REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. REPORT DATE *(DD-MM-YYYY)*
29-11-2011

2. REPORT TYPE
Conference Paper

3. DATES COVERED *(From - To)*

4. TITLE AND SUBTITLE

Functionalized Fluoroalkyl Polyhedral Oligomeric Silsesquioxane (F-POSS)

5a. CONTRACT NUMBER

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)
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5d. PROJECT NUMBER

5f. WORK UNIT NUMBER
23030521

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

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8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)

Air Force Research Laboratory (AFMC)
AFRL/RZS
5 Pollux Drive
Edwards AFB CA 93524-7048

10. SPONSOR/MONITOR'S ACRONYM(S)

11. SPONSOR/MONITOR'S NUMBER(S)
AFRL-RZ-ED-TP-2011-558

12. DISTRIBUTION / AVAILABILITY STATEMENT

Approved for public release; distribution unlimited (PA #111052).

13. SUPPLEMENTARY NOTES
For presentation at the American Chemical Society National Conference, San Diego, CA 25-29 Mar 2012.

14. ABSTRACT

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.

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			**17. LIMITATION OF ABSTRACT**	**18. NUMBER OF PAGES**	**19a. NAME OF RESPONSIBLE PERSON**
					Dr. Joseph M. Mabry
a. REPORT	**b. ABSTRACT**	**c. THIS PAGE**	SAR	4	**19b. TELEPHONE NUMBER** *(include area code)*
Unclassified	**Unclassified**	**Unclassified**			N/A

Standard Form 298 (Rev. 8-98)
Prescribed by ANSI Std. 239.18

FUNCTIONALIZED FLUORINATED POLYHEDRAL OLIGOMERIC SILSESQUIOXANE (F-POSS)

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FUNCTIONALIZED FLUOROALKYL POLYHEDRAL OLIGOMERIC SILSESQUIOXANE (F-POSS)

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Introduction

Recently, Fluorinated Polyhedral Oligomeric SilSesquioxanes (F-POSS), contain a Si-O core [$SiO_{1.5}$] 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 (γ_{sv} = 9.3 mN/m) for a crystalline solids.[2] The incorporation of F-POSS in polymers has led to the development of both superhydrophobic and superoleophobic surfaces.[3,4] 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/superoleophobic 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, ^{13}C, ^{19}F, and ^{29}Si NMR spectra were obtained on a Bruker 300-MHz or 400-MHz spectrometer. A heteronuclear inverse gated decoupling pulse sequence (NONOE) with a 12 sec delay was used to acquire ^{29}Si NMR spectra. Contact angle measurements were taken on an optical contact angle system OCA (Dataphysic).

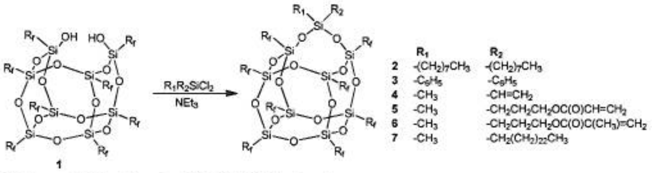
General synthesis of functionalized F-POSS. This synthesis will be discussed in detail in future publication. *Synthesis of compound* (**3**). **1** (2.90, 0.72 mmol) is dissolved in hexafluorobenzene. To this diphenyldichlorosilane (0.182 g, 0.72 mmol) is added and this was subsequently stirred for 15 min. Then triethylamine (0.19 mL, 1.44 mmol) is 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 ($CDCl_3$:AK-225G: ppm) δ 7.69 (mm, 4H), 7.46 (mm, 6H), 2.12 (br m, 16H), 1.06 (mm, 8H), 0.99 (mm, 8H). ^{13}C NMR (C_6F_6, ppm) δ 133.4, 133.0, 127.07, 126.7, 123-105 (m, CF_2, CF_3), 24.4 (m), 2.0, 1.4, 0.9. ^{29}Si NMR (C_6F_6, ppm) δ -45.0, -65.8, -68.0, -68.2 (1:2:2:4). ^{19}F NMR ($CDCl_3$:C_6F_6, ppm) δ -82.3 (3F), -116.9 (2F), -122.8 (6F), -123.7 (2F), -124.3 (2F), -127.3 (2F). IR (25 °C, KBr, cm^{-1}) 2987, 2943, 1729, 1149, 1213, 1153, 976, 904, 814, 706, 663. m.p. = 120.2 -122.8 °C. Anal. Calcd. for $C_{92}H_{42}F_{136}O_{13}Si_9$ (found): C, 26.36 (26.22), H, 1.01 (0.91), F, 61.64 (61.38).

General Polymerization of F-POSS monomers. Methyl methacrylate (MMA, 1.52 g, 15.2 mmol), **7** (0.80 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 N_2 for 25 min to remove any O_2 and was immediately submerged in a 65 °C oil bath for 36 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 main side product isolated during the reaction was closed-cage F-POSS. Multinuclear NMR (^1H, ^{29}Si, ^{19}F), FT-IR, and elemental analysis were used to confirm the structure of compound **3**. The ^{29}Si peaks were observed at resonances 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.



***Scheme 1.** Synthesis of F-POSS derivatives.*

Contact angle measurements of F-POSS monomers. The wetting properties of F-POSS make it one of the lowest surface energy materials known. To demonstrate that functionalized F-POSS structures retain their impressive wetting properties, advancing (θ_{adv}) and receding (θ_{rec}) contact angle measurements were taken with water and hexadecane. Compared to unfunctionalized F-POSS and open-caged **1**, these modified F-POSS structures possess similar wetting properties to their predecessors. For example, compound **3** possess a low hysteresis, allowing for low sliding angles for hydrocarbons such as hexadecane (Figure 2). Initial observations will be explored in further detail to elucidate the impact of functionality on the wetting-properties of F-POSS.

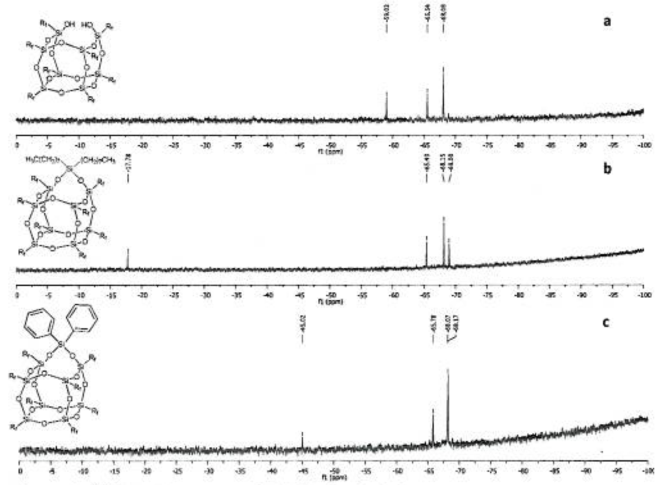


Figure 1. ^{29}Si NMR spectra of a) **1** b) **2** and c) **3**.

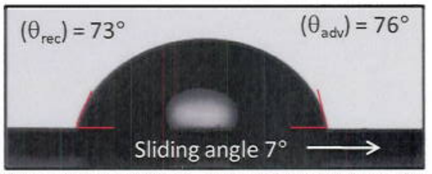


***Figure 2.** Sliding angle of a 10 uL drop of hexadecane rolling of Si wafer coated with compound 3.*

Synthesis of copolymers. Copolymerizations of methyl methylacrylate (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 monomers. The wetting behavior of these polymers is being investigated as well.

Conclusions

Functionalized F-POSS were synthesized in a simple one-stop 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 novel structures can be used in the development of new superhydrophobic and oleophobic materials.

Acknowledgements. The authors would like to thank the Air Force Office of Scientific Research the Air Force Research Laboratory Propulsion Directorate for financial support.

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