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Hydrophobic Nanoroughened Surfaces from Processable POSS PFCB Polymer Composites

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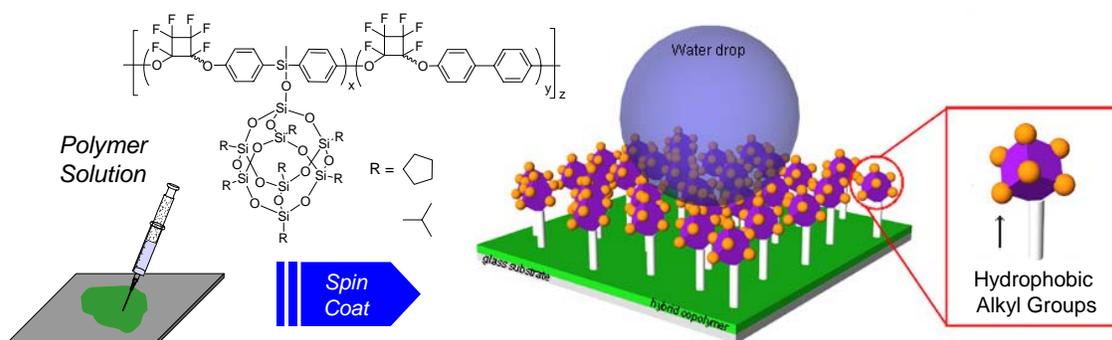
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The first preparation of processable, semi-fluorinated PFCB aryl ether polymers possessing covalently bound pendant POSS cages is reported. These copolymers exhibit increased hydrophobicity attributed to the surface migration of the nanometer-sized POSS aggregates, producing nanoroughness that mimics surface features of the lotus leaf.

Keywords: PFCB Polymers, Polyhedral oligomeric silsesquioxanes, Hydrophobicity, Nanoroughness

TOC Graphic



There remains great interest in the fabrication of low surface energy materials that mimic biological systems possessing high degrees of ultrahydrophobicity.¹ In particular, many plant species such as the lotus leaf exhibit a peculiar self-cleaning phenomenon resulting from micron-sized nodes decorated on the surface, which induce water beading. These water beads are naturally repelled from the surface, removing any foreign debris with them.^{2,3} There are many noteworthy examples of coatings that successfully produce artificial ultrahydrophobic lotus leaf-like surfaces; examples include self-assembly⁴⁻⁶ and chemical deposition^{7,8} of low surface energy molecules, lithographic patterning of micron-sized ordered arrays,^{9,10} and surface etching.^{11,12} The caveat of the aforementioned examples is they produce materials that either require aggressive post chemical and/or thermal surface treatments, use of expensive starting materials, or necessitate the need for limitedly accessible lithography methods. As such, there still exists a need to efficiently produce hydrophobic materials amenable for large scale production.

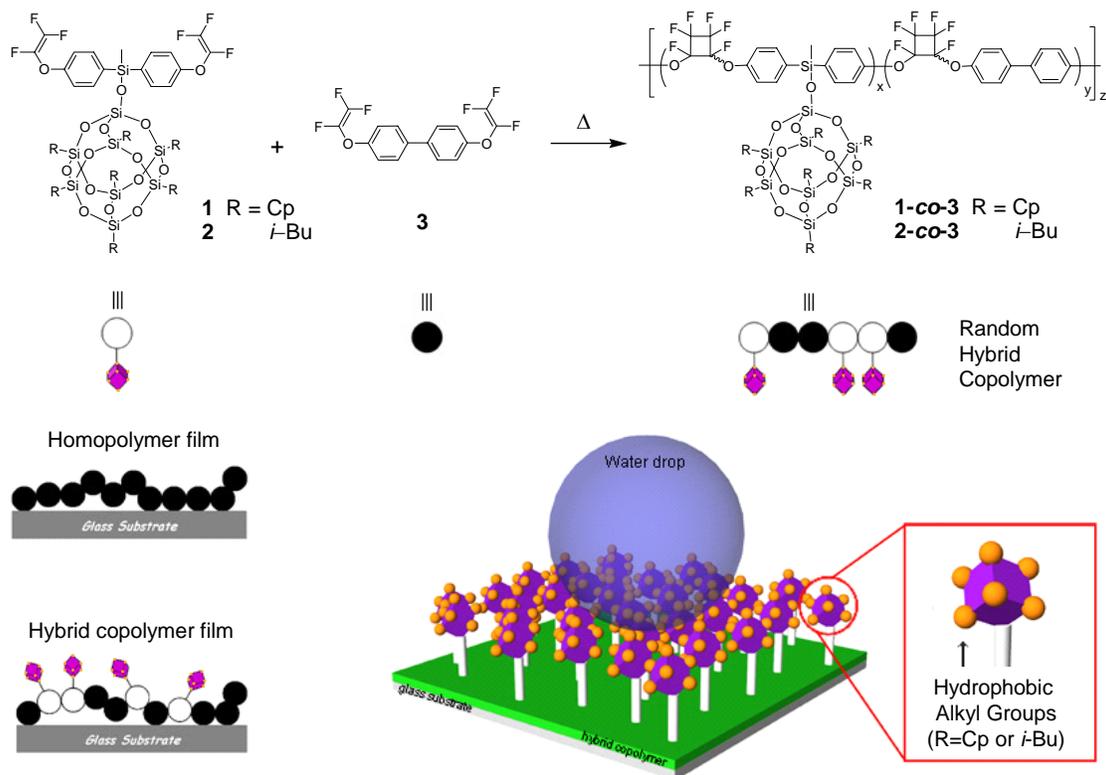
Fluoropolymers continue to be of global significance for a broad range of advanced material applications.¹³ They are chemically inert, thermally robust, and possess low surface energies. Because they are intrinsically highly crystalline, they present costly processing challenges. On the other hand, perfluorocyclobutyl (PFCB) aryl ether polymers are an emerging class of next-generation processable, amorphous semi-fluorinated polymers.^{14,15} PFCB aryl ether polymer systems possess tunable refractive indices, controllable glass transition temperatures, and are thermally robust. As a consequence, they are of particular interest in a multitude of material applications including high performance optics,¹⁶

polymer light-emitting diodes (PLEDs),¹⁷⁻¹⁹ electro-optics,^{20,21} atomic oxygen resistant coatings,²² and proton exchange membranes (PEMs) for fuel cells.²³

Polyhedral oligomeric silsesquioxanes (POSS) are thermally robust, discreetly nano-sized building blocks for the development of high performance materials in aerospace as well as commercial markets.^{24,25} Numerous examples show that POSS can be either blended or covalently linked into a matrix polymer.²⁶ These materials produce hybrid “ceramic-like” composites improving bulk properties including glass transition temperature, mechanical strength, thermal and chemical resistance, and ease of processing.

In this work, we show the first example of processable, semi-fluorinated PFCB aryl ether polymers covalently bound to pendant POSS cages (Scheme 1). The composites are easily prepared in nearly quantitative recovery and demonstrate increased hydrophobicity comparable to that of commercial Teflon[®]. The hydrophobicity is attributed to the surface migration of the nanometer-sized POSS aggregates, producing nanoroughness that mimicks surface features of the lotus leaf.

Scheme 1. Preparation of POSS PFCB hybrid copolymers (1-co-3 and 2-co-3) via thermal polymerization of POSS monomers (1 and 2) with monomer 3. Hydrophobic surfaces are produced from the hybrid copolymers films as a result of POSS surface migration producing nanoroughness in addition to their hydrophobic alkyl content.



POSS functionalized monomers **1** (R = cyclopentyl, Cp) and **2** (R = *iso*-butyl, *i*-Bu) were prepared by an efficient condensation of commercial POSS alcohols with 4,4'-bis(4-trifluorovinyl)oxy)biphenyl(methyl)chlorosilane previously reported by Smith *et al.* using a metal-halogen exchange methodology.^{27,28} The monomers were isolated with a high degree of purity confirmed by NMR (¹H, ¹⁹F, ¹³C, and ²⁹Si), ATR-FTIR, GPC, and elemental combustion analysis (see Supporting Information). Homopolymer (**poly3**) and copolymers (**1-co-3** and **2-co-3**) were prepared from the respective monomers by bulk polymerization at 190 °C producing POSS PFCB aryl ether copolymers. Selected polymer properties are shown in Table 1.

Table 1. Selected Properties of Polymers.

poly	wt% (mol%) POSS ^a	$M_n \times 10^{-3}$ GPC ^b	M_w/M_n	T_g (°C) ^c	T_d (°C) ^d	
1-co-3	20 (7.1)	21.5	5.2	134	447 (439)	
2-co-3	10 (3.3)	24.9	1.4	133	452 (442)	
2-co-3	20 (6.6)	20.5	3.2	128	440 (438)	
poly1	100	6.6	3.5	131	--	
poly2	100	6.3	2.5	138	--	
2-b-3	10 (3.4)	21.9	3.4	149	450 (506)	<i>a</i>
2-b-3	20 (6.7)	19.5	4.5	142	462 (501)	<i>p</i>
poly3	0	25.0	2.1	140	450 (446)	<i>e</i> <i>r</i>

cent of POSS monomer **1** or **2**. ^b GPC in CHCl₃ using polystyrene as standard. ^c DSC (10 °C min⁻¹) in nitrogen determined by second re-heating cycle. ^d TGA onset (10 °C min⁻¹) of chain extended polymers.

All copolymers prepared showed similar molecular weight distribution compared to the PFCB aryl ether homopolymer *via* the step-growth polymerization. Polymer conversions were monitored using ¹⁹F NMR and GPC analysis (Figure 1). ¹⁹F NMR of copolymer **2-co-3** with 20 wt% POSS showed the resulting multiplet -130.0–(-135.5) ppm of the PFCB aryl ether ring from the thermal cyclodimerization with no evidence of residual trifluorovinyl aryl ether peaks of monomer **2**. These are typically represented by an AMX pattern resulting in three 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). Copolymer **1-co-3** functionalized with cyclopentyl groups showed the highest polydispersity, likely due to the insolubility of the polymer. In addition, no POSS PFCB aryl ether macrocycles were observed *via* the intramolecular cyclodimerization of monomers (**1** or **2**) from GPC analysis.

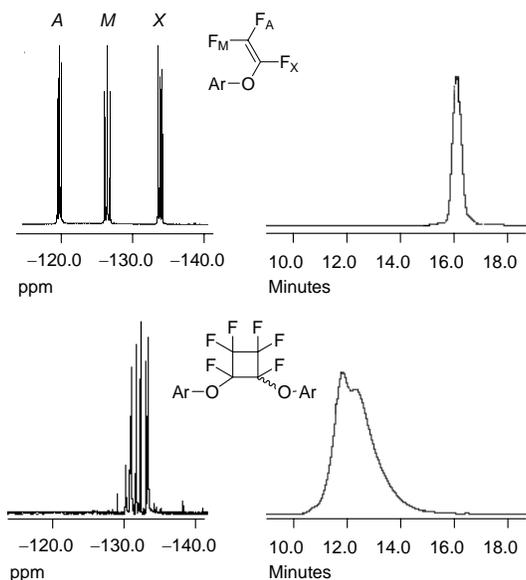


Figure 1. ^{19}F NMR spectrum and GPC trace comparison showing the conversion of POSS monomer **2** (top) to 20 wt% POSS PFCB copolymer **2-co-3** (bottom).

Differential scanning calorimetry (DSC) indicated a plasticizing effect observed by the lowering of glass transition temperature (T_g) upon incorporation of POSS. The decrease was most notable for copolymers with *iso*-butyl groups ($R = i\text{-Bu}$) and further increased with higher POSS loadings. POSS incorporation typically increases the T_g of polymer systems retarding chain mobility. However, the observed decrease could be a result of POSS incompatibility with the fluoropolymer matrix essentially acting as molecular ball bearings. POSS PFCB aryl ether homopolymers were also prepared by thermal polymerization with monomers **1** and **2**, producing **poly1** and **poly2** with an average of five POSS molecules in each chain segment ($n = 5$). These were used to prepare block copolymers (**2-b-3**) by thermal polymerization with monomer **3**. The block polymers showed an increase in T_g demonstrating the POSS block segments hinder chain mobility. Furthermore, the block copolymers **2-b-3** showed an increase in the thermal decomposition temperature observed from thermal gravimetric analysis (TGA) compared with copolymers **1-co-3** and **2-co-3**. Interestingly, the block copolymers showed a 50 °C increase in decomposition temperature in air compared with nitrogen in excess of 500 °C.

Copolymers with up to 20 wt% *iso*-butyl functionalized POSS produced optically transparent, semi-flexible films. POSS loadings greater than 20 wt% produced polymers that were difficult to solution

process. All the examples shown here can be solution processed either as spin cast films (SCF) or drop cast films (DCF) using common organics solvents such as THF or cyclopentanone.

The films were studied using electron microscopy. Scanning electron microscopy (SEM) showed no evidence of micron-sized POSS aggregation. However, transmission electron microscopy (TEM) analysis (Figure 2) revealed nanometer-sized POSS clusters with varying sizes ranging 5–20 nm as confirmed by energy dispersive X-ray (EDX) analysis. The observation also shows the discretely-sized POSS cage aggregates are well dispersed within the PFCB aryl ether matrix. These nanometer POSS aggregates attribute to the surface roughening of the film surface (*vide infra*).

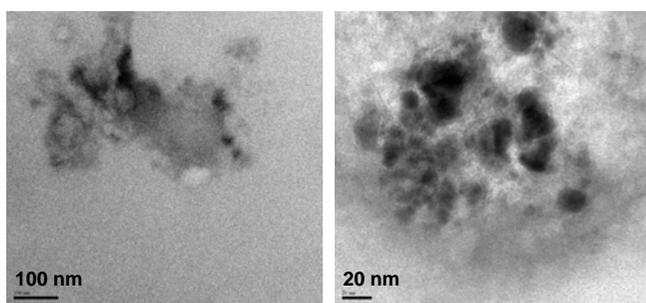


Figure 2. Images of 20 wt% POSS PFCB copolymer composite **2-co-3** at different magnifications exposing nanometer sized POSS aggregates, shown as dark shapes in TEM micrographs.

The hydrophobicity of the copolymer films functionalized with *iso*-butyl POSS were tested using water drop shape analysis and measured for the corresponding water contact angle (Figure 3). The relationship of contact angle and surface energy is governed by Young's equation which relates interfacial tensions among the surface to the liquid and gas phases of water.²⁹ Furthermore, it is well known that surface roughness imparts increased hydrophobicity of a material as demonstrated by Cassie and Wenzel.^{30,31} Compared with the homopolymer **poly3**, copolymer **2-co-3** showed an increase in water contact angle with increasing POSS content. The highest increase in water repellency was 16% for 20 wt% POSS copolymer **2-co-3** with an average contact angle of 104.7° compared with homopolymer **poly3** that averaged 91.3°. Furthermore, block copolymer **2-b-3** also showed a similar increase in water repellency compared with that of copolymer **2-co-3**. It was shown using 3D white light optical profilometry, the degree of surface roughness correlates with increased water contact

angles. Figure 4 shows the visual comparison of homopolymer **poly3** with that of copolymer composite **2-co-3**. Profilometry analysis reveals significant surface roughening of the POSS copolymer **2-co-3** compared with homopolymer **poly3** with an average surface roughness (r.m.s.) of 4.20 nm and 0.36 nm, respectively. The average size of the surface protrusions were measured as the peak-to-valley ratio and were 38 nm for **2-co-3** and 17 nm for **poly3**. In all cases, composites prepared by the drop cast film (DCF) method showed a slightly higher average surface roughness as high as 1.3 nm 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 (**2-b-3**) that were prepared by spin casting showed the highest surface roughness. As a further comparison, 20 wt% of fully-condensed *iso*-butyl₈T₈ POSS was solvent blended into **poly3** and spin cast as a film. The resulting film's water contact angle was 15% lower than compared with PFCB homopolymer **poly3**. 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 aryl ether matrix results in decreased water repellency.

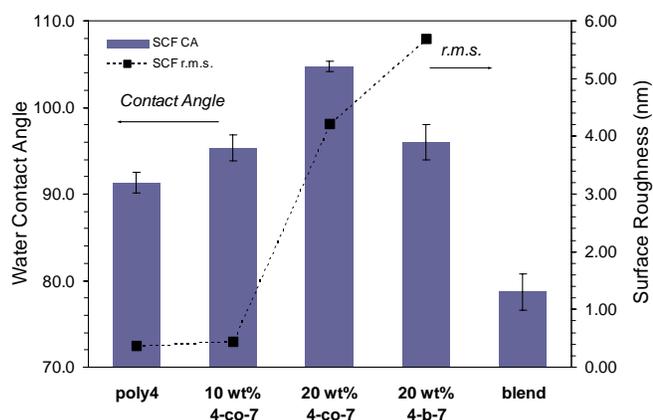


Figure 3. Water contact angle and surface roughness (r.m.s) measurements of polymers.

It has recently been shown that POSS covalently bound into polyurethanes improves dewetting, due to the increase in the nanometer surface roughness as well as hydrophobic alkyl groups on the POSS

structures.³² Furthermore, the existence of nanoroughness has been shown to theoretically and experimentally contribute analogous hydrophobic behaviour similar to that caused by the micron-relief texture of the lotus leaf.^{33–35} However, as it is pointed out, the impact of the coined ‘lotus effect’ is due to microstructuring and produces a large change in hydrophobicity due to macroscopic interaction of the water and surface. Depending on the lotus leaf species, water contact angles have been experimentally measured and vary to as low as 28° and as high as 160°.³ On the other hand, the observation of nanostructuring has a subtle increase in water repellency due to surface molecular perturbation of the water droplet.

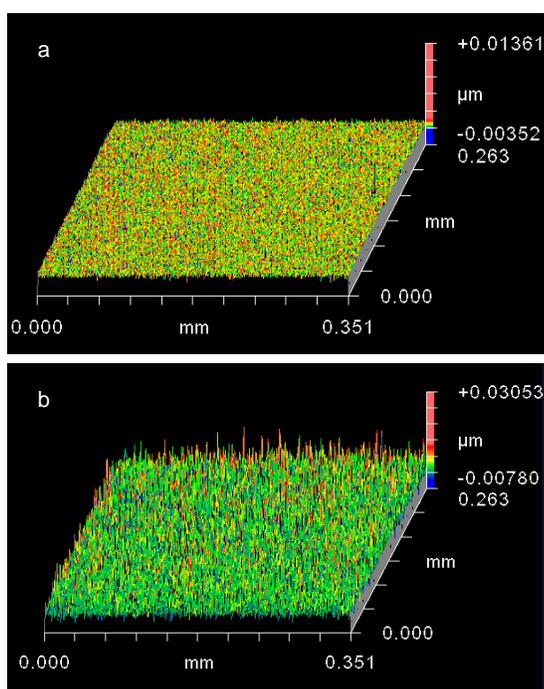


Figure 4. 3D surface projections of **poly3** (a) and copolymer **2-co-3** (b) obtained from white light optical profilometry.

We show that our results are consistent with this observation in that the surface roughening due to the presence of nanometer-sized surface migration of POSS molecules attributes to increasing the hydrophobicity. The POSS cages essentially serve as a vehicle for introducing aggregation in addition to incorporating hydrophobic alkyl character from the silsesquioxane cubes. Nanostructural ordering of POSS has been shown to produce controlled growth of lamellae with a defined lateral length.³⁶ The hydrophobicity can be further influenced by the substitution of the alkyl substituents on the POSS cages

with fluorinated alkyl chains. Such an intuitive design has been demonstrated with 3,3,3-trifluoropropyl groups on POSS encapped poly(methylmethacrylates)³⁷ and is the subject of our ongoing investigations.

In summary, we have prepared solution processable POSS pendant PFCB aryl ether copolymers and block copolymers that produce nanometer-sized surface roughness when cast as films. Our findings show POSS incorporation into PFCB aryl ether polymers has improved the hydrophobicity and is now comparable to various grades of commercial fluoropolymers including DuPont's Teflon[®] and Teflon[®]-AF with water contact angles of 100° and 105°, respectively.^{38,39} More so, we find the ability to easily process these POSS functionalized fluoropolymers makes them particularly attractive for a broad range of manufacturing techniques for hydrophobic material applications including fibers, coatings, and bulk components. The forethought of utilizing our ability to artificially fabricate nanostructures combined with microstructuring could afford a potentially new class of materials possessing unique liquid discriminating surface properties not exclusive to just water, but also industrial solvents, hazardous biological waste, microorganisms, and also for antifouling.

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Supporting Information Available: Experimental details and characterization of all new compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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