Mn[a]	PDI[a]	Tg (^{0}C)[b]	Td [c]	
					N_2	air
14	19,000	14,000	1.3	-1	435	385
27a	44,000	26,000	1.7	-10	440	420
27b	90,000	52,000	1.7	-12	445	405

a. Determined by GPC using THF as the eluent at 30^{0}C, relative to polystyrene standards.
b. Midpoint in the change in slope of the DSC thermogram obtained using a heating rate of 10^{0}C / min.
c. Temperature at which a 5 % weight loss occurred when subjected to TGA using a heating rate of 10^{0}C / min.

The crosslinking of copolymer 14 was accomplished in a similar manner to 24 and 25. In this case, after the Mn reached approximately 10,000 g/mol, the residue was dissolved in chloroform and washed with water to neutralize any residual chlorosilane end-groups. After 66 and dibutyltindilaurate were added, the chloroform was allowed to evaporate over 1 d. The residue was then heated at 50^{0}C in 100 % relative humidity for 5 d.

Random perfluorocyclobutane-containing silarylene-siloxane copolymers

Copolymers 28a-f were prepared from 17 and a α,ω-disilanol-terminated fluorosilicone oligomer (11) using a KOH-mediated technique similar to that described by Grassie (Scheme 10, Table 3).[9] Copolymers 29a-d were prepared from 23 and the fluorosilicone oligomer in a similar manner (Scheme 11, Table 4). Similar to homopolymer 25, 29a-d had reduced thermal stability when prepared with KOH, unless the copolymers were washed repeatedly with dilute acetic acid. Therefore, sodium hydride was again used to prepare copolymers 29a-d.

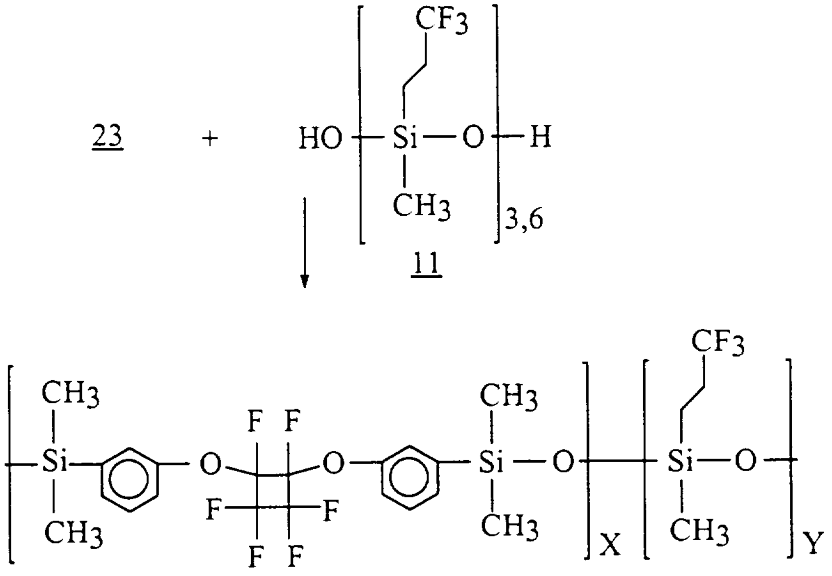


Scheme 10

Table 3. Properties of random copolymers 28a-f.

Polymer	X	Y [a]	Mw [b]	Mn[b]	PDI	Tg [c]	Td [d]	
							N_2	air
28a	1	2.7	77,000	44,000	1.7	-20	445	385
28b	1	4.4	65,000	44,000	1.5	-38	405	370
28c	1	5.5	135,000	74,000	1.8	-42	440	375
28d	1	6.5	68,000	45,000	1.5	-44	440	375
28e	1	8.0	132,000	87,000	1.5	-52	----	------
28f	1	12	21,000	15,000	1.3	-60	405	335
Commercial fluorosilicone	0	1	73,000	48,000	1.5	-68	385	340

a. Copolymer composition determined by ^{1}H-NMR. X and Y refer to the repeat unit ratios shown as in Scheme 10.
b. Determined by GPC at 30^{0}C using THF as the eluent, relative to polystyrene standards.
c. Midpoint in the change in slope of the DSC thermogram obtained using a heating rate of 10^{0}C / min.
d. Temperature at which a 5 % weight loss occurred when subjected to dynamic TGA using a heating rate of 10^{0}C / min.



29a-d

Scheme 11

Table 4. Properties of random *meta*-catenated copolymers <u>29a-d</u>.

Polymer	X	Y[a]	Mw[b]	Mn[b]	PDI	Tg[c]	Td[d]	
							N2	air
<u>29a</u>	1	2.8	45,000	34,000	1.3	-34	415	385
<u>29b</u>	1	3.8	39,000	30,000	1.3	-40	415	385
<u>29c</u>	1	6.0	50,000	38,000	1.3	-50	430	390
<u>29d</u>	1	7.5	44,000	34,000	1.3	-55	390	375
Commercial Fluorosilicone	0	1	73,000	48,000	1.5	-68	385	340

a. Copolymer composition determined by ^{1}H-NMR. X and Y refer to the repeat unit ratios shown as in Scheme 11.
b. Determined by GPC at 30^{0}C using THF as the eluent, relative to polystyrene standards.
c. Midpoint in the change in slope of the DSC thermogram obtained using a heating rate of 10^{0}C / min.
d. Temperature at which a 5 % weight loss occurred when subjected to dynamic TGA using a heating rate of 10^{0}C / min.

A considerable amount of cyclization occurred during the copolymerizations. The products were mixtures of a unimodal high molecular weight polymer that contained low molecular weight fluorosilicone cyclics. The cyclics were separated from the linear polymers during their isolation in methanol (Figure 9). The amount of cyclics, which remained in methanol, ranged from approximately 30 to 75 % (w/w), depending on the amount of fluorosilicone oligomer in the feed. Concurrently, the yield of copolymer decreased with increasing amounts of fluorosilicone monomer (Figure 10, Table 5). A monomer feed / copolymer composition relationship was established (Figure 11). Due to competing cyclization and the randomizing nature of the basic catalyst, reactivity ratios could not be established. Randomization occurs because reactions do not occur exclusively between silanol end-groups.[28] The silanolate intermediate can react with siloxane bonds in the backbone of the copolymer. Any fluorosilicone oligomer generated could then cyclize. Thus, the copolymer composition is determined more by a thermodynamic equilibrium rather than by kinetics.

Table 5. Yield of copolymers 28a-f.

Copolymer	Monomer feed ratio of (11/17) (mol/mol)	Mol % 11 in feed	Copolymer yield (%)
28a	3 / 1	0.75	73
28b	9 / 1	0.90	45
28c	12 / 1	0.92	40
28d	17 / 1	0.94	25
28e	23 / 1	0.96	20
28f	50 / 1	0.98	20

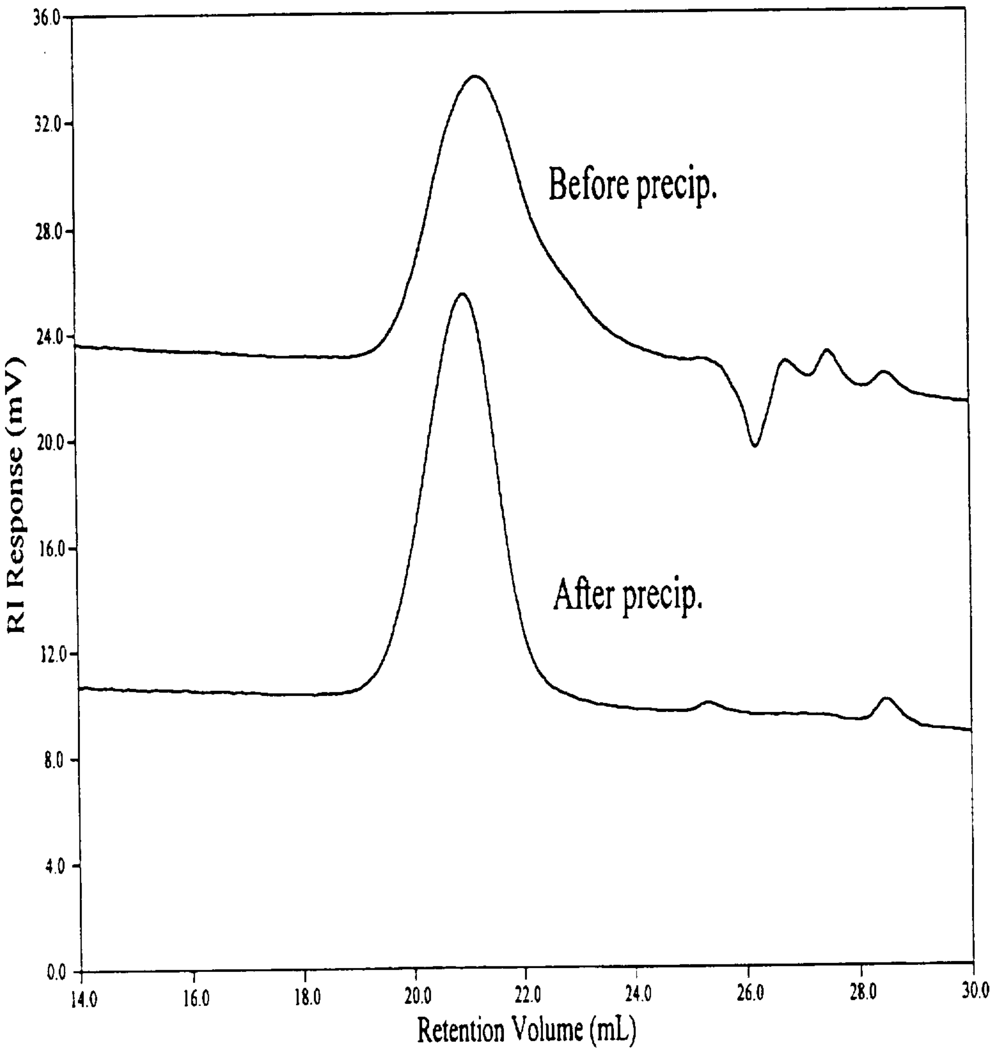


Figure 9. GPC chromatograms of copolymer 29c before and after precipitation in methanol.

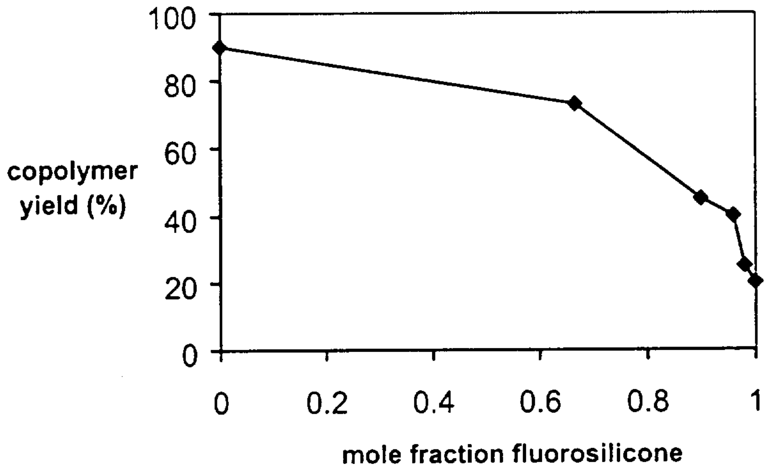


Figure 10. Yield of copolymer 28 vs. mole fraction of fluorosilicone in feed.

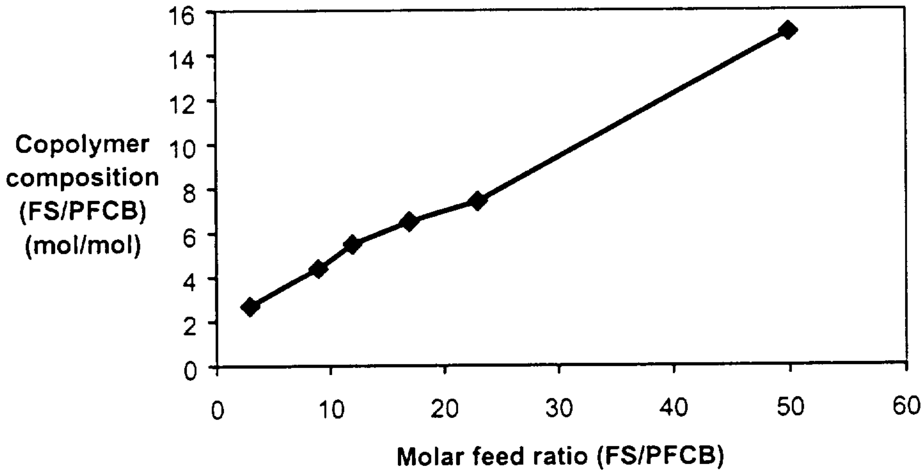


Figure 11. Copolymer composition of 28 vs. monomer feed ratio (FS / PFCB).

The use of the randomizing catalyst KOH was expected to result in the formation of random copolymers. However, the copolymers were still subjected to DSC analysis in an attempt to identify any block structures. All of the copolymers exhibited one Tg (Figure 12). To determine if blocks of the two components would phase-separate, several attempts were made to solution blend a high molecular weight homopolymer of 24 with a commercial fluorosilicone homopolymer. In each case, a two phase system was obtained that exhibited two Tgs.

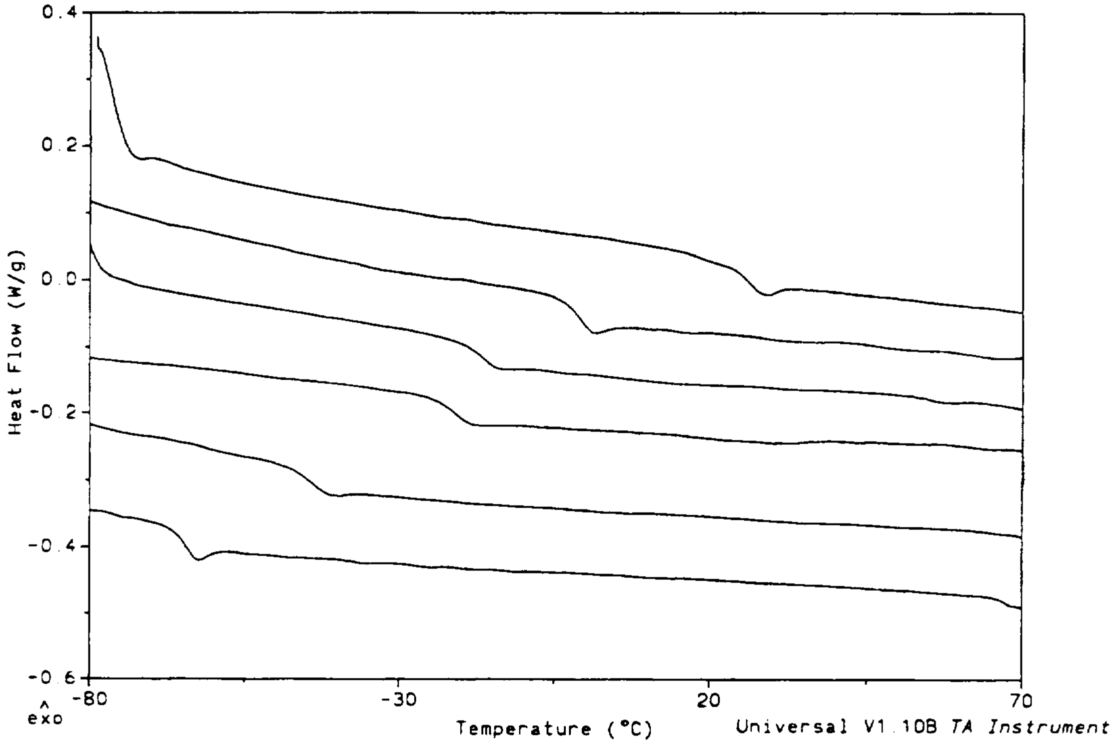


Figure 12. DSC thermograms of *para*-catenated copolymer series. From top to bottom; 24, 14, 28a, 28b, 28d, and fluorosilicone homopolymer.

The low polydispersitites of the copolymers can primarily be attributed to fractionation during the methanol precipitation (Figure 9). The polydispersity of the polymers prior to precipitation was between 1.6 and 2.0. After precipitation, the polydispersities of the lower molecular weight copolymers were as low as 1.3. The higher molecular weight copolymers had polydispersities between 1.5 and 1.8, approaching the theoretical polydispersity of 2.0. Interestingly, polymers prepared by non-randomizing silanol condensation reactions exhibit polydispersities approaching 1.4.[29] It has been postulated that this occurs because of the invalidity of the fundamental assumption by Flory that polymer end-groups have reactivities nearly identical to those of analogous low molecular weight compounds.

An attempt was made to crosslink copolymer 28e, after it was precipitated in methanol, with 66 and dibutyltin dilaurate. However, a soluble product was obtained. Since the Mn of 28e was 87,000 g/mol, the concentration of reactive end-groups was very low, which may account for the lack of reactivity. Instead of using a condensation cure, crosslinking was accomplished via radical reactions with a 50 % dispersion of 2,4-dichlorobenzoylperoxide.[30] After mixing the components in a blender, a lengthy degassing period was necessary to prevent bubbling during the cure cycle. The crosslinking of the commercial fluorosilicone homopolymer was accomplished in a similar manner.

Copolymer compositions

Copolymer compositions were determined with ^{1}H-NMR (Figure 13). The integrated areas of the absorptions of the protons in the aromatic region of the perfluorocyclobutane (PFCB) repeat unit (7.0-7.5 ppm), after subtraction of the chloroform absorption, were compared to the area under the absorption peak of the hydrogens in the methylene group adjacent to the trifluoromethyl group (2 ppm) in the fluorosilicone (FS) repeat unit.

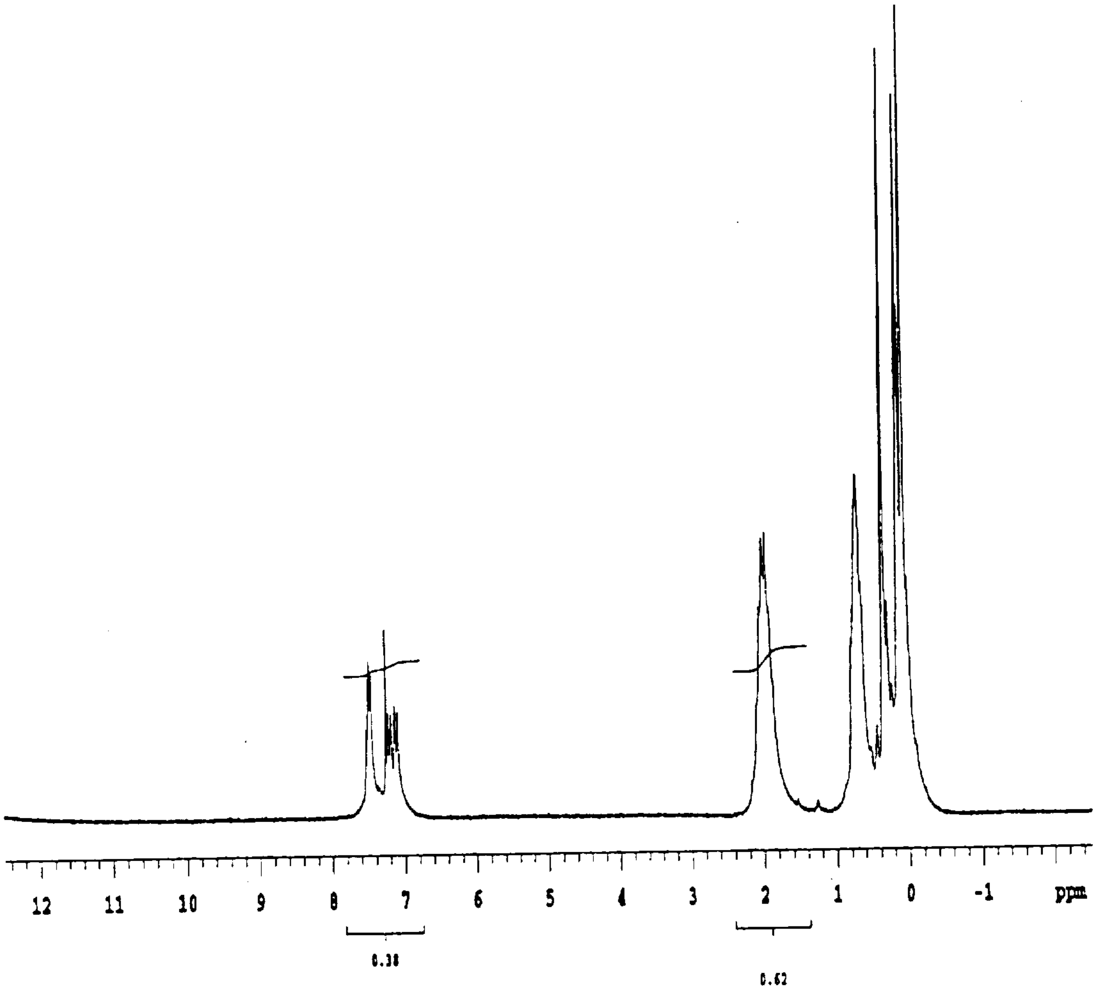


Figure 13. ^{1}H-NMR spectrum of <u>28d</u>.

The following expression was used to determine copolymer compositions:

$$[\, A / B \,] = [\, 8 / 2y \,]$$

where A = the area under the aromatic proton absorptions (7.0 – 7.5 ppm); B = the area under the proton absorption of the methylene group adjacent to the trifluoromethyl group (2.0 ppm); and y = the number of fluorosilicone repeat units in the copolymer, when the number of perfluorocyclobutane repeat units in normalized to 1.

A similar analysis was done with ^{19}F-NMR by comparing the area under the absorptions of the fluorine atoms in the perfluorocyclobutane ring (-132 to –138 ppm) to the area under the absorption of the fluorine atoms of the trifluoromethyl group (-74 ppm) (Figure 14). Due to the asymmetric nature of the PFCB, there are twelve different absorptions (6 from the *cis* isomer and 6 from the *trans* isomer) observed for this moiety.[10] The algebraic expression used was similar to that above except that the integer 6 was used in the numerator and the integer 3 was used in the denominator. The copolymer compositions determined by ^{19}F-NMR were within 10 % of the compositions determined by ^{1}H-NMR.

Polymer and copolymer thermal properties

Isothermal TGA analyses in nitrogen showed that polymers 24, 14 and copolymers 28a-f were more thermally stable than a commercial fluorosilicone homopolymer that was neutralized with acetic acid and precipitated in methanol (Figure 15). The copolymer thermal stability did start to decrease when the molar copolymer composition reached about 8 / 1 (FS / PFCB). However, even a copolymer with a molar composition of 12 / 1 (FS / PFCB) underwent significantly less weight loss than a fluorosilicone when heated above 250^{0}C. This is consistent with the results of a previous study with polydimethylsiloxane containing random silphenylene repeat units.[9] It is likely that degradation initiates at the chain end and proceeds until a perfluorocyclobutane repeat unit is encountered, and then slows or stops at that point.

The relative stabilities of the copolymers from isothermal TGA was consistent with dynamic TGA in both inert and oxidizing atmospheres. The temperatures at which 5 and 25 % weight losses occurred in N_2 were about 30-50^{0}C higher for 24, 14 and 28a-f, relative to a fluorosilicone homopolymer (Table 4, Figure 16). The same relative trend was observed in air, however, the temperatures for a given weight loss were about 30^{0}C lower.

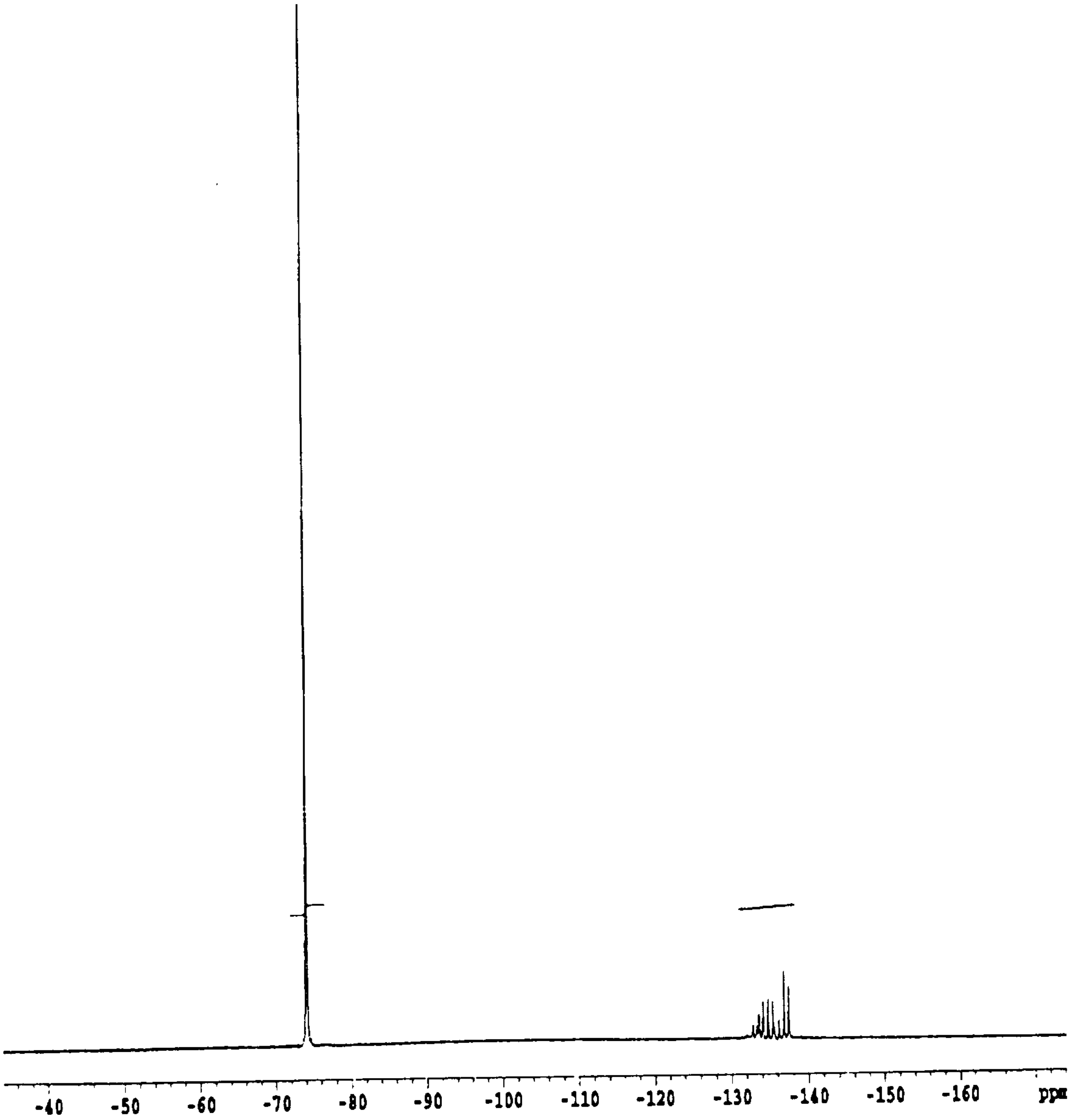


Figure 14. ^{19}F-NMR spectrum of polymer <u>28d</u>.

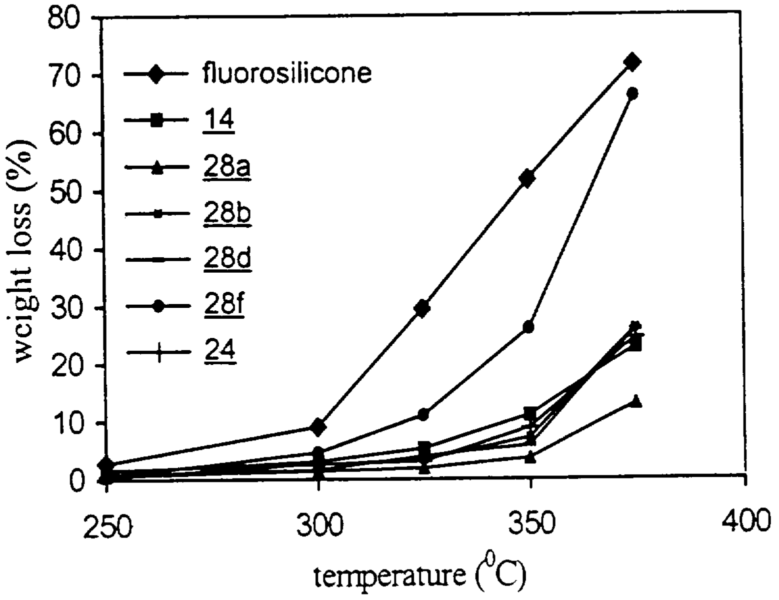


Figure 15. Isothermal weight loss of polymers and copolymers after 2 h of heating under N_2.

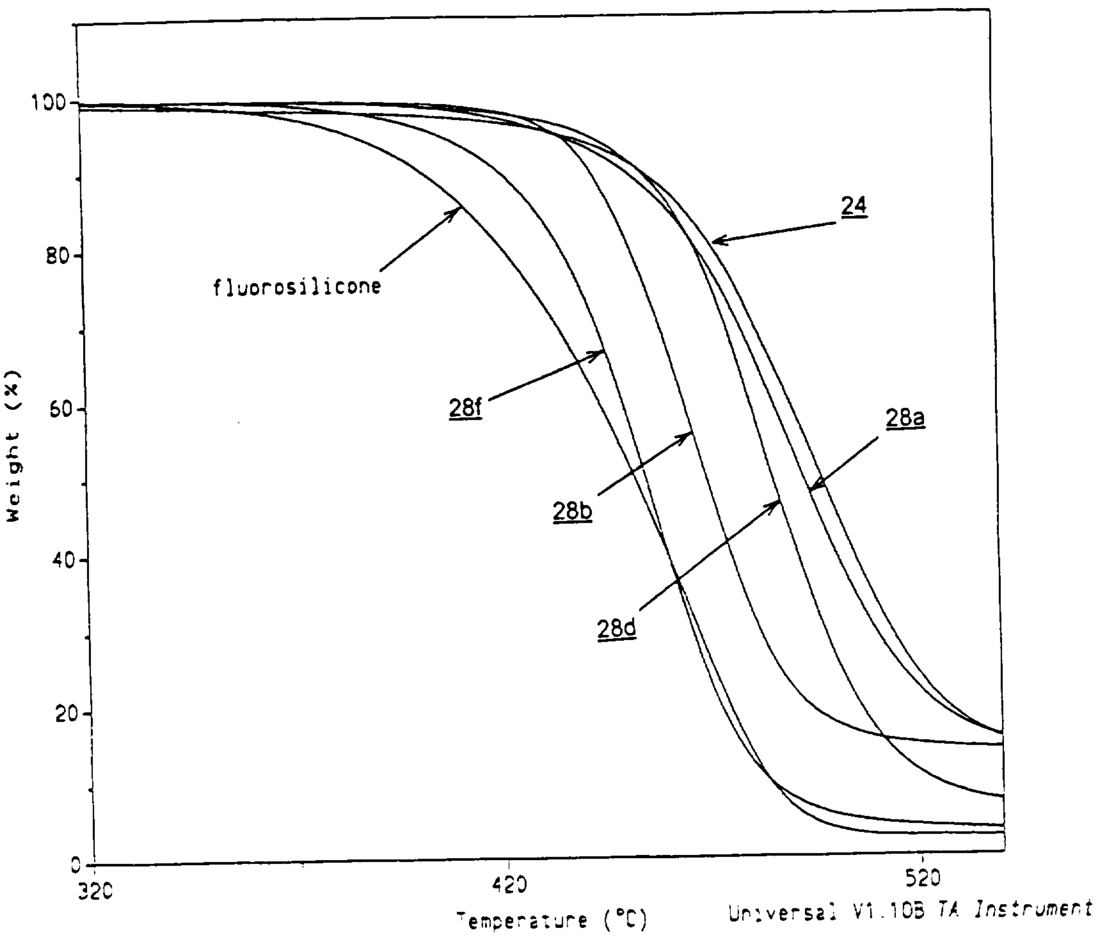


Figure 16. Dynamic TGA thermograms of fluorosilicone and *para*-catenated copolymers obtained under N_2 at 10^0C / min.

Polymer 25 and copolymers 29a-d also displayed thermal stabilities greater than a fluorosilicone homopolymer control (Figure 17). The isothermal stability of the *meta*-catenated copolymers also decreased dramatically when the molar copolymer composition of 23 to fluorosilicone reached about 1 to 7. Similar to the *para*-catenated copolymers, the *meta*-catenated copolymers also displayed greater stability than a fluorosilicone when subjected to dynamic TGA (Figure 18).

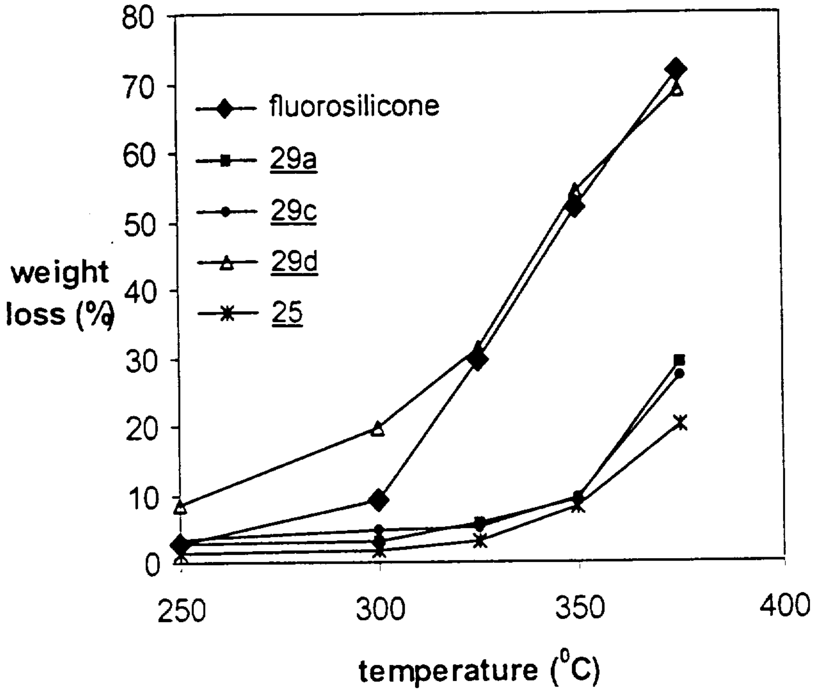


Figure 17. Isothermal weight loss of polymers and copolymers after 2 h of heating under N_2.

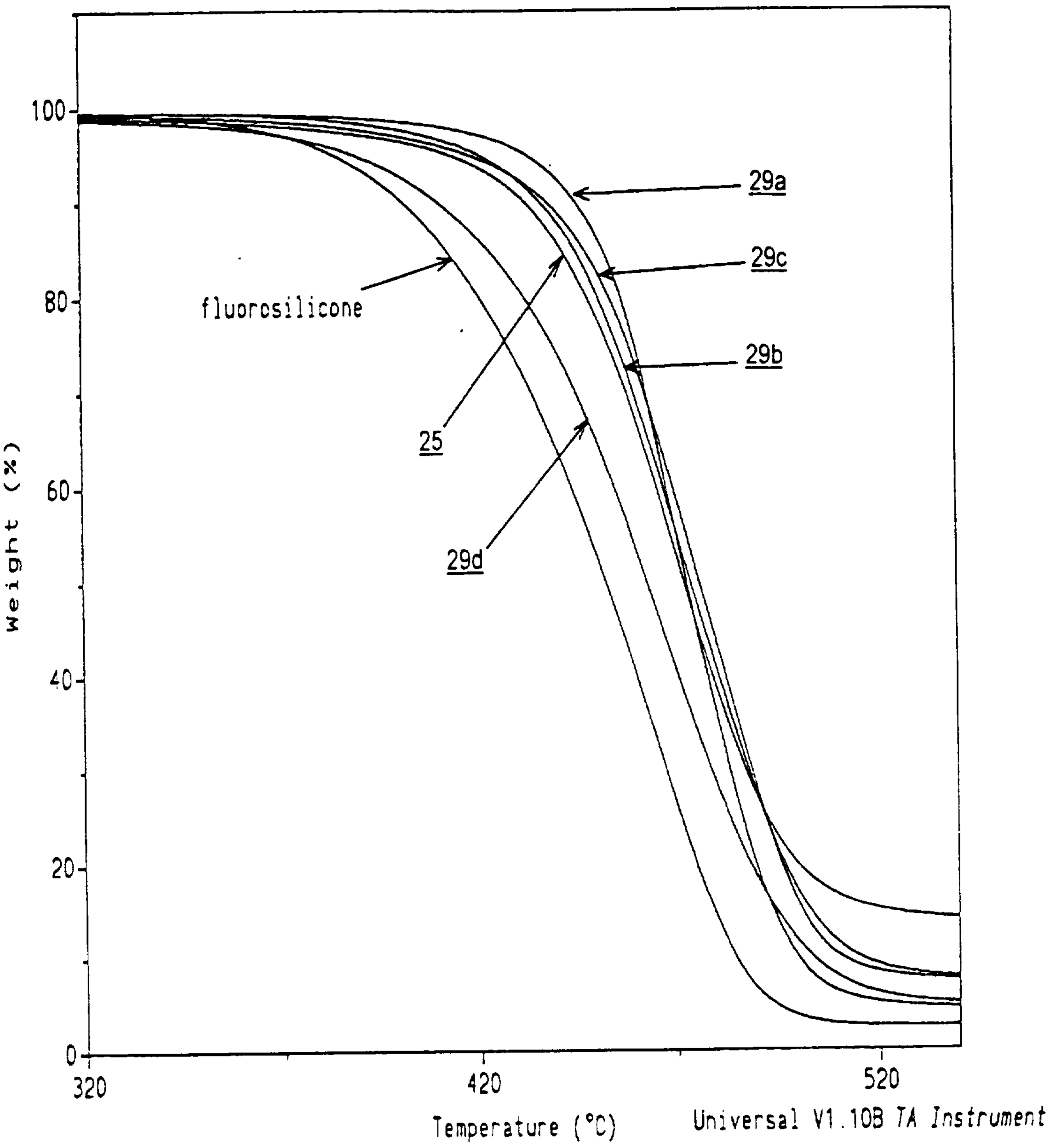


Figure 18. Dynamic TGA thermograms of fluorosilicone and *meta*-catenated copolymers obtained under N_2 at 10^0C / min.

The Tg of polymer 24 was strongly dependent on Mn up to an Mn of about 50,000 g/mol (Figure 19, Table 1). The Tg of 27^{0}C appeared to be independent of Mn beyond this point. Smith and Babb had suggested that the Tg becomes independent of Mn near 20,000 g/mol, where the Tg is 18^{0}C.[10] The previously reported melt-like transitions at -25^{0}C and 50^{0}C were not observed.[10] Polymer 25, which contained the *meta*-catenated aromatic ring, had a Tg of –12^{0}C when the Mn was 48,000 g/mol. This indicates that *meta*-catenation reduced the Tg by nearly 40^{0}C.

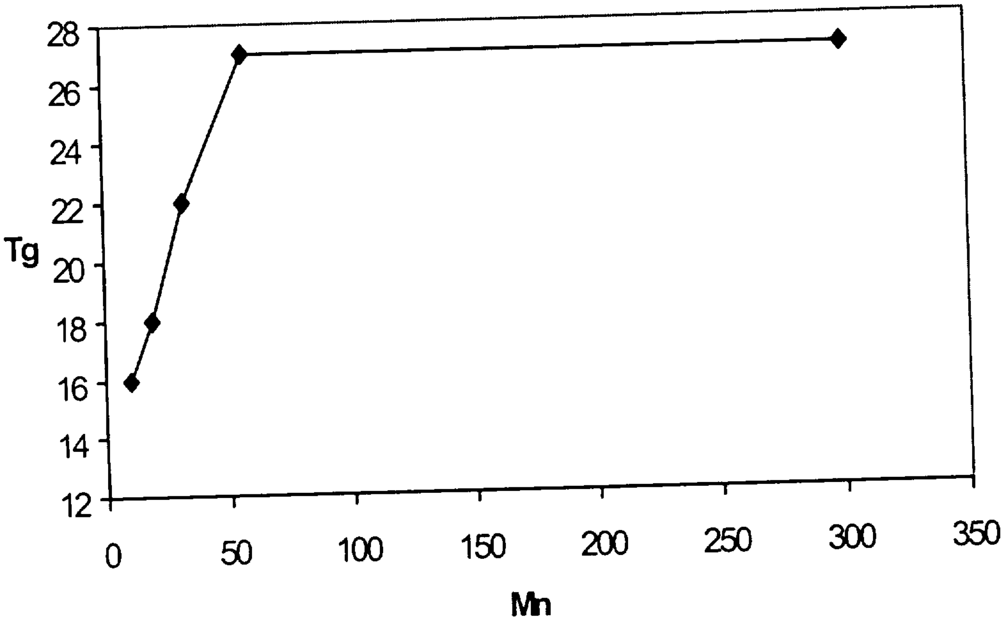


Figure 19. Tg (^{0}C) vs Mn (x 10^{-3}) for polymer 24.

The Tgs of the *para*-catenated polymer 24 and copolymers 28a-f linearly decreased from -1^0C to -60^0C as the amount of fluorosilicone in the copolymer increased from 25 wt % to 80 wt % (Figure 20). The HSCT required a fuel tank sealant with low temperature flexibility at -54^0C.[1] The Figure shows that a Tg of -54^0C would be displayed by a copolymer containing 75 wt % fluorosilicone. The Tgs of the *meta*-catenated copolymers 29a-d were also linearly dependent on the fluorosilicone content, decreasing from -34^0C to -55^0C as the wt % of the fluorosilicone increased from 48 % to 70 %.

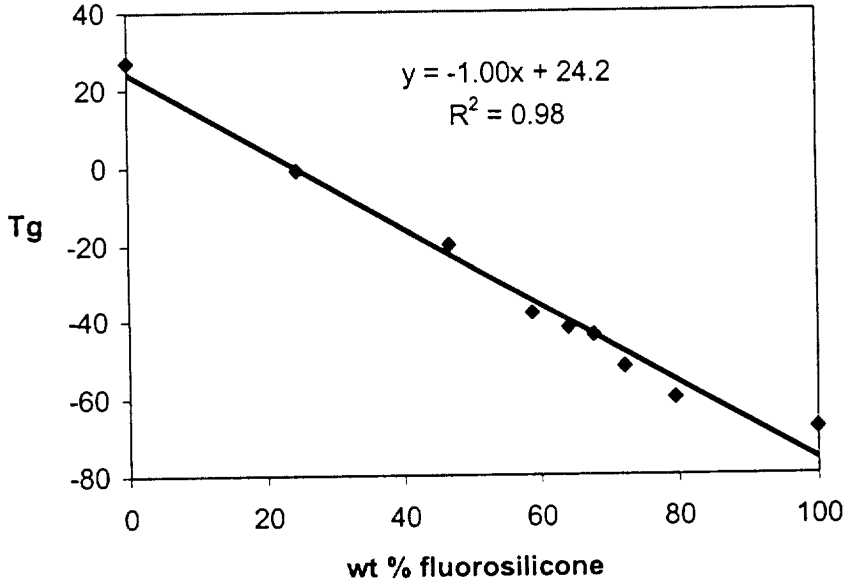


Figure 20. Tg (^{0}C)vs. wt % fluorosilicone in polymer series 28.

The crosslinking of polymers 24, 14, 25, 28e and the fluorosilicone homopolymer resulted in Tg increases of 1 to 3^0C. This is consistent with the formation of a lightly crosslinked network.[31] The Shore A hardnesses of the networks ranged from about 15-20, typical of unfilled polysiloxane elastomers. The amount of extractables in the crosslinked networks ranged from 8 to 15 %. The amount of extractables was highest with solvents whose solubility parameter most closely matched that of the network (Tables 6 and 7). The moderately low amount of soluble materials indicates that the curing processes were rather efficient.

Swelling behavior of crosslinked polymers

In order for a polymer to be useful as a fuel tank sealant, it is important that it displays very low swell in hydrocarbon solvents. Highly swollen networks have very low elongation, tear strength and tensile strength.[32,33] This reduction in properties of highly swollen networks has been attributed to a loss of viscoelastic and other dissipative processes.[32] Jet fuel is generally a blend of 80 % (v/v) branched aliphatic hydrocarbons and 20 % (v/v) aromatic hydrocarbons.[34] For laboratory testing purposes, 2,2,4-trimethylpentane is used to simulate the aliphatic portion of jet fuel and toluene is used to simulate the aromatic portion of jet fuel.[35]

It was initially postulated that the perfluorocyclobutane-containing fluorosilicones would have good fuel resistance due to the high concentration of fluorine in the polymer structure. Prior to testing this hypothesis, the fuel resistance of the perfluorocyclobutane homopolymer was determined for comparative purposes. Thus, the crosslinked network of 24 was subjected to swelling measurements in several different solvents according to ASTM D-471 (Table 6). Surprisingly, the lightly crosslinked network underwent significant swelling in hydrocarbon solvents (Figure 21).

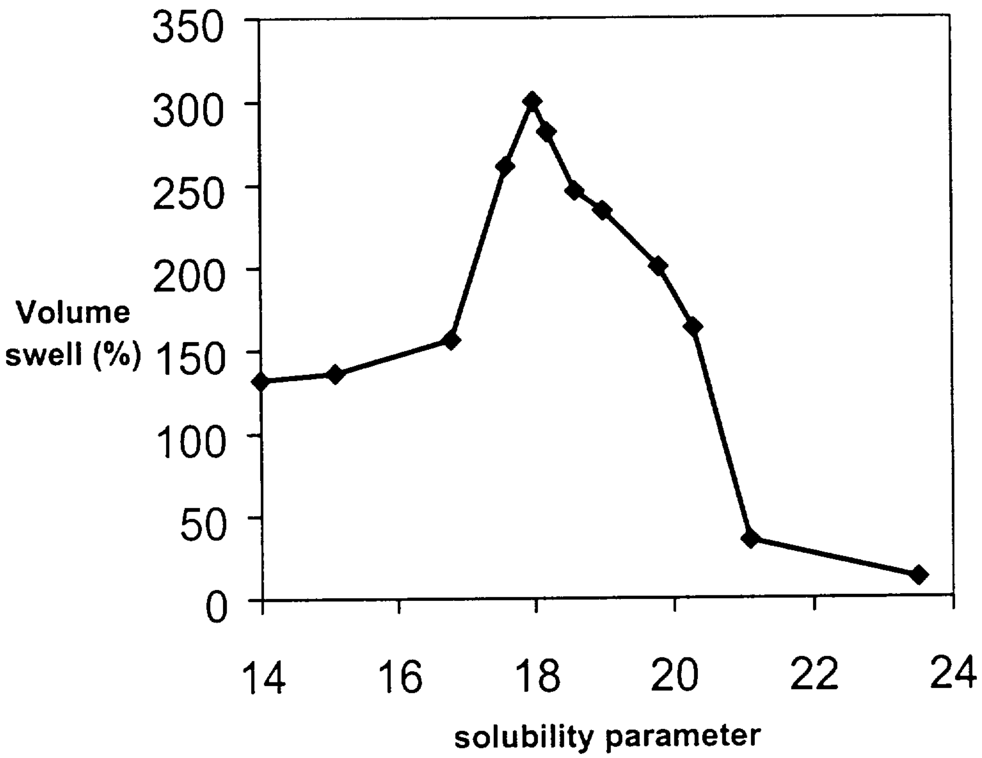


Figure 21. Volume swell (%) vs. solvent solubility parameter (J $^{1/2}$ m $^{-3/2}$) for polymer 24.

The maximum volume swell was 300 % in toluene (δ = 18.2 J $^{1/2}$ m $^{-3/2}$).[36] This suggests that the fluorinated cyclobutane structure does not shield the hydrocarbon portions of the network as effectively as the trifluoromethyl group in crosslinked fluorosilicone[37], which undergoes less than 20 % volume swell in hydrocarbon solvents.[38] The dramatic difference in swelling behavior may also be partially attributable to differences in the systems' fluorine contents (23.8 wt % vs. 36.5 wt %).

Table 6. Volume swell of polymers 24 and 25 in various solvents.

Solvent	Solubility parameter ($J^{1/2}$ $m^{-3/2}$)[36]	Volume swell (%) 76[a]	Volume swell (%) 113[a]
Isooctane	14.0	132 (11)[b]	80 (15)[b]
Heptane	15.1	136 (12)	65 (15)
Cyclohexane	16.8	156 (11)	106 (15)
Carbon tetrachloride	17.6	261 (11)	160 (14)
m-xylene	18.0	282 (12)	---
Toluene	18.2	300 (12)	190 (17)
Ethyl acetate	18.6	246 (12)	163 (16)
Chloroform	19.0	234 (12)	160 (17)
Methylene chloride	19.8	200 (12)	110 (15)
Acetone	20.3	163 (10)	---
Acetic anhydride	21.1	35 (9)	34 (13)
Isopropanol	23.5	12 (6)	25 (12)

a. Most of the volume swell values represent the mean of 3 samples and have a standard deviation of about 5-10 % of the mean.

b. The value in parentheses represents the % of material extracted in that particular solvent ((initial weight of specimen – final weight after drying) / initial weight).

After immersion in toluene and the chlorinated solvents, the swollen crosslinked polymer of 24 was very brittle and crumbled under slight stress. Intrinsic viscosity measurements of the linear polymer 24 in different solvents were consistent with the observed maxima in toluene (Figure 22, Table 7). However, there is considerably less precision in these measurements.

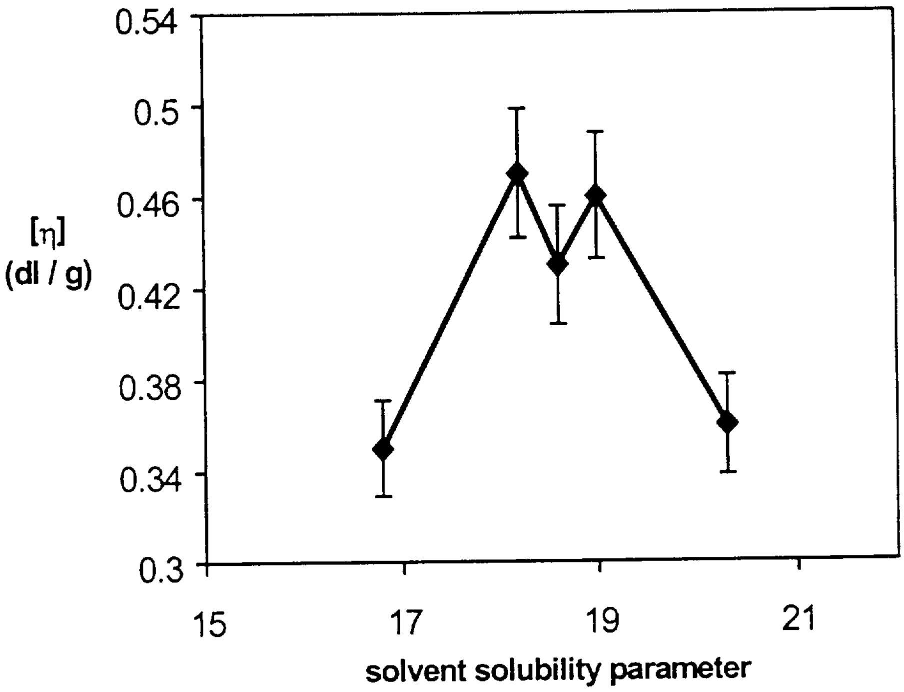


Figure 22. Plot of intrinsic viscosity (dl/g) of 24 (Mn = 58,000 g/mol, GPC) vs. solvent solubility parameter (J $^{1/2}$ m $^{-3/2}$).

Table 7. Intrinsic viscosity of polymer 24 in various solvents.

Solvent	Solubility parameter ($J^{1/2}$ $m^{-3/2}$)[37]	Intrinsic Viscosity (dL / g)
Cylcohexane	16.8	0.35
Toluene	18.2	0.47
Ethyl acetate	18.6	0.43
Chloroform	19.0	0.46
Acetone	20.3	0.36

The hydrocarbon resistance of the crosslinked network of copolymer 14 was only slightly better than that of crosslinked 24. The copolymer, which had a fluorine content of 26.9 %, underwent maximum swelling in chloroform ($\delta = 19.0$ $J^{1/2}$ $m^{-3/2}$) (Table 8). The hydrocarbon resistance of the PFCB containing fluorosilicone network 28e was similar to that of a pure fluorosilicone (Figure 23, Table 8). Since the copolymer fluorine content was only slightly less than that of a pure fluorosilicone, it appears that the PFCB-containing repeat unit did not enhance the fluorosilicone resistance to hydrocarbons. Similar to fluorosilicone, the crosslinked network swelled considerably in solvents with δs higher than those of hydrocarbons. The maximum volume swell for 28e was over 300 % in methylene chloride ($\delta = 19.8$ $J^{1/2}$ $m^{-3/2}$). The δ of this solvent is very close to the reported δ of fluorosilicone ($\delta = 19.6$ $J^{1/2}$ $m^{-3/2}$).[39]

Table 8. Volume swell of crosslinked *para*-catenated copolymers in various solvents.

Solvent / Solubility paramter ($J^{1/2}\ m^{-3/2}$)	Volume swell (%)		
	14	28e	24
Isooctane / 14.0	130 (15)[a]	35 (2)	132 (11)
Cyclohexane / 16.8	150 (11)	30 (3)	156 (11)
Toluene / 18.2	255 (15)	68 (2)	300 (12)
Chloroform / 19.0	280 (18)	180 (6)	234 (12)
Methylene chloride / 19.8	250 (18)	380 (7)	200 (12)
Acetic anhydride / 21.1	50 (10)	60 (2)	35 (9)
Isopropyl alcohol / 23.5	15 (8)	15 (0)	12 (6)

a. The value in parentheses represents the % of material extracted in that particular solvent ((initial weight of specimen – final weight after drying) / initial weight).

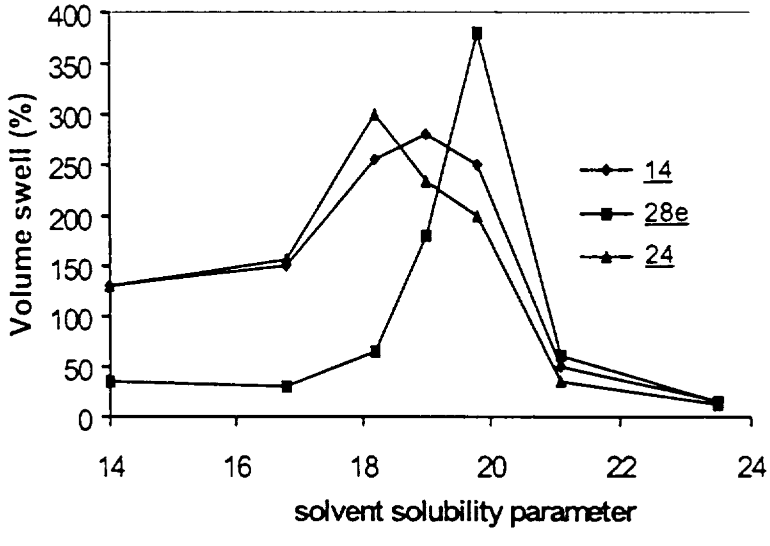


Figure 23. Volume swell of 24, 14, and 28e vs. solvent solubility parameter.

The volume swell of the crosslinked systems evaluated in this study in toluene and isooctane are plotted vs. their fluorosilicone contents in Figure 24. It is assumed that the effect of crosslink density on the magnitude of swell is small relative to the effect of chemical structure. It appears that a fluorosilicone content of 75 wt % (fluorine content 33.3 %) is needed to achieve hydrocarbon resistance comparable to that of fluorosilicone. This is consistent with the results of a study of silalkarylene-siloxane copolymers with pendant trifluoropropyl groups that showed that a fluorine content of 30 wt % was needed in order to achieve acceptable hydrocarbon resistance.[40]

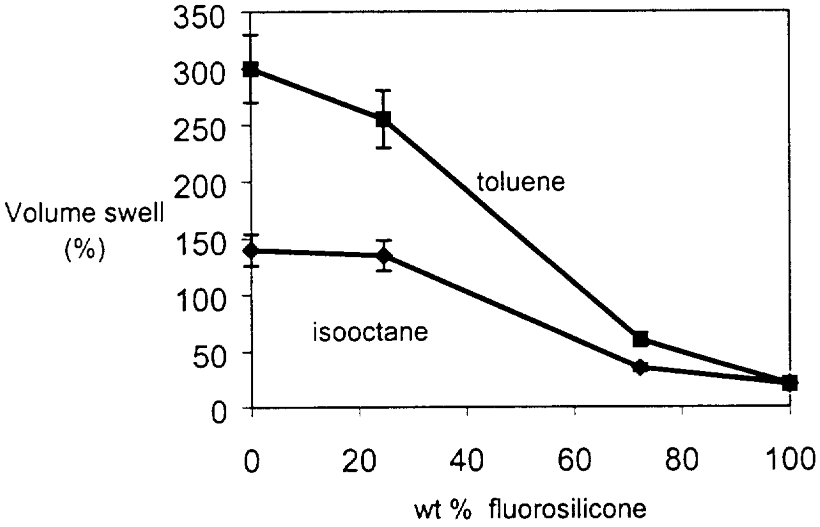


Figure 24. Volume swell vs. fluorosilicone content (wt %) of *para*-catenated copolymers.

A lightly crosslinked network of polymer 25 was also subjected to swelling measurements. The relative swelling behavior was identical to that of polymer 24, however, the magnitude of swell was considerably lower (Figure 25). This difference in magnitude can not be attributed to minor variations in the crosslink densities of the networks. Instead, it is postulated that the shorter hydrocarbon segment length in the *meta*-catenated polymer, relative to the *para*-catenated polymer, is responsible for this reduction in swell magnitude.

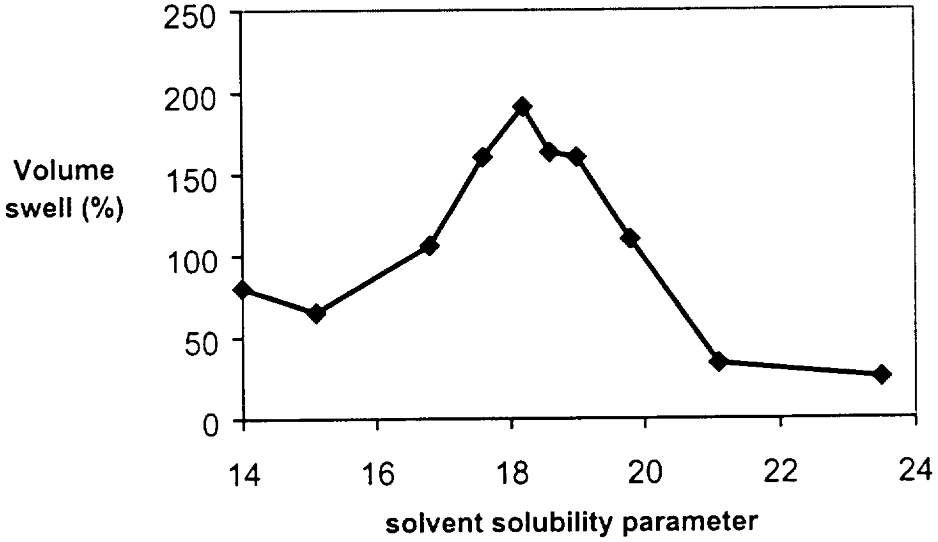


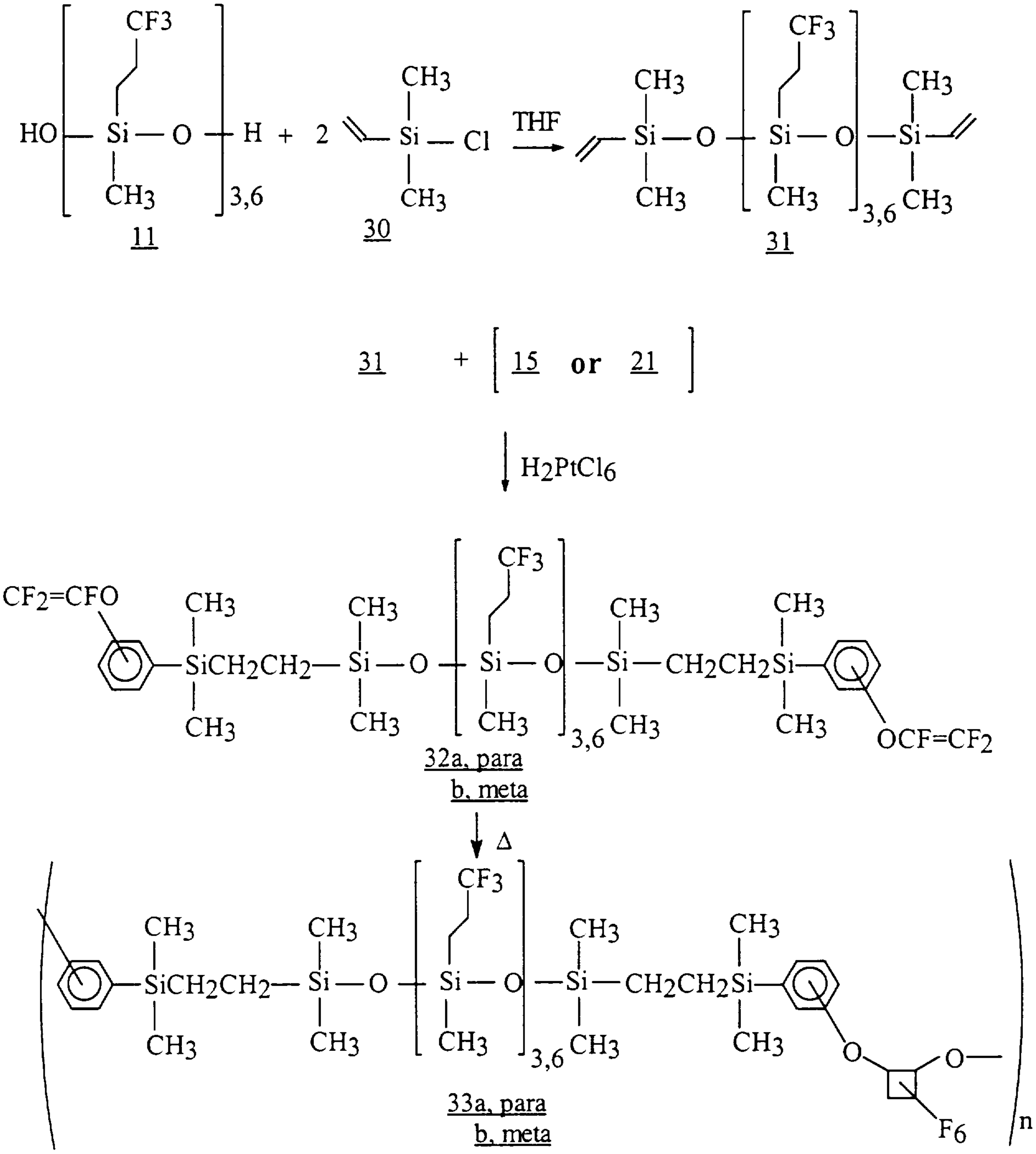
Figure 25. Volume swell (%) of 25 vs. solvent solubility parameter (J $^{1/2}$ m $^{-3/2}$).

3. POLYMERIZATION BY CYCLODIMERIZATION

Preparation of trifluorovinylether-terminated fluorosilicone oligomers

A two-step synthetic route was developed for the preparation of trifluorovinylether-terminated fluorosilicone oligomers (Scheme 12). The first step involved the preparation of a vinyl-terminated fluorosilicone oligomer 31 via the condensation of two equivalents of chlorodimethylvinylsilane with the α,ω-silanol-terminated fluorosilicone oligomer 11. The disappearance of the strong O-H stretch at 3350 cm^{-1} in the IR spectrum, the appearance of absorptions in the 5-6 ppm range in the ^{1}H-NMR spectrum, and an increase in molecular weight relative to the starting oligomer provided evidence of the vinyl termination.

A hydrosilation reaction was used to couple the silanes 15 and 21 with the vinyl-terminated fluorosilicone oligomer. This reaction gave a high yield of the desired trifluorovinylether-terminated fluorosilicone oligomer. The IR spectrum of the product contained bands at 1500 (aromatic stretch), 1600 (aromatic stretch), and 1833 (trifluorovinyl stretch) cm^{-1}. The disappearance of the vinyl group, along with the appearance of aromatic protons was confirmed with ^{1}H-NMR. Due to overlapping peaks, ^{1}H-NMR was ineffective in determining the orientation of addition of the silane to the vinyl group. Usually, the silane adds to the carbon atom β to the vinyl silane.[41] Using (distortionless enhancement by polarization transfer) DEPT ^{13}C-NMR, the orientation of addition of oligomer 32a was determined to be nearly 100 % β addition (Figure 26).[42] The Figure indicates the absence of any methine (C-H) protons (other than the aromatic protons at 118 ppm and 135 ppm), which would be present if α addition had occurred. In addition, two new methylene (CH_2) peaks were observed at 6 and 8 ppm. Absolute assignments were not made, however, it is speculated that the peak at 8 ppm is from the hydrogens adjacent to the aromatic silicon.


11
30
THF
31
31 + [15 or 21]
H2PtCl6
CF2=CFO
OCF=CF2
32a, para
b, meta
Δ
33a, para
b, meta
F6
3,6
n

Scheme 12

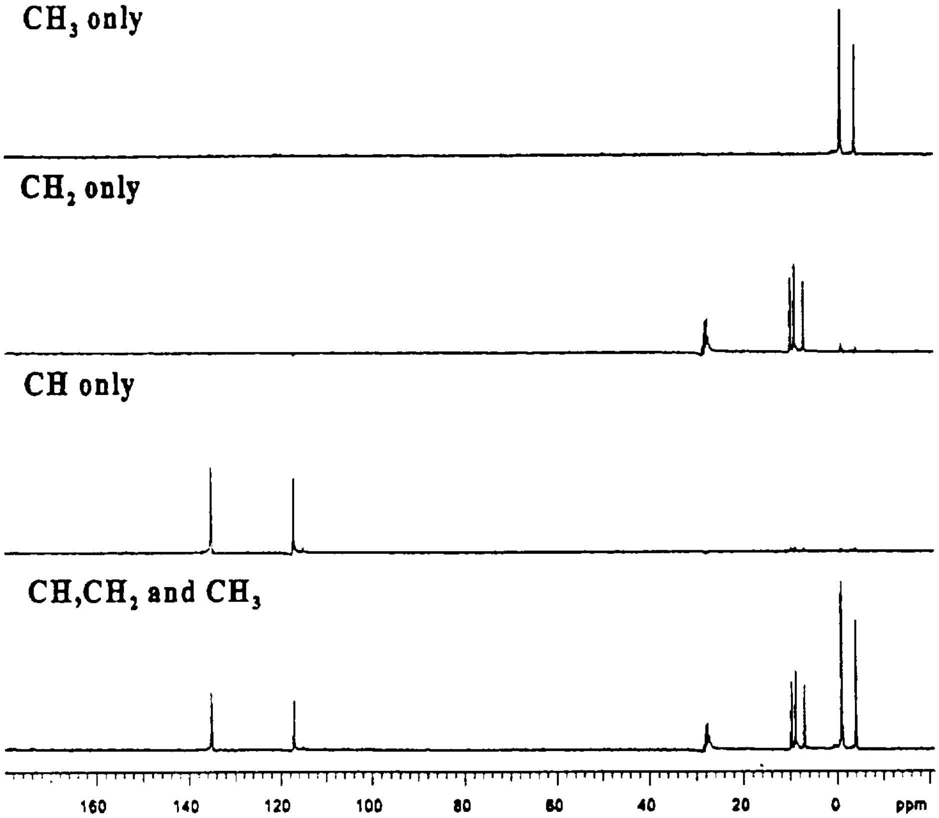


Figure 26. DEPT ^{13}C-NMR of oligomer 32a.

The hydrosilation reaction occured exclusively at the vinylsilane moiety. The trifluorovinylether group was found to be inert to hydrosilation with platinum catalysis even under rigorous reaction conditions. A possible explanation for this behavior is that the fluorine atoms shorten the π bonds of the alkene making the initial coordination with platinum difficult. The selective reactivity of vinylsilanes to the exclusion of trifluorovinyl groups had been observed by Tarrant.[43]

Properties of fluorosilicone oligomers prepared via cyclodimerization

Chain extension was accomplished by heating oligomer 32a and b for 6 h at 185^{0}C. ^{19}F-NMR proved to be a useful technique for the characterization of these polymers (Figure 27). After precipitation of 33a in methanol, integration of the area under the peak of the trifluoromethyl group (-74 ppm), compared to the area under the peaks of the perfluorocyclobutane groups (-132 to –138 ppm), suggested a 3.9 to 1 repeat unit ratio. This is consistent with the expected ratio based on the difunctional fluorosilicone oligomer. In addition, the molecular weight can be calculated by using the following formula: Mn = 1260 [(area of perfluorocyclobutane) / (area of trifluorovinylether) + 2]where 1260 is the molecular weight of one repeat unit, using the calculated repeat unit ratio of 3.9 to 1. A value of 13,300 g/mol for 33a was obtained using this technique.

The trifluorovinylether group has three non-equivalent fluorine atoms. With ^{19}F-NMR, each of these fluorine atoms couples to the other two non-equivalent fluorine atoms to give three doublet of doublets which are centered at -124, -132, and -140 ppm. These peaks have been assigned by Babb as the *cis*, *trans*, and geminal fluorine absoptions, respectively.[10] As mentioned earlier, the perfluorocyclobutane ring has 12 non-equivalent fluorines (six from the *cis* isomer and six from the *trans* isomer) due to the asymmetry of the cyclobutane ring. These peaks are centered between -132 and -140 ppm and have not been individually assigned.

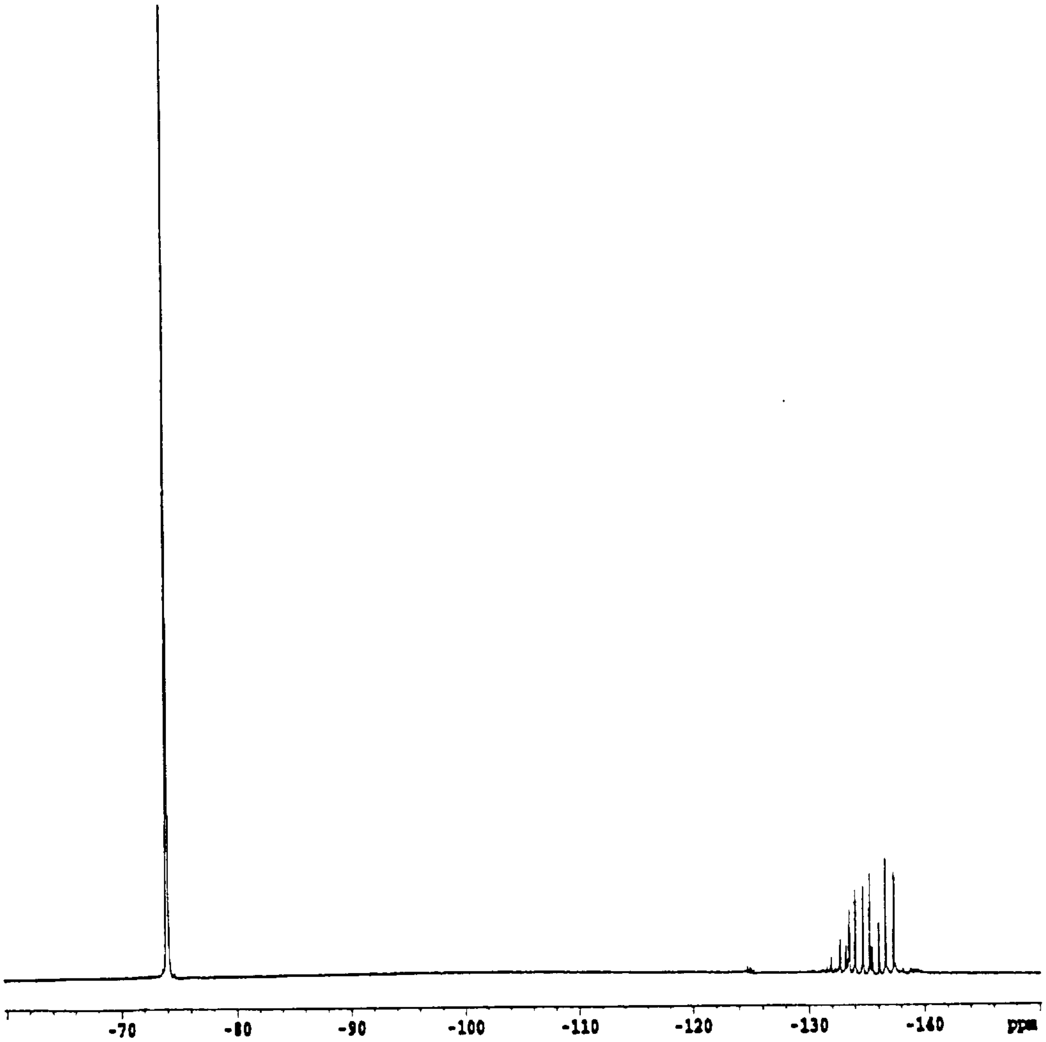


Figure 27. ^{19}F-NMR spectrum of polymer 33a.

Thermal properties

The temperatures at which 5 % and 25 % weight losses occurred during TGA in both air and nitrogen were lower for oligomers 33a and b than for a non-functionalized fluorosilicone (Table 9). Zhdanov and coworkers carried out the hydrosilation polymerization of 1,4-bis(dimethylsilyl)benzene with a α,ω-vinyl-terminated PDMS oligomer.[44] The linear polymer prepared by these workers displayed very similar thermal stability to the polymers in this study. Although degradation catalyzed by traces of residual catalyst can not be completely ruled out, it is possible that the Si-CH_2CH_2-Si linkage adjacent to a siloxane linkage is a weak link.

Table 9. Properties of polymers prepared from trifluorovinylether-terminated oligomers.

Polymer	Tg [a] (°C)	Td (N_2) [b] 5 %	Td (N_2) [b] 25 %	Td (air) [b] 5 %	Td (air) [b] 25 %	Mw [c] (g/mol)	Mn [c] (g/mol)	PDI
33a	-41	330	405	320	360	22,000	15,600	1.4
33b	-47	330	405	310	370	24,200	16,800	1.5

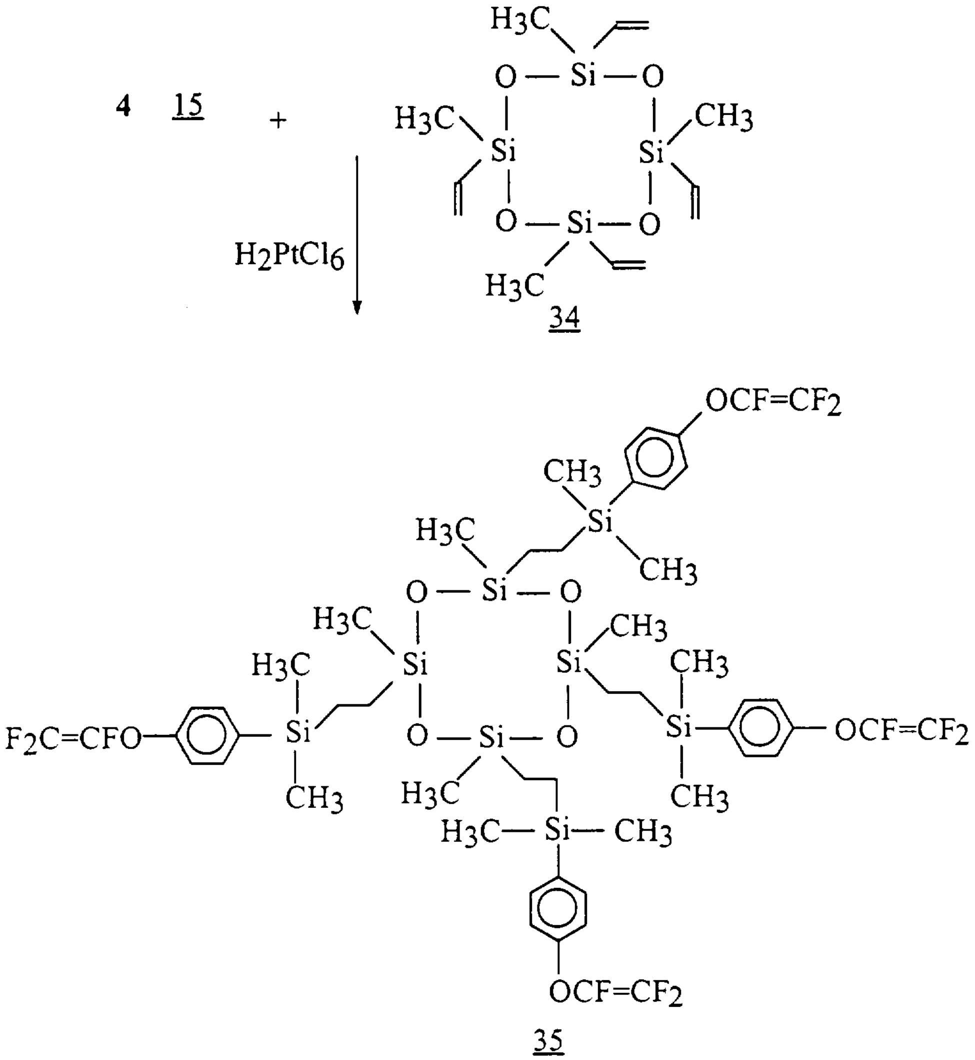
a. Midpoint in the change in slope of the DSC thermogram obtained using a heating rate of 10°C / min.
b. Temperature at which the indicated % weight loss occurred during dynamic TGA using a heating rate of 10°C / min.
c. Determined by GPC at 30°C using THF as the eluent, relative to polystyrene standards.

The Tgs for oligomers 33a and b were slightly lower than predicted by the linear equation given in Figure 20. Evidently, the lower molecular weights and the presence of the methylene linkages in the polymer backbone depressed the Tgs. A 6°C lower Tg was observed for the polymer containing the *meta*-catenated aromatic PFCB, relative to the *para*-catenated aromatic PFCB. Again, only one transition was observed in the temperature region from −100°C to 125°C.

Synthesis of 2,4,6,8-tetramethyl-2,4,6,8-tetrakis{2-[4-trifluorovinyl(oxy)phenyl dimethylsilyl]ethyl}cyclotetrasiloxane (35)

Several trifunctional trifluorovinylether-containing compounds have been prepared.[45,46] All of these compounds, however, crosslink to give networks with Tgs greater than 400^{0}C. The incorporation of one of these crosslinking agents in the polymers prepared in this study could have increased the Tg of the crosslinked network by 10^{0}C or more. Therefore, the flexible tetrafunctional crosslinking agent 35 was prepared by a hydrosilation reaction (Scheme 13). Similar to the preparation of oligomers 32a,b, the hydrosilation reaction was essentially complete in 3 h at 60^{0}C. The siloxane ring showed no evidence of ring-opening during the hydrosilation reaction. GPC analysis revealed that the product after column purification had a polydispersity of 1.01 with an Mn of 1430 g/mol, close to the calculated value of 1273 g/mol. Thus, no tri, di, or mono-substituted impurities were present.

Prior to cyclodimerization, 35 displayed a Tg at –55^{0}C. Compound 35, when fully thermally self-cured, displayed a Tg at 54^{0}C (Figure 28). IR analysis showed very little O-H stretching in the crosslinked product, which would be present if a significant amount of ring-opening had occurred. Compound 35 lost 5 % of its weight at 380^{0}C during TGA when heated at a rate of 10^{0}C / min under N_2. Due to the low thermal stability of oligomers 32a and b, all attempts to crosslink these oligomers with 35 resulted in severe degradation of the network.



Scheme 13

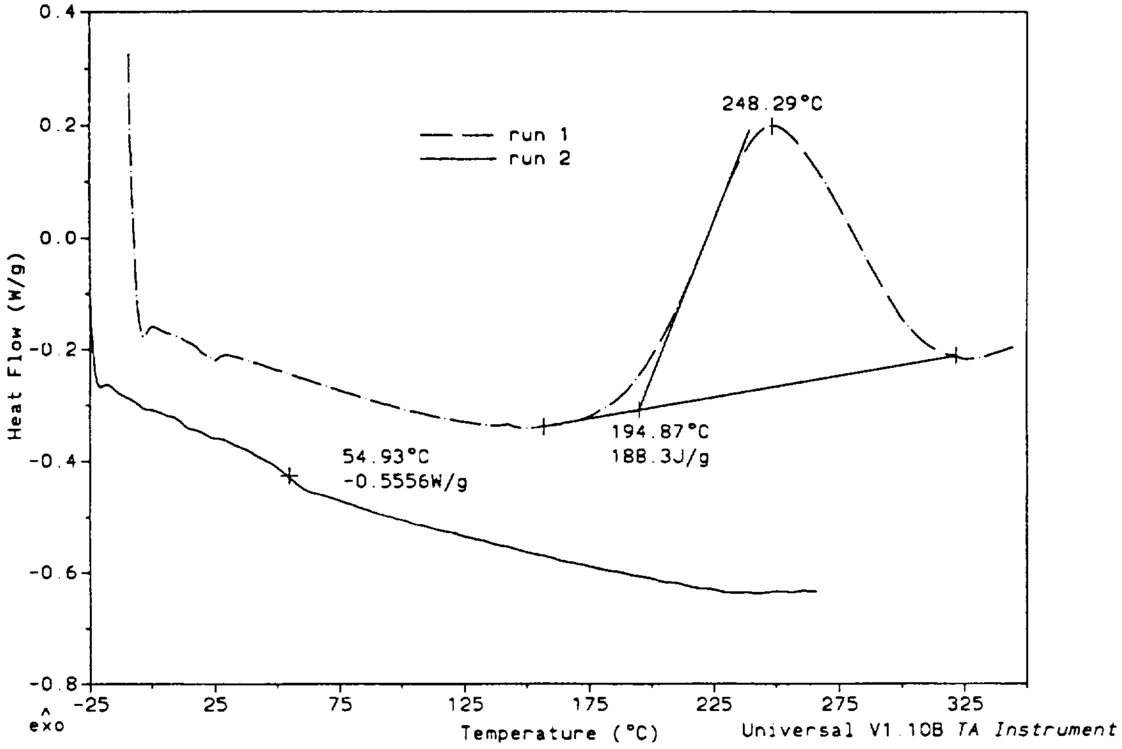


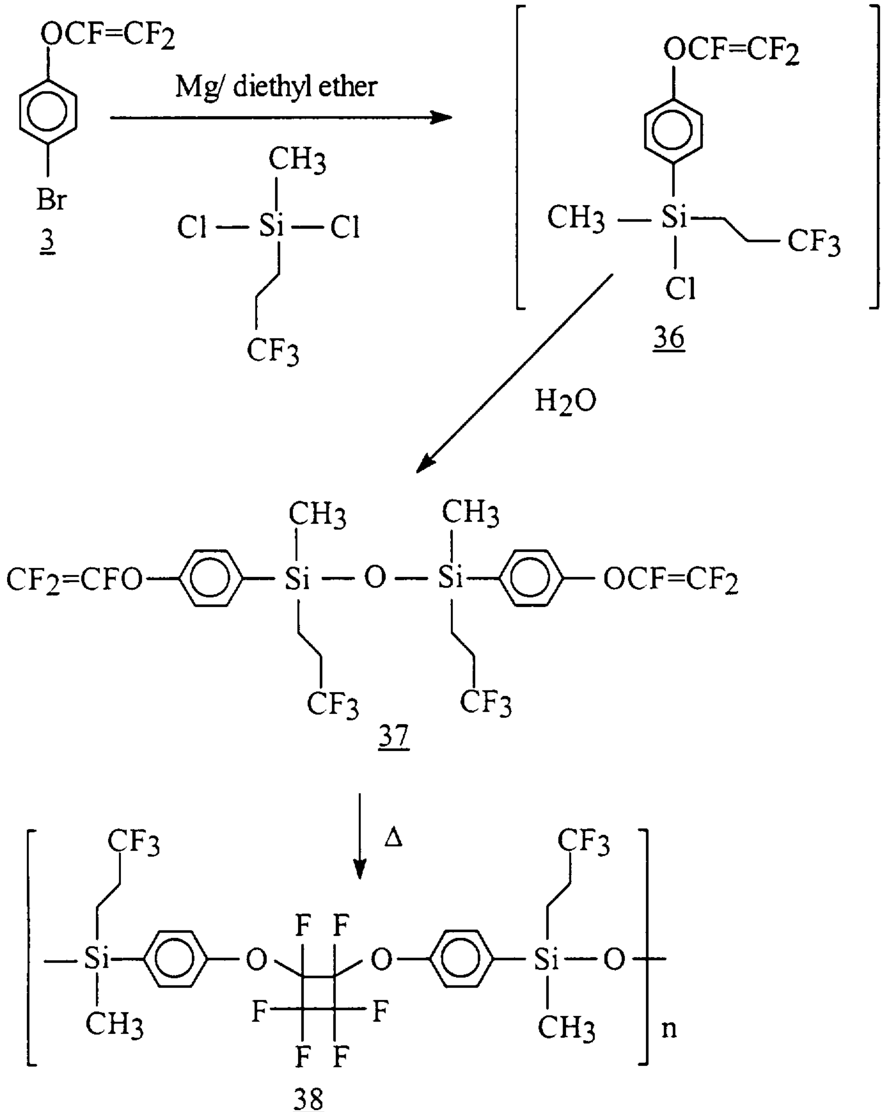
Figure 28. DSC thermograms of compound 35 using a heating rate of 10^0C / min.

Preparation of PFCB-containing polymers with pendant trifluoropropyl groups

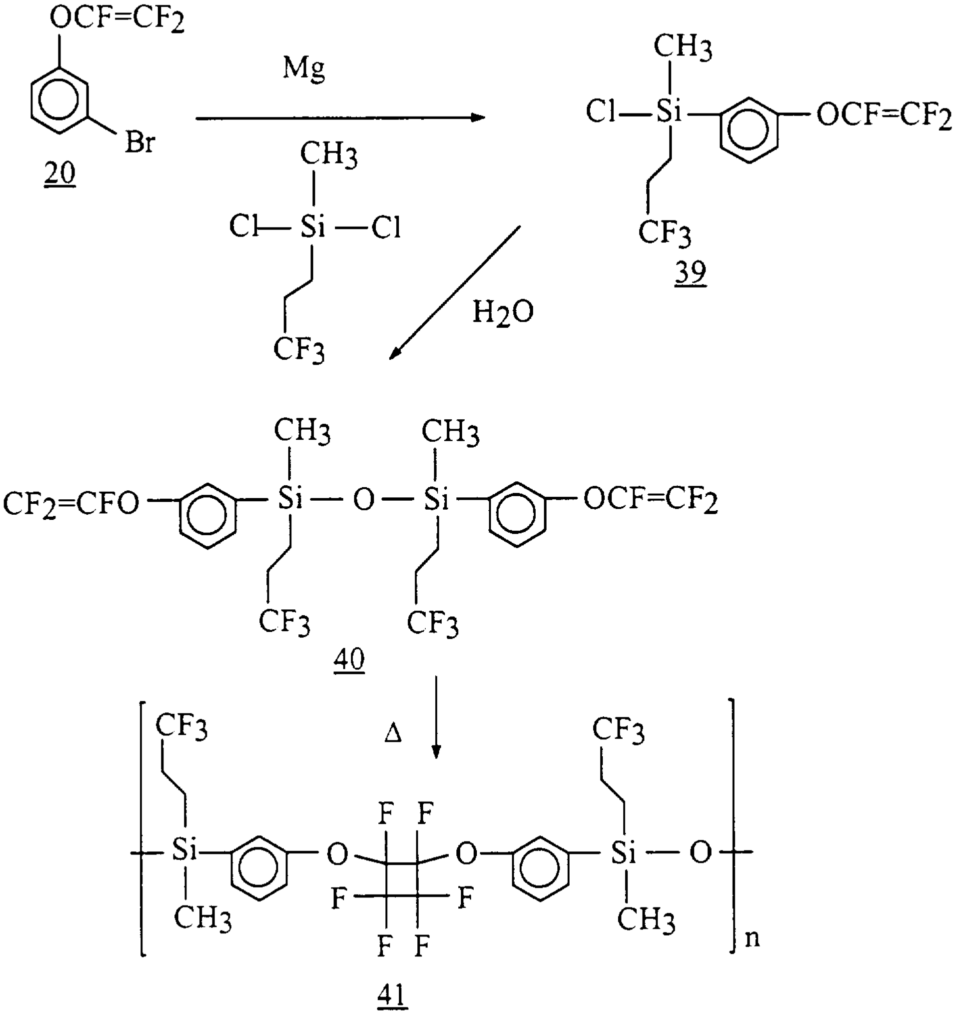
Synthesis of 1,3-bis[4-trifluorovinyl(oxy)phenyl]1,3-(3,3,3-trifluoropropyl)dimethyldisiloxane (37) and 1,3-bis[3-trifluorovinyl(oxy)phenyl]1,3-(3,3,3-trifluoropropyl)dimethyldisiloxane (41)

An attempt was made at preparing PFCB polymers that undergo less swelling by incorporating trifluoropropyl groups pendant to the polymer backbone. The approach used to prepare the *meta* and *para*-catenated structures is shown in Schemes 14 and 15. The monofunctional chlorosilane 36 was prepared from 3 using an *in situ* Grignard reaction in diethylether. Rosenberg and Choe had demonstrated that maximum yields are obtained when 2.5

equivalents of dichlorosilane are used per equivalent of aromatic halide.[47] The use of THF and dichlorosilanes has been shown to lead to side reactions.[48]



Scheme 14



Scheme 15

Compound 36 was distilled and then hydrolyzed for over 20 h in diethyl ether to the silanol. The HCl byproduct was removed by passing a light flow of N_2 under the surface of the reaction mixture. To promote siloxane formation, 1 % (w/w) of tetramethylguanidine di-2-ethylhexanoate was then added. Toluene was also added to promote azeotropic removal of water.

Compound 40 was prepared in an analogous manner starting from reagent 20. The low yields of the hydrolysis reactions were primarily due to material losses involved in the difficult separation of a mono-functional impurity via column chromatography.

Polymerizations of 37 and 40 were accomplished by heating at 195^{0}C for 8 h (Table 10). ^{19}F-NMR was used to monitor the disappearance of the trifluorovinylether absorptions (-124, -132, and -140 ppm) and the appearance of the perfluorocyclobutane ring absorptions (-132 to -138 ppm) absorptions. IR could also be used to qualitatively monitor the polymerization. The trifluorovinyl moiety displayed a weak vinyl stretch at 1833 cm^{-1} that diminished during polymerization. A new peak, which has been attributed to the hexafluorocyclobutane ring[10], began to appear at 960 cm^{-1}. Polymer 41 was crosslinked by first oligomerizing this compound to an Mn of about 3,000 g/mol and then heating with 35 at 200^{0}C for 16 h. The resulting flexible, light-yellow gel displayed a Tg at 2^{0}C, 4^{0}C higher than the linear polymer.

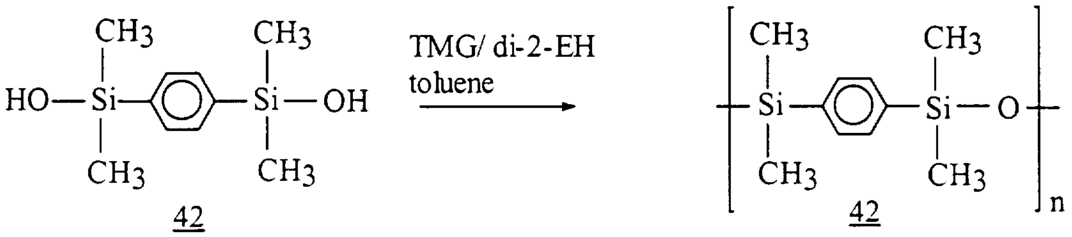
Table 10. Properties of silarylene-siloxane polymers with pendant trifluoropropyl groups (38, 41).

Polymer	Mw[a] (g/mol)	Mn[a] (g/mol)	PDI	Tg[b] (^{0}C)	Td (^{0}C) (air)[c] 5 %	Td (^{0}C) (air)[c] 25 %	Td (^{0}C)(N$_2$)[c] 5 %	Td (^{0}C)(N$_2$)[c] 25 %
38	54,000	30,000	1.8	28	375	420	390	445
41	117,000	61,000	1.9	- 2	380	425	395	450

a. Determined by GPC using THF as the eluent at 30^{0}C, relative to polystyrene standards.
b. Mid-point in the change in slope of a DSC thermogram obtained using a heating rate of 10^{0}C / min.
c. Temperature at which the indicated % weight loss occurred during dynamic TGA using a heating rate of 10^{0}C / min.

Thermal properties of 38 and 41

Polymers 38 and 41 displayed very good thermal stability in both air and N_2. There was very little difference in both the isothermal and dynamic stability between the polymers with pendant trifluoropropyl groups and the polymers with all methyl groups (Figure 29). For comparative purposes, a pure silphenylene-siloxane copolymer was prepared from 1,4-bis(dimethylhydroxysilyl)benzene using the technique of Grassie (Scheme 16).[9] The properties of this polymer are shown (Table 11). Polymer 43 does have slightly better thermal stability than either 41 or 25, however, all three polymers have considerably enhanced thermal stability relative to the fluorosilicone homopolymer.



Scheme 16

Table 11. Properties of silphenylene-siloxane polymer 43.

Mw[a] (g/mol)	Mn[a] (g/mol)	PDI[a]	Tg[b] (^{0}C)	Tm[b] (^{0}C)
240,000	128,000	1.9	N.D.[c]	124

a. Determined by GPC in THF at 30^{0}C, relative to polystyrene standards.
b. Maximum of the melting endotherm in a DSC thermogram obtained using a heating rate of 10^{0}C / min.
c. N.D. = not detected. Previous authors have reported a Tg of −18^{0}C.[27]

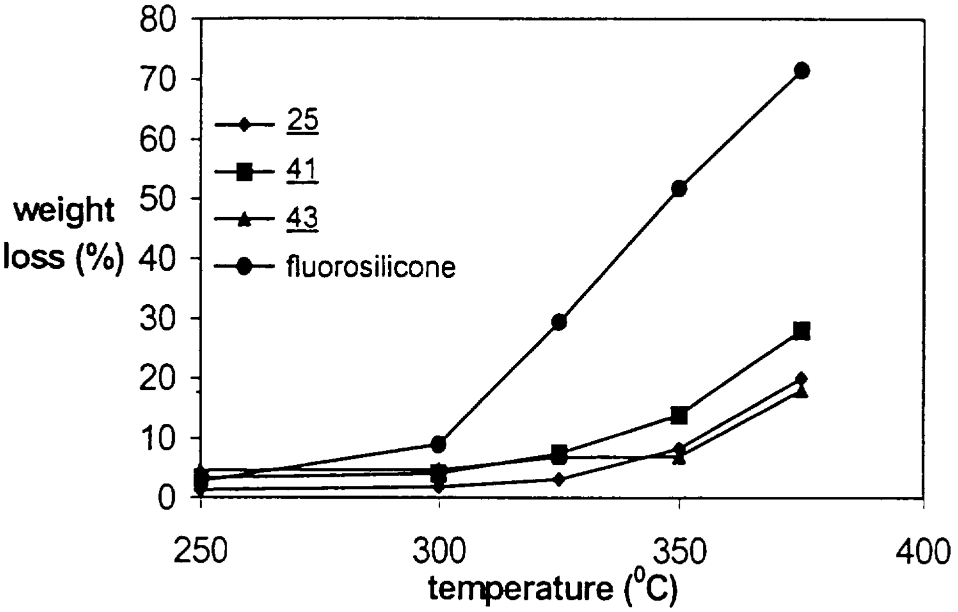


Figure 29. Isothermal weight loss after 2 h of heating under N_2.

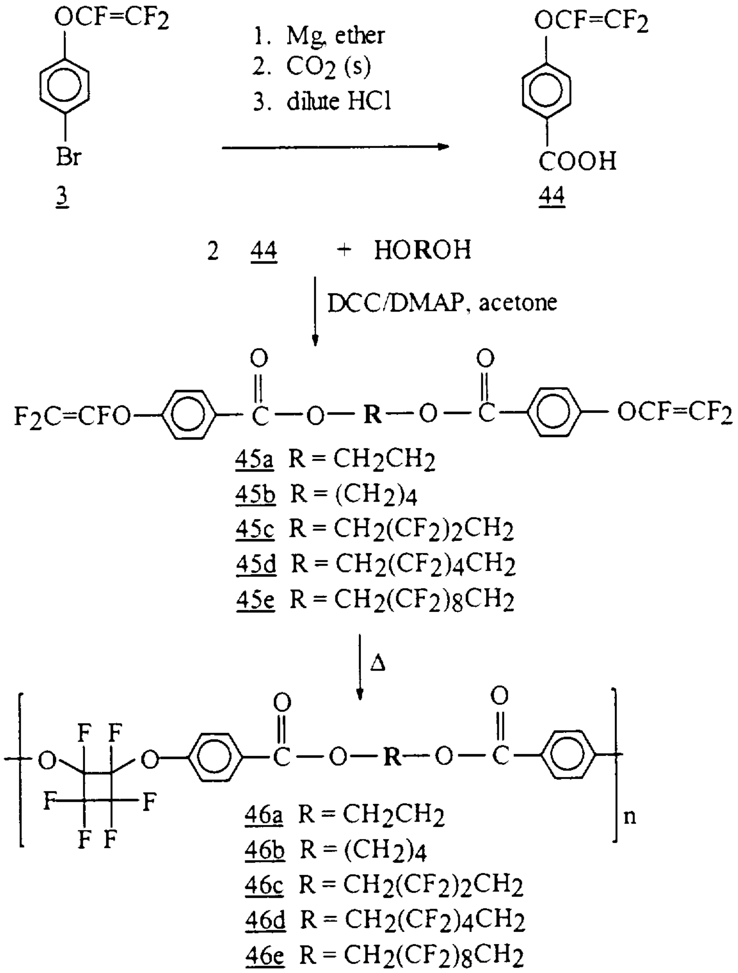
The Tgs of 38 and 41 were 6 and 10°C higher than the tetramethyl-substituted polymers 24 and 25 at equivalent molecular weights. However, the Tg increase was not as large as expected. Rosenberg and Choe found with similar polymers that the Tg increased 8-10°C per trifluoropropyl group.[47]

Swelling properties

The presence of the pendant trifluoropropyl goups in 41 was expected to significantly enhance the fuel resistance of the crosslinked form of this polymer relative to 25. In isooctane, the volume swell dropped considerably to about 40 %. However, in toluene and other aromatic solvents (mesitylene, xylene etc.) the swelling was still over 200 %. Thus, the aromatic portion of jet fuel would still cause considerable swelling of this structure.

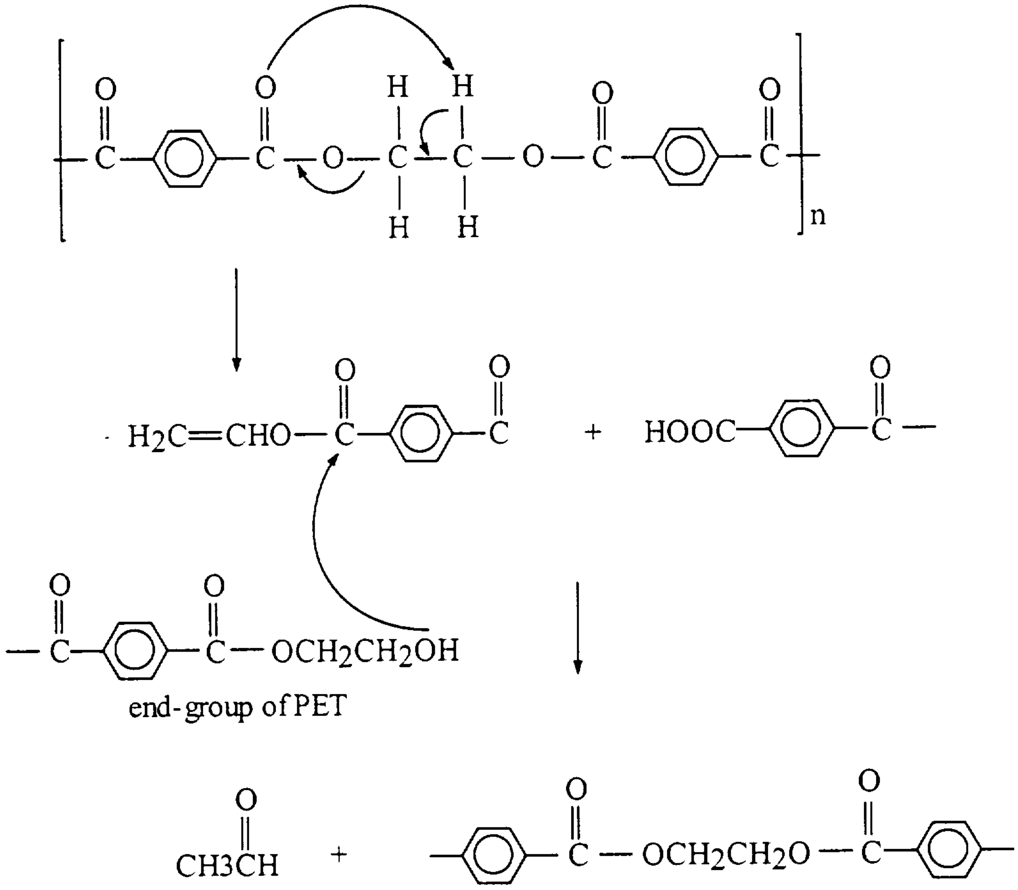
4. SYNTHESIS OF TRIFLUOROVINYLETHER-TERMINATED FLUOROETHERS AND FLUOROCARBONS

Prior to treating a trifluorovinyl-ether containing carboxylic acid derivative with the chain ends of a commercial Fluorolink D^R oligomer, a series of model compounds was prepared to determine the thermal stability of the ester group. The approach involved the preparation of 4-[trifluorovinyl(oxy)]benzoic acid (<u>44</u>) and its subsequent reaction with a series of commercially available α,ω-fluorinated and hydrogenated diols (Scheme 17). The resulting oligomers were to be chain-extended via thermal cyclodimerization.



Scheme 17

Polyesters are not generally known as having high thermal stability. The degradation of poly(ethylene terephthalate) (PET) involves the abstraction of a β hydrogen from the aliphatic portion of the molecule (Scheme 18).[49] This reaction leads to the formation of a vinyl ester end-group and a carboxylic acid moiety. Further reaction of the vinyl ester end-group with the terminal hydroxyl groups of the PET polymer leads to the evolution of acetaldehyde, the primary degradation product. The degradation pathway shown in Scheme 18 would not be available to polymers 46c-e because of a lack of β hydrogens. In fact, completely aromatic polyesters, which have no aliphatic hydrogens available for abstraction, have excellent thermal stability.



Scheme 18

Synthesis of the fluorinated and hydrogenated diesters (45a-e)

Compound 44 was prepared by forming the Grignard reagent of 3, followed by carbonation and acidification. The best procedure involved formation of the Grignard reagent in diethyl ether, followed by direct addition of solid CO_2. After mixing for about 1 h, an excess of 10 % aqueous HCl was added to the brown gel. The product was then extracted with ether, washed with water, and recrystallized twice from hexane. A large amount of material loss occurred in the recrystallization step, reducing yields to about 40 %. Compound 44 had been prepared by Babb and coworkers using a different technique.[50]

A dicyclohexylcarbodiimide (DCC)-promoted esterification was used to form the diester compounds containing terminal trifluorovinylether moieties 45a-e.[51] All reactions were carried out in acetone containing dimethylaminopyridine (DMAP). The diesters were purified by column chromatography using neutral alumina with methylene chloride / hexane eluent mixtures. Higher proportions of methylene chloride (8/2; v/v) were needed for purification of the hydrogenated diesters 45a-b. The monomers had melting points ranging from 20 to 74^0C (DSC) (Table 12). Compound 45e, which had eight CF_2 groups, exhibited two crystalline melting points at 43 and 48^0C (Figure 30).

Polymerization and polymer properties

Compounds 45a-e were polymerized by heating, in the absence of mixing, at 200^0C for 8 h. The properties of the resulting polymers (46a-e) are shown in Table 13. It is postulated that the polydispersities were broad because of the lack of agitation. The Tgs of the polymers ranged from 39 to 72^0C, and increased with decreasing carbon chain lengths. A comparison of polymers 46b and 46c indicates that the presence of fluorine increases the Tg very slightly. The thermal stabilities of the polymers indicate that the ester linkage is reasonably stable to heat. The

Table 12. Melting points of diester monomers.

Monomer	Melting point (^0C)	
45a	43^a	$(43\text{-}46)^b$
45b	20^a	-------
45c	74^a	$(72\text{-}74)^b$
45d	64^a	$(61\text{-}63)^b$
45e	$43, 48^a$	$(44\text{-}47)^b$

a. Minimum of the melting endotherm using DSC with a heating rate of 10^0C/min.
b. Melting range obtained with a Mel-temp apparatus with a heating rate of approximately 2^0C / min.

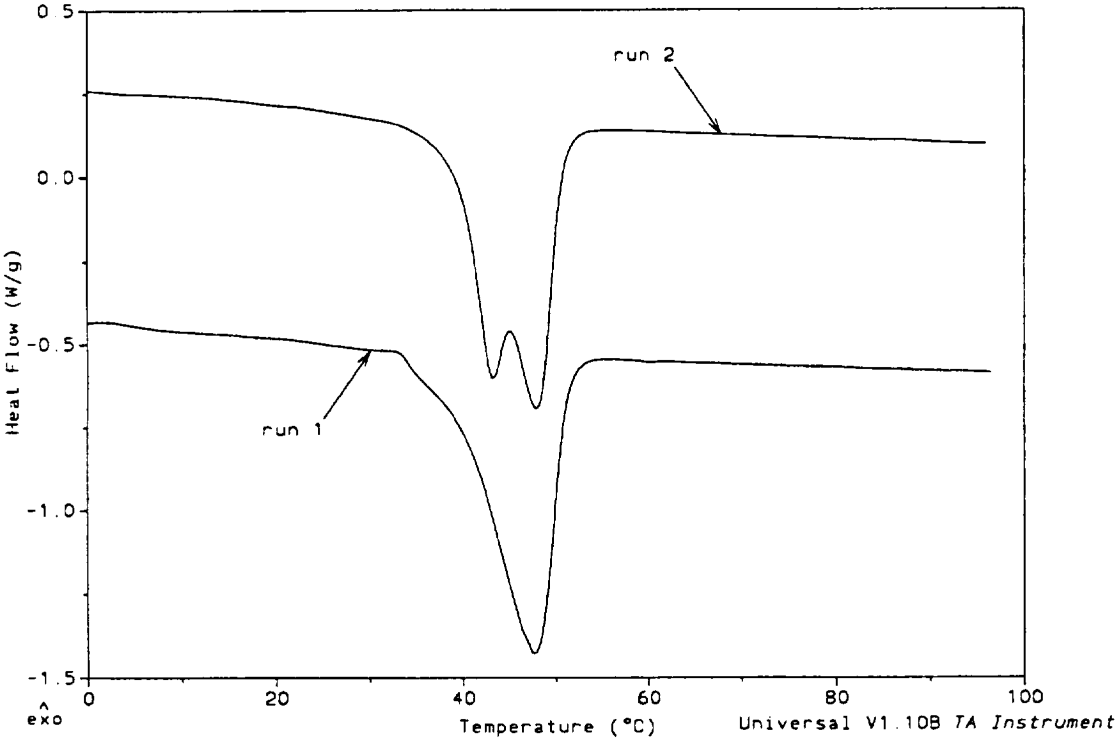


Figure 30. DSC thermograms of monomer 45e obtained with a heating rate of 10^0C / min.

hydrogenated polymers displayed considerably reduced stability compared to the polymers with fluorinated carbon chains. This is likely due to the absence of β hydrogens in the fluorinated polyesters. The high thermal stabilities offered promise for functionalization of the Fluorolink D^R oligomer. This oligomer has end-groups identical to the end-groups of the α,ω-hydroxy terminated fluorinated alcohols.

Table 13. Properties of polymers 46a-e.

polymer	Mw^a (g/mol)	Mn^a (g/mol)	PDI^a	Tg^b (^{0}C)	Td (^{0}C)^c Air	Td (^{0}C)^c N_2
46a	49,400	10,400	4.8	72	370	385
46b	50,300	14,600	3.4	49	365	390
46c	30,900	11,800	2.6	53	410	425
46d	49,900	14,700	3.4	40	415	415
46e	49,100	16,300	3.0	8,39	425	435

a. Determined by GPC using THF as the eluent at 30^{0}C, relative to polystyrene standards.

b. Mid-point in the change in slope of a DSC thermogram obtained using a heating rate of 10^{0}C / min.

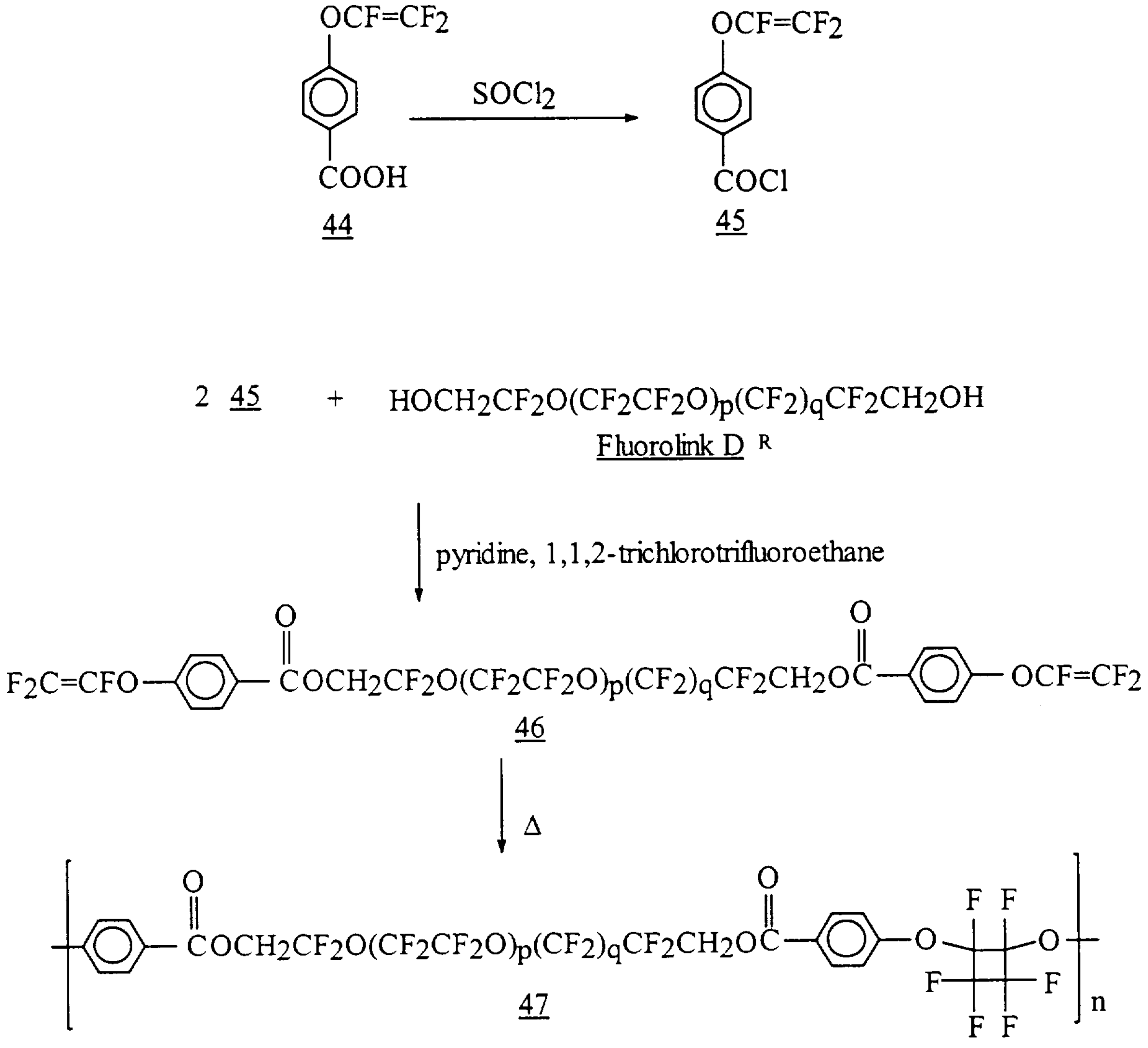
c. Temperature at which a 5 % weight loss occurred when subjected to TGA using a heating rate of 10^{0}C / min.

Functionalization of Fluorolink D^R

The DCC-mediated esterification reaction used for the preparation of monomers 45a-e gave moderate yields. Since the solubility of these small molecules was very high in common solvents, purification techniques such as column chromatography could be used effectively to separate the diester from the dicyclohexylurea by-product and unreacted alcohol and carboxylic acid. The Fluorolink D^R oligomer, with an Mn of 1500 g/mol, has extremely low solubility in organic solvents.[52] In fact, the only solvents that can dissolve this oligomer are 1,1,2-trichlorotrifluoroethane and perfluorocarbon fluids. The high cost, toxicity and volatility of the latter compounds prohibited their use. Furthermore, due to the low polarity of 1,1,2-trichlorotrifluoroethane, DCC and 44 are not soluble in this solvent. Therefore, compound 45 was prepared by treating 44 with thionyl chloride. This reaction proceeded smoothly at room temperature to form a light brown oil (Scheme 19). Babb had prepared this acid chloride by treating 44 with oxalyl chloride.[50]

Functionalization of the Fluorolink D^R oligomer was accomplished by dissolving the oligomer in 1,1,2-trichlorotrifluoroethane and adding slightly greater than two equivalents of 45. This reaction was allowed to proceed at room temperature in the presence of pyridine (an acid acceptor) for 24 h. The solution was then filtered through a 0.45 μ filter and added to methanol to precipitate the functionalized oligomer. The functionalized oligomer was then heated in a vacuum oven at 70^0C for 16 h in an attempt to remove any residual pyridine hydrochloride (bp 224^0C)[53] and unreacted acid chloride.

IR analysis showed the disappearance of the strong O-H stretch of the hydroxy-terminated oligomer and the appearance of bands at 1833 ($CF=CF_2$) and 1745 (C=O ester) cm^{-1}. GPC analysis revealed an increase in the Mn from 1460 g/mol to 2100 g/mol, consistent with the addition of two aromatic groups at the chain ends (Figure 31). Because of the poor solubility in common deuterated solvents, ^{1}H-NMR was not effective in establishing functionalization. This probably would have been difficult anyway, since the only expected change in the spectrum would have been a slight shift in the absorption of the CH_2 group upon conversion of the hydroxyl end-groups to ester groups. GPC and IR analysis did reveal the presence of what appeared to be some unreacted acid chloride, which could not be removed even after precipitation in methanol.


OCF=CF2
SOCl2
COOH
44
OCF=CF2
COCl
45
2 45 + HOCH2CF2O(CF2CF2O)p(CF2)qCF2CH2OH
Fluorolink D R
pyridine, 1,1,2-trichlorotrifluoroethane
F2C=CFO
O
COCH2CF2O(CF2CF2O)p(CF2)qCF2CH2OC
O
OCF=CF2
46
Δ
O
COCH2CF2O(CF2CF2O)p(CF2)qCF2CH2OC
O
O
F F
O
F
F
F F
n
47

Scheme 19

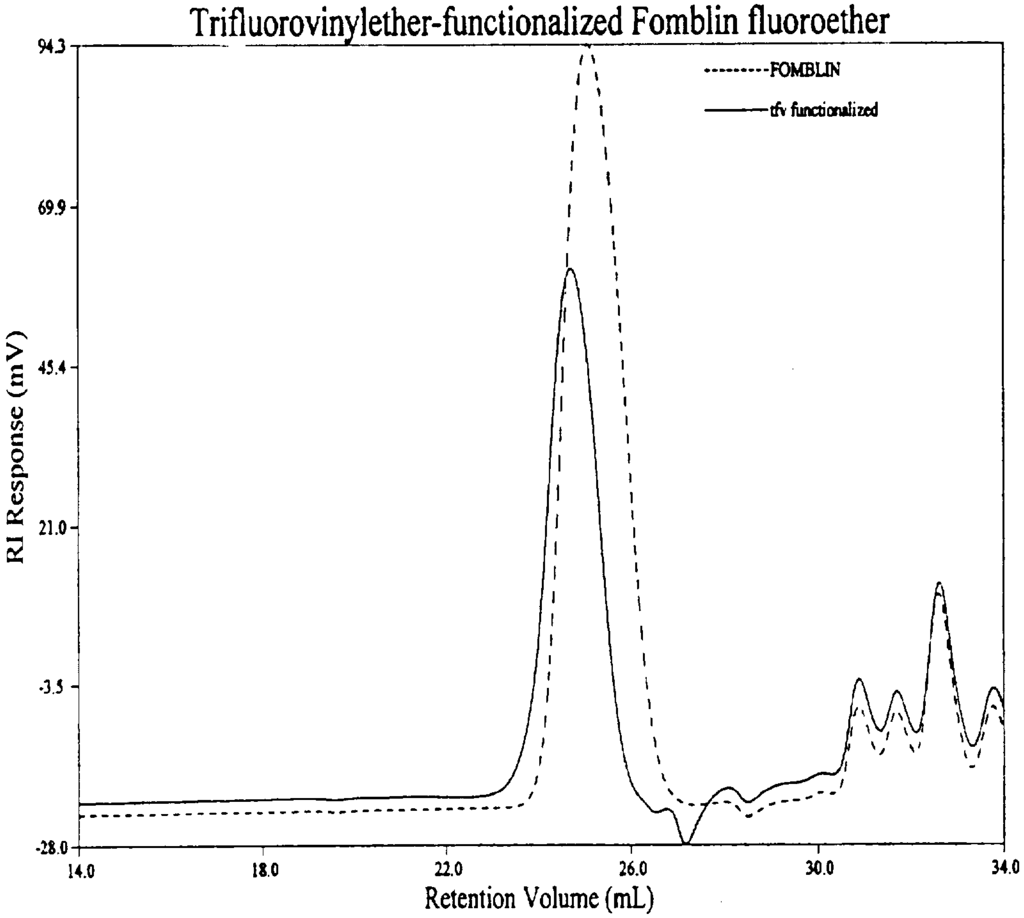


Figure 31. GPC chromatogram before and after functionalization of Fluorolink D^R.

Chain extension and crosslinking of the functionalized oligomer

Chain extension was carried out by heating oligomer 46 at 170^{0}C for 18 h. A significant increase in viscosity was observed along with the disappearance of the trifluorovinyl stretch in the IR spectrum (Figure 32). GPC measurements in THF indicated that the oligomer Mn increased slightly to 2900 g/mol with an Mw of 3400 g/mol. However, the solubility of the oligomer in THF was very poor. Several attempts were made to increase the molecular weight of 47 by repeated reprecipitations in methanol followed by reheating. For example, heating a sample, which had been precipitated twice, at 195^{0}C for 8 h did not result in a significant increase in the Mn. The chain-extended polymer 47 had moderate thermal stability displaying a 5 % weight loss in air and nitrogen at 365^{0}C (Figure 33). The low stability of Fluorolink D^R, relative to other perfluoropolyethers, has been attributed to the presence of difluoroacetal linkages in the polymer backbone.[52] There was no evidence of any transitions in the DSC thermogram from –110^{0}C to 150^{0}C. Possible explanations of the low Mn observed include: (1) insolubility of the higher molecular weight polymer in THF which resulted in lower observed values; (2) intramolecular reactions of the trifluorovinylether end-groups resulting in cyclization; and (3) the presence of the mono-functional trifluorovinylether-terminated 45. The clearly visible increase in viscosity upon heating supports the first explanation.

Oligomer 46 was mixed with 10 pbw of 35, and the resulting two-phase mixture was heated at 185^{0}C for 18 h. The crosslinked gel obtained was extracted with 1,1,2-trichlorotrifluoroethane to remove about 25 % of soluble material. The crosslinked gel was slightly tacky and underwent a volume swell of less than 20 % in both isooctane and toluene.

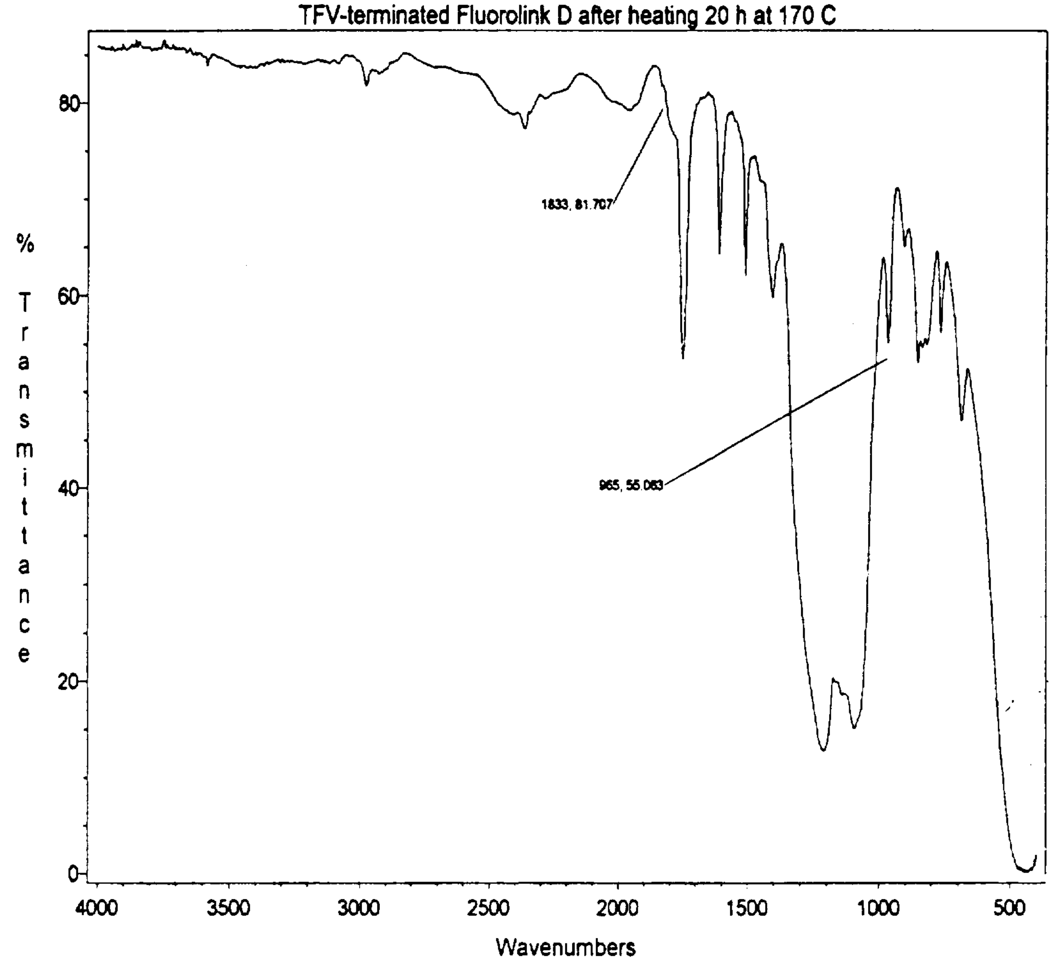


Figure 32. IR spectrum of chain-extended perfluoropolyether containing perfluorocyclobutane rings (47).

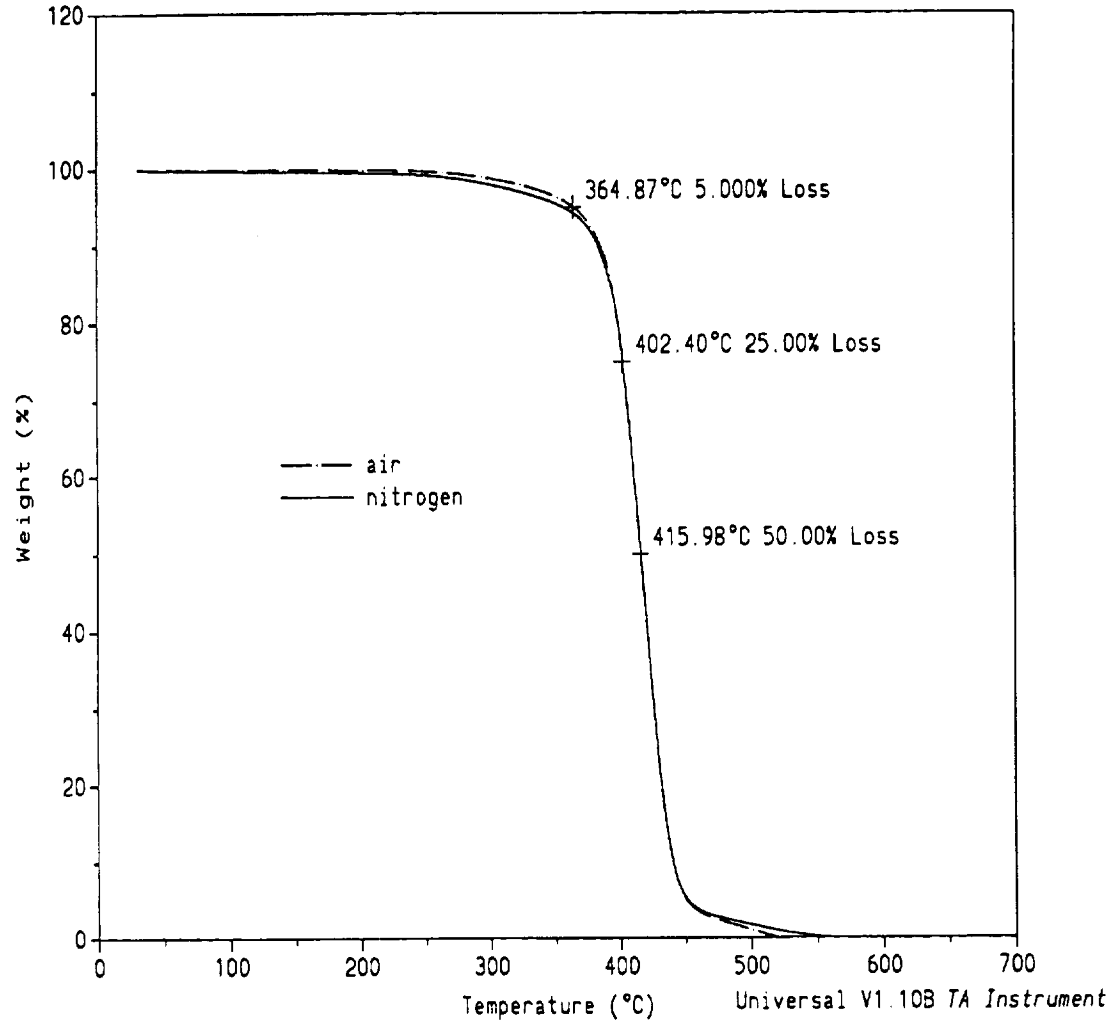


Figure 33. TGA thermograms of 47 obtained under air and N_2 using a heating rate of 10^0C / min.

SUMMARY

In the first portion of this work, 1,2,3,3,4,4-hexafluoro-1,2-bis[4-(dimethyl hydroxysilyl)phenoxy]cyclobutane and 1,2,3,3,4,4-hexafluoro-1,2-bis[3-(dimethyl hydroxysilyl)phenoxy]cyclobutane were prepared and homopolymerized to afford polymers with excellent thermal stability and Tgs of 27^0C and -12^0C, respectively. Despite the moderately high wt % of fluorine in the polymer structure (23.8 %), these polymers had poor fuel resistance. In fact, swelling measurements indicate that these polymers had apparent solubility parameters of about 18.2 $J^{1/2}\ m^{-3/2}$ (toluene). Copolymerization of the disilanol monomers with fluorosilicone monomers afforded copolymers that displayed one Tg and excellent thermal stability. Copolymers containing 20-30 wt % of the perfluorocyclobutane-containing structure displayed adequate fuel resistance, enhanced thermal stability, and a Tg low enough to meet the requirements of a HSCT fuel tank sealant.

In the second part of this work, trifluorovinylether-terminated oligomers were prepared and polymerized via cyclodimerization. Initially, an α,ω-silanol-terminated fluorosilicone was end-capped with trifluorovinylether end groups via a two-step synthetic sequence. The oligomer was thermally cyclodimerized to a polymer that displayed thermal stability similar to that of a fluorosilicone homopolymer. Second, 1,3-bis[4-trifluorovinyl(oxy)phenyl]-1,3-(3,3,3-trifluoropropyl)dimethyldisiloxane and 1,3-bis[3-trifluorovinyl(oxy)phenyl]-1,3-(3,3,3-trifluoropropyl)dimethyldisiloxane were prepared and cyclodimerized to afford polymers that contained pendant trifluoropropyl groups. The pendant trifluoropropyl groups did enhance solvent resistance in aliphatic hydrocarbon solvents, however, no improvement was observed in aromatic hydrocarbon solvents. These polymers also displayed excellent thermal stability.

In the last part of this work, a series of monomers was prepared by the DCC-promoted esterification of 4-[trifluorovinyl(oxy)]benzoic acid with α,ω-functionalized hydrogenated and partially fluorinated alcohols. The monomers were cyclodimerized to the corresponding polymers. The polymers that did not contain β hydrogens displayed significantly higher thermal stability than the fully hydrogenated polymers. A commercially-available α,ω-hydroxy-terminated perfluoropolyether was then functionalized with 4-[trifluorovinyl(oxy)]benzoyl chloride. An attempt was made to polymerize the resulting oligomer via the cyclodimerization of the terminal trifluorovinylether moieties. Although the viscosity of the oligomer increased significantly during polymerization, GPC analysis revealed that the THF soluble portion of the polymer did not have high molecular weight.

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