**Functionalized Fluoroalkyl Polyhedral Oligomeric Silsesquioxane (F-POSS)**

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A variety of functionalized Fluorinated Polyhedral Oligomeric SilSesquioxanes (F-POSS) were synthesized and characterized. The chemical structures were confirmed using multinuclear NMR spectroscopy ($^1$H, $^{13}$C, $^{19}$F, and $^{29}$Si), FT-IR, and combustion analysis. Dynamic contact angle measurements of these compounds were taken with water and hexadecane. Copolymers containing F-POSS were synthesized from monomer functionalized F-POSS. These novel structures can be used as initial building blocks for the development of low surface energy materials.
FUNCTIONALIZED FLUORINATED POLYHEDRAL
OLIGOMERIC SILSESQUIOXANE (F-POSS)

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OLIGOMICERIC SİLSESQUIOXANE (F-POSS)

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Discussion

Introduction

Recently, Fluorinated Polyhedra1 Oligoorganic Silsesquioxanes (F-POSS) contain Si-C-O core [SiOCH3] with long-chain fluorinated alkyl group periphery, were developed for low surface energy applications.1 F-POSS was found to possess the lowest surface energy values known (γsv = 9.3 mN/m) for a crystalline solid.2 The incorporation of F-POSS in polymers has led to the development of both superhydrophobic and superoleophilic surfaces.34 These composites were based on the physical blending of F-POSS into a polymer matrix. Currently, there are no methods to functionalize long-chain F-POSS, thereby limiting its potential in other low-surface-energy applications due to poor mechanical robustness and abrasion resistance. Herein, we report the synthesis and characterization of functionalized F-POSS. The functionalized compounds can both be physically blended and covalently bound to polymer matrices. These materials possess potential applications in superhydrophobic/superoleophilic coatings and low-surface-energy materials.

Experimental

Materials All dichlorosilanes were purchased from Gelest. All reactions were performed under a nitrogen atmosphere unless otherwise noted. Instrumentation 1H, 2H, 2F, and 29Si NMR spectra were obtained on a Bruker 500-MHz or 400-MHz spectrometer. A heteronuclear inverse gated decoupling pulse sequence (NONO) with a 12 sec delay was used to acquire 29Si NMR spectra. Contact angle measurements were taken on an optical contact angle system OCA (Dataphysics).

General synthesis of functionalized F-POSS. This synthesis will be discussed in detail in future publication. Synthesis of compound (3). 1 (2.90, 0.72 mmol) was added to hexafluorobenzene. To this diphenyldichlorosilane (0.182 g, 0.72 mmol) was added and this was then stirred for 15 min. Then triethylamine (0.19 mL, 1.44 mmol) was added slowly and the solution was stirred for an additional 12 hr. This product is subsequently precipitated from an ethyl acetate/hexafluorobenzene solvent mixture to yield compound 3. Yield 55%. 1H NMR (CDCl3); δ 7.69 (mm, 4H), 7.76 (mm, 6H), 7.42 (mm, 6H), 7.33 (mm, 6H), 1.25 (mm, 6H), 1.10 (mm, 6H), 0.89 (mm, 6H). 13C NMR (CDCl3); δ 133.4, 133.0, 127.07, 126.7, 123-105 (mm, CF3, CF2), 24.4 (mm, C6H5), 2.0, 1.4, 0.9. 29Si NMR (CDCl3); δ -54.5, -65.8, -68.0, -68.2 (1:2:2:4). 2F NMR (CDCl3); δ -82.3 (3F), -116.9 (2F), -123.7 (2F), -124.3 (2F), -127.3 (2F). IR (25 °C, KBr, cm-1) 2987, 2943, 2927, 2873, 1419, 1213, 1153, 976, 1041, 1037, 1106, 1063, m.p. = 120.2 °C. Anal. Calcd for C30H10F5O4Si: 26.30 (26.22), H: 1.01 (0.91), F: 61.64 (61.28).

General Polymerization of F-POSS monomers. Methyl methacrylate (MMA), 1,5 g, 15.2 mmol), 7 (0.8 g, 0.002 mmol), and azobisisobutyronitrile (AIBN, 50 mg, 0.3 mmol) were dissolved in a fluorinated solvent:THF mixture (4:1). This solution was purged with N2 for 25 min to remove any O2 and was immediately submerged in a 65 °C oil bath for 3 hrs. The resulting solution was precipitated in hexanes, filtered, and dried to yield a white powder (0.88 g, 58%).

Contact angle measurements. F-POSS compounds (10 mg/mL) were dissolved in a fluorinated solvent and spun cast at a rate of 900 rpm for 30 seconds onto oxygen-plasma treated 1-inch silicon wafers.

Results and Discussion

Synthesis of Functionalized F-POSS. The incompletely-condensed silsesquioxane 1 can be readily reacted with a variety of dichlorosilanes (Scheme 1). For example, the reaction of 1 with diphenyldichlorosilane in the presence of triethylamine produced compound 3 (yield 55%). The side product isolated during the reaction was closed-cage F-POSS. Multinuclear NMR (1H, 29Si, 2F) and elemental analysis were used to confirm the structure of compound 3. The 29Si peaks were observed at resonance of -45.2, -65.8, -68.0, and -68.2, with a ratio of 1:2:2:4 (Figure 1). The resonance at -45.2 ppm was attributed to the diphenyl functionalized Si.

Figure 1. 29Si NMR spectra of a) 1 b) 2 and c) 3.

Synthesis of copolymers. Copolymerizations of methyl methacrylate (MMA) modified F-POSS (6) and MMA via thermally-initiated AIBN-produced PMMA-co-F-POSS copolymers. Currently, molecular weights of these polymers are being obtained to determine the impact of F-POSS in the polymerization of these copolymers. The wetting behavior of these polymers is being investigated as well.

Conclusions

Functionalized F-POSS were synthesized in a simple one-step reaction from a variety of dichlorosilanes. Dynamic contact angle measurements of these structures were taken to determine the influence of functionalized group on surface energy. Monomer functionalized F-POSS compounds were found to copolymerize readily. These new structures can be used in the development of new superhydrophobic and oleophobic materials.
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References


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