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Synthesis and thermal properties of fluorosilicones containing perfluorocyclobutane rings

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Abstract

Two disilanol monomers containing perfluorocyclobutane rings, 1,2-bis[4-(dimethylhydroxysilyl)phenoxy]-1,2,3,3,4,4-hexafluorocyclobutane and 1,2-bis[3-(dimethylhydroxysilyl)phenoxy]-1,2,3,3,4,4-hexafluorocyclobutane, were prepared and self-polymerized by treatment with base. The glass transition temperatures (T_gs) of the two high-molecular-weight polymers obtained were 27 and −12°C, respectively. The two monomers were also copolymerized with an α,ω-silanol-terminated 3,3,3-trifluoropropylmethylsiloxane (fluorosilicone) oligomer to form copolymers with varying compositions. The T_gs of the copolymers, which ranged from −60 to −1°C, increased as the amount of the perfluorocyclobutane-containing silphenylene repeat units increased. Copolymers containing more than 20 wt% of this repeat unit displayed less weight loss at elevated temperatures than a fluorosilicone homopolymer when subjected to isothermal gravimetric analysis. One of the copolymers, which contained about 30 wt% of the perfluorocyclobutane-containing repeat unit, was crosslinked with 2,4-dichlorobenzoyl-peroxide. The crosslinked network displayed a volume swell of under 40% in isooctane, similar to a crosslinked fluorosilicone.

Keywords: Fluorosilicone; Perfluorocyclobutane; Fuel tank sealant

1. Introduction

The work presented herein was directed towards developing elastomers that could lead to high temperature fuel tank sealants. Fuel tank sealants are urgently needed and are considered to be enabling technology for high speed civil transports (HSCTs). The sealant must exhibit a combination of properties such as high elongation, moderate peel strength, fuel resistance, and performance for 60,000 h at 177°C. No commercial sealant meets the requirement of the HSCT. The high temperature requirement is because aerodynamic heating while in flight at Mach 2.4 is projected to cause the fuel tank sealant (when the tank is empty) to reach temperatures approaching 177°C [1]. This work 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 make a decision on HSCT go-ahead. The HSCT in this program was a commercial passenger airplane for transoceanic flights that could fly at speeds approaching Mach 2.4.

The most popular commercially available fuel tank sealant that can be used at a temperature of around 177°C 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 rigid silanol-functionalized monomers that were copolymerized with siloxane monomers to form alternating copolymers [4–6]. For example, silphenylene–siloxane and silalkarylene–siloxane copolymers have been synthesized that display increased thermal stability. However, the incorporation of the rigid repeat units in the siloxane backbone also significantly increased the glass transition temperature (T_g), 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

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consistent with other studies that have shown that polysiloxanes undergo both intra- and intermolecular exchange reactions at temperatures below the degradation temperature [8]. In fact, Grassie showed that the random incorporation of as little as 0.15 mol% silphenylene repeat units imparts considerable thermal stability to polydimethylsiloxane [9].

The objective 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 T_g. The incorporation of additional fluorine atoms in the backbone was also expected to result in enhanced fuel (hydrocarbon) resistance. The approach selected to the desired copolymers involved the condensation of silanol-terminated fluorosilicone oligomers with silanol-terminated perfluorocyclobutanes. The effects of the incorporation of the cyclobutane units on the copolymer T_gs, thermal stabilities, and resistance to hydrocarbons were then determined.

2. Experimental

2.1. Materials

3-Bromophenol was purchased from Lancaster Chemical Co. A α,ω-silanol-terminated fluorosilicone oligomer [70% of which had a degree of polymerization of 3, and 30% of which had a degree of polymerization of 6] and a fluorosilicone homopolymer (lot # 88673) were provided by the General Electric Company. Prior to thermal analysis, the commercial fluorosilicone homopolymer was dissolved in methylene chloride, washed with dilute acetic acid and distilled water, and then added to methanol to precipitate the polymer. This treatment removed the low-molecular weight cyclic impurities. 1,2-Dibromotetrafluoroethane was provided by the Dow Chemical Company. All other chemicals were purchased from Aldrich Chemical Co.

2.2. Instrumentation

^{1}H NMR spectra were obtained using a Varian 200-MHz spectrometer. Elemental analyses were performed by Galbraith Laboratories. IR spectra were recorded with a Mattson Genesis Series FTIR. Differential scanning calorimetry (DSC) were performed on a Dupont model 2910 DSC using a heating rate of 10°C/min. Thermogravimetric analysis (TGA) data were obtained using a Hi-Res TGA 2950 Thermogravimetric Analyzer from TA Instruments. Gel permeation chromatography (GPC) was carried out at 30°C using a Waters 410 differential refractometer with tetrahydrofuran (THF) as the eluent.

2.3. Synthesis of intermediates and monomers

2.3.1. 4-[2-Bromotetrafluoroethoxy]bromobenzene (**1**) [10]

To a 2 l, three-neck flask equipped with a Dean–Stark trap, a condenser, a thermometer, and a mechanical stirrer were added 173.0 g (1.00 mol) of 4-bromophenol, 175 ml of *m*-xylene, 700 ml of dimethylsulfoxide, and 70.00 g (1.06 mol) of potassium hydroxide (KOH) pellets. The mixture was heated to 80°C. After the KOH dissolved, the pressure was reduced to 15 mm Hg, and the *m*-xylene/water azeotrope was removed by distillation. After heating at 80°C for 80 h, the system was allowed to come to atmospheric pressure and cooled to 30°C. The Dean–Stark trap and condenser were replaced with an addition funnel containing 286.0 g (1.10 mol) of 1,2-dibromotetrafluoroethane. The reagent was slowly added over 2 h to the reaction mixture, which was maintained at 20–30°C using a water bath. After 4 h of stirring at room temperature, the mixture was heated to 50°C for 14 h, and then added to 2 l of distilled water. The organic phase, which was more dense than the aqueous phase, was separated and washed with 500 ml of a 5% (w/w) sodium carbonate solution, and then with 500 ml of distilled water. The light brown liquid was then distilled to give 216.0 g (61%) of a clear, colorless liquid: bp 50–60°C, 3 mm Hg [Ref. [10] 100–110°C, 20 mm Hg]; ^{1}H NMR ($CDCl_3$) δ: 7.07 (2 H, d, Ar) and 7.47 ppm (2 H, d, Ar); IR (neat) 1484, 1201, 1164, 1132 and 933 cm^{-1}.

2.3.2. 4-[Trifluorovinyl(oxy)]bromobenzene (**2**) [10]

To a suspension of 50.00 g (0.765 mol) of activated zinc in 380 ml of acetonitrile was added 215.0 g (0.611 mol) of **1** over 1 h. The reaction mixture was heated at reflux for 16 h and then cooled to room temperature. The acetonitrile was removed by evaporation under reduced pressure, and 1.4 l of hexane was added to the off-white slurry to extract the product. The hexane extract was separated and concentrated under reduced pressure to give a yellow liquid, which was distilled under reduced pressure to afford 110.0 g (71%) of a clear, colorless liquid: bp 35–42°C, 3 mm Hg. [Ref. [10] 65–75°C, 20 mm Hg]; ^{1}H NMR ($CDCl_3$) δ: 6.95 (2 H, d, Ar) and 7.43 ppm (2 H, d, Ar); IR (neat) 1833 ($CF{=}CF_2$), 1483, and 825 cm^{-1}.

2.3.3. {4-[Trifluorovinyl(oxy)]phenyl}dimethylsilane (**3**) [10]

To a stirred mixture of 6.34 g (0.261 mol) of 50 mesh magnesium powder, 0.001 g of iodine, 45.00 g (0.476 mol) of chlorodimethylsilane, and 320 ml of THF at room temperature was added 60.00 g (0.237 mol) of 4-[trifluorovinyloxy]bromobenzene. After the mixture began to exotherm and darken, it was cooled to 0–5°C using an ice bath. After the addition was complete, the mixture was allowed to slowly warm to room temperature over 5 h. After 15 h of stirring at room temperature, the reaction was quenched with 25 ml of water and 200 ml of hexane, filtered through silica gel and concentrated under reduced pressure. The off-yellow liquid was distilled under reduced pressure to afford 34.60 g (63%) of a clear, colorless liquid: bp 34–38°C, 3 mm Hg [Ref. [10] 80°C, 20 mm Hg]; ^{1}H NMR ($CDCl_3$) δ: 0.32 (6 H, d, CH_3), 4.44 (1 H, heptet, Si–H), 7.08 (2 H, d, Ar), and 7.52 ppm (2 H, d, Ar); IR (neat) 2125 (Si–H), 1833 ($CF{=}CF_2$), and 1591 (Ar) cm^{-1}.

2.3.4. 1,2,3,3,4,4-Hexafluoro-1,2-bis[4-(dimethylsilyl)phenoxy]cyclobutane (4)

To a three-neck flask equipped with a stir bar, N_2 inlet, a condenser, and a thermometer was added 30.00 g of **3**, which was heated at 150°C for 7 h. The reaction mixture was allowed to cool to room temperature, and then transferred to a short-path distillation apparatus. The unreacted starting material was removed by distillation under reduced pressure. The product was also removed by distillation under reduced pressure to give 13.3 g of a clear, colorless oil. The unreacted starting material was heated at 150°C for 7 h, and then distilled to give an additional 6.80 g of the product resulting in an overall yield of 20.10 g (67%): bp 125–136°C, 3 mm Hg; ^{1}H NMR ($CDCl_3$) δ: 0.33 (12 H, s, CH_3), 4.40 (2 H, m, Si–H), 7.13–7.22 (4 H, d, Ar), and 7.287.40 ppm (4 H, d, Ar); IR (neat) 2962 (C–H), 2124 (Si–H), 1591 (Ar), 1498 (Ar), 1396, 1305, 1020, 962 (hexafluorocyclobutane), 885, 829 and 766 cm^{-1}.

Anal. Calcd. For $C_{20}H_{22}F_6O_2Si_2$: C, 51.71%; H, 4.77%. Found: C, 51.74%; H, 4.86%.

2.3.5. 1,2,3,3,4,4-Hexafluoro-1,2-bis[4-(dimethylhydroxysilyl)phenoxy]cyclobutane (5)

To a 500-ml, three-neck flask were added 7.40 g of **4**, 125 ml of diethylether, and 0.50 g of a 5% Pd/C catalyst. The reaction mixture was cooled to 0–5°C with an ice bath, and then 15 ml of distilled water was added dropwise over 15 min. After the addition was complete, the two-phase mixture was stirred an additional 30 min until all bubbling ceased, and then filtered. The filtrate was washed with distilled water. The ether layer was collected and evaporated to dryness under reduced pressure. The white residue was recrystallized from a 100/3 hexane/diethylether mixture and dried under reduced pressure to give 5.40 g (68%) of white crystals: mp 96–98°C; ^{1}H NMR ($CDCl_3$) δ: 0.40 (12 H, s, C–H), 1.90 (2 H, s, O–H), 7.00–7.20 (4H, dd, Ar), and 7.50–7.60 ppm (4H, dd, Ar); IR (KBr) 3400 (O–H), 2963 (C–H), 1591 (Ar), 1503 (Ar), 1321, 1206, 1116, 965 (hexafluorocyclobutane), 870, and 824 cm^{-1}.

Anal. Calcd. For $C_{20}H_{22}F_6O_4Si_2$: C, 48.38%; H, 4.47%. Found: C, 48.20%; H, 4.57%.

2.3.6. 3-[2-Bromotetrafluoroethoxy]bromobenzene (6)

This compound was prepared by the procedure described for **1**, using 3-bromophenol as the starting phenol. A 68% yield of a clear, colorless liquid was obtained: bp 47–54°C, 1 mm Hg; ^{1}H NMR ($CDCl_3$) δ: 7.14–7.50 ppm (4 H, m, Ar); IR (neat) 1586, 1473 (Ar), 1328, 1204, 1165, 1135, 1103, 937, 875, 861, 808, 767, and 672 cm^{-1}.

Anal. Calcd. For $C_8H_4Br_2F_4O$: C, 27.30%; H, 1.15%. Found: C, 27.44%; H, 1.19%.

2.3.7. 3-[Trifluorovinyl(oxy)]bromobenzene (7)

This compound was prepared by the procedure described for **2**. A 77% yield of a clear, colorless liquid was obtained: bp 36–42°C, 5 mm Hg; ^{1}H NMR ($CDCl_3$) δ: 7.00–7.36 ppm (4 H, m, Ar); IR (neat) 1833 ($CF{=}CF_2$),1588, 1473 (Ar), 1316, 1275, 1192, 1142, 876, 770 and 675 cm^{-1}.

Anal. Calcd. For $C_8H_4BrF_3O$: C, 37.98%; H, 1.59%. Found: C, 38.03%; H, 1.61%.

2.3.8. {3-[Trifluorovinyl(oxy)]phenyl}dimethylsilane (8)

This compound was prepared by the procedure described for **3**. A 76% yield of a clear, colorless liquid was obtained: bp, 32–36°C, 3 mm Hg; ^{1}H NMR ($CDCl_3$) δ: 0.34 (6 H, s, CH), 4.41 (1 H, heptet, Si–H), and 7.00–7.36 ppm (4 H, m, Ar); IR (neat) 3064, 2963 (C–H), 2905, 2128 (Si–H), 1833 ($CF{=}CF_2$), 1571 (Ar), 1477 (Ar), 1414, 1313, 1192, 1145, 899, 872, 764 and 735 cm^{-1}.

Anal. Calcd. For $C_{11}H_{10}F_3OSi$: C, 51.71%; H, 4.77%. Found: C, 52.10%; H, 4.99%.

2.3.9. 1,2,3,3,4,4-Hexafluoro-1,2-bis[3-(dimethylsilyl)phenoxy]cyclobutane (9)

This compound was prepared by the procedure described for **4**. A 65% yield of a clear, colorless, viscous oil was obtained: bp 115–125°C, 3 mm Hg; ^{1}H NMR ($CDCl_3$) δ: 0.34 (12 H, s, C–H), 4.41 (2 H, m, Si–H), and 7.13–7.37 ppm (8 H, m, Ar); IR (neat) 3060, 2962, 2904, 2127 (Si–H), 1571 (Ar), 1480 (Ar), 1416, 1305, 1262, 1198, 968 (hexafluorocyclobutane), 888, 834, 765 and 735 cm^{-1}.

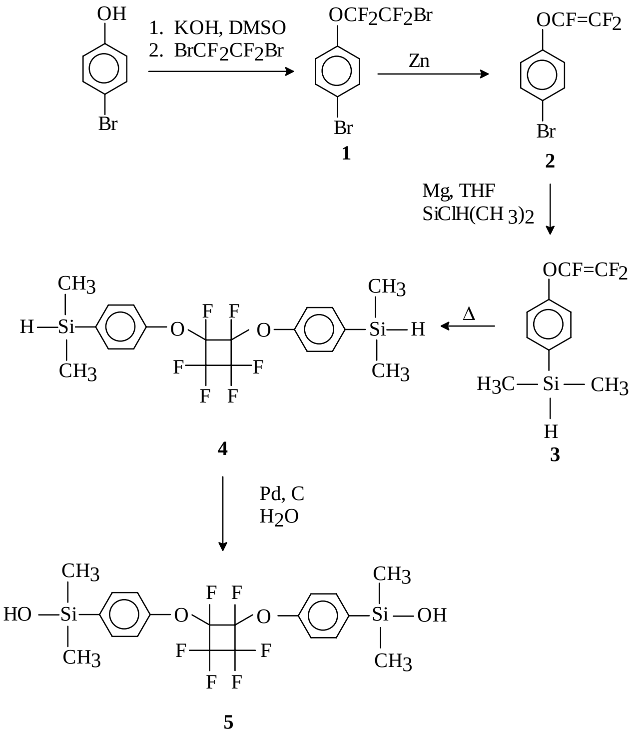
Anal. Calcd. For $C_{20}H_{22}F_6O_2Si_2$: C, 51.71%; H, 4.77%. Found: C, 51.70%; H, 4.81%.

2.3.10. 1,2,3,3,4,4-Hexafluoro-1,2-bis[3-(dimethylhydroxysilyl)phenoxy]cyclobutane (10)

This compound was described by the procedure described for **5**. A 90% yield of a viscous oil which contained about 90% monomer and 10% higher molecular weight siloxane oligomers, as determined by GPC analysis, was obtained. ^{1}H NMR ($CDCl_3$) δ: 0.34 (12 H, s, CH), 2.10 (2 H, s, O–H), and 7.10–7.50 ppm (8 H, m, Ar); IR (neat) 3400 (O–H), 2962, 1571, 1480, and 968 (hexaflurocyclobutane) cm^{-1}. No further purification was attempted.

2.3.11. 4-Diethoxymethylsilyl[trifluorovinyl(oxy)]benzene (11) [11]

To a 500 ml, three-neck, round-bottomed flask equipped with a mechanical stirrer, a condenser, an addition funnel, and an Argon inlet were added 4.64 g of magnesium powder, 113.0 g methyltriethoxysilane, 190 ml of THF, and two crystals of iodine. The mixture was heated to reflux (approximately 70°C), and then 32.00 g of **2** in 30 ml of THF were added over 30 min. After a 1 h induction period, the mixture began to exotherm with vigorous boiling. The



Scheme 1.

mixture was stirred an additional 16 h at reflux, cooled to room temperature, and filtered through Celite. After the THF and methyltriethoxysilane were removed by distillation, the residue was also distilled under reduced pressure to afford 13.00 g (34%) of a clear, colorless liquid: bp 103–110°C, 10 mm Hg [Ref. [11] 87–92°C, 5 mm Hg]; ^{1}H NMR ($CDCl_3$) δ: 0.30 (3 H, s, C–H), 1.20 (6 H, t, CH_2CH_3), 3.70 (4 H, q, OCH_2CH_3), 7.0–7.1 (2 H, d, Ar), and 7.55–7.65 ppm (2H, d, Ar); IR (neat) 1833 ($CF{=}CF_2$), 1594 (Ar), and 1500 cm^{-1} (Ar).

2.3.12. 1,2,3,3,4,4-Hexafluoro-1,2-bis[4-(diethoxymethylsilyl)phenoxy]cyclobutane (12)

To a 50-ml, three-neck flask equipped with a stir bar, a N_2 inlet, a condenser, and a thermometer was added 12.90 g of **11**. The compound was heated at 165–170°C for 7 h. After the starting material was removed by distillation under reduced pressure, the residue was also distilled under reduced pressure to give 6.30 g (49%) of a clear, colorless liquid: bp 165–180°C, 3 mm Hg; ^{1}H NMR ($CDCl_3$) δ: 0.3 (6 H, s, C–H), 1.20 (12 H, t, CH_2CH_3), 3.8 (8 H, q, OCH_2CH_3), 7.1–7.3 (4H, m, Ar), and 7.6–7.7 ppm (4 H, m, Ar); IR (neat) 2960 (C–H) and 965 (hexafluorocyclobutane) cm^{-1}.

Anal. Calcd. For $C_{26}H_{34}F_6O_6Si_2$: C, 50.97%; H, 5.59%; F, 18.60%. Found: C, 51.12%; H, 5.65%; F, 18.63%.

2.4. Polymerization procedure for copolymer 14

Equimolar quantities of 3,3,3-trifluoropropylmethyldichlorosilane and **5** were dissolved in the amount of THF required to give a 20% (w/w) solution. The solution was stirred at room temperature for 24 h, and then added to methanol to precipitate the copolymer.

2.5. General polymerization procedure for the homopolymers 13 and 16 and the random copolymers 15a–15f and 17a–17d

To a three-neck flask were added various amounts of the silanol-terminated fluorosilicone oligomer **5** (or **10**), 0.1% of either KOH or sodium hydride, and sufficient toluene to afford a solution containing 50% (w/w) reactants. After the mixture was heated at 90–100°C for 1 h, the toluene and water were removed by azeotropic distillation. The residue was heated an additional 2 h at 150°C, dissolved in diethylether and washed with excess dilute acetic acid, and then with distilled water. The ether solution was added to methanol to precipitate the copolymer. The perfluorocyclobutane homopolymers **13** and **16** were prepared using this procedure without the fluorosilicone fluid.

2.6. Crosslinking of polymers 13 and 14

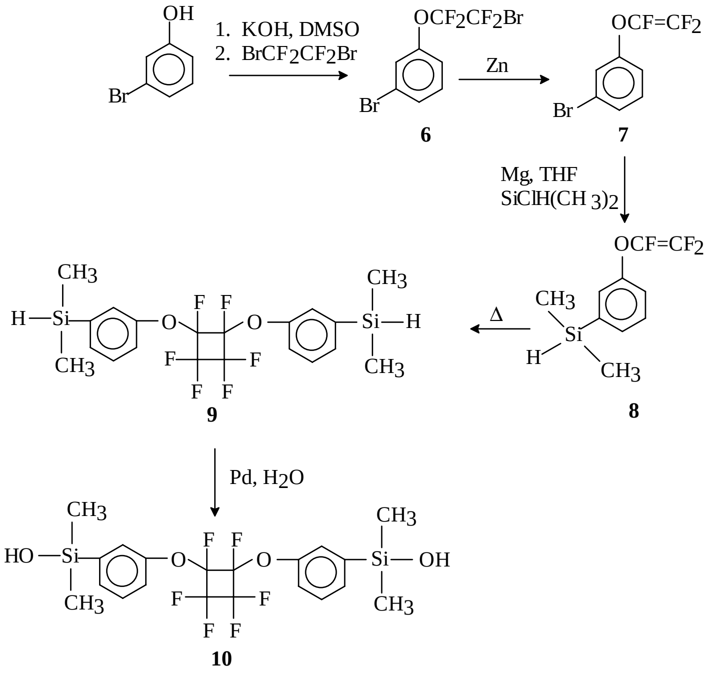
An oligomer with an $\bar{M}_n$ of approximately 10,000 was prepared by the previous procedure, and then dissolved in a 50/50 mixture of chloroform and toluene to give an oligomer concentration of approximately 30% (w/w). After 8% by weight of **12**, and 1% by weight of dibutyltindilaurate were added, the solution was placed in a shallow petri dish, and the solvents were allowed to evaporate over 48 h. The resulting gel was heated at 50°C in 100% relative humidity for 5 d. The crosslinked polymers were extracted with methanol in a Soxhlet extraction apparatus and then dried.

2.7. Crosslinking of 15e and the fluorosilicone homopolymer

Due to the large amount of cyclics that formed during the copolymerization, and the high molecular weight of the copolymer, peroxide crosslinking was carried out after precipitation of copolymer **15e** in methanol. The commercial fluorosilicone homopolymer was crosslinked in a similar manner. To the neat polymer was added 1.5 pbw of a 50% dispersion of 2,4-dichlorobenzoylperoxide (Varox). The components were mixed in a blender, degassed in a vacuum oven at room temperature for 24 h, and then placed in a mold at 110°C for 1 h at atmospheric pressure. After cooling, the crosslinked polymer was extracted with methanol in a Soxhlet apparatus.

2.8. Swelling measurements

The volume swell (%) of the polymers and copolymers was determined by immersing a sample (dimensions approximately 1 mm thick by 1 cm by 1 cm) in each solvent for 22 h at room temperature. Equilibrium was generally established within 3 h. Volume swell (%) was then

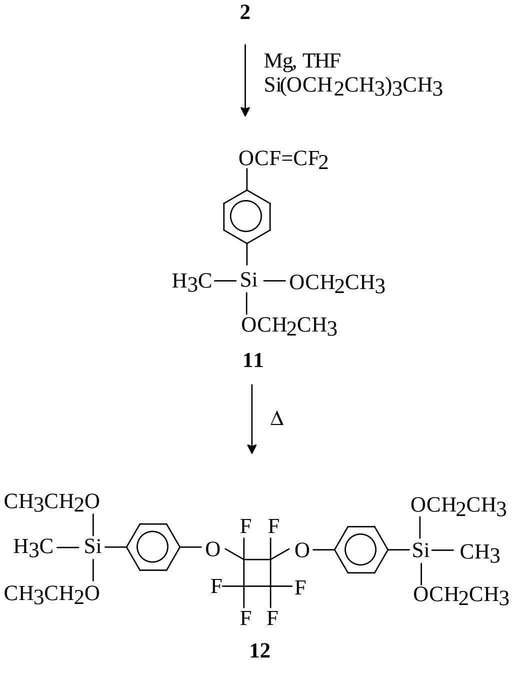


Scheme 2.

determined by the following equation:

$$\text{Volume swell}(\%) = \frac{\Delta V}{V} = \frac{\rho_{\text{polymer}}}{\rho_{\text{solvent}}} \frac{S - D}{D} \times 100;$$

where ρ is the density; S the swollen weight; D the weight after complete removal of solvent.



Scheme 3.

3. Results and discussion

3.1. Monomer syntheses

Compounds **1–3** were prepared previously by Smith and Babb (Scheme 1) [10]. These workers were the first to utilize the thermal cyclodimerization of aromatic trifluorovinyl ether moieties to perfluorocyclobutane rings as a polymerization mode of propagation. In this work, compound **3** was cyclodimerized at 150°C for 6–7 h to afford the silane dimer **4** (Scheme 1). Extended heating above 175°C promoted side reactions, which resulted in a product that was difficult to purify by distillation. The thermal cyclodimerization reaction is known to generate an approximately 50/50 mixture of *cis*/*trans* isomers of a 1,2-disubstituted cyclobutane [12]. The broad boiling point of **4** is likely a consequence of the slightly different physical properties of the *cis*/*trans* isomers. Compound **4** was hydrolyzed to the disilanol **5** in the presence of a 5% palladium-on-carbon catalyst. The use of a pH 7 buffer and lower temperatures reduced the amount of oligomerization during the hydrolysis. The oligomers that formed were removed by recrystallization of **5** from hexane.

The *meta*-catenated isomers of **1–5** (**6–10**) were prepared from 3-bromophenol by the same procedures used for the *para*-substituted compounds (Scheme 2). Compound **7** formed a Grignard reagent with magnesium at about the same rate as compound **2**. Only slight physical property differences were displayed by the *meta*- and *para*-substituted isomers. Compound **10** was a viscous oil that resisted crystallization. GPC analysis showed that **10** was a mixture containing 90% disilanol and about 10% higher molecular

Table 1
Properties of the polymers and copolymers

Polymer no.	Copolymer composition [a]		Fluorosilicone (wt%)[a]	$\bar{M}_n$[b] (g/mol)	PDI[b]	T_g[c]	TGA (5% weight loss) (°C)[d]	
	X	*Y*					Air	N_2
13	1	0	0	58,000	2.0	27	380	410
14	1	1	24.6	14,500	1.3	−1	385	435
15a	1	2.7	46.8	45,000	1.7	−20	385	445
15b	1	4.4	58.9	43,000	1.5	−38	370	405
15c	1	5.5	64.2	75,000	1.8	−42	375	440
15d	1	6.5	67.9	45,000	1.5	−44	375	440
15e	1	8.0	72.3	87,000	1.5	−52	—	—
15f	1	12	79.6	15,600	1.4	−60	335	405
Fluorosilicone	0	1	100	48,000	1.5	68	340	385
16	1	0	0	48,000	2.3	−12	385	415
17a	1	2.8	47.7	34,000	1.3	−34	385	420
17b	1	3.8	55.3	30,000	1.3	−40	385	415
17c	1	6.0	66.1	38,000	1.3	−50	390	430
17d	1	7.5	71.0	34,000	1.3	−55	375	395

[a] Determined by ^{1}H NMR. *X* and *Y* refer to repeat units as shown in Scheme 7.
[b] Determined by GPC using polystyrene standards in THF at 30°C. The samples were analyzed after precipitation in methanol.
[c] Mid-point in change in slope in DSC thermogram obtained with a heating rate of 10°C/min.
[d] Temperature at which a 5% weight loss occurred when the sample was subjected to TGA with a heating rate of 10°C/min.

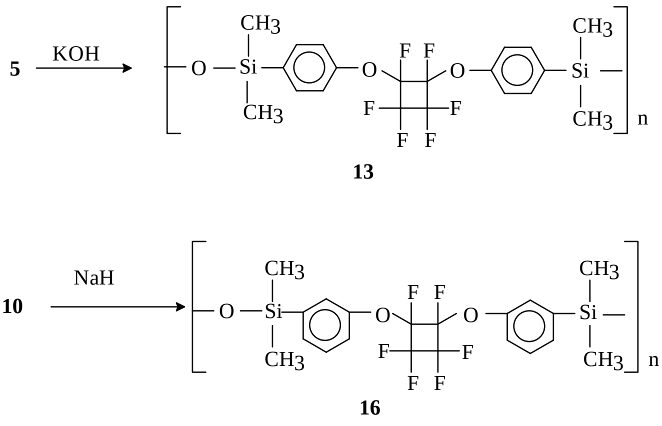
weight siloxane oligomers. IR and ^{1}H NMR analyses clearly showed the presence of an O–H group and the complete disappearance of the Si–H bond. The small amount of higher molecular weight oligomers did not interfere with the polymerization of the disilanol.

The crosslinking agent **12** was prepared from the Grignard reagent of **2**, which was generated in the presence of methyltriethoxysilane (Scheme 3). A higher temperature was required for this reaction than for the reaction of the Grignard reagent with chlorodimethylsilane, due to the lower reactivity of alkoxysilanes relative to chlorosilanes. Reaction times longer than 4 h were necessary in order to ensure complete reaction of **2**. The thermal cyclodimerization of **11** gave **12**.

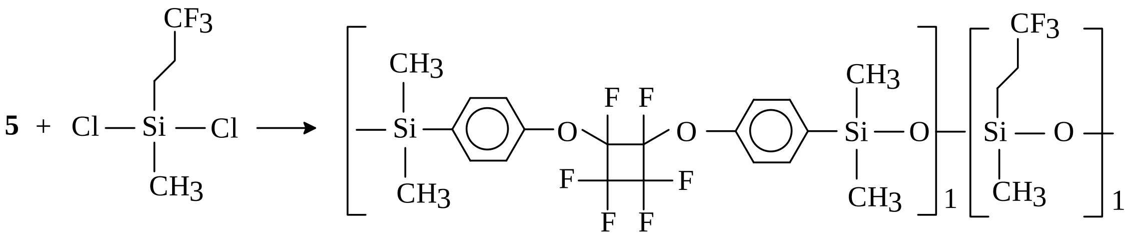
3.2. Polymerizations

3.2.1. Homopolymers

Polymer **13** was prepared by base (KOH)-catalyzed, self-condensation of the disilanol monomer **5** (Table 1, Scheme 4). The number-average molecular weight ($\bar{M}_n$), which ranged from 19,000 to 300,000 g/mol, increased with decreasing amounts of added base, consistent with previous findings [13]. For optimum thermal stability, the base was neutralized with dilute acetic acid after the polymerization. This treatment provided silanol (Si–OH) end-groups, thereby, eliminating possible end-group degradation effects [2]. Polymer **13**, with trifluorovinylether end groups, had been prepared previously by Smith and Babb who utilized



Scheme 4.



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Scheme 5.

the thermal self cyclodimerization of 1,3-bis{4-[(trifluorovinyl)oxy]phenyl]}-1,1,3,3-tetramethyldisiloxane. However, the cyclodimerization route provided a considerably lower molecular weight than obtained in this study.

Although the first attempt to prepare polymer **16** from monomer **10** 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.

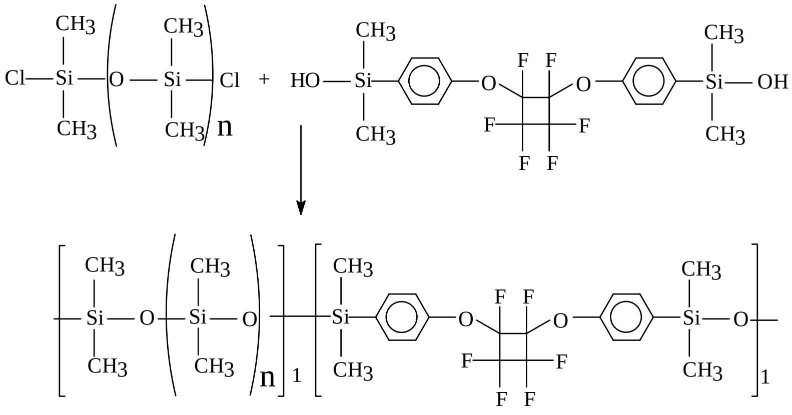
The crosslinking of homopolymer **13** was accomplished by first chain extending **5** using KOH. When an $\bar{M}_n$ of approximately 10,000 g/mol was reached, the reaction was terminated by the addition of dilute acetic acid. After the oligomer was dissolved in a 50/50 (v/v) mixture of toluene and chloroform, the tetrafunctional alkoxysilane **12** and dibutlytindilaurate were added. After the solvent was removed by evaporation, the sample was heated at 50°C in 100% relative humidity for 5 days.

3.2.2. Copolymer **14**

Copolymer **14** (Table 1, Scheme 5) was prepared by the room temperature condensation of **5** with 3,3,3-trifluoropropylmethyldichlorosilane. This type of polymerization has been shown to produce copolymers with significant blockiness [14]. Thus, even with controlled monomer addition and a strong inert gas flow, the hydrogen chloride evolved can react with the siloxane bonds in the polymer backbone leading to redistribution of the repeat units. The amount of monomer alternation retained has been shown to depend on the pendant substituents [14].

The $\bar{M}_n$ of the copolymer obtained from the dichlorosilane-disilanol condensation was only 14,500 g/mol, even though the monomers and solvent were quite pure. The reaction of **5** with dichlorodimethylsilane gave a copolymer with an $\bar{M}_n$ of 26,000 g/mol, and the reaction of **5** with 1,3-dichlorotetramethyldisiloxane gave an M_n of 52,000 g/mol using identical reaction conditions (Scheme 6, Table 2). It is likely that the 3,3,3-trifluoropropyl group slows the condensation reaction sterically. The higher molecular weights observed with the less sterically hindered dichlorosilanes, and the successful curing of the trifluoropropylmethyl substituted oligomer suggests that any competing desilylation reactions are insignificant [15,16]. The lower purity of monomer **10** relative to **5**, prevented the preparation of a *meta*-catenated isomer of **14**. Attempts at copolymerizing **10** with 3,3,3-trifluoropropylmethyldichlorosilane failed due to problems in attaining the proper stoichiometry.

The crosslinking of copolymer **14** was accomplished in a similar manner to **13**. In this case, after the $\bar{M}_n$ reached



Scheme 6.

Table 2
Properties of copolymers shown in scheme 6

n	T_g	M_n	PDI	TGA (5% weight loss)	
				Air	N_2
0	− 10	26,000	1.7	420	445
1	− 12	52,000	1.7	405	445

approximately 10,000 g/mol, the residue was dissolved in chloroform and washed with water to remove any chlorosilane functional groups. After the crosslinking agent and dibutyltindilaurate were added, the sample was heated in 100% relative humidity for 5 days.

3.2.3. Random copolymers

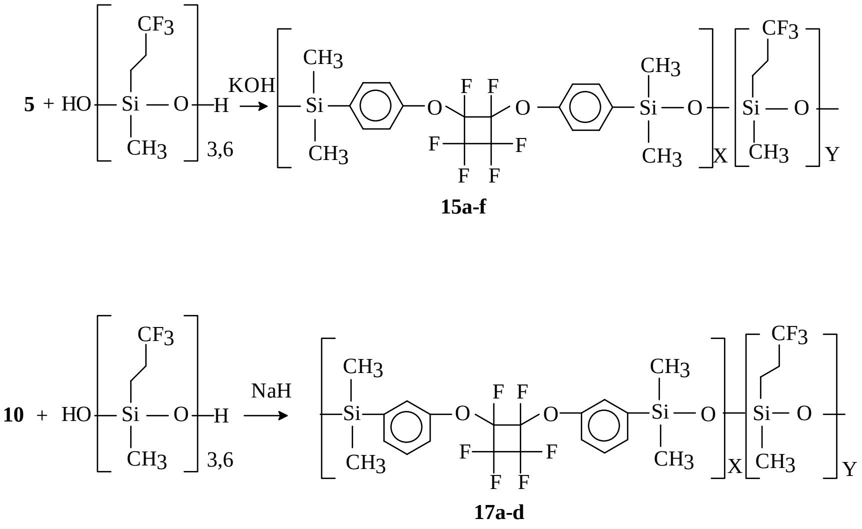
Copolymers **15a**–**15f** were prepared from **5** and a α,ω-disilanol-terminated fluorosilicone oligomer using a KOH mediated technique similar to that of Grassie (Table 1, Scheme 7) [9]. Copolymers **17a**–**17d** were prepared from **10** and the fluorosilicone oligomer in an analogous manner using KOH and sodium hydride as the catalyst. Similar to homopolymer **16**, copolymers **17a**–**17d** had reduced thermal stability when prepared with KOH, unless the copolymers were washed repeatedly with dilute acetic acid.

A considerable amount of cyclization of the fluorosilicone occurred during the copolymerizations. The products were mixtures that contained a unimodal high molecular weight copolymer with low-molecular-weight fluorosilicone cyclics. The cyclics were separated from the linear copolymers during their isolation in methanol. The amount of cyclics, which remained in the methanol, ranged from approximately 30–65% (w/w), depending on the amount of fluorosilicone oligomer in the feed. Based on GPC analysis, the major component in the cyclics appeared to be a tetramer (eight-membered ring). The equilibration of a fluorosilicone homopolymer in the bulk state has been shown to give a 20% yield of linear polymer and an 80% yield of low molecular weight cyclics [17]. IR and ^{1}H NMR analysis of the methanol-soluble fraction provided no evidence for the presence of the perfluorocyclobutane group. Thus, the perfluorocyclobutane monomer did not form homocyclics or cocyclics with the fluorosilicone oligomer. All of the copolymers and the commercial fluorosilicone control were washed with dilute acetic acid, and then with distilled water to provide silanol end-groups. As stated earlier, this treatment served to eliminate possible end-group degradation effects [2].

The use of the randomizing catalyst KOH was expected to result in the formation of random copolymers [9,18]. However, the copolymers were still subjected to DSC analysis in an attempt to identify any block structures. All of the copolymers exhibited one T_g. To determine if blocks of the two components would phase separate, several attempts were made to solution blend a high molecular weight homopolymer of **13** with a fluorosilicone homopolymer. In each case, a two-phase system was obtained that exhibited two T_gs.

The low polydispersities of the copolymers (Table 1) can primarily be attributed to fractionation during the methanol precipitation. The polydispersity of the polymers prior to precipitation was usually between 1.6 and 2.0. After precipitation, the polydispersities of the low 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 for step-growth polymers.

An attempt was made to crosslink copolymer **15e** using the tetrafunctional alkoxysilane **12** and dibutyltindilaurate. However, a soluble product was obtained. Since the $\bar{M}_n$ of **15e** was 87,000 g/mol, the concentration of reactive end groups was extremely low, which may account for the copolymers lack of reactivity. Crosslinking was accomplished using a 50% dispersion of 2,4-dichlorobenzoylperoxide



15a-f

17a-d

Scheme 7.

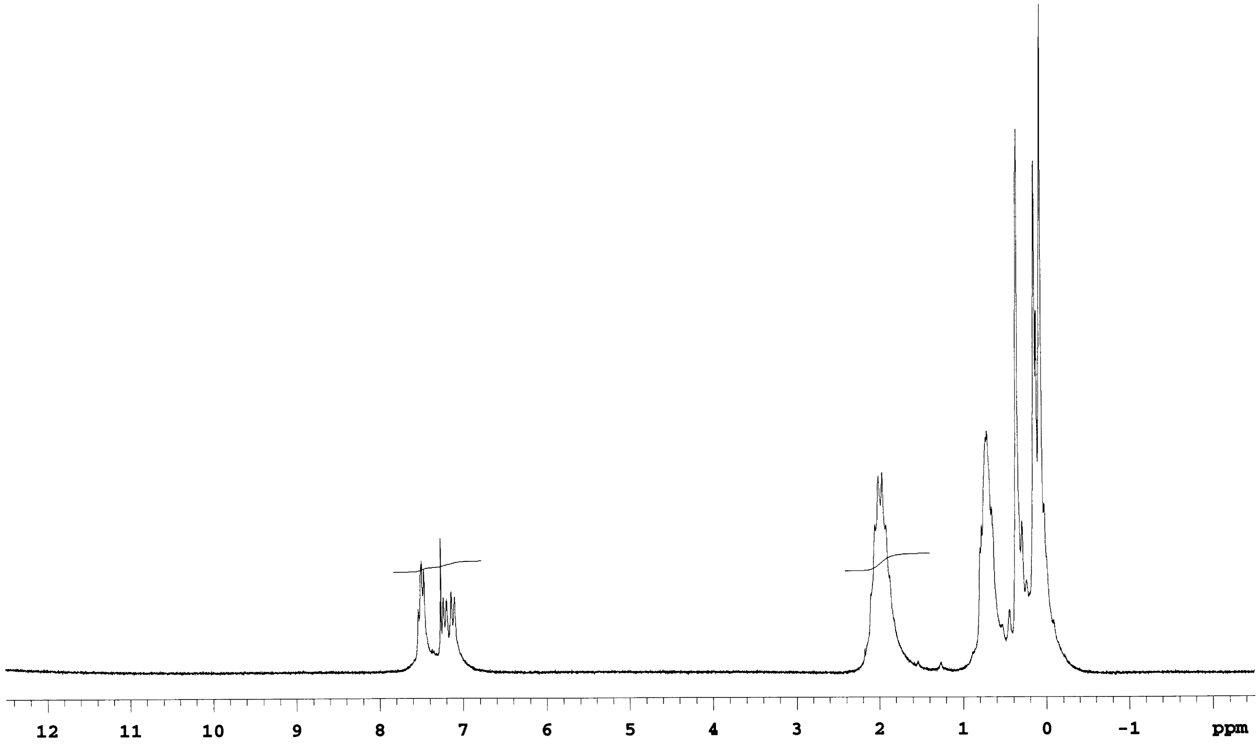


Fig. 1. ^{1}H NMR spectrum of copolymer **15d**.

(Varox) [19]. 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.

3.3. Copolymer composition

Copolymer compositions were determined with ^{1}H NMR (Fig. 1). The integrated areas of the absorptions of the aromatic region of the perfluorocyclobutane repeat unit (77.5 ppm) after subtraction of the chloroform absorption, were compared to the area under the absorption peak of the methylene group adjacent to the trifluoromethyl group (2 ppm) in the fluorosilicone repeat unit. The following expression was used to determine copolymer compositions:

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

where A is the area under the aromatic absorptions (7.0–7.5 ppm) after subtraction of the chloroform absorption; B is the area under the absorption of the methylene group adjacent to the trifluoromethyl group (2.0 ppm); and y the number of repeat units of fluorosilicone, when the number of perfluorocyclobutane repeat units is 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 trifluoromethyl group (-74 ppm). The algebraic expression used was similar to that above except 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 agreed well with those determined by ^{1}H NMR.

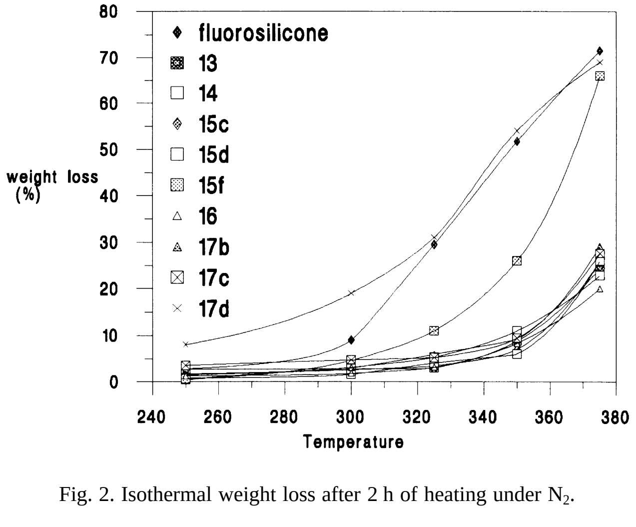


Fig. 2. Isothermal weight loss after 2 h of heating under N_2.

3.4. Thermal properties

Dynamic and isothermal TGA analyses in nitrogen showed that polymer **13** and copolymers **14** and **15a–15f** were more thermally stable than the fluorosilicone homopolymer control (Fig. 2, Table 1). The copolymer thermal stability did abruptly decrease when the molar ratio of **5** to

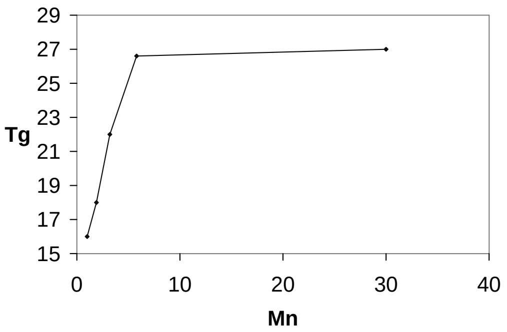


Fig. 3. T_g vs $\bar{M}_n$ ($\times 10^4$) for homopolymer **13**.

the fluorosilicone in the copolymer reached about 1:12. However, the copolymer still underwent significantly less weight loss than a fluorosilicone when heated above 250°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 ends and proceeds through cyclic formation until a perfluorocyclobutane repeat unit is encountered, and then slows down or stops at that point. Only one mode of degradation was observed in the dynamic thermograms. Smith and Babb reported a similar thermal stability for polymer **13** with trifluorovinylether end-groups [10].

Polymers **16** and **17a–17d** also displayed thermal stabilities greater than the fluorosilicone homopolymer control (Fig. 2, Table 1). The thermal stability of the *meta*-catenated copolymers also decreased dramatically when the ratio of **10** to the fluorosilicone reached 1:8.

The T_g of polymer **13** was strongly dependent on $\bar{M}_n$ up to an $\bar{M}_n$ of approximately 50,000 g/mol (Fig. 3). The T_g of 27°C appeared to be independent of $\bar{M}_n$ beyond this point. (Smith and Babb had suggested that the T_g becomes independent of $\bar{M}n$ near 20,000 g/mol, where the T_g is 18°C [10].) The previously reported melt-like transitions near 50°C were not observed [10]. Polymer **16**, which contained the *meta*-catenated aromatic ring, had a T_g of −12°C when the $\bar{M}_n$ was 48,000 g/mol. This indicates that the *meta*-catenation reduced the T_g by nearly 40°C.

Table 3
Solvents used in the swelling studies

Solvent	δ ($J^{1/2}$ $m^{-3/2}$)
Isooctane	14.3
Heptane	15.1
Cyclohexane	16.8
Carbon tetrachloride	17.6
Xylene	18
Toluene	18.2
Ethyl acetate	18.6
Chloroform	19.0
Methylene chloride	19.8
Acetone	20.3
Acetic anhydride	21.1
Isopropanol	23. 5

The T_gs of the *para*-catenated copolymers **14** and **15a–15f** linearly decreased from −1 to 60°C as the amount of fluorosilicone in the copolymer increased from 25 to 80 wt% (Fig. 4). The HSCT required a sealant with flexibility at −54°C [1]. The figure shows that a T_g of −54°C would be displayed by a copolymer containing 75 wt% fluorosilicone. The T_gs of the *meta*-catenated copolymers **17a–d** were also linearly dependent on the fluorosilicone content, decreasing from −34 to −55°C as the wt% of fluorosilicone increased from 48 to 70%.

Crosslinking polymers **13**, **14**, **15e**, and the fluorosilicone homopolymer resulted in T_g increases of 1–3°C. This is consistent with the formation of a lightly crosslinked network [20]. The Shore A hardnesses of the networks ranged from about 15 to 20, typical of unfilled polysiloxane elastomers. The amount of extractables in the crosslinked networks ranged from 8 to 15%. In general, the most material was extracted by the solvent whose solubility parameter (δ) most closely matched that of the network. The moderately low amounts of soluble materials indicate that the curing processes were rather efficient.

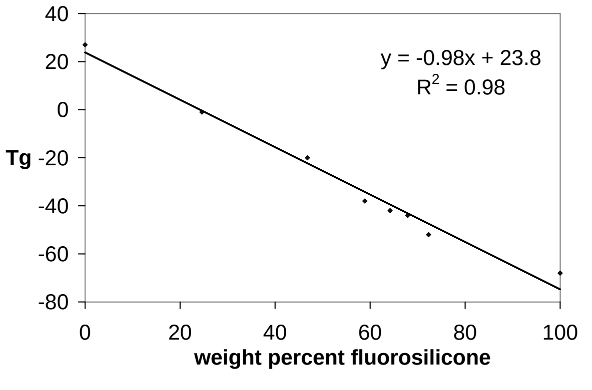


Fig. 4. T_g vs. fluorosiilcone content (wt%) of the *para*-catenated copolymers.

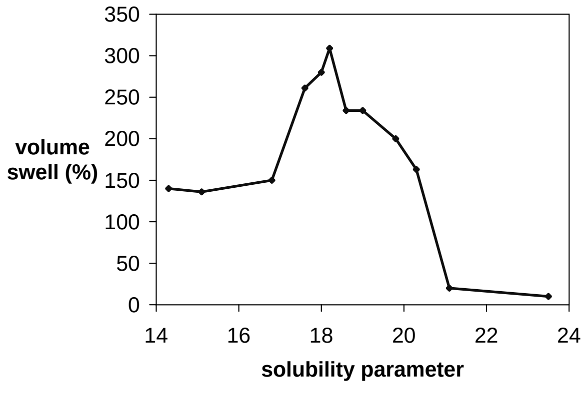


Fig. 5. Volume swell (22 h immersion, room temperature) vs. solubility parameter ($J^{1/2}$ $m^{-3/2}$) of the crosslinked network of **13**.

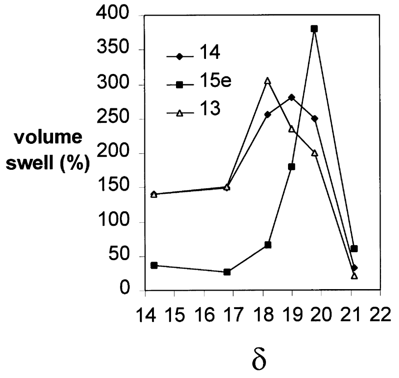


Fig. 6. Swelling behavior of polymer **13** and copolymers **14** and **15e**.

3.5. Swelling behavior

It was initially postulated that the perfluorocyclobutane containing fluorosilicones would have good fuel (hydrocarbon) resistance due to the high concentration of fluorine in the polymer structure. Prior to testing this hypothesis, an attempt was made to determine the contribution of perfluorocyclobutane rings to the fuel resistance of a silphenylene–siloxane system. Thus, the crosslinked network of **13** was subjected to swelling measurements in several different solvents according to ASTM D-471 (Table 3). Surprisingly, the crosslinked network underwent significant swelling in hydrocarbon solvents (Fig. 5). The maximum volume swell was 300% in toluene ($\delta = 18.2\ \mathrm{J}^{1/2}\ \mathrm{m}^{-3/2}$) [21]. 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 [22], which undergoes less than 20% volume swell in hydrocarbon solvents [23]. The dramatic difference in swelling behavior may also be attributable to the differences in the systems fluorine contents (23.8% vs. 36.5%). After immersion in toluene and the chlorinated solvents, the swollen crosslinked polymer was very brittle and crumbled under slight stress. The reduction in tear and tensile properties of highly swollen networks has been attributed to a loss of viscoelastic and other dissipation processes [24].

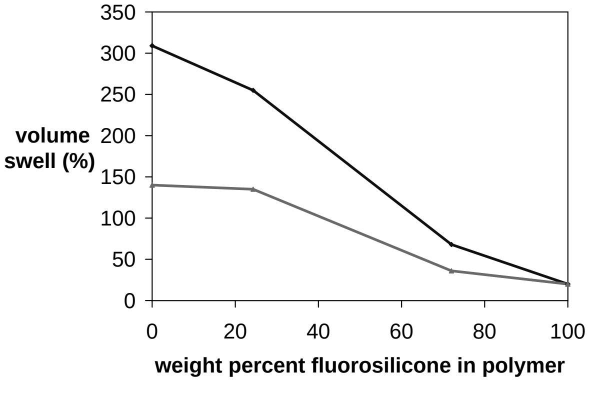


Fig. 7. Volume swell (22 h immersion, room temperature) vs. fluorosilicone content (wt%) of the *para*-catenated copolymers (◆ toluene; ▲ isooctane).

The hydrocarbon resistance of the crosslinked network of copolymer **14** was only slightly better than that of crosslinked **13**. The copolymer, which had a fluorine content of 26.9%, underwent maximum swelling in chloroform ($\delta = 19.0\ \mathrm{J}^{1/2}\ \mathrm{m}^{-3/2}$). Thus, the incorporation of 50 mol% fluorosilicone units in the backbone shifted the δ value approximately $0.8\ \mathrm{J}^{1/2}\ \mathrm{m}^{-3/2}$.

The hydrocarbon resistance of the perfluorocyclobutane-containing fluorosilicone network of **15e** was similar to that of a pure fluorosilicone (Fig. 6). Since the copolymer fluorine content (33.3% wt%) was only slightly less than that of pure fluorosilicone (36.5 wt%), it appears that the perfluorocyclobutane rings did not enhance the fluorosilicone resistance to hydrocarbons. Similarly to fluorosilicone, the crosslinked network swelled considerably in solvents with δs higher than those of hydrocarbons. The maximum volume swell was over 300% in methylene chloride ($\delta = 19.8\ \mathrm{J}^{1/2}\ \mathrm{m}^{-3/2}$). The δ of this solvent is very close to the reported δ of fluorosilicone ($\delta = 19.6\ \mathrm{J}^{1/2}\ \mathrm{m}^{-3/2}$) [25].

The volume swell of the crosslinked systems evaluated in this study in toluene and isooctane are plotted vs. their fluorosilicone contents in Fig. 7. It appears that a fluorosilicone content of approximately 75 wt% (fluorine content = 33.3 wt%) 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 [26].

4. Conclusions

The incorporation of as low as 20 wt% of a perfluorocyclobutane-containing silphenylene repeat unit in a fluorosilicone backbone resulted in a polymer that had significantly lower weight loss than a fluorosilicone when heated in nitrogen for 2 h at temperatures above 250°C. The incorporation of the repeat unit, however, also increased the T_g. The T_g became unacceptably high (> -54°C) when more than 25 wt% of the fluorosilicone was replaced. The incorporation of the repeat unit also decreased the hydrocarbon resistance of crosslinked fluorosilicone networks. No more than 25 wt% of the fluorosilicone could be replaced before the fluorosilicone hydrocarbon resistance was compromised. Thus, the optimum performance was achieved when approximately 20–25 wt% of the fluorosilicone was replaced with the perfluorocyclobutane-containing silphenylene repeat units.

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