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Polyhedral Oligomeric Silsesquioxane- Functionalized Perfluorocyclobutyl Aryl Ether Polymers (Preprint)

**An Overview of the Synthesis and Properties of Polyhedral
Oligomeric Silsesquioxanes (POSS) Functionalized with
Perfluorocyclobutyl (PFCB) Aryl Ether Polymer Blends and
Copolymers**

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Perfluorocyclobutyl (PFCB) aryl ether polymers are semi-fluorinated polymers that produce processable, optically transparent materials for a multitude of materials applications. Incorporating low surface energy polyhedral oligomeric silsesquioxanes (POSS) into the PFCB polymer matrix

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produced enhanced hydro- and oleo-phobicity. PFCB polymers functionalized with POSS nanostructures include blends, copolymers, and block copolymers. For copolymers, trifluorovinyl aryl ether (TFVE) POSS monomers were prepared in good yields using an operationally simple corner capping methodology from commercial POSS trisilanols. The surface analysis of POSS functionalized PFCB polymer blends and copolymers using microscopy and optical profilometry showed the POSS structures produced sub-micron to nanometer roughness that contributes to enhanced water and hexadecane repellency.

Introduction

Many plant species such as the lotus leaf exhibit a peculiar self-cleaning mechanism resulting from micron-sized nodes decorated on the surface. These nodes are covered with nano-sized wax particles on the surface. This structure induces the beading of water, which is naturally repelled from the surface, removing any entrained foreign debris.^{1,2} There are many noteworthy examples of coatings that successfully produce artificial ultrahydrophobic lotus leaf-like surfaces.³ However, many of these examples are prepared using aggressive post chemical and/or thermal surface treatments, expensive starting materials, or necessitate the need for lithography methods. As a consequence, there still exists a need to efficiently produce low surface energy materials, albeit not exclusively limited to hydrophobicity, amenable for large scale application.

Fluoropolymers continue to be of great interest for a wide range of material applications, particularly for low energy surfaces.⁴ Incorporating fluorine into a polymer backbone creates an interesting irony in terms of physical properties. On one hand, highly fluorinated polymers possess a high degree of chemical resistance, thermal stability, and excellent insulating ability. Conversely, perfluorinated polymers, like poly(tetrafluoroethylene) (PTFE), are intrinsically crystalline, leading to high processing costs. Therefore, interest continues in developing new fluoropolymers to overcome processing limitations while maintaining performance. Perfluorocyclobutyl (PFCB) aryl ether polymers are prepared by condensate-free, step-growth [2+2] thermal cyclodimerization of

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trifluorovinyl aryl ether (TFVE) monomers (Figure 1).^{5,6} The cycloaddition event proceeds via a biradical intermediate in a predominately head-to-head fashion.⁷ The stereorandom nature of the PFCB aryl ether linkage affords an entirely amorphous, semi-fluorinated thermoplastic that is solution processable. TFVE monomers are easily functionalized for desired applications employing a halogen-metal exchange methodology developed by Smith *et al.* using the intermediate, 4-bromo(trifluorovinyl) aryl ether, as a commercial starting material.^{8,9} As a result of this tailorability, material applications of PFCB polymers include high performance optics,¹⁰ polymer light-emitting diodes (PLEDs),¹¹ atomic oxygen (AO) resistant coatings,¹² polymeric proton exchange membranes (PEMs) for fuel cells,¹³ and liquid-crystalline polymers.¹⁴

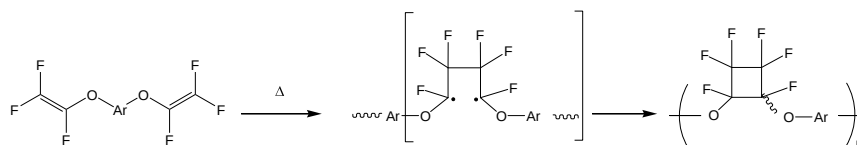


Figure 1. Thermal [2+2] cyclopolymerization of trifluorovinyl aryl ethers.

Polyhedral oligomeric silsesquioxane (POSS) compounds comprised of a functionalized nanometer-sized silicon-oxygen core framework have received much interest as robust building blocks for the development of high performance materials.¹⁵ POSS incorporation into polymers, either as blends or covalently bound copolymers, produces hybrid organic-inorganic composites. Modified properties of the virgin polymer include changes in glass transition temperature, crystallinity, mechanical toughness, chemical resistance, ease of processing, fire resistance, and atomic oxygen resistance.¹⁵

Herein, recent focus expands on the utility of PFCB polymers by introducing blended and covalently bound POSS cages for improving water and hexadecane repellency. These POSS-modified PFCB polymers produced hybrid composites with improved properties such as thermal stability, mechanical integrity, tunable refractive index, and gas permeability.

Experimental

Materials. Chemicals and solvents were purchased through Sigma Aldrich and purified according to reported procedures.¹⁶ POSS triols **1** and **2** were obtained from Hybrid Plastics. Fluorinated POSS (F-POSS) compounds were donated by

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the Air Force Research Laboratory, Propulsion Directorate or prepared according to previously published procedures.¹⁷ POSS trisodium silanolate salt **3** was prepared according to previously published procedures by Fukuda.¹⁸ Experimental procedures and spectroscopic data for POSS functionalized TFVE monomers **1c–3c** and **6–7** are reported elsewhere.^{19,20} 4,4'-Bis(4-trifluorovinyloxy)biphenyl (**4**) and 2,2-bis(4-trifluorovinyloxybiphenyl)-1,1,1,3,3,3-hexafluoropropane (**5**) were generously donated and are commercially available from Tetramer Technologies, L.L.C., Pendleton, SC and distributed through Oakwood Chemicals, Inc.

General Procedures. All reactions were carried out under ultra high purity grade nitrogen. Flasks and syringes were flame-dried under vacuum and allowed to cool in a desiccator filled with Ca_2CO_3 prior to use. ^1H , ^{13}C (proton decoupled), and ^{19}F (proton decoupled), and ^{29}Si NMR data were obtained on a JOEL Eclipse⁺ 300. Gel permeation chromatography (GPC) data were collected in CHCl_3 using polystyrene as a standard (Polymer Labs Rascal PS-2) using a Waters 2690 Alliance System with UV-Vis detection. Differential scanning calorimetric (DSC) analysis and thermal gravimetric analysis (TGA) were performed on a TA Q1000 instrument and Mettler-Toledo 851 instrument, respectively. Transmission electron microscopy (TEM) micrographs were obtained from a Hitachi H9500 300 eV at the Clemson University Electron Microscope Facility. Surface analysis and roughness was performed on a Zygo New View 6300 3D white light optical profiler or a Digital Instruments Dimension 3100 atomic force microscopy (AFM) system.

Contact Angle Measurements. Contact angle analyses were performed on a FDS Data physics Contact Analyzer System or a Rime-Hart 100-00 115 Goniometry. Liquid drops were either automatically or manually dispensed with 8–10 μL drop sizes. The contact angles were determined via the software suite or via graphical fitting of the contact tangents in the captured image. Both approaches gave the same nominal value within ± 2 degrees. Static contact angle values report an average of the three values measured on various areas of the coated surface. Deionized water and hexadecane were used as test fluids to measure static contact angles.

Results and Discussion

POSS PFCB Polymer Blends

Fluorinated POSS (F-POSS) compounds were blended into PFCB polymer **poly5** ($M_{\text{an}} = 22000$, PDI = 2.2; GPC in CHCl_3 using PS as standard) by

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dissolving a weight percentage of F-POSS relative to the polymer matrix in a minimal amount of hexafluorobenzene (Figure 2). Although the POSS and PFCB polymer dissolved in solvent produced a readily homogenous solution, the mixture was rigorously blended with a magnetic stirrer for five minutes. The solution was then spin cast onto borosilicate plates (ca. 0.5-0.75µm thick), producing optically transparent films for loadings less than 20 wt%.

Previous work by Mabry and Vij, showed the fluorodecyl₈T₈ POSS (**FP₈T₈**) compound possesses the highest degree of hydro- and oleo-phobicity.¹⁷ The measured static contact angles of **FD₈T₈** was reported as 154° and 87° for water and hexadecane, respectively. Although other F-POSS compounds produce suitable free standing films from spin casting, the following blending work will focus on PFCB polymer blends with **FD₈T₈** since these produce the highest water and hexadecane contact angles.

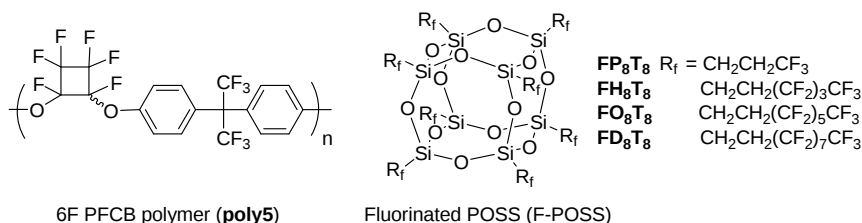


Figure 2. Fluorinated POSS is solvent blended into 6F PFCB polymer matrix.

Increasing **FD₈T₈** POSS wt% loadings shows a gradual increase in water and hexadecane contact angle (Figure 3). The 6F PFCB polymer (**poly5**) is considered hydrophobic with no F-POSS incorporation with water and hexadecane contact angles of 95° and 27°. **FD₈T₈** POSS loadings up to 15 wt% developed a water repellency plateau; the blend shows an overall 32% increase in water contact angle. At optimized **FD₈T₈** loadings of 10 wt%, a maximum hexadecane contact angle of 80° was observed increasing oleophobicity by 158%. While films prepared from 15 wt% **FD₈T₈** POSS loading still appeared transparent and homogenous, at 20 wt% **FD₈T₈** POSS, significant incompatibility was observed producing opaque films. Work is currently in progress to determine liquid drop hysteresis by measuring advancing and receding contact angles.

Blending **FD₈T₈** into the PFCB polymer introduced additional fluorine content and increased surface roughness. These two characteristics produced a composite with lower surface energy. The relationship of contact angle and

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surface energy is governed by Young's equation which relates interfacial tensions among the surface to the liquid and gas phases of water.²¹ Furthermore, it is well known that surface roughness imparts increased hydrophobicity of a material as demonstrated by Cassie and Wenzel.^{22,23} Analysis of 15 wt% POSS PFCB polymer composite film surface by SEM analysis using energy dispersive X-ray (XDS) elemental mapping showed excellent dispersion of the POSS within the PFCB matrix.

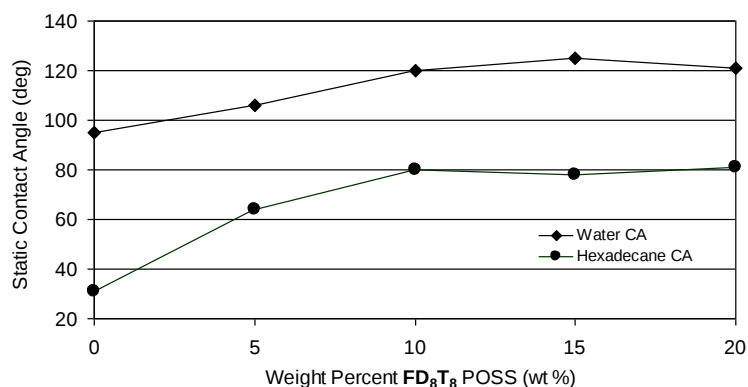


Figure 3. Water and hexadecane static contact angle versus wt % of FD_8T_8 blended into **poly5**.

AFM analysis of 15 wt% FD_8T_8 blend compared with the virgin PFCB polymer showed a marked increase in surface roughness (Figure 4). From AFM analysis, virgin **poly5** and 15 wt% FD_8T_8 composite blend gave a measured surface roughness (r.m.s.) of 0.527 nm and 1.478 nm, respectively. The incorporation of the nanosized F-POSS structures produces a three-fold increase in surface roughness possibly due to blooming and aggregation of these structures on the surface during the spin casting process. Additional surface characterization remains ongoing to determine the concentration gradient of the F-POSS structures on the surface compared to entrained F-POSS in the bulk material.

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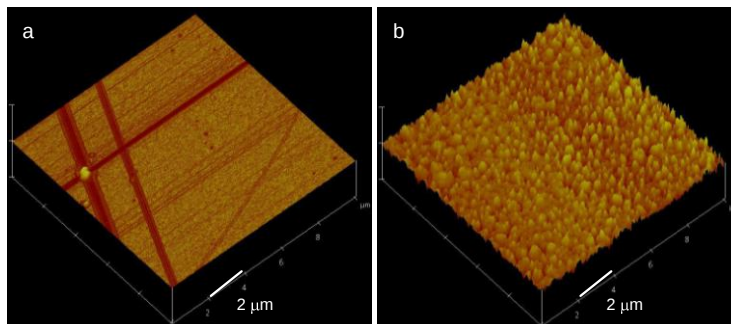


Figure 4. AFM of (a) virgin PFCB polymer **poly5** and (b) 15 wt% **FD₈T₈** POSS **poly5** blend.

Solvent blending demonstrated good compatibility of F-POSS with PFCB polymers. Significant increases in the hydrophobicity and oleophobicity of PFCB polymers was observed with minimal F-POSS loadings by the increase in fluorine content and surface nanoroughness. The suppression of surface migration and increased POSS loading could be achieved by incorporating POSS structures covalently bound to a polymer backbone. This is the focus of the following sections where initial attempts to introduce non-fluorinated POSS would serve as model studies to understand effects on bulk copolymer properties. Consequently, the incorporation of fluorinated POSS as copolymers would serve to ultimately enhance hydro- and oleo-phobicity.

Chain Terminated POSS PFCB Copolymers

Monomer Synthesis. The preparation of TFVE POSS monomers for chain terminated copolymers is shown in Figure 5.¹⁹ POSS-functionalized TFVE monomers **1c** and **2c** were prepared from commercially available POSS triols **1** and **2**. Monomer **3c** was synthesized via the hydrolytic condensation of trifluoropropyltrimethoxysilane affording the trisodium silonate salt (**3**).¹⁸ Initial corner-capping via the condensation of POSS triols **1–3** with acetooxyethyltrichlorosilane affords the POSS T₈ cages **1a–3a**. POSS alcohols **1b–3b** are produced in nearly quantitative yield by deprotection of the POSS esters **1a–3a** under mild acidic conditions. Dicyclohexyldicarbimide (DCC) coupling with 4-(trifluorovinyl)oxy)benzoic acid (available through Oakwood Chemicals) produces the desired monomers **1c–3c**. The overall, optimized four-step monomer synthesis produces modest to good yields of 40–76% for **1c–3c**.

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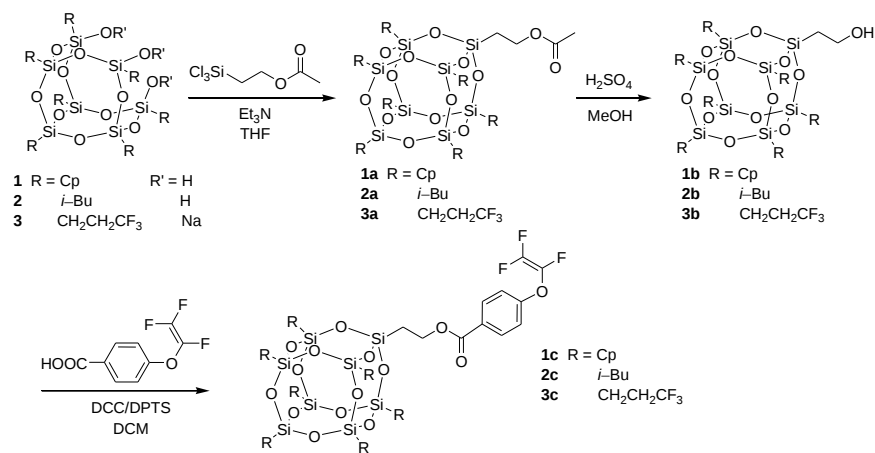


Figure 5. Synthesis of POSS monomers functionalized with TFVE.

Polymerization. Copolymerization of POSS functionalized PFCB aryl ether monomers **1c–3c** with bisfunctionalized TFVE monomer 4,4'-bis(4-trifluorovinyl)oxybiphenyl (**4**) was performed in bulk at 180 °C for 48–96 h in vacuum-sealed ampoules (Figure 6).

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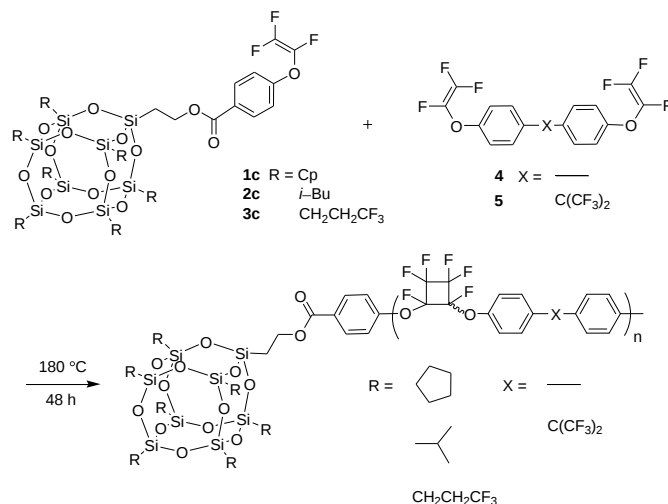


Figure 6. Preparation of POSS chain terminated PFCB copolymers.

Selected properties of the chain terminated copolymers are shown in Table 1. POSS-functionalized copolymers produce optically transparent, free-standing films from either THF drop- or spin-casting. In all cases, the bulk polymerization produces nearly quantitative mass recovery after precipitation. Molecular weights of copolymers **2c-co-4** and **3c-co-4** are similar to the corresponding homopolymer **poly4**. The cyclopentyl-substituted POSS functionalized copolymers **1c-co-4** showed significantly lower M_n values compared to homopolymer **poly4**. This is due to the fact the monomer **1c** does not melt below 200 °C, nor is it soluble in the monomer melt at bulk polymerization temperature of 180 °C. Molecular weights were the highest for copolymers **3c-co-4** functionalized with the trifluoropropyl POSS. The compatibility of fluorinated POSS in the semi-fluorinated PFCB matrix is further evidenced by copolymer **3c-co-5**. In this case, the polymer backbone introduces the hexafluoroisopropylidene moiety increasing fluorine content by 33%.

Table 1. Selected Properties of POSS Chain Terminated PFCB Copolymers

polymer	wt% POSS	$M_n \times 10^{-3}$ GPC ^a	M_w/M_n	T_g (°C) ^b	T_d (°C) N ₂ (air) ^c
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poly4	0	13.3	2.2	140	450 (446)
1c-co-4	10	2.1	1.7	133	322, 464 (330, 489)
1c-co-4	20	7.0	2.0	131	316, 518 (355, 479)
2c-co-4	10	10.3	1.8	124	304, 461 (306, 563)
2c-co-4	20	12.6	2.3	109	307, 521 (297, 558)
3c-co-4	10	22.2	3.0	138	325, 450 (300, 450)
3c-co-4	20	28.8	4.3	131	319, 467 (310, 460)
poly5	0	4.0	1.9	97	466 (457)
3c-co-5	20	8.8	1.6	100	318, 474 (310, 460)

^a GPC in CHCl₃ using polystyrene as standard. ^b DSC (10 °C/min) in nitrogen determined by second re-heating cycle. ^c TGA onset at 10 °C/min.

Thermal Properties. Table 1 shows the DSC analysis of homopolymers and copolymers functionalized with POSS. As previously reported, T_g for amorphous, semi-fluorinated PFCB homopolymers **poly4** and **poly5** are 140 °C and 97° C, respectively. A plasticizing effect was observed with **2c-co-4**, particularly with increasing POSS content, lowering T_g by 28% using 20 wt% monomer. On the other hand, compatibility was achieved using fluorinated POSS monomers in copolymer systems **3c-co-5** with no deviation in T_g .

Degradation Analysis. Composite thermal stability was studied in nitrogen and air using thermogravimetric analysis (TGA) as shown in Table 1. Homopolymers **poly4** and **poly5** exhibit a high degree of thermal stability with recorded thermal decomposition temperatures (T_d) of 450 and 466 °C in nitrogen and 446 and 457 °C in air. For all copolymers studied, two onsets of degradation were observed in nitrogen and air. TGA indicated the onset of degradation in nitrogen and air results in a mass loss proportional to the weight percent of POSS content in the copolymers. Char yields randomly varied in the range of 11–54% in nitrogen for all copolymers studied using TGA analysis.

Pendant POSS PFCB Copolymers

New linear chain terminated PFCB polymers functionalized with POSS have been prepared through the facile corner capping of POSS triols. The composites produced moderate molecular weight, transparent polymers with excellent solvent processability and, in some cases, improvement in thermo-oxidative stability. Wettability analysis of the copolymer films did not show a significant improvement in water or hexadecane contact angle over the homopolymers. The preparation longer fluoroalkyl TFVE POSS monomers is the interest of future investigations in order to improve water and hexadecane

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repellency.

Monomer Synthesis. The preparation of POSS monomers with bifunctional TFVE moieties **6** and **7** were prepared by an efficient condensation of commercial POSS silanols with 4,4'-bis(4-trifluorovinylether)biphenyl methylchlorosilane previously reported by Smith *et al.* using a metal-halogen exchange methodology (Figure 7).²⁰ The monomers were isolated in acceptable yields (29–30%) with a high degree of purity.

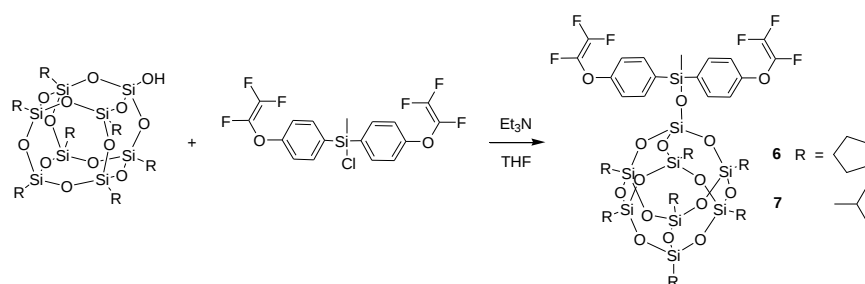


Figure 7. Synthesis of bifunctionalized TFVE POSS monomers.

Monomer characterization was confirmed by multi-nuclei NMR (^1H , ^{19}F , ^{13}C , and ^{29}Si) spectroscopy and elemental analysis. Figure 8 shows a representative ^{29}Si NMR of POSS TFVE monomer **7** in CDCl_3 . Symmetry arrangement of the silicon atoms exhibits four resonance peaks with ratios 1:3:4:1 for peak assignments *a*, *c*, *d*, *b*, respectively. The bridgehead *M* silicon atom (assigned as *a*) with adjoining diaryltrifluorovinylether moieties is shifted furthest downfield at -9.6 ppm. The *Q* silicon in the POSS cage assigned *b* is shifted at -109.9 ppm. The remaining regions pertain to the apex *T* silicon atoms of the POSS cage and shift -66.3 ppm and -67.2 ppm for *c* and *d*, respectively.

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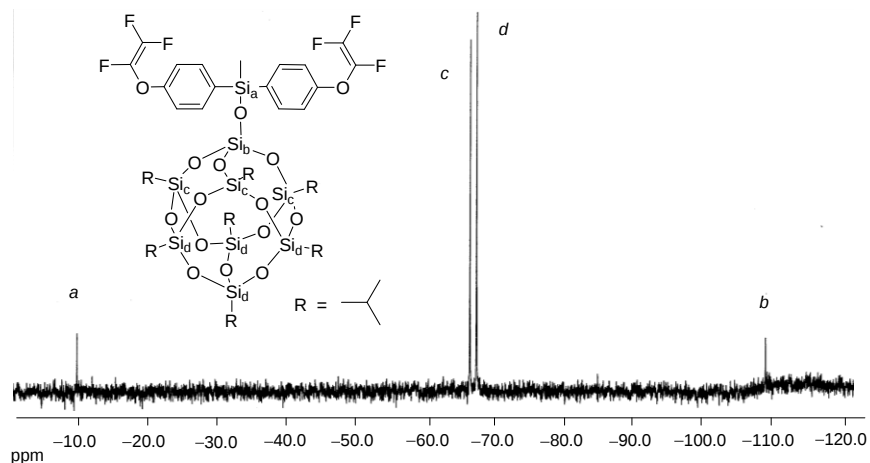


Figure 8. ^{29}Si NMR (60 MHz, inverse gate proton decoupled) of POSS TFVE monomer **7** in CDCl_3 .

Polymerization. Homopolymers (**poly4** and **poly5**) and copolymers (**4-co-6** and **4-co-8**) were prepared from the respective monomers by bulk polymerization at 190 °C producing POSS PFCB aryl ether copolymers (Figure 9). Selected polymer properties are shown in Table 2. All copolymers prepared showed similar molecular weight distribution compared to the PFCB aryl ether homopolymer *via* the thermal step-growth cyclopolymerization.

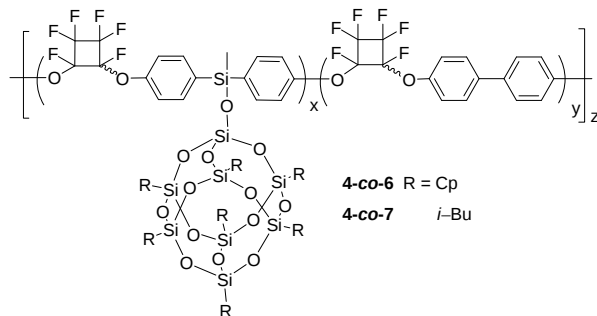


Figure 9. Pendant POSS PFCB random copolymers.

^{19}F NMR analysis indicated complete conversion of the POSS monomers

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that were incorporated into the PFCB copolymer (Figure 10). The TVFE peaks are typically observed using ^{19}F NMR by three sets of doublet of doublets at -119.5 ppm (*cis*-Ar-O-CF=CF₂), -126.4 ppm (*trans*-Ar-O-CF=CF₂), and -133.8 ppm (Ar-O-CF=CF₂). ^{19}F NMR of copolymer **4-co-7** with 20 wt% POSS showed the resulting multiplet -130.0 –(-135.5) ppm of the perfluorocyclobutyl aryl ether ring from the thermal cyclodimerization. Copolymer **4-co-6** functionalized with cyclopentyl groups showed the highest polydispersity, likely due to the insolubility of higher molecular weight polymers.

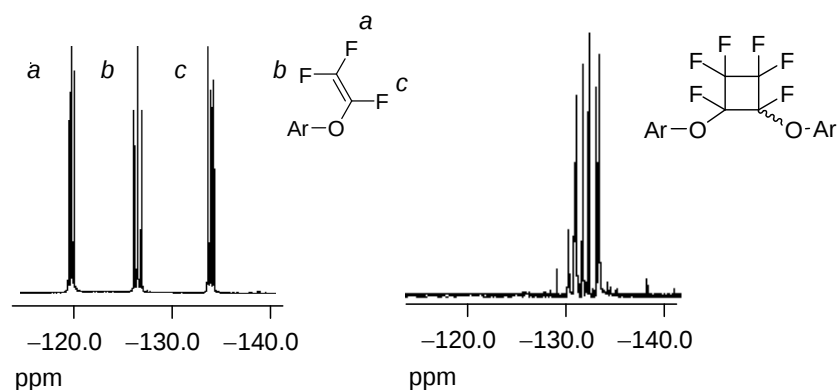


Figure 10. ^{19}F NMR (283 MHz) in CDCl_3 showing the conversion of POSS TFVE monomer 7 (left) incorporated into the random copolymer **4-co-7** (right).

Differential scanning calorimetry (DSC) indicated a plasticizing effect shown by the decrease in the glass transition temperature (T_g) with POSS copolymers. The decrease was most noticeable for copolymers with *iso*-butyl groups ($R = i\text{-Bu}$) and further increased with higher POSS loadings up to 20 wt%, similar to the chain terminated PFCB polymers. The observed decrease may be the result of POSS incompatibility with the semi-fluorinated PFCB polymer matrix or may be due to the flexibility of the POSS isobutyl groups. POSS PFCB aryl ether homopolymers were also prepared by thermal polymerization with monomers **6** and **7**, producing **poly6** and **poly7**; the average chain segment length is five POSS molecules ($n = 5$) as determined by GPC analysis. These POSS prepolymers were used to produce block copolymers (**4-b-7**) via thermal polymerization with monomer **4**. Compared to the POSS PFCB copolymers, the block polymers showed an increase in T_g demonstrating that the POSS block segments hinder chain mobility. Furthermore, the block copolymers

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4-b-7 showed an increase in the thermal decomposition temperature observed from TGA compared with the two POSS PFCB copolymers **4-co-6** and **4-co-7**. Introducing block segments into the copolymer showed a 50 °C increase in thermal decomposition temperature in air compared with nitrogen in excess of 500 °C.

Table 2. Selected Properties of Pendant POSS PFCB Copolymers

polymer	wt% POSS	$M_n \times 10^{-3}$ GPC ^a	M_w/M_n	T_g (°C) ^b	T_d (°C) N ₂ (air) ^c
poly4	0	13.3	2.2	140	450 (446)
4-co-6	20	21.5	5.2	134	447 (439)
poly6	100	6.6	3.5	131	--
4-co-7	10	24.9	1.4	133	452 (442)
4-co-7	20	20.5	3.2	128	440 (438)
poly7	100	6.3	2.5	138	--
4-b-7	10 ^d	21.9	3.4	149	452 (506)
4-b-7	20 ^d	19.5	4.5	142	462 (501)
poly5	0	8.0	2.0	100	466 (457)
5-co-7	15	13.2	4.2	89	--

^a GPC in CHCl₃ using polystyrene as standard. ^b DSC (10 °C/min) in nitrogen determined by second re-heating cycle. ^c TGA onset at 10 °C/min.

^d Value indicates wt% of **poly4** or **poly5** used as a block unit.

Film Preparation and Surface Analysis. Copolymers with up to 20 wt% *iso*-butyl functionalized POSS produced solution processable, optically transparent, semi-flexible films. However, POSS loadings greater than 20 wt% produced polymers that were difficult to solution process producing gelled solids. Copolymers and block copolymers were solution processed (in THF) to prepare spin cast films (SCF) or drop cast films (DCF). TEM and EDX analysis revealed nanometer POSS clusters with varying sizes ranging from 5–20 nm.

The hydrophobicity of the copolymer films functionalized with *iso*-butyl POSS were tested using contact angle analysis (Table 3 and Figure 11). Compared with the homopolymer **poly4**, copolymer **4-co-7** showed an increase in water contact angle with increasing POSS content. The highest increase in water repellency was 16% for 20 wt% POSS copolymer **4-co-7** with an average contact angle of 104.7° compared with homopolymer **poly4** that averaged 91.3°.

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Furthermore, block copolymer **4-b-7** also showed a similar increase in water repellency compared with that of homopolymer **poly4**. The degree of surface roughness correlated with the increased water contact angles, as indicated by 3D white light optical profilometry,. Profilometry analysis also reveals significant surface roughening of the POSS copolymer **4-co-7** compared with homopolymer **poly4** with an average surface roughness (r.m.s.) of 4.20 nm and 0.36 nm, respectively. In all cases, composites prepared by the drop cast film (DCF) method showed a 1.3 nm higher average surface roughness compared with the smoother spin cast films (SCF). More importantly, incorporation of the POSS nanofillers increases the surface roughness up to 12–19 times compared to that of the homopolymer films. Block copolymers **4-b-7** that were prepared by spin casting showed the highest surface roughness. As a further comparison, 20 wt% of fully-condensed *iso*-butyl₈T₈ POSS (Hybrid Plastics) was solvent blended into **poly4** and spin cast as a film. The resulting film's water contact angle was 15% lower than compared with PFCB homopolymer **poly4**. The surface roughness was not obtained because the blend produces a white opaque, heterogeneous film and cannot be measured by optical profilometry. However, upon visual inspection, a porous substrate with irreproducible film morphologies was observed suggesting incompatibility of *iso*-butyl POSS in the semi-fluorinated PFCB polymer matrix results in decreased water repellency.

Because the POSS PFCB polymers are highly solution processable in common organic solvents (e.g., THF), contact test fluids such as hexadecane and iodomethane failed to produce any measurable repellency and thus completely wetted the surface.

Table 3. Water Contact Angles of POSS PFCB Polymer Films

polymer	SCF	SCF	DCF	DCF
	CA (°)	r.m.s. (nm)	CA (°)	r.m.s. (nm)

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poly4	91.3	0.36	92.0	0.38
4-co-7	95.3	0.44	98.7	0.46
4-co-7	104.7	4.20	98.3	5.62
4-b-7	96.0	5.67	100.0	6.88
blend	78.8	--	--	--

The existence of nanoroughness has been shown to theoretically and experimentally contribute analogous hydrophobic behaviour similar to that caused by the texture of the lotus leaf.^{24,25} However, the ‘lotus effect’ is due to nano- and micro-structuring, which produces a large change in hydrophobicity due to macroscopic interaction between the water and surface. On the other hand, the observation of nanostructuring has a subtle increase in water repellency due to surface molecular perturbation of the water droplet. The subtle, yet enhanced hydrophobicity reported for pendant POSS PFCB copolymers is consistent with this observation by the presence of surface roughening due to nanometer-sized surface migration of hydrophobic alkyl functionalized POSS molecules. Continued work includes the preparation of fluorinated POSS functionalized TFVE monomers employing the aforementioned synthetic methodology. This would introduce the lower surface energy fluorinated POSS cages to enhance hydro- and oleo-phobicity.

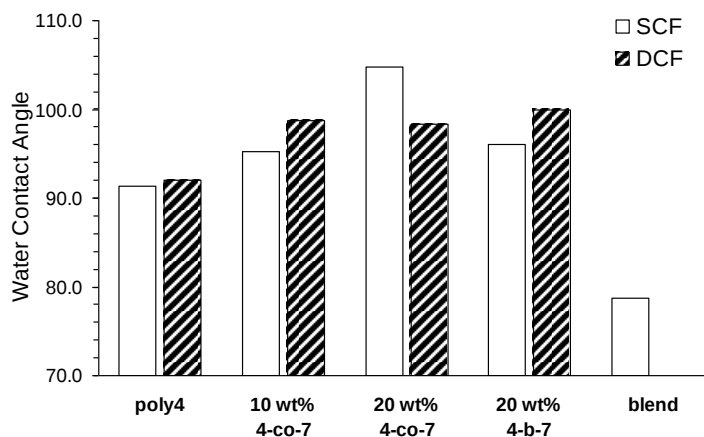


Figure 11. Water contact angles of spin cast films (SCF) and drop cast films (DCF) of various film surfaces.

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Conclusions

POSS has been successfully used as a low surface energy nanofiller for the preparation of hydro- and oleo-phobic PFCB polymer blends, copolymers, and block copolymers. The fluorinated POSS PFCB polymer blends showed a significant improvement in both water and hexadecane repellency due to surface roughening as well as the increase in fluorine content. Within the family of copolymers, POSS chain terminated and pendant POSS copolymers produced solution processable films. These copolymer and block copolymer films exhibit modest increase in hydrophobicity due to POSS that produced nanoroughening. The ability to easily process these POSS functionalized fluoropolymers makes them particularly attractive for hydrophobic material applications including fibers, coatings, and bulk components. Utilizing the ability to artificially fabricate low surface energy, nanosized surface features combined with microstructuring could afford a potentially new class of materials possessing liquid or gas discrimination.

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