Perfluorocyclobutane Aromatic Polyethers. Synthesis and Characterization of New Siloxane-Containing Fluoropolymers†

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ABSTRACT: The synthesis and characterization of siloxane-containing perfluorocyclobutane (PFCB) aromatic polyethers, a new class of fluorosiloxane polymers possessing a well-defined linear structure of alternating disiloxanyl-*p*-phenylene (*cis*/*trans*)-1,2-disubstituted perfluorocyclobutyl ether linkages with known fluoroolefin end groups, is described. The unexpected formation of an aryl Grignard reagent from 4-[(trifluorovinyl)oxy]bromobenzene (**2**) allowed for the high-yield synthesis of 4-[(trifluorovinyl)oxy]phenyldimethylsilane (**3**) which was dehydrogenatively hydrolyzed *in situ* and condensed to bis[1,3-[4-[(trifluorovinyl)oxy]phenyl]]-1,1,3,3-tetramethyldisiloxane monomer (**4**). Thermal cyclopolymerization in the bulk produces poly(1,1,3,3-tetramethyldisiloxanyl-*p*-phenylene-1-oxaperfluorocyclobutylene-2-oxa-*p*-phenylene) (**5**) as a clear, flexible, and thermally stable elastomeric film. Copolymerization of **4** with a trifunctional PFCB monomer gives a toughened thermoset with good thermal stability. Monomers and polymers were characterized by ^{1}H, ^{13}C, and ^{19}F NMR and FTIR spectroscopy. Number-average molecular weights were determined by gel permeation chromatography and, when possible, quantitative ^{19}F NMR end group analysis. Synthesis, characterization, thermal analyses, and current scope of PFCB polymer chemistry are discussed.

Introduction

Polymers containing fluorine continue to lead in the development of advanced materials exhibiting high thermal and thermal oxidative stability, chemical resistance and superior electrical insulating ability.[1−3] Highly fluorinated polymers like poly(tetrafluoroethylene) (PTFE),[2] however, illustrate the challenging "trade-off" between properties and processability that currently dictates high-performance polymer design in general. Practical application of these typically crystalline or otherwise ordered polymers is often precluded by prohibitive process costs. A recent focus has been the synthesis of partially fluorinated polymers, where placement of fluorine-containing segments or substituents within the repeat unit enhances valuable properties such as low dielectric constant and thermal stability without sacrificing—and frequently improving—processability.[3,4] Fluorinated poly(aryl ethers)[3] and polyimides[4] have enjoyed considerable attention in this area as the quest for next-generation materials for microelectronics applications continues.

We recently reported the thermal [$2\pi + 2\pi$] cyclopolymerization of aryl trifluorovinyl ethers, thereby providing new thermoplastics and thermosets possessing the perfluorocyclobutane (PFCB) aromatic ether linkage.[5] Cyclodimerization is favored thermodynamically for fluoroolefins due to an increased double-bond strain,[6a] a lower C═C π-bond energy,[6b] and the strength of the resulting fluorinated C—C single bond adducts in contrast to most hydrocarbon analogs. As generalized in Figure 1, predominant head-to-head cycloaddition proceeds to form the more stable diradical intermediate followed by rapid ring closure giving a mixture of *cis*- and *trans*-1,2-disubstituted perfluorocyclobutanes (Figure 1).[7]

The thermal cyclodimerization of fluorinated olefins has been well established[8−12] since the first reports on the cycloaddition of tetrafluoroethylene.[9] Substituted trifluorovinyl dimerizations are also well-known.[10] The thermal cyclodimerization of α,β,β-trifluorostyrenes has been reported,[11] and recently, fluorinated polyimides have been prepared containing trifluorovinyl pendant groups which could be used for cross-linking.[12]

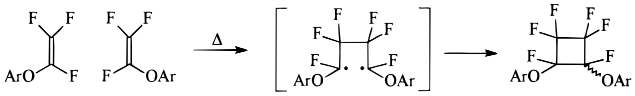

Figure 1. Perfluorocyclobutane (PFCB) aromatic ether formation.

Trifluorovinyl ethers, however, have received less attention.[13−17] Perfluoroalkyl trifluorovinyl ethers were shown by Beckerbauer[13] in 1968 to undergo thermal cyclopolymerization giving low molecular weight perfluoroalkyl polymers containing the hexafluorocyclobutane linkage. In addition to melt-processable fluoroplastics,[1d] fluoroelastomers,[1e] and coatings,[1f] trifluorovinyl ethers are currently used as monomers for the preparation of fluorinated ion exchange resins[14] and ionomer membranes.[1g,15] Recently, new ω-alkenyl vinyl ethers have been cyclopolymerized radically giving fluoropolymers containing five and six-membered rings.[16] In addition, trifluorovinyl ether ω-alcohols were shown to undergo base-catalyzed step addition polymerization affording new perfluoropolyethers.[17]

Our approach has been to combine flexible, yet thermally robust, aromatic ethers with fluorocarbon linkages via the cyclopolymerization of trifluorovinyl ether monomers.[5] We have found that this method gives high molecular weight PFCB thermoplastic polymers and solution advanced thermosetting prepolymers which can be easily processed. Advanced PFCB thermoplastics and cured thermosets of this type exhibit high T_g's, excellent thermal stability,[5e] optical clarity, and isotropic dielectric constants below 2.5 at 1 MHz.

The thermally induced step growth addition type polymer chemistry which proceeds here does not require catalysts or initiators. Cycloaddition polymerization results in well-defined polymers containing known trifluorovinyl terminal groups which are completely void of condensation byproducts.[5d] Our program thus far has

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† This paper is dedicated to Professor George B. Butler on the occasion of his 80th birthday.

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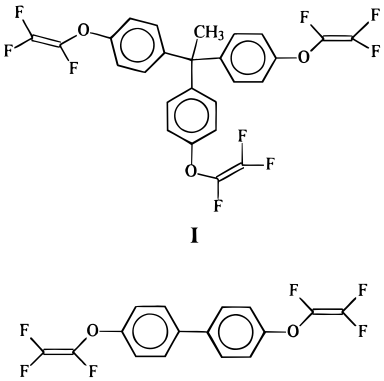

I

II

Figure 2. Previously studied aromatic trifluorovinyl ether monomers.

focused on trifluorovinyl ethers prepared from readily available bis- and trisphenols, such as, tris(hydroxyphenyl)ethane **I** and biphenol **II** (Figure 2).[5a]

While these structures provide high-T_g polymers with good thermal stability and mechanical properties, we have undertaken a study to examine other functionalities which may complement existing PFCB polymer properties. One such group predicted to exhibit compatibility with PFCB polyethers is the versatile siloxane linkage. Fluorinated siloxane polymers in general are currently employed commercially as high-temperature lubricants, elastomers, and adhesives with excellent chemical, thermal, and oxidative resistance.[18]

Tremendous effort has been devoted to the synthesis of organofunctional siloxane polymers due to their unique combination of properties including low-temperature flexibility, hydrophobicity, thermal stability, low dielectric, biocompatability, and gas permeability.[19] In particular, siloxane incorporation has been used to tailor specific properties of an existing base macromolecular function to give hybrid polymers possessing a tunable range of performance. These hybrid systems include the following: poly(silarylene−siloxane)s,[20] poly(imide−siloxane)s,[21] sol−gels,[22] siloxane-modified epoxy resins,[23] phenolic compounds,[24,25] vinyl ester resins,[26] polysulfones,[27] polycarbonates,[28] polyurethanes,[29] polyesters,[30] and a variety of block copolymers.[31]

Here we describe our initial efforts at constructing new siloxane-containing aryl trifluorovinyl ether monomers and PFCB polymers therefrom. It was found that Grignard reagents can be prepared from aryl bromides containing the trifluorovinyl ether functionality. This surprising result allowed for the preparation of disiloxane monomer **4** described herein and has continued to be of valuable synthetic utility. Silicon-containing perfluorocyclobutane aromatic polyethers were not known previously.

Experimental Section

General Information. ^{1}H NMR 400-MHz, proton-decoupled ^{13}C NMR 100-MHz, and ^{19}F NMR 376-MHz spectra were obtained with a Varian Unity Plus NMR Superconducting Spectrometer system. Quantitative ^{13}C and ^{19}F NMR spectra were collected using a gated decoupled sequence with a pulse delay of 60 (16 h acquisition) and 20 s (4 h acquisition), respectively. Chloroform-*d* was used as solvent, and chemical shifts reported are internally referenced to tetramethylsilane (0 ppm), $CDCl_3$ (77 ppm), and $CFCl_3$ (0 ppm) for ^{1}H, ^{13}C, and ^{19}F nuclei, respectively. Infrared analyses were performed on neat oils between NaCl plates or on free-standing polymer films using an ATI Mattson Genesis Series FTIR spectrophotometer. Gas chromatography/mass spectrometry (GC/MS) data were obtained from a Varian Saturn GC/MS using a 30 m × 0.25 mm × 0.25 mm DB-1 capillary column. High-resolution electron impact mass spectroscopic (EI/HRMS) data were obtained on a Fisons Autospec mass spectrometer and the sample was introduced by direct exposure probe (DEP).

Gel permeation chromatography (GPC) data were collected using a Waters model 150-C gel permeation chromatograph at 30 °C equipped with two Polymer Labs PLGel 5 μm Mixed-C columns. Data acquisition and manipulation were performed using GPC-PRO software from Viscotek. The eluting solvent was HPLC grade THF at a flow rate of 1.0 mL/min. Retention times were calibrated against Polymer Labs Easical PS-2 polystyrene standards.

Differential scanning calorimetry (DSC) data were obtained from a Mettler TA4000 System under a nitrogen atmosphere at a scan rate of 10 °C/min. thermogravimetric analysis (TGA) was performed on a DuPont Instruments 951 Thermogravimetric Analyzer with program heating at 10 °C/min in nitrogen and air with a flow rate of 50 mL/min.

All starting materials, reagents, and solvents were obtained from commercial sources and used as received unless otherwise stated.

4-(2-Bromotetrafluoroethoxy)bromobenzene (1). To a 5-L vessel fitted with a Dean−Stark azeotropic distillation assembly were added 1007.33 g (5.82 mol) of 4-bromophenol, 373.79 g (5.82 mol) of KOH, 3.2 L of DMSO, and 0.8 L xylene. The mixture was heated to 100 °C (ca. 200 mmHg) for 48 h during which time H_2O was removed giving a dry salt solution (800 ppm H_2O). The solution was cooled to 30 °C, and 1665.09 g (6.40 mol) of $BrCF_2CF_2Br$ was added slowly in 4 h with constant cooling such that the temperature did not exceed 30 °C. The solution was allowed to stir for 12 h at 22 °C and then for 10 h at 35 °C whereafter the reaction was diluted with H_2O and extracted with methylene chloride, and the organic phase was washed three times with H_2O, dried over $MgSO_4$, and concentrated *in vacuo* giving 1477.9 g (72%) of the bromotetrafluoroethyl ether **1** as a clear liquid: bp 100−110 °C (20 mmHg). To date, the only significant byproduct produced during fluoroalkylation is a small quantity (<5%) of the tetrafluoroethyl ether ($ArOCF_2CF_2H$) and is more effectively removed after elimination to the fluoroolefin **2** by flashing over neutral alumina in hexane. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.07 (2H, d, $J = 8.4$ Hz), 7.47 (2H, d, $J = 8.8$ Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 110.40 (m, CF_2), 113.52 (m, CF_2), 115.79 (m, CF_2), 118.54 (m, CF_2), 120.30, 123.41, 132.91, 147.85. ^{19}F NMR (376 MHz, $CDCl_3$): δ −86.60 (t, $J = 4.58$ Hz), −68.58 (t, $J = 4.58$ Hz). IR (neat): ν 1484 (st, Ar), 1328, 1201 (st, br), 1164, 1132, 1099, 1012 (w), 933 (st) cm^{-1}. GC/MS (M^+ calcd as $C_8H_4Br_2F_4O = 349.86$) *m/z* (%): 354 (46) 352 (100), 351 (39), 157 (25), 155 (25), 63 (40), 50 (27). HRMS obsd. M^+ 349.8558 (calcd 349.8565).

4-[(Trifluorovinyl)oxy]bromobenzene (2). To a 5-L dry vessel under nitrogen was added 1477.9 g of bromo ether **1** (4.2 mol) slowly over 3 h to a stirring mixture of 302.03 g (4.62 mol) of Zn turnings in 3.5 L of acetonitrile at 80 °C. The mixture was refluxed for 10 h then evaporated; the crude product was extracted from the salts successively with hexane, concentrated, and distilled (bp 65−75 °C, 20 mmHg) giving 843.5 g (79.4%) of **2** as a clear liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.95 (2H, d, $J = 8.8$ Hz), 7.43 (2H, d, $J = 8.8$ Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 117.4, 132.8, 132.97, 133.63 (ddd, *C*F=CF$_2$, $^1J = 136$ Hz, $^2J = 129$, 90 Hz), 146.98 (ddd, CF=*C*F$_2$, $^1J = 61$ Hz, $^2J = 274$, 279 Hz), 154.2. ^{19}F NMR (376 MHz, $CDCl_3$): δ −119.8 (1F, dd, *cis*-CF=C*F*$_2$, F$_a$), −126.7 (1F, dd, *trans*-CF=C*F*$_2$, F$_b$), −134.9 (1F, dd, C*F*=CF$_2$, F$_c$) ($J_{ab} = 96$ Hz, $J_{ac} = 58.0$ Hz, $J_{bc} = 109.9$ Hz). IR (neat): ν 1832 (w, $CF{=}CF_2$), 1483 (st, Ar), 1317, 1288 (st), 1200, 1165, 1143, 1074 (w), 1015 (w), 822 (w) cm^{-1}. GC/MS (M^+ calcd as $C_8H_4BrF_3O$ 252) *m/z* (%): 254 (72) 253 (12), 252 (75), 173 (51), 157 (36), 155 (40), 63 (16), 50 (72). HRMS obsd M^+ 251.9391 (calcd 251.9397).

[4-[(Trifluorovinyl)oxy]phenyl]dimethylsilane (3). To a stirring mixture of 2.95 g (0.1212 mol, 1.1 equiv) of magnesium powder, 20.86 g (0.2205, 2.0 equiv) chlorodimethylsilane, and 150 mL of dry THF under nitrogen was added **2** (27.3 g, 0.1102 mol, 1.0 equiv) in 30 mL of dry THF dropwise

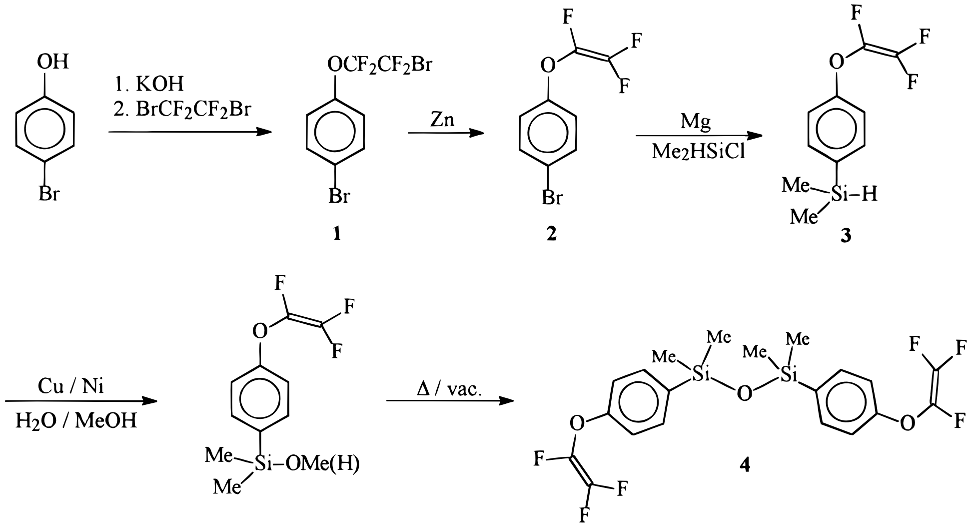

Figure 3. Synthesis of disiloxanyl monomer **4** via Grignard chemistry.

at −1 to 10 °C over 1.5 h. The mixture was stirred at room temperature for 13 h and then quenched with 10 mL of H_2O and 100 mL of hexane, filtered over neutral alumina, and concentrated *in vacuo.* The crude product was dissolved in methylene chloride and washed three times with 50 mL of H_2O, dried over anhydrous $MgSO_4$, and distilled (bp 80 °C, 20 mmHg), giving clear liquid **3** in 87% yield. ^1H NMR (400 MHz, $CDCl_3$): δ 0.32 (6H, d, J = 3.7 Hz), 4.44 (1H, hept, J = 3.7 Hz), 7.08 (2H, d, J = 8.8 Hz), 7.52 (2H, d, J = 8.8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ −3.82, 115.38, 133.40 (ddd, $CF{=}CF_2$, ^1J = 136 Hz, ^2J = 129, 90 Hz), 133.89, 135.89, 147.17 (ddd, $CF{=}CF_2$, ^1J = 62, 273 Hz, ^2J = 279 Hz), 156.25. ^{19}F NMR (376 MHz, $CDCl_3$): δ −119.0 (1F, dd, *cis*-$CF{=}CF_2$, F_a), −125.8 (1F, dd, *trans*-$CF{=}CF_2$, F_b), −132.9 (1F, dd, $CF{=}CF_2$, F_c) (J_{ab} = 96.1 Hz, J_{ac} = 58.0 Hz, J_{bc} = 109.9 Hz). IR (neat): ν 1252 (st, SiMe), 1496 (br, SiAr), 1591 (st, Ar), 1837 (w, $CF{=}CF_2$), 2124 (st, Si−H) cm^{-1}. GC/MS (M^+ calcd for $C_{10}H_{11}OF_3Si$ 232.28 g/mol) m/z (%): 232 (21) 231 (100), 135 (74), 134 (39), 120 (46), 119 (78), 108 (64), 107 (69), 105 (66), 93 (31), 91 (32), 77 (91), 59 (49). Anal. Calcd for $C_{10}H_{11}OF_3Si$ (found): C, 51.71 (52.55); H, 4.77 (5.16).

Bis[1,3-[4-[(trifluorovinyl)oxy]phenyl]]-1,1,3,3-tetramethyldisiloxane (4). To a stirring mixture of 0.4 g (0.0062 mol, 0.3 equiv) of copper powder, 0.1 g of nickel powder, 4.89 g of H_2O and 4 mL of methanol was added dropwise at 25 °C over 25 min 4.8 g (0.021 mol, 1.0 equiv) of **3** in 5 mL THF. The mixture was heated to reflux for 74 h, filtered, and concentrated under reduced pressure at 70 °C (2 mmHg) for 10 h and then at 100 °C (20 mm Hg) for 8 h, giving **4** as a clear liquid in 43% yield. ^1H NMR (400 MHz, $CDCl_3$): δ 0.36 (12H, s), 7.10 (4H, d, J = 8.06 Hz), 7.55 (4H, d, J = 8.06 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 0.76, 115.19, 133.55 (ddd, $CF{=}CF_2$, ^1J = 126.59 Hz, ^2J = 129.17, 90.05 Hz), 134.93, 136.12, 147.13 (ddd, $CF{=}CF_2$, ^1J = 62, 273.09 Hz, ^2J = 278.99 Hz), 156.23. ^{19}F NMR (376 MHz, $CDCl_3$): δ −118.63 (2F, dd, *cis*-$CF{=}CF_2$, F_a), −125.46 (2F, dd, *trans*-$CF{=}CF_2$, F_b), −132.69 (2F, dd, $CF{=}CF_2$, F_c) (J_{ab} = 97.66 Hz, J_{ac} = 57.98 Hz, J_{bc} = 109.9 Hz). FTIR (neat): ν 1250 (s, SiMe), 1500 (s, SiAr), 1590 (s, Ar), 1837 (w, $CF{=}CF_2$), 1025 (br, Si−O−Si) cm^{-1}. GC/MS (M^+ calcd for $C_{18}H_{20}O_3F_6Si_2$ 478.54 g/mol) m/z (%): 463 (M^+ − 15, 100) 281 (62), 183 (20), 155 (25), 151 (28), 91 (24). Anal. Calcd for $C_{18}H_{20}O_3F_6Si_2$ (Found): C, 50.20 (49.20); H, 4.18 (4.1).

Homopolymerization of Monomer 4 to Polymer 5. Bulk polymerization of monomer **4** (0.51 g) was carried out by heating the neat liquid on a glass plate at 180 °C under nitrogen for 0.5 h and then heating at 210 °C for 14 h. Upon cooling, polymer **5a** was recovered as a clear flexible tack-free film in essentially quantitative yield. ^1H NMR (400 MHz, $CDCl_3$): δ 0.31 (12H, s), 7.14 (4H, dd, J = 38.1, 7.3 Hz), 7.47 (4H, m). Quantitative ^{13}C NMR (100 MHz, $CDCl_3$): δ 0.73 (4C, s), 105.8 (m, cyclobutyl-F_6), 108.7 (m, cyclobutyl-F_6), 109.9 (m, cyclobutyl-F_6), 112.8 (m, cyclobutyl-F_6), 115.7, 117.23 (4C, s), 119.0, 134.56 (2C, 54% *trans* C_o), 134. 7 (2C, 46% *cis* C_o), 136.25 (1C, 55% *trans* C_{ipso}), 136.49 (1C, 45% *cis* C_{ipso}), 153.61 (1C, *trans* C_{ipso}), 153.67 (1C, *cis* C_{ipso}). Quantitative ^{19}F NMR (376 MHz, $CDCl_3$): δ trifluorovinyl end groups at −119.48 (2F, dd, *cis*-$CF{=}CF_2$, Fa, F_b not resolved), −133.7 (2F, dd, $CF{=}CF_2$, F_c); cyclobutyl-F_6 at −126.4, −127.4, −127.9, −128.5, −129.2, −129.9, −130.4, −131.0, −131.6 (total cyclobutyl-F_6 160F, DP = 27, M_n = 13 300). FTIR (neat film): ν 1250 (s, SiMe), 1500 (s, SiAr), 1590 (s, Ar), 1025 (br, Si−O−Si), 960 (s, st, cyclobutane-F_6) cm^{-1}. Sealed tube DSC analysis (10 °C/min) of monomer **4** gave ΔH = −495 J/g (−56.5 kcal/mol) with an onset of polymerization at 139 °C and a maximum exotherm at 233 °C. GPC in THF and relative to polystyrene gave monomodal distribution with M_w = 33 600 and M_n = 10 000 (M_w/M_n = 3.4). DSC (20 °C/min, 2nd heat) gave T_g = 16 °C and TGA (10 °C/min, N_2) gave T_d (onset) = 428 °C.

Copolymerization of 4 with 1,1,1-Tris[4-[(trifluorovinyl)oxy]phenyl]ethane (I). In a covered aluminum pan, 0.2104 g (44.0 mmol, 1.1 equiv) of monomer **4** and 0.2201 g (40.5 mmol, 1 equiv) of **I** were mixed at 120 °C for 5 min then heated at 180 °C for 12 h under a nitrogen atmosphere. The temperature was then increased to 200−210 °C and heating continued for 19 h, yielding a transparent insoluble disk. FTIR (film): ν 1591 (w), 1503 (SiAr) 1205 (st), 1260 (s, SiMe), 1058 (br, Si−O−Si), 962 (s, st, cyclobutane-F_6) cm^{-1}. DSC (10 °C/min) gave T_g = 120 °C and TGA (10 °C/min) gave T_d (onset) = 471 °C in nitrogen and 461 °C in air.

Results and Discussion

Monomer Synthesis. Initial efforts toward the synthesis of siloxane-containing aryl trifluorovinyl ether monomers focused on the preparation of bisphenol intermediates[24,25] which could be easily transformed to the bis(trifluorovinyl ether) by standard methods.[5] The target bisphenol, 1,3-bis(4-hydroxyphenyl)-1,1,3,3-tetramethyldisiloxane—although previously reported[25]—was not isolated pure by either of two protection routes attempted. Deprotection of the methyl ether or the trimethylsilyl ether bisphenols prepared via silicon Grignard chemistry[32] with dichlorodisiloxane resulted in decomposition and formation of phenol. Attempts at reproducing previous work[25] that detailed rearranging the dimethylsilyl ether of bromophenol via *in situ* Grignard formation to hydroxyphenyldimethylsilane were also unsuccessful.

Efforts were then focused on the synthesis of a functionalized trifluorovinyl ether intermediate which could be converted directly to a siloxane-containing difunctional monomer (Figure 3). Fluoroalkylation of bromophenol to give dibromo intermediate **1** followed by zinc-mediated elimination gave trifluorovinyl ether

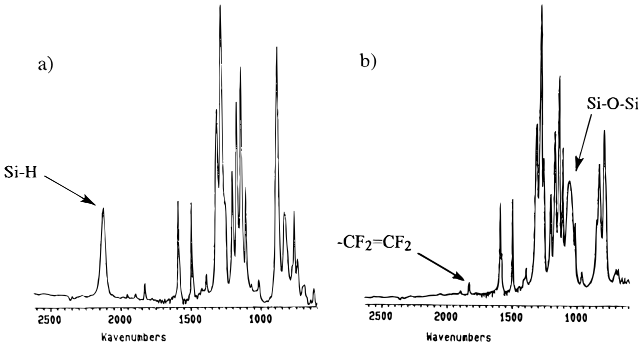

Figure 4. FTIR spectra of silane intermediate **3** (a) and monomer **4** (b).

compound **2** by standard procedures.[5a] As detailed elsewhere,[5a,33] the only significant side reaction during fluoroalkylation is protonation of an intermediate tetrafluoroethyl ether anion—presumably by adventitious water—giving a small quantity of tetrafluoroethyl ether (Ar-OCF$_2$CF$_2$H). This troublesome impurity functions as a terminating agent if not removed (see experimental procedures for **1**) and therefore limits the molecular weight during subsequent step growth cyclopolymerization.

Upon treatment of aromatic bromide **2** with Mg powder in the presence of chlorodimethylsilane, *in situ* Grignard formation and substitution gave silane intermediate **3** in good yield (Figure 3). Although reluctant to prepare nucleophilic organometallic complexes in the presence of perfluoroolefins, we found no reference objecting to the formation of aryl Grignards on the same molecule containing this electrophilic group. Conjugative and inductive effects conceivable in **2** may play a beneficial role in the formation and stability of this useful Grignard reagent.

Addition of carbon nucleophiles to fluorinated olefins is known to be among the best reactions in organofluorine chemistry[34] and known additions to trifluorovinyl ethers, albeit less common,[35] were perceived to be no exception. Despite these preconceptions, however, aryl trifluorovinyl ether Grignard chemistry proceeds smoothly at low temperature with or without the addition of chlorosilane in THF solutions (3−4 M). It was also found in subsequent reactions that the Grignard from **2** is stable in THF solutions even at elevated temperatures (67 °C). Theoretical calculations at the semiempirical level suggest that electron density on Grignard **2** is greatly delocalized by the *para*-substituted perfluorovinyl ether group. This delocalization of charge density may account for both a reduction in nucleophilicity of the magnesium adduct and the electrophilicity of the olefin.[36]

Silane **3** is a versatile intermediate in itself and could provide access to a variety of phenyl trifluorovinyl ether functional compounds via well-established hydrosilation[37] or condensation[38] chemistry. Condensation of **3** via dehydrogenative hydrolysis/methanolysis was carried out as described previously.[25] Hydrogen evolution accompanied the slow consumption of silane **3** (by GC) within 74 h. Methoxysilane and silanol intermediates (Figure 3) were observed by GC/MS yet were not isolated since condensation to monomer **4** had already begun during reflux (ca. 20%) and was completed simply by further heating under vacuum.

Figure 4 depicts the conversion of silane **3** to monomer **4** by FTIR. Spectrum a of silane **3** exhibits the Si−H stretch at 2124 cm^{-1} whereas spectrum b of monomer **4** illustrates the resulting disappearance of this vibration and the addition of a new broad absorbance at 1025 cm^{-1} representing the Si−O−Si bending mode. Also present in the two spectra is the weak perfluoroolefin absorbance found at 1837 cm^{-1}.

The conversion of silane **3** is characterized further by the disappearance of the Me$_2$Si−H group in the ^{1}H NMR spectrum. Silane (Si−H) proton signals represented as a neatly resolved heptet centered at 4.4 ppm in the spectrum of **3** disappear and the SiMe proton signals

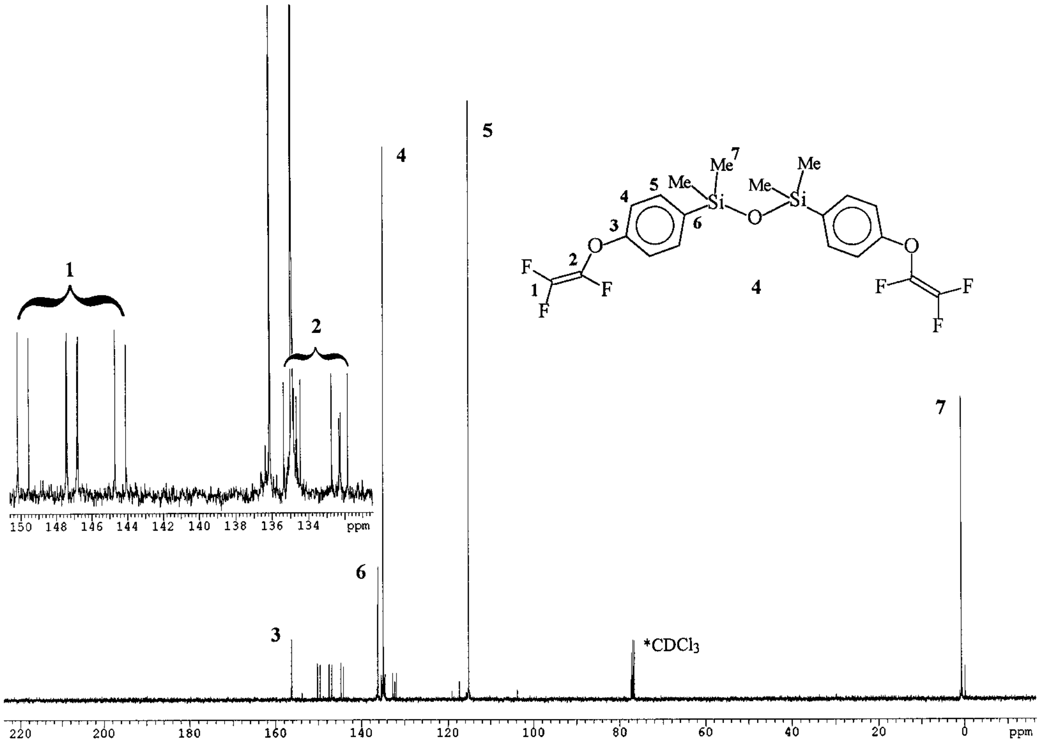

Figure 5. Quantitative ^{13}C NMR spectrum of monomer **4**.

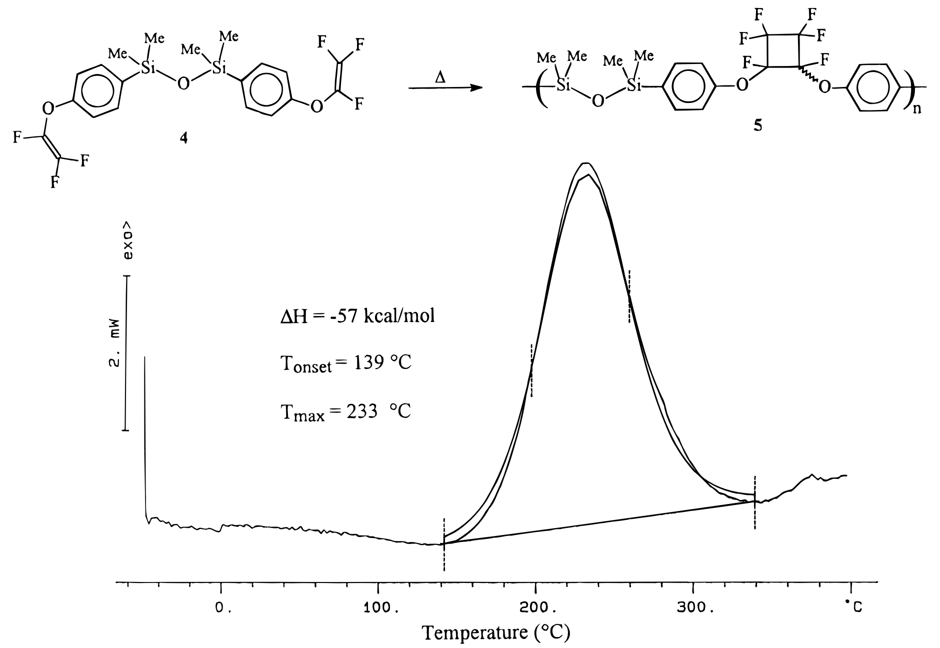

Figure 6. Homopolymerization of monomer **4** by DSC (10 °C/min).

change as predicted from a doublet at 0.32 ppm for **3** to a singlet at 0.36 ppm in the spectrum for monomer **4**. Figure 5 shows the quantitative ^{13}C NMR spectrum of disiloxane monomer **4**. Four aromatic carbon signals are clearly resolved as are the terminal vinylic carbon signals ($CF{=}\mathit{C}F_2$) represented as a fluorine-coupled ddd pattern from 144 to 150 ppm (Figure 5 inset). The internal vinylic carbon ($\mathit{C}F{=}CF_2$) ddd pattern appears partially overlapped with an aromatic carbon signal from 132 to 135 ppm.

Cyclopolymerization. Difunctional monomers possessing the aromatic trifluorovinyl ether group undergo exothermic cyclodimerization affording linear PFCB-containing aromatic polyethers.[5] PFCB polymers, in general, constitute a recent addition to the field of cyclopolymerization established by Butler.[39]

As mentioned earlier (Figure 1), a weak and strained C=C π-bond[6] is thermodynamically responsible for spontaneous cyclopolymerization of fluoroolefins at elevated temperatures. The cyclodimerization of tetrafluoroethylene was reported to proceed with a $\Delta H = -50$ kcal/mol[40] due to this unique fluoroolefin reactivity. For trifluorovinyl ether monomers synthesized in our laboratories, exothermic polymerization reaches a measurable rate (DSC at 10 °C/min)[41] near 140 °C and polymerizations are typically carried out at temperatures between 150 and 210 °C. Monomer **4** is no exception (Figure 6) in that bulk polymerization gave exothermic $T_{\text{onset}} = 139$ °C and $T_{\max} = 233$ °C and a measured $\Delta H = -57$ kcal/mol (DSC, 10 °C/min).

Homopolymerization of monomer **4** to siloxane PFCB polymer **5a** was accomplished by heating **4** in the bulk at 210 °C for 14 h, yielding a clear flexible tack-free film. Although mechanical properties have not yet been determined, polymer **5** does possess a certain degree of elasticity above T_g. Table 1 contains some comparative physical data for the PFCB polymers described herein.

PFCB polymer chemistry proceeds by step growth addition type propagation giving well-defined linear polymers terminated with known perfluoroolefin end groups. Cyclopolymerization is thermally initiated without the use of catalysts, such that polymerization ceases upon the removal of heat, leaving quantifiable end groups intact. This asset allows for the exact determination of number-average molecular weight (M_n) by quantitative ^{19}F NMR end group analysis for various stages of polymerization below complete conversion. The homopolymerization of **4** was terminated just before the concentration of terminal fluoroolefin fell below the limit of detection for our quantitative ^{19}F NMR conditions so that accurate quantitation was possible (Figure 7). Integration of the terminal vinylic fluorine signals at −119.48 ppm (F_a, dd, *cis*-$CF{=}C\mathit{F}_2$) vs the various cyclobutyl fluorine signals from −126.4 to −131.6 ppm gave DP = 27 or $M_n = 13\,300$. This measurement happens to agree well with a relative $M_n = 10\,000$ determined by GPC when using polystyrene standards. As shown in Figure 7, geminal F_a and *cis*-F_c fluorine end groups are easily resolved at this stage of polymer advancement. Geminal fluorine F_b, however, is not distinguished due to the cluster of signals representing the six nonequivalent fluorines on each *cis*- and *trans*-disubstituted PFCB ring.

Table 1. Siloxane-Containing Perfluorocyclobutane Aromatic Polyethers

polymer	M_n GPC[a]	M_n NMR[b]	M_w	M_w/M_n	T_g (°C) DSC[c]	T_d (°C) N_2 (air)[d]
5a	10 000	13 300	34 000	3.4	16	428
5b	20 000	nd[h]	66 000	3.4	18	435 (423)
6	thermoset				120	471 (461)
polyI[e]	thermoset				>400[f]	475[g]

[a] In THF relative to polystyrene. [b] By quantitative ^{19}F NMR end group analysis. [c] 10 °C/min heating rate. [d] TGA onset at 10 °C/min heating rate. [e] Homopolymer[5a] of **I** in Figure 2. [f] DMS, see ref 5a. [g] See ref 5b for a complete thermal stability study. [h] End groups not detected.

The presence of well-defined reactive end groups—by definition—places PFCB polymers within an important class of α,ω-difunctional macromolecules, or telechelic polymers.[42] Subsequent homopolymerization or copolymerization of PFCB telechelomers with other trifluorovinyl ether monomers or polymers can be achieved by simple thermal advancement. For example, further heating **5a** at 180−200 °C for 19 h gave advanced polymer **5b**. Step growth addition polymerization proceeded without agitation and resulted in a 2-fold

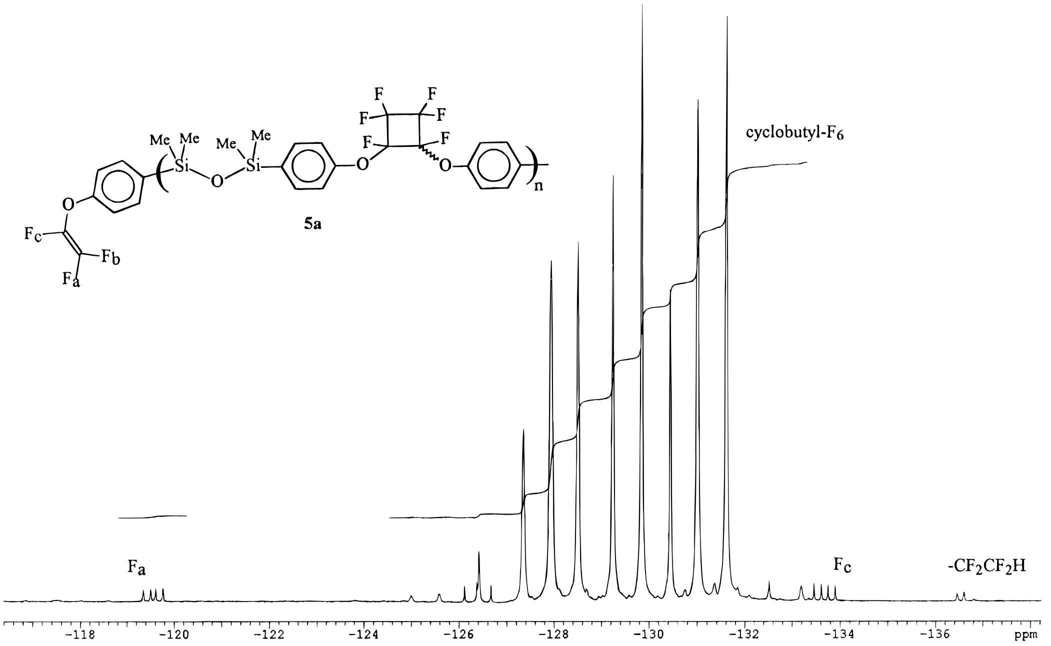

Figure 7. Quantitative ^{19}F NMR spectrum of polymer **5a**.

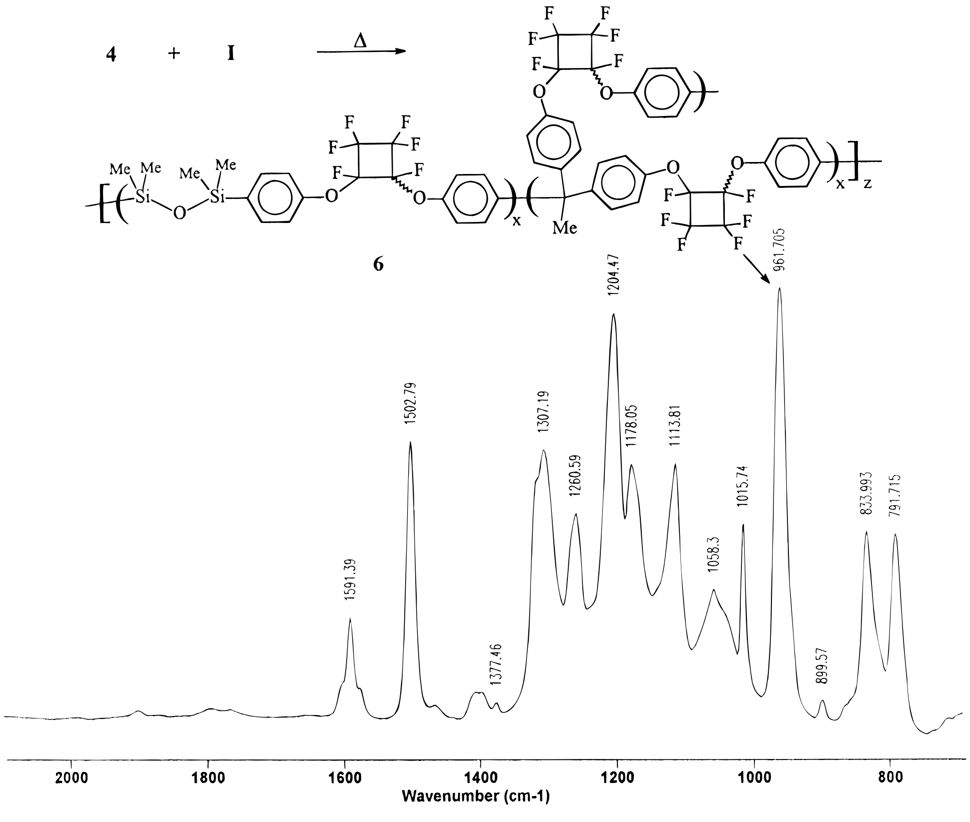

Figure 8. Copolymerization of **4** and **I** with resulting FTIR spectrum of polymer **6**.

increase in molecular weight (GPC $M_n = 20\,000$) while an identical polydispersity ($M_w/M_n = 3.4$) was maintained. The capability of PFCB polymer chemistry to be further advanced to variable and exact molecular weights provides an opportunity to construct well-defined block copolymers with controlled block lengths.

The terminal fluoroolefin end groups of polymer **5b** fell below the limits of detection for our quantitative ^{19}F NMR conditions at 376 MHz. As described earlier, one known factor limiting the molecular weight of PFCB polymers is the presence of a small quantity of tetrafluoroethyl ether (Ar-OCF$_2$CF$_2$H) in the monomer. This impurity is evident in the ^{19}F NMR spectrum in Figure 7 by two faint triplets at −136.24 and −136.62 ppm (<0.05% F).

Other particularly useful methods of characterization available to PFCB polymers include FTIR and ^{13}C NMR spectroscopy (see Experimental Section). A strong sharp band in the IR near 960 cm^{-1} is diagnostic for the presence of the hexafluorocyclobutane group. This easily resolved absorption has proven to be a useful analytical tool since this region in the IR is rarely occupied by other functionalities (Figure 8). Methods by which the cure kinetics of PFCB thermosets can be determined (provided both *cis* and *trans* isomers are represented by this vibration) are currently under development.

The 1,2-disubstituted perfluorocyclobutane group is further identified in the ^{13}C NMR spectrum of polymer **5** by the presence of at least four separate multiplets from 106 to 113 ppm at 100 MHz. These unresolved cyclobutane carbon signals representing both *cis* and *trans* geometric isomers, in addition, are all coupled to each nonequivalent fluorine atom attached to the cyclobutane ring. Vinylic carbon signals present in the carbon spectrum of monomer **4** (Figure 5) are not observed for polymer **5** under our quantitative conditions at 100 MHz.

The aromatic carbons of polymer **5** adjacent (*ipso*) and *ortho* to the perfluorocyclobutyl ether linkage do give separate signals dictated by the 1,2-disubstituted *cis*/*trans* (*Z*/*E*) configuration of the ring. Although the carbon assignments for each isomer are not yet unequivocally known, we tentatively assign the carbon signal consistently in slight excess as the *E* or *trans* isomer due to its presumed greater stability. Quantitative carbon integration of the *ipso* carbon signals at 136.3 (presumably *trans*) and 136.5 ppm (*cis*) gave 55% *trans* whereas *ortho* carbon signals at 134.6 (*trans*) and 134.7 ppm (*cis*) gave 54% *trans* disubstitution.

Essentially equal geometric isomer distribution seems to be inherent to PFCB polymer chemistry. Identical results were also found for the biphenyl thermoplastic polymer from monomer **II** (Figure 2). These NMR results also agree well with synthetic model studies[5a] which indicated completely random formation of *cis* and *trans* isomers for other PFCB thermoplastics. Furthermore, *ab initio* calculations (6/31G*) have predicted a difference of only 1.2 kcal/mol in the total energies, $\Delta E_{\mathrm{cis/trans}}$, for representative isomers.[5d]

Aromatic trifluorovinyl ether monomers prepared to date have shown no significant difference in reactivity when combined to form copolymers. PFCB copolymers are therefore random in nature and copolymer composition is dictated by initial comonomer ratios. In order to begin to identify the potential toughening effect of siloxane monomer **4** on PFCB thermosets, a copolymer with trifunctional monomer **I** (Figure 2) was prepared. A 50% (w/w) mixture of the two compounds was mixed and heated as described earlier giving copolymer **6** as an insoluble transparent film. Figure 8 illustrates the copolymerization reaction and the FTIR spectrum of copolymer **6**. As discussed earlier, the strong perfluorocyclobutane absorbance at 962 cm^{-1} is typical for PFCB polymers in general. Also evident in the IR is the presence of the Si−Me (1260 cm^{-1}) and the broad Si−O−Si (1058 cm^{-1}) absorbances. The perfluorovinyl end group absorbance which usually appears near 1840 cm^{-1} in the IR is not detected for this advanced thermoset.

Thermal Properties. As is typical for polymers containing significant incorporation of the flexible siloxane linkage in the main chain, polymer **5** exhibits a T_g below room temperature. Figure 9 contains the DSC thermograms for the first (a) and second (b) heatings of polymer **5a** indicating a slight dependence on thermal history. A meltlike transition at 50 °C and $T_g = 21$ °C are observed on first heating whereas a less defined endotherm occurs at −25 °C with $T_g = 16$ °C on the second and subsequent heatings at 10 °C/min. These data suggest that some degree of order had formed in the film upon initial slow cooling after polymerization. Although crystalline phases have not been identified in PFCB polymers before, it is conceivable that the flexible siloxane linkage allows interchain interactions not possible with other PFCB polymers constructed thus far. Increasing the molecular weight 2-fold had no significant effect on the T_g of polymer **5**. Advanced polymer **5b** exhibits a $T_g = 18$ °C under identical measuring conditions. Additional transitions are not observed for polymer **5b** upon subsequent heating cycles or controlled cooling below 0 °C.

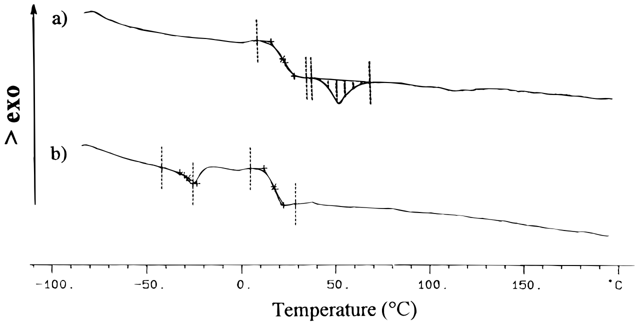

Figure 9. DSC first (a) and second (b) heatings of polymer **5a** (10 °C/min).

Upon 50% (wt) incorporation of siloxane monomer **4** into a thermoset (**6**) with trifunctional monomer **I**, a $T_g = 120$ °C is observed compared to $T_g > 400$ °C for **polyI** homopolymer.[5a] This substantial effect on T_g suggests that toughening PFCB thermosets with lower levels of **4** may be possible without sacrificing other properties. Table 1 illustrates the limits upon the range of T_g's possible from monomers **4** and **I**.

Figure 10 depicts the thermal stability of polymer **5b** (a) and copolymer **6** (b) by TGA analysis. Homopolymer **5b** exhibits typical thermal stability for main-chain aromatic siloxane-based systems[19b,20] where the onset of degradation does not occur until 435 and 423 °C in nitrogen and air atmospheres, respectively, at a heating rate of 10 °C/min. As expected, slightly higher thermal stability is observed for thermoset copolymer **6** where the onset of degradation ensues at 471 and 461 °C in nitrogen and air, respectively. It is interesting to note that both polymers **5b** and **6** exhibit significant char yields in nitrogen. Almost 10% of the initial weight is retained for **5b** and 30% remains for copolymer **6** at temperatures exceeding 650 °C. This is in agreement with previous results from a more thorough thermal degradation study of **polyI** homopolymer which retains nearly 50% of its weight when decomposed in nitrogen.[5e]

Conclusions

An aryl Grignard reagent containing the trifluorovinyl ether group was prepared, providing a new and useful route to aryl trifluorovinyl ether monomers from inexpensive starting materials. This chemistry resulted in the facile and high-yield synthesis of a versatile silane intermediate which is easily dehydrogenatively hydrolyzed *in situ* and condensed to a new disiloxane bis(trifluorovinyl ether) monomer **4**. Thermal bulk cyclopolymerization of **4** gave the first siloxane-containing PFCB polymer **5** as a clear flexible tack-free film of reasonable molecular weight, low T_g, and good thermal stability. PFCB polymer molecular weight and the *cis*/*trans* ratio of the 1,2-disubstituted perfluorocyclobutane linkage were accurately determined by quantitative ^{19}F NMR end group analysis and quantitative ^{13}C NMR, respectively. Telechelic polymer **5**, containing reactive trifluorovinyl terminal groups, was also thermally ad-

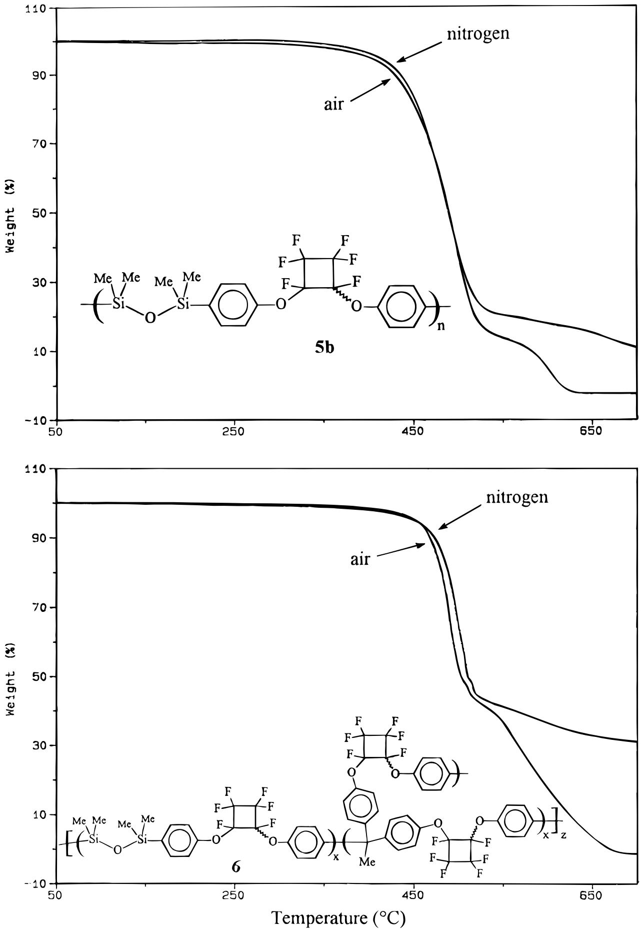

Figure 10. TGA of polymer **5b** and copolymer **6** in air and nitrogen (10 °C/min).

vanced to higher molecular weight. Monomer **4** copolymerizes with an existing trifunctional monomer giving a toughened PFCB thermoset with good thermal stability. Siloxane-containing PFCB polymers could be expanded into a useful class of fluorosilicones by extension of the siloxane linkage within the main chain or by pendant functionality of the trifluorovinyl phenyl ether group onto known polysiloxane systems.

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