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14. ABSTRACT A new class of perfluorocyclobutyl (PFCB) polymers covalently functionalized with polyhedral oligomeric silsesquioxanes (POSS) is presented. Three discreetly functionalized POSS monomers possessing thermally reactive trifluorovinyl aryl ethers (TFVE) were prepared in good yields. The POSS TFVE monomers were prepared by initial corner capping of cyclopentyl (-C5H9), iso-butyl (-CH2CH(CH3)2), or trifluoropropyl (-CH2CH2CF3) functionalized POSS trisilanols with acetoxyethyltrichlorosilane followed by sequential acid-catalyzed deprotection and coupling with 4-(trifluorovinyl)oxybenzoic acid. TFVE functionalized POSS monomers were thermally polymerized with 4,4'-bis(4-trifluorovinyl)oxybiphenyl or 2,2-bis(4-trifluorovinyl)oxybiphenyl-1,1,1,3,3,3-hexafluoropropane monomers via a condensate-free, [2+2] step-growth polymerization. The polymerization afforded solution processable PFCB polymers with POSS macromers installed on the polymer chain ends. POSS monomers and their corresponding copolymers were characterized by 1H, 13C, 19F, and 29Si NMR, GPC, ATR-FTIR, and elemental combustion analysis. GPC trace analysis showed agreeable number-average molecular weight for various weight percent of iso-butyl and trifluoropropyl chain terminated POSS PFCB copolymers. DSC analysis showed the introduction of increasing POSS weight percent in the endcapped PFCB copolymers lowers glass transition temperatures as high as 31 °C. On the other hand, the trifluoropropyl POSS endcapped PFCB polymer glass transition temperature was unaffected when copolymerized with the more fluorinated 2,2-bis(4-trifluorovinyl)oxybiphenyl-1,1,1,3,3,3-hexafluoropropane monomer. TGA analysis of POSS PFCB copolymers showed step-wise decomposition of copolymers resulting from the initial degradation of the POSS cages at 297–355 °C in nitrogen and air which was confirmed by pyrolysis coupled with GC–MS. This initial weight loss was proportional to the weight percent POSS incorporated into the polymer. The balance of decomposition was observed at 450–563 °C in nitrogen and air which is higher than the PFCB homopolymers in most cases. Polymer surface characterization was performed on spin cast transparent, flexible films. These composite films exhibited good POSS dispersion within the matrix PFCB polymer as was shown by TEM analysis.					
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Synthesis, Characterization, and Properties of Chain Terminated Polyhedral Oligomeric Silsesquioxane-Functionalized Perfluorocyclobutyl Aryl Ether Copolymers

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A new class of perfluorocyclobutyl (PFCB) polymers covalently functionalized with polyhedral oligomeric silsesquioxanes (POSS) is presented. Three discreetly functionalized POSS monomers possessing thermally reactive trifluorovinyl aryl ethers (TFVE) were prepared in good yields. The POSS TFVE monomers were prepared by initial corner capping of cyclopentyl (-C₅H₉), *iso*-butyl (-CH₂CH(CH₃)₂), or trifluoropropyl (-CH₂CH₂CF₃) functionalized POSS trisilanols with acetoxymethyltrichlorosilane followed by sequential acid-catalyzed deprotection and coupling with 4-(trifluorovinyl)benzoic acid. TFVE functionalized POSS monomers were thermally polymerized with 4,4'-bis(4-trifluorovinyl)oxybiphenyl or 2,2-bis(4-trifluorovinyl)oxybiphenyl-1,1,1,3,3,3-hexafluoropropane monomers *via* a condensate-free, [2+2] step-growth polymerization. The polymerization afforded solution processable PFCB polymers with POSS macromers installed on the polymer chain ends. POSS monomers and their corresponding copolymers were characterized by ¹H, ¹³C, ¹⁹F, and ²⁹Si NMR, GPC, ATR-FTIR, and elemental combustion analysis. GPC trace analysis showed agreeable number-average molecular weight for various weight percent of *iso*-butyl and trifluoropropyl chain

terminated POSS PFCB copolymers. DSC analysis showed the introduction of increasing POSS weight percent in the endcapped PFCB copolymers lowers glass transition temperatures as high as 31 °C. On the other hand, the trifluoropropyl POSS endcapped PFCB polymer glass transition temperature was unaffected when copolymerized with the more fluorinated 2,2-bis(4-trifluorovinyloxybiphenyl)-1,1,1,3,3,3-hexafluoropropane monomer. TGA analysis of POSS PFCB copolymers showed step-wise decomposition of copolymers resulting from the initial degradation of the POSS cages at 297–355 °C in nitrogen and air which was confirmed by pyrolysis coupled with GC–MS. This initial weight loss was proportional to the weight percent POSS incorporated into the polymer. The balance of decomposition was observed at 450–563 °C in nitrogen and air which is higher than the PFCB homopolymers in most cases. Polymer surface characterization was performed on spin cast transparent, flexible films. These composite films exhibited good POSS dispersion within the matrix PFCB polymer as was shown by TEM analysis.

Keywords: perfluorocyclobutyl (PFCB) polymer; polyhedral oligomeric silsesquioxanes; POSS

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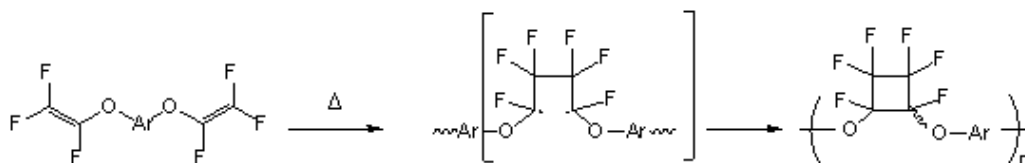
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1. Introduction

Fluoropolymers are important for a broad range of advanced material applications [1]. Introducing fluorine into a polymer backbone creates an interesting paradox in terms of desired properties. In one sense, highly fluorinated polymers are desired due to their inherent high degree of chemical resistance, superior thermal stability, excellent insulating ability, and low surface energy. However, perfluorinated polymers, like

poly(tetrafluoroethylene) (PTFE), are intrinsically highly crystalline and thus present challenges in terms of high processing cost. Therefore, interest continues to develop next generation fluoropolymers motivated by the need to overcome processing limitations while maintaining performance-enhancing properties.

Perfluorocyclobutyl (PFCB) polymers [2] have gained much interest as processable, semi-fluorinated polymers advancing a multitude of technology corridors such as high performance optics [3], polymer light-emitting diodes (PLEDs) [4], atomic oxygen (AO) resistant coatings [5], polymeric proton exchange membranes (PEMs) for fuel cells [6], high temperature fluorosilicones [7], and liquid-crystalline polymers [8]. PFCB polymers are prepared by condensate-free, step-growth [2+2] thermal dimerization of trifluorovinyl aryl ethers (TFVE) (Scheme 1) [9]. The cycloaddition event has been studied by Raman spectroscopy and was shown to proceed *via* a biradical intermediate producing nearly exclusive formation of 1,4-perfluorocyclobutyl aryl ether rings in the chain extended polymer system [10]. The stereo-random nature of the PFCB aryl ether linkage typically affords an amorphous thermoplastic attractive for solution processing. As a consequence of the aromatic ether structure, PFCB polymers have an intrinsically high glass transition temperature and possess a high degree of thermal stability in air. TFVEs are easily functionalized from versatile organometallic reagents derived from 4-bromo(trifluorovinyl)benzene as a commercial starting material [11].



Scheme 1. Thermal [2+2] cyclopolymerization of trifluorovinyl aryl ethers.

Since their seminal inception by Vogt and Scott [12], polyhedral oligomeric silsesquioxane (POSS) compounds comprised of a functionalized silicon-oxygen core framework have received much interest as robust nanometer-sized building blocks for the development of high performance materials [13]. POSS incorporation, either in polymer blends or covalently bound as copolymers, produces hybrid organic-inorganic composites improving on the properties of the virgin polymer such as glass transition temperature, mechanical toughness, chemical resistance, ease of processing, fire resistance, and atomic oxygen resistance.

Octa(aminophenyl)silsesquioxane (OAPS) with TFVE moieties installed on each apex silicon of the POSS T_8 cage has been reported [14]. Thermal polymerization of the TFVE-functionalized OAPS with PFCB oligomers produced crosslinked materials possessing excellent thermal stability while retaining the optical integrity of the matrix polymer. Similarly, PFCB thermoplastics as well as thermosets possessing siloxane linkages have also been prepared [7] contributing to the established class of poly(fluorosilicones) as lubricants and adhesives [15].

In this report, our aim is to expand on the utility of PFCB polymers by introducing covalently bound ceramic-like POSS cages while maintaining the processability of the semi-fluorinated matrix. We anticipate the introduction of POSS cages attached on the polymer chain ends would produce hybrid polymers with controlled molecular weight that could enhance bulk properties as hydro- and oleophobicity, thermal stability, mechanical integrity, tunable refractive index, low dielectric values, and improved gas permeability.

2. Experimental Section

2.1. General Information and Materials

Chemicals and solvents were purchased through Sigma Aldrich and purified according to reported procedures unless otherwise stated [16]. POSS triols **1** and **2** were donated by the Air Force Research Laboratory, Propulsion Directorate and commercially available through Hybrid Plastics. 4,4'-Bis(4-trifluorovinyloxy)biphenyl (**4**) and 2,2-bis(4-trifluorovinyloxybiphenyl)-1,1,1,3,3,3-hexafluoropropane (**5**) were donated by Tetramer Technologies, L.L.C. and are commercially distributed through Oakwood Chemicals, Inc. All reactions were carried out under ultra high purity grade nitrogen. Flasks and syringes were flamed-dried under vacuum and allowed to cool in a desiccator filled with Drierite prior to use.

2.2. Instrumentation

2.2.1. NMR Spectrometry. ^1H , ^{13}C (proton decoupled), ^{19}F , and ^{29}Si NMR data were obtained on a JOEL Eclipse⁺ 300 and chemical shifts were reported in part per million (δ ppm). ^1H NMR data were internally referenced to tetramethylsilane (δ 0.0), ^{13}C NMR chemical shifts were reported relative to the center peak of the multiplet for CDCl_3 (δ 77.0 (t)), and ^{19}F NMR was referenced to CFCl_3 . ^{29}Si NMR data were referenced to tetramethylsilane (δ 0.0) and were recorded with inverse-gated proton decoupling with a six second pulse delay.

2.2.2. IR Spectroscopy. Attenuated total reflectance Fourier transform infrared (ATR–FTIR) analysis of neat samples was performed on a ThermoNicolet Magna IR 550 FTIR spectrophotometer.

2.2.3. Chromatography. Gel permeation chromatography (GPC) data were collected in CHCl_3 using polystyrene as a standard (Polymer Labs Easical PS-2) using a Waters 2690 Alliance System with UV-Vis detection. GPC samples were eluted in series through

Polymer Labs PLGel 5 mm Mixed-D and Mixed-E columns at 35 °C. See Table 1 for polymer molecular weights.

Gas chromatography (GC) coupled with mass spectrometry (MS) was performed on a Shimadzu GC-17A gas chromatograph coupled with a Shimadzu QP5000 mass spectrometer (EI at 70 eV) with initial temperature of 60 °C at a ramp of 10 °C/min.

2.2.4. Thermal Analysis. Differential scanning calorimetry (DSC) analysis and thermal gravimetric analysis (TGA) were performed on a TA Q1000 instrument and Mettler-Toledo 851 instrument, respectively. Glass transitions temperatures (T_g) of polymers were obtained from the third heating cycle using DSC analysis at a temperature ramp of 10 °C/min. See Table 1 for glass transition temperature (T_g) and Table 2 for thermal decomposition temperature (T_d) in nitrogen and air of polymers. Melting points were measured using either DSC or a Mel-Temp melting point apparatus. Combustion analysis was obtained from Atlantic Microlab, Inc., P.O.Box 2288, Norcross, GA 30091. High resolution mass spectra of **3c** was obtained at the Mass Spectrometry Laboratory, School of Chemical Sciences, University of Illinois, Urbana-Champaign, IL 61801 using a high resolution Micromass FAB 70-SE-4F. Pyrolysis analysis was carried out on Frontier Lab single-shot at 500 °C interfaced with the GC-MS.

2.2.5. Microscopy. Transmission electron microscopy (TEM) micrographs were obtained from a Hitachi H9500 with accelerating voltage of 300 kV at the Clemson University Electron Microscope Facility. Samples were prepared by casting polymer solutions from THF onto copper TEM grids and allowed to dry in a desiccator 24 h prior to use.

2.3 Synthesis of 1a

Acetoxyethyltrichlorosilane (2.1 mL, 12.0 mmol) was added drop wise to a stirred solution of trisilanolcyclopentyl-POSS **1** (10 g, 11.4 mmol) and triethylamine (5.8 mL,

42.0 mmol) in THF (120 mL). After 5 h, the solution was filtered and concentrated under vacuum. The solid was then dispersed in methanol (200 mL), filtered, washed repeatedly with methanol (2×100 mL), and dried under vacuum to afford **1a** as a white, free-flowing powder (10.6 g, 94%). ATR-FTIR (neat) ν 2953 (w), 1464 (w), 1229 (w), 1087 (vs), 1035 (m), 838 (w), 744 (w) cm^{-1} ; ^1H NMR (CDCl_3 , 300 MHz) δ 4.17 (t, $J = 6.0$ Hz, 2H), 2.02 (s, 3H), 1.86–1.38 (m, 56H), 1.07 (t, $J = 6.0$ Hz, 2H), 1.04–0.92 (m, 7H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 171.2, 61.3, 27.4, 27.1, 22.3, 21.2, 13.5; ^{29}Si NMR (CDCl_3 , 59 MHz) δ –65.9, –66.0, –69.2 (3:4:1). Anal. calcd for $\text{C}_{39}\text{H}_{70}\text{O}_{14}\text{Si}_8$: C, 47.43; H, 7.14. Found: C, 47.23; H, 7.31.

2.4. Synthesis of **1b**

Concentrated H_2SO_4 (0.8 mL) was added to **1a** (4 g, 4.05 mmol) dissolved in methanol (200 mL) and chloroform (200 mL). After 48 h, the solution was concentrated under vacuum. The crude concentrate was redissolved in ethyl acetate (200 mL), washed repeatedly with water (2×100 mL), dried (MgSO_4), filtered, and concentrated under vacuum to afford **1b** as a white, crystalline powder (3.7 g, 97%). ATR-FTIR (neat) ν 2948 (m), 2864 (m), 1086 (vs) cm^{-1} ; ^1H NMR (CDCl_3 , 300 MHz) δ 4.17 (t, $J = 15.5$ Hz, 2H), 1.95–1.41 (m, 56H), 1.08–0.92 (m, 9H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 58.9, 27.4, 27.1, 22.3, 17.7; ^{29}Si NMR (CDCl_3 , 59 MHz) δ –65.9, –68.1 (7:1). Anal. calcd for $\text{C}_{37}\text{H}_{68}\text{O}_{13}\text{Si}_8$: C, 47.00; H, 7.25. Found: C, 46.75; H, 7.28.

2.5. Synthesis of **1c**

4-(Trifluorovinyloxy)benzoic acid (254 mg, 1.16 mmol) was added to a solution of dicyclohexylcarbodiimide (DCC) (254 mg, 1.27 mmol), 4-(dimethyl-amino)pyridinium 4-toluenesulfonate (DPTS) (107 mg, 0.35 mmol), and **1b** (1 g, 1.06 mmol) in

dichloromethane (20 mL). After 24 h, the solution was filtered and concentrated under vacuum. Purification of the residue by flash chromatography on silica gel using 5% ethyl acetate–95% hexanes (v/v) for elution afforded **1c** as a white solid (1 g, 83%). R_f 0.50 (5% ethyl acetate–95% hexanes (v/v)); mp >260 °C; ATR-FTIR (neat) ν 2949 (m), 1723 (w), 1271 (w), 1084 (vs) cm^{-1} ; ^1H NMR (CDCl_3 , 300 MHz) δ 8.09 (d, J = 8.6 Hz, 2H), 7.12 (d, J = 8.6 Hz, 2H), 4.45 (t, J = 7.9 Hz, 2H), 1.78–0.84 (m, 65H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 155.6, 158.2, 132.0, 127.5, 115.4, 62.1, 29.8, 27.4, 27.0, 22.3, 13.5; ^{19}F NMR (CDCl_3 , 283 MHz) δ –118.7 (dd, J = 95.5, 55.4 Hz, *cis*-CF=CF₂, 1F), –125.5 (dd, J = 111.9, 95.5 Hz, *trans*-CF=CF₂, 1F), –134.2 (dd, J = 111.9, 52.4 Hz, CF=CF₂, 1F); ^{29}Si NMR (CDCl_3 , 59 MHz) δ –65.9, –68.0, –69.1 (4:3:1). Anal. calcd for C₄₆H₇₁F₃O₁₅Si₈: C, 48.22; H, 6.25; F, 4.97. Found: C, 48.22; H, 6.25; F, 4.97. GPC in CHCl₃ relative to polystyrene gave a monomodal distribution with M_n = 842 (M_w/M_n = 1.0).

2.6. Synthesis of **2a**

Trisilanolisobutyl-POSS **2** (9 g, 11.4 mmol) was used following the procedure outlined for the preparation of **1a** to obtain **2a** as a white solid (9.1 mg, 88%). ATR-FTIR (neat) ν 2953 (w), 1745 (w), 1229 (w), 1085 (vs), 1037 (m), 838 (w), 739 (w) cm^{-1} ; ^1H NMR (CDCl_3 , 300 MHz) δ 4.17 (t, J = 8.6 Hz, 2H), 2.01 (s, 3H), 1.91–1.78 (m, 7H), 1.08 (t, J = 8.6 Hz, 2H), 1.01–0.93 (m, 42H), 0.60–0.58 (m, 14H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 171.0, 61.1, 25.8, 23.9, 22.5, 21.1, 13.5; ^{29}Si NMR (CDCl_3 , 59 MHz) δ –67.0, –67.4, –70.0 (3:4:1). Anal. calcd for C₃₂H₇₀O₁₄Si₈: C, 42.54; H, 7.81. Found: C, 42.50; H, 7.96.

2.7. Synthesis of **2b**

2a (5.5 g, 6.09 mmol) was used following the procedure outlined for the preparation of **1b** to obtain **2b** as a white solid (4.1 mg, 80%). ATR-FTIR (neat) ν 2948 (m), 2864 (m),

1086 (vs) cm^{-1} ; ^1H NMR (CDCl_3 , 300 MHz) δ 4.17 (t, J = 7.9 Hz, 2H), 1.92–1.78 (m, 7H), 1.63 (s, OH), 1.06 (t, J = 7.8 Hz, 2H), 0.96–0.94 (m, 42H), 0.61–0.59 (m, 14H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 58.8, 25.7, 23.9, 22.5, 17.8; ^{29}Si NMR (CDCl_3 , 59 MHz) δ –67.1, –67.3, –69.1 (3:4:1). Anal. calcd for $\text{C}_{30}\text{H}_{68}\text{O}_{13}\text{Si}_8$: C, 41.82; H, 7.96. Found: C, 41.20; H, 8.11.

2.8. Synthesis of **2c**

2b (5.5 g, 6.09 mmol) was used following the procedure outlined for the preparation of **1c** to obtain **2c** as a white solid (1.8 mg, 73%). Mp 75–77 °C; ATR-FTIR (neat) ν 2953 (m), 1725 (w), 1273 (w), 1086 (vs) 740 (w) cm^{-1} ; ^1H NMR (CDCl_3 , 300 MHz) δ 8.09 (d, J = 8.9 Hz, 2H), 7.12 (d, J = 8.9 Hz, 2H), 4.45 (t, J = 7.9 Hz, 2H), 1.85–1.82 (m, 7H), 1.24 (t, J = 7.9 Hz, 2H), 0.97–0.93 (m, 42H), 0.59 (t, J = 7.5 Hz, 14H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 165.5, 158.2, 132.0, 127.5, 115.5, 61.9, 25.8, 23.9, 22.6, 13.5; ^{19}F NMR (CDCl_3 , 283 MHz) δ –118.7 (dd, J = 95.5, 55.4 Hz, *cis*- $\text{CF}=\text{CF}_2$, 1F), –125.4 (dd, J = 111.9, 95.5 Hz, *trans*- $\text{CF}=\text{CF}_2$, 1F), –134.4 (dd, J = 111.9, 52.4 Hz, $\text{CF}=\text{CF}_2$, 1F); ^{29}Si NMR (CDCl_3 , 59 MHz) δ –67.0, –67.3, –69.9 (3:4:1). Anal. calcd for $\text{C}_{39}\text{H}_{71}\text{F}_3\text{O}_{15}\text{Si}_8$: C, 44.12; H, 6.74; F, 5.37. Found: C, 43.98; H, 6.99; F, 5.09. GPC in CHCl_3 relative to polystyrene gave a monomodal distribution with $M_n = 1052$ ($M_w/M_n = 1.0$).

2.9. Synthesis of **3c**

Hepta(3,3,3-trifluoropropyl)-tricycloheptasiloxane trisodium silanolate **3** (3.0 g, 3.42 mmol) was used for the preparation of **3a** and **3b** previously reported by Fukada [18]. **3b** was used following the procedure outlined for the preparation of **1c** to obtain **3c** as a white solid (1.85 mg, 40%). Mp 75–76 °C; ATR-FTIR (neat) ν 2954 (m), 1723 (m), 1216 (vs), 1112 (vs), 903 (w), 837 (w) cm^{-1} ; ^1H NMR (CDCl_3 , 300 MHz) δ 8.09 (d, J = 8.9

Hz, 2H), 7.13 (d, $J = 8.9$ Hz, 2H), 4.45 (t, $J = 7.9$ Hz, 2H), 2.20–2.05 (m, 14H), 1.33 (t, $J = 7.9$ Hz, 2H), 0.96–0.86 (m, 14H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 165.3, 131.9, 128.9, 126.9, 125.3, 115.6, 60.7, 28.3, 27.9, 27.5, 27.0, 4.01; ^{19}F NMR (CDCl_3 , 283 MHz) δ –68.6 (s, $\text{CH}_2\text{CH}_2\text{CF}_3$, 21F), –118.5 (dd, $J = 95.5, 55.4$ Hz, *cis*- $\text{CF}=\text{CF}_2$, 1F), –125.4 (dd, $J = 111.9, 95.5$ Hz, *trans*- $\text{CF}=\text{CF}_2$, 1F), –134.5 (dd, $J = 111.9, 52.4$ Hz, $\text{CF}=\text{CF}_2$, 1F); ^{29}Si NMR (CDCl_3 , 59 MHz) δ –67.5, –67.6, –68.6 (4:3:1). Anal. Calcd for $\text{C}_{32}\text{H}_{36}\text{F}_{24}\text{O}_{15}\text{Si}_8$: C, 28.66; H, 2.71; F, 33.99. Found: C, 29.86; H, 2.86; F, 33.01. HRMS–FAB (m/z) $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{32}\text{H}_{36}\text{F}_{24}\text{O}_{15}\text{Si}_8$, 1340.9900; found, 1340.9907. GPC in CHCl_3 relative to polystyrene gave a monomodal distribution with $M_n = 1060$ ($M_w/M_n = 1.0$).

2.10. Preparation of Copolymer **1c-co-4**

In a flame-dried, vacuum sealed glass ampoule, a specified amount of **1c** and 4,4'-bis(4-trifluorovinyloxy)biphenyl **4** were heated to 180 °C for 48 h. After cooling and opening the ampoule, the polymer was dissolved in a minimal amount of THF and precipitated in methanol, filtered, washed repeatedly with methanol, and dried under vacuum to afford a pale yellow–white fibrous solid in nearly quantitative yield. ATR-FTIR (neat) ν 2950 (w), 1606 (w), 1496 (vs), 1196 (vs), 1109 (vs), 957 (vs), 823 (m) cm^{-1} ; ^1H NMR (CDCl_3 , 300 MHz) δ 7.48–7.46 (m, 6H), 7.24–7.16 (m, 6H), 4.10 (t, $J = 7.8$ Hz, 2H), 1.80–0.85 (m, 65H); ^{19}F NMR (CDCl_3 , 283 MHz) δ –128.0–(–131.4) (m, cyclobutyl- F_6).

2.11. Preparation of Copolymer **2c-co-4**

2c and **4** were used following the procedure outlined for the preparation of **1c-co-4** to obtain **2c-co-4** as a pale yellow–white fibrous solid in nearly quantitative yield. ATR-

FTIR (neat) ν 29570 (w), 1606 (w), 1495 (vs), 1301 (s), 1193 (vs), 1107 (s), 953 (vs), 821 (s) cm^{-1} ; ^1H NMR (CDCl_3 , 300 MHz) δ 7.60–7.45 (6H), 7.26–7.18 (6H), 3.76–3.72 (m, 2H), 1.87–1.83 (m, 2H), 1.60–1.54 (m, 7H), 0.96–0.92 (42H), 0.61–0.57 (m, 14H); ^{19}F NMR (CDCl_3 , 283 MHz) δ –126.5–(–131.2) (m, cyclobutyl- F_6).

2.12. Preparation of Copolymer **3c-co-4**

3c and **4** were used following the procedure outlined for the preparation of **1c-co-4** to obtain **3c-co-4** as a pale yellow–white, fibrous solid in nearly quantitative yield. ATR-FTIR (neat) ν 2926 (w), 1606 (m), 1496 (vs), 1305 (vs), 1199 (vs), 962 (vs), 851 (s), 600 (m) cm^{-1} ; ^1H NMR (CDCl_3 , 300 MHz) δ 7.60–7.45 (6H), 7.23–7.03 (6H), 4.42 (t, J = 7.9 Hz, 2H), 2.17–2.08 (m, 14H), 1.26 (t, J = 7.9 Hz, 2H), 0.96–0.86 (m, 14H); ^{19}F NMR (CDCl_3 , 283 MHz) δ –68.5 (21F), –126.4–(–131.2) (m, cyclobutyl- F_6).

2.13. Preparation of Copolymer **3c-co-5**

3c and **5** were used following the procedure outlined for the preparation of **1c-co-4** except heating was prolonged for 96 h to obtain **3c-co-5** as a pale yellow–white, fibrous solid in nearly quantitative yield. ATR-FTIR (neat) ν 2950 (w), 1512 (m), 1174 (vs), 1117 (s), 1305 (vs), 962 (s), 831 (s) cm^{-1} ; ^1H NMR (CDCl_3 , 300 MHz) δ 7.40–7.06 (12H), 4.44 (t, J = 7.9 Hz, 2H), 2.18–2.11 (m, 14H), 1.29 (t, J = 7.9 Hz, 2H), 0.96–0.86 (m, 14H); ^{19}F NMR (CDCl_3 , 283 MHz) δ –63.9 (6F), –68.6 (21F), –127.2–(–132.8) (m, cyclobutyl- F_6).

2.14. Preparation of Homopolymers **poly4** and **poly5**

In a flame-dried, vacuum sealed glass ampoule, a specified amount of **4** or **5** was heated to 180 °C for 48 h. After cooling and opening the ampoule, the polymer was

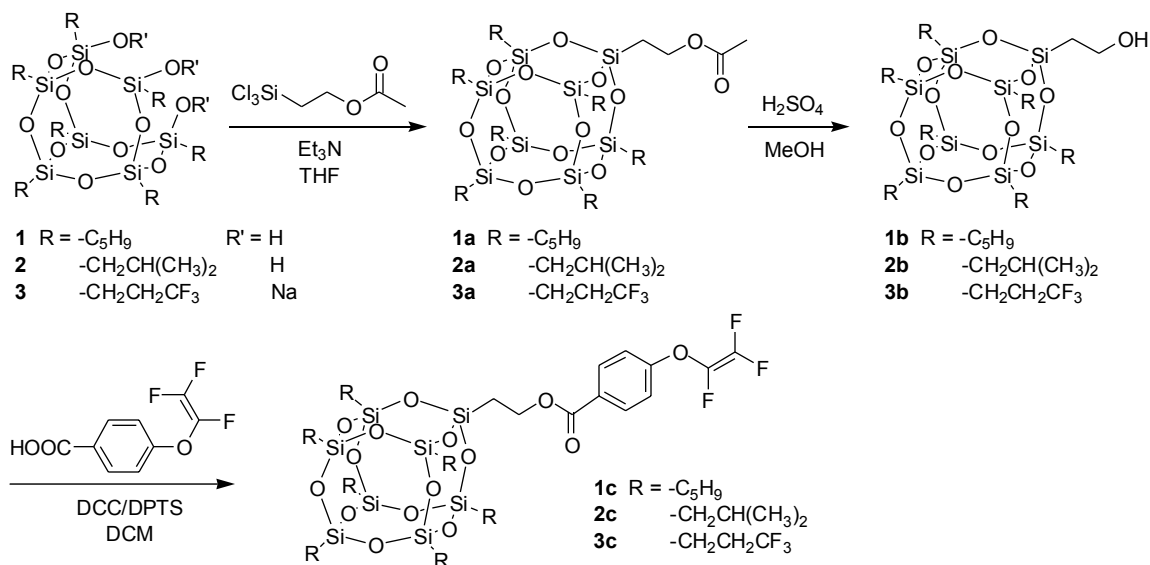
dissolved in a minimal amount of THF and precipitated in methanol, filtered, washed repeatedly with methanol, and dried under vacuum to afford a white fibrous solid in nearly quantitative yield. Their characterization has been previously reported [9a,17].

3. Results and discussion

3.1. Monomer Synthesis

POSS-functionalized TFVE monomers **1c** and **2c** were prepared from commercially available functionalized POSS triols **1** and **2**. Monomer **3c** was synthesized *via* the hydrolytic condensation of trifluoropropyltrimethoxysilane under basic conditions in the presence of potassium hydroxide affording the trisodium silanolate **3** [18]. Initial corner-capping *via* the condensation of POSS triols **1–3** with acetoxyethyltrichlorosilane afforded the POSS T₈ cages **1a–3a**. POSS alcohols **1b–3b** were produced in nearly quantitative yield by deprotection of the POSS esters **1a–3a** under mild acidic conditions. Dicyclohexyldicarbimide (DCC) coupling with 4-(trifluorovinyloxy)benzoic acid produced the desired POSS functionalized TFVE monomers **1c–3c**.

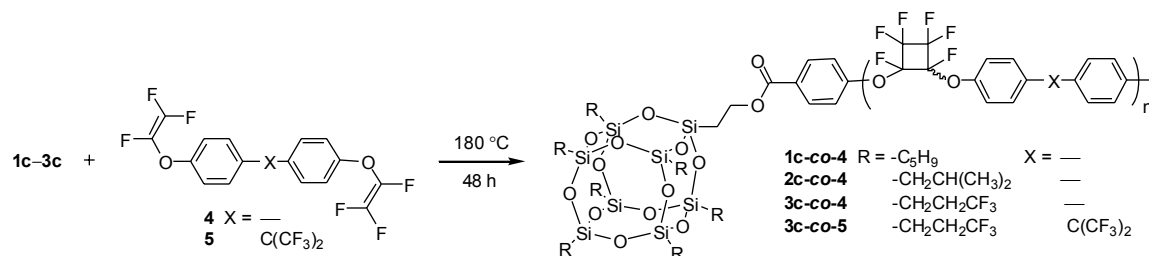
The overall four-step monomer synthesis produced good yields of 40–76% for **1c–3c**. Characterization and purity of POSS functionalized TFVE monomers were confirmed by NMR (¹H, ¹³C, ¹⁹F, and ²⁹Si), GPC, IR, and elemental analysis (C, H, and F). Sharp melting points at 75–77 °C were observed for monomers **2c** and **3c**; however, the cyclopentyl POSS-functionalized TFVE monomer **1c** showed no measurable melting < 200 °C. All monomers are soluble in common polar and non-polar organic solvents (hexanes, THF, CHCl₃, acetone, and DMSO).



Scheme 2. Synthesis of silsesquioxane-functionalized trifluorovinyl ether monomers.

3.2. Polymerization

Copolymerization with POSS functionalized PFCB monomers **1c–3c** with commercial bisfunctionalized TFVE monomer 4,4'-bis(4-trifluorovinyloxy)biphenyl (**4**) were performed in bulk at 180 °C for 48–96 h in vacuum-sealed ampoules (Scheme 3). Selected polymer properties are shown in Table 1. Copolymerization of **3c** with commercial 2,2-bis(4-trifluorovinyloxybiphenyl)-1,1,1,3,3,3-hexafluoropropane (**5**) required extended heating at 180 °C for 96 due to the established lower cyclodimerization rate for deactivated aryl TFVE monomers [11a]. Polymers were purified by dissolving material in a minimal amount of THF, precipitated in MeOH, followed by filtration to afford fibrous yellow-white material. In all cases, nearly quantitative weight recovery was observed for the purified polymers. Copolymer POSS incorporation was confirmed by ¹H NMR analysis and agreed with calculated weight percents (Table 1).



Scheme 3. Copolymerization of POSS TFVE monomers **1c–3c** with bisfunctionalized TFVE monomers **4** and **5**.

^{19}F NMR was a diagnostic tool used to observe the conversion of TFVE monomers to PFCB polymers. The conversion of POSS-functionalized TFVE monomer **3c** to copolymer **3c-co-5** by ^{19}F NMR is shown in Figure 1. The diagnostic trifluorovinyl AMX pattern at -118.5 ppm (F_A), -125.4 ppm (F_M), and -134.5 ppm (F_X) converts to the perfluorocyclobutyl- F_6 multiplet at -127.2 –(-132.8) ppm. Using either ^1H or ^{19}F NMR analysis, it was difficult to determine if POSS end groups were present on one or both ends of the linear polymer, albeit no terminal TFVE end groups were observed.

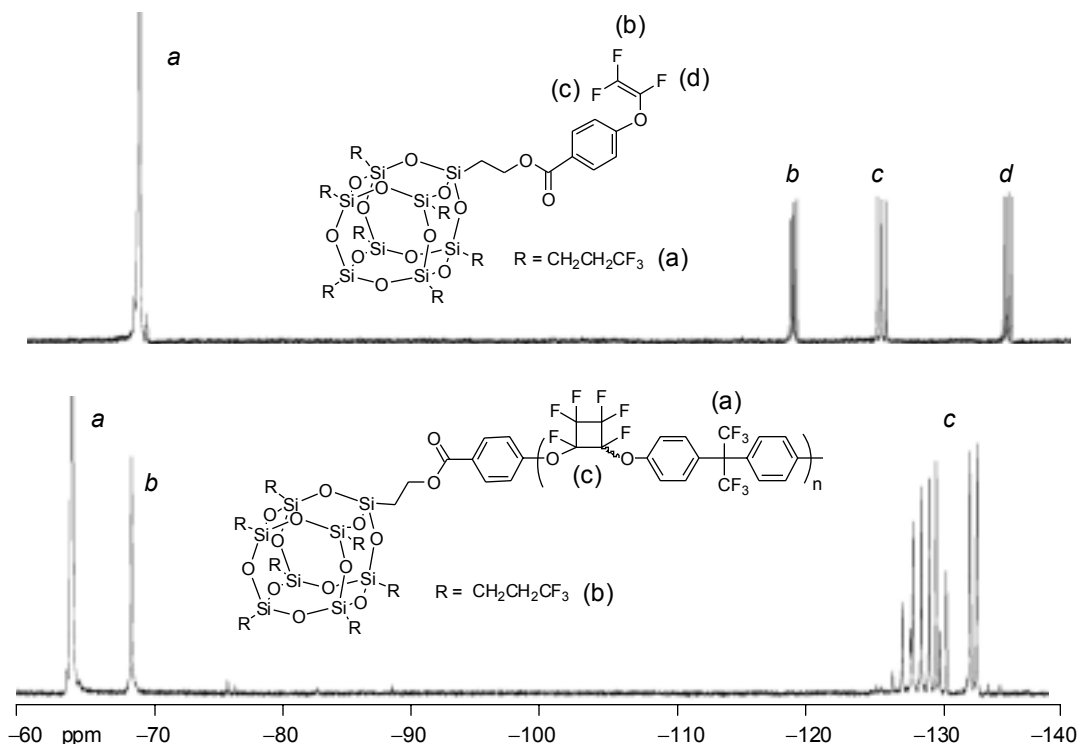


Figure 1. ^{19}F NMR (in CDCl_3) overlay of trifluorovinylether functionalized POSS **3c** (top) and 20 wt% POSS copolymer **3c-co-5** (bottom).

The cyclopentyl and *iso*-butyl endcapped POSS functionalized copolymers **1c-co-4** and **2c-co-4** showed significantly lower M_n values compared to homopolymer **poly4** (Table 1). This is possibly due to the high melting point ($>200\text{ }^\circ\text{C}$) of monomer **1c** and its poor solubility in monomer **4** melt at bulk polymerization temperature of $180\text{ }^\circ\text{C}$. Similarly, the *iso*-butyl terminated POSS copolymer **2c-co-4** showed a factor of two lower M_n compared with homopolymer **poly4** possibly due to increasing copolymer insolubility in the melt, however still produced good film forming properties. GPC analysis illustrates the conversion of POSS functionalized TFVE monomer **2c** to a monomodal distribution of **2c-co-4** as shown in Figure 2. GPC traces of all crude copolymers showed no evidence of unreacted POSS-functionalized monomer. Clearly, from copolymers **1c-co-4** and **2c-co-4**, TFVE POSS monomers behave as chain terminators and they lower the M_n compared

with homopolymer **poly4**. On the other hand, the trifluoropropyl POSS copolymers **3c-co-4** and **3c-co-5** produced similar M_n compared with **poly4** and **poly5**, respectively.

In all cases, the relative GPC M_n appears to increase slightly within the copolymer series with increasing POSS monomer weight percent. This may be due to the increasing hydrodynamic volume due to bulky POSS cages appended to both single polymer chain ends. It should also be noted that solubility between biphenyl monomer **4** and fluorinated POSS monomer **3c** is dramatically increased over non-fluorinated POSS monomers. Therefore, the increase in relative GPC M_n for the **3c** copolymer series could be attributed to both hydrodynamic volume increases as well as enhanced polymerization rate due to solubility. While most polydispersities were nearly the same for all copolymers compared with their respective homopolymers, copolymer **3c-co-4** showed the highest polydispersity and broadened with increased POSS content as expected from the increased conversion and higher molecular weight.

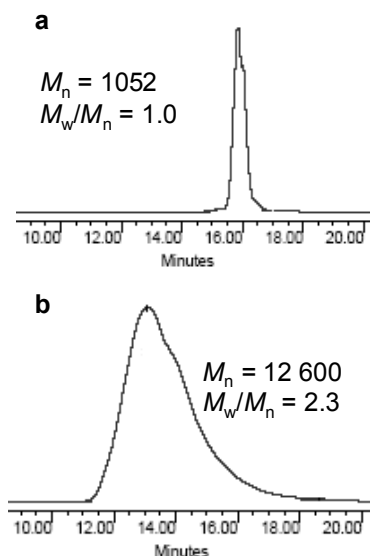


Figure 2. Gel permeation chromatogram in CHCl_3 of TFVE POSS monomer **2c** (a) and copolymer **2c-co-4** with 20 wt% POSS (b).

3.3. Thermal properties

Table 1 shows the DSC analysis of homopolymers and copolymers functionalized with POSS. Glass transition temperatures (T_g) for amorphous, semi-fluorinated PFCB homopolymers **poly4** and **poly5** were 140 °C and 97° C, respectively. These values agree with previously reported work [3]. Increasing POSS content lowered T_g 's in all copolymers and, for example, a 28% decrease in T_g was observed for **2c-co-4** with 20 wt% POSS compared with homopolymer **poly4** (Figure 3). Although, this observation may be attributed to low number-average molecular weight (particularly with **1c-co-4** and **2c-co-4**), incorporation of POSS does significantly affect T_g since a PFCB homopolymer of **poly4** prepared with a comparable number-average molecular weight (M_n of 13300) gave a similar T_g of 139 °C. On the other hand, compatibility was observed using fluorinated POSS monomers in copolymer system **3c-co-4** with 10 wt% POSS and **3c-co-5** with 20 wt% POSS resulting in little deviation of T_g .

Table 1. Selected Properties of Polymers

polymer	wt% POSS	calcd mol% POSS	found mol% POSS ^a	$M_n \times 10^{-3}$ GPC ^b	M_w/M_n	T_g (°C) ^c
poly4	0	0.0	--	25.0	2.1	140
1c-co-4	10	3.7	2.0	5.7 ^d	2.0	122
1c-co-4	20	7.9	6.5	6.4 ^d	2.2	119
2c-co-4	10	4.0	2.3	10.3	1.8	124
2c-co-4	20	8.5	8.0	12.6	2.3	109
3c-co-4	10	3.2	1.7	22.2	3.0	138
3c-co-4	20	6.9	3.6	28.8	4.3	131
poly5	0	0.0	--	11.2	2.1	97
3c-co-5	20	8.5	4.4	8.8	1.6	100

^a Measured by ¹H NMR using integration ratio of aryl to POSS alkyl peaks.

^b GPC in CHCl₃ using polystyrene as standard. ^c DSC (10 °C/min) in nitrogen determined by third re-heating cycle. ^d Average of two polymerizations.

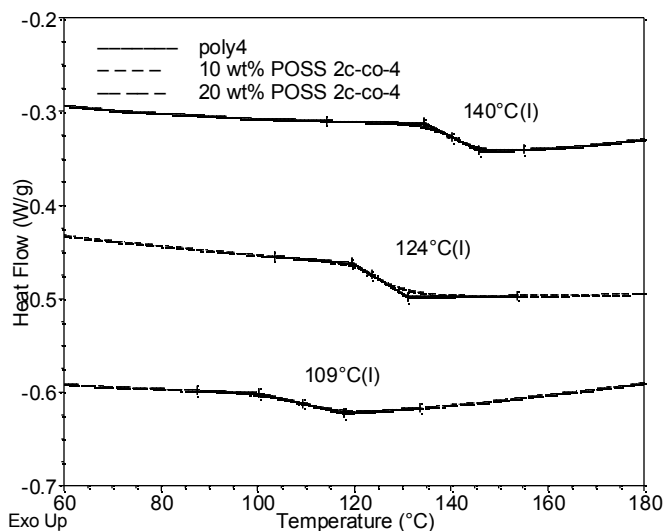


Figure 3. DSC traces of homopolymer **poly4** and copolymer **2-co-4** with 10 and 20 wt% POSS.

3.4. Degradation analysis

Copolymer thermal stability was studied in nitrogen and air using thermal gravimetric analysis (TGA) as shown in Table 2. Homopolymers **poly4** and **poly5** exhibit a high degree of thermal stability with recorded thermal decomposition temperatures (T_d) of 450 °C and 466 °C in nitrogen and 446 °C and 457 °C in air, respectively. For all copolymers studied, two onsets of degradation were observed in nitrogen and air. Figure 4 illustrates the step-wise decomposition of POSS PFCB copolymer **1c-co-4** in comparison with the homopolymer **poly4**. TGA showed the onset of degradation in nitrogen and air results in a weight loss proportional to the weight percent of POSS content in the copolymers.

The comparison of GC–MS pyrolysis analysis of monomer **1c** with **1c-co-4** revealed evidence of similar POSS cage decomposition to siloxane fragments. This fragmentation pattern shows $[M]^+$ with m/z (relative intensity): 284 (53%), 249 (12%), 214 (7%), 142 (15%), 107 (8%), 71 (5%). Molecular weights of 284, 214, and 142 primarily elude to siloxane fragments of $[(\text{CySiO})_2\text{SiCH}_2\text{CH}_2]^+$, $[\text{CySiO}_3]^+$, and $[\text{CH}_2\text{CH}_2\text{SiO}_3]^+$,

respectively. The main components of GC analysis for **1c-co-4** produced phenolic species as a result of expulsion of the hexafluorocyclobutene from the PFCB ring. This has been previously shown by Babb based on the thermal degradation of PFCB polymers [10]. TGA analysis showed a significant increase in final decomposition temperature (T_d >500 °C) of copolymers **1c-co-4** with 20 wt% POSS (in nitrogen) and **2c-co-4** with 10 and 20 wt% POSS (in nitrogen and air) relative to the PFCB homopolymer **poly4**. In most other cases, a modest increase in final T_d was observed for copolymers containing POSS. POSS has been shown to improve polymer thermal stability [19] possibly by a self-passivating mechanism ultimately creating layer silicon oxide [20]. Char yields were in the range of 11–54% in nitrogen at 600 °C for all copolymers studied using TGA analysis; no char was observed by measurements performed in air at that temperature.

Table 2. Summary of Thermal Decomposition of Copolymers

polymer	wt% POSS	in N ₂			in air	
		T_d (°C) ^a	initial weight loss (%)	char (%)	T_d (°C) ^a	initial weight loss (%)
poly4	0	450	--	45	446	--
1c-co-4	10	322, 464	6.3	41	330, 489	3.0
1c-co-4	20	316, 518	14.6	37	355, 479	7.0
2c-co-4	10	304, 461	6.8	40	306, 563	5.9
2c-co-4	20	307, 521	14.2	54	297, 558	12.1
3c-co-4	10	325, 450	10.0	30	300, 450	10.0
3c-co-4	20	319, 467	15.0	32	310, 460	12.6
poly5	0	466	--	25	457	--
3c-co-5	20	318, 474	12.2	20	310, 460	12

^a TGA onset at 10 °C/min of chain extended polymers.

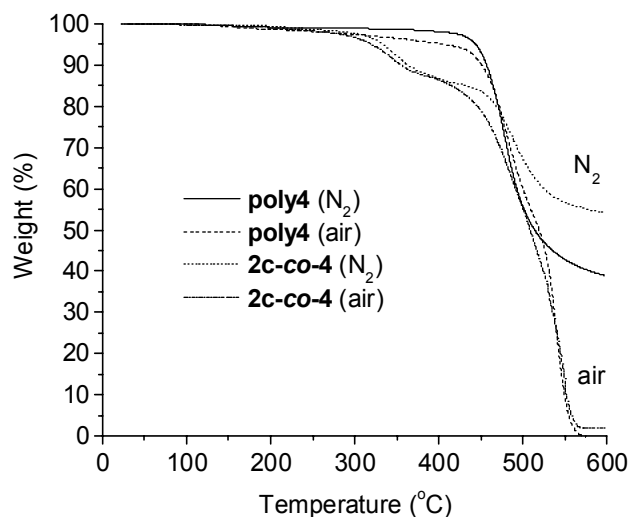


Figure 4. TGA comparison of homopolymer **poly4** and copolymer **2c-co-4**.

3.5. Surface analysis of copolymers

Films of the copolymers were prepared from spin casting using a minimal amount of THF (approximately 80 wt% solids) producing 3–5 μm thick films. The films produced were transparent and flexible. Initial surface characterization using SEM showed no micron-sized POSS aggregates; however, the use of TEM revealed the presence of 50-150 nm POSS clusters confirmed by energy dispersive X-ray spectroscopy (EDS) (Figure 5). These POSS clusters were observed on various areas on the TEM grid and best represent that of the entire sample.

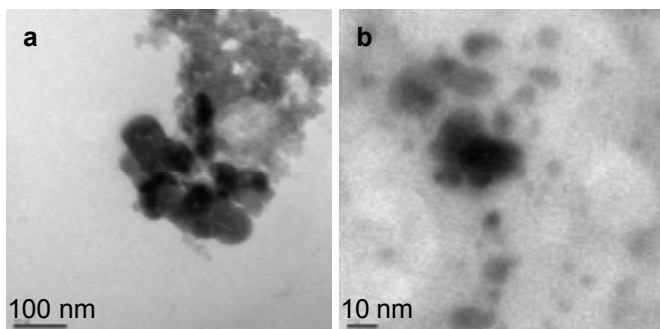


Figure 5. TEM images of **2c-co-4** with 20 wt% POSS illustrating POSS aggregates as darkened areas.

4. Conclusions

A new PFCB polymer endcapped with POSS has been prepared through the facile functionalization of commercial POSS triols and commercial PFCB precursor intermediates. The copolymers exhibited moderate to high molecular weight, lower T_g 's, and gave transparent creasable spin cast films with excellent solvent processability. In some cases, the copolymers functionalized with POSS produced a higher degree of stability in nitrogen and air. We anticipate this new class of POSS functionalized PFCB polymers for use as a versatile material in a multitude of high performance fluoropolymer applications possessing processability and high thermal resistance.

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