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To be super-resistant to wetting, surfaces generally require both nano- and micro-scale roughness, as well as low surface energy. Based on calculations, to have a smooth superoleophobic surface would require a surface energy lower than any known material. Increasing the length of the fluorinated chains may lead to molecules with even lower solid surface energies and therefore even better hydrophobic and oleophobic properties. We present the synthesis of the longest chain fluorinated POSS molecules reported: fluorododecylPOSS (FDD). The synthesis is performed *via* the base-catalyzed, one-step condensation of the corresponding trialkoxysilane.

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SYNTHESIS AND CHARACTERIZATION OF LONG-CHAIN FLUORINATED POLYHEDRAL OLIGOMERIC SILSESQUIOXANES (F-POSS)

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Abstract: To be super-resistant to wetting, surfaces generally require both nano- and micro-scale roughness, as well as low surface energy. Based on calculations, to have a smooth superoleophobic surface would require a surface energy lower than any known material. Increasing the length of the fluorinated chains may lead to molecules with even lower solid surface energies and therefore even better hydrophobic and oleophobic properties. We present the synthesis of the longest chain fluorinated POSS molecules reported: fluorododecylPOSS (FDD). The synthesis is performed *via* the base-catalyzed, one-step condensation of the corresponding trialkoxysilane.

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Introduction

Continuing the search for improved materials that are resistant to wetting by both water and oils is of considerable interest. Non-wetting materials find application as seals, fingerprint resistant touch screens, and anti-icing materials.[1] Superhydrophobicity and superoleophobicity, defined as having a contact angles of greater than 150° and low contact angle hysteresis,[2] are two very desirable properties. To be super-resistant to wetting, surfaces generally require both nano- and micro-scale roughness, as well as low surface energy. Based on calculations, to have a smooth superoleophobic surface would require a surface energy lower than any known material.[3]

Polyhedral Oligomeric SilSesquioxanes (POSS) cages consist of a silicon-oxygen core framework possessing alkyl functionality on the periphery. They are thermally robust and may exhibit low surface energies[4]. Previous reports illustrate the importance of long chain fluorinated hydrocarbons for superhydrophobic properties. Fluorodecyl POSS (FD), which is surrounded by eight 10-carbon alkyl groups with eight carbon atoms on each group being fully fluorinated, is found to have the lowest solid surface energy currently available.[4] Increasing the length of the fluorinated chains may lead to molecules with even lower solid surface energies and therefore even better hydrophobic and oleophobic properties.[4]

Herein, we present the synthesis of the longest chain fluorinated POSS molecules reported: fluorododecylPOSS (FDD). The molecular weight of the POSS cage is 4793.73 g/mol. The synthesis is performed *via* the base-catalyzed, one-step condensation of the corresponding trialkoxysilane.

Experimental

Materials. Fluorinated olefins have been purchased from SynQuest Labratories and Matrix Scientific and used without further purification. Ttriethylorthoformate and trichlorosilanes were obtained from Gelest. Ethanol, dichloropentafluoropropane, hexachloroplatinic acid hydrate, and potassium hydroxide were obtained from Aldrich and were used without further purification.

Instrumentation. ^1H, ^{19}F, and ^{29}Si NMR spectra were obtained on a Bruker 300-MHz spectrometer. IR spectra of KBr pellets were obtained using a Nicolet 710 FT-IR spectrometer. DSC measurements were taken using a TA Instruments DSC 2010 Differential Scanning Calorimeter. Contact Angle analyses were performed on a First Ten Angtroms 110 series system using a syringe metering pump.

Synthesis of 1H,1H,2H,2H-perfluorododecyl POSS (FDD). FluorododecylPOSS was produced by the base-catalyzed hydrolysis of fluorododecyltriethoxysilane. This silane was made via catalytic hydrosilylation using hexachloroplatinic acid hydrate in *iso*-propanol (Speier's catalyst). Running the reaction in a sealed system, where a slight pressure increase is created upon heating, also improved the yield of the desired hydrosilylation products.[5] Refluxing in triethylorthoformate was used to convert the trichlorosilane to the triethoxysilane.

Characterization. $(1H,1H,2H,2H\text{-perfluorododecyl})_8Si_8O_{12}$ (Fluorododecyl POSS). Mp 168.9 °C; ^{29}Si NMR ($(CD_3)_2CO$, 59.6 MHz): δ -66.69; ^{19}F NMR ($(CD_3)_2CO$, 282.4 MHz): δ -83.6 (24F), -118.6 (16F), -123.5 (80F), -124.5 (16F), -125.1 (16F), -128.2 (16F); Anal. Calcd for $C_{96}H_{32}F_{168}O_{12}Si_8$: C, 24.05; H, 0.67; F, 66.58. Found: C, 24.19; H, 0.54; F, 66.84.

Results and Discussion

The synthesis of FDD has stemmed from the need for lower surface energy solids, which yield higher contact angles with all liquids. Contact angle is related to the surface energy and roughness of a surface and the surface tension of the liquid.[4] Water has a surface tension (γ_{lv}) of 72.1 mN/m, which is much higher than organic liquids such as hexadecane (γ_{lv} =27.5 mN/m).[2, 3] The higher surface tension explains the larger contact angles for water than for hexadecane on the same surface. By measuring the contact angles of water and hexadecane on surfaces with varied POSS cages the importance of the side chain length is clearly visible (Figure 1). Although it may appear that the smooth surface water contact angle has reached a plateau in the top graph, when roughness is introduced the contact angles are still increasing with respect to side chain length.[1] The contact angles for the hexadecane, in the lower graph below, are rising consistently with the length of side chain.[6] This suggests that side chain lengths of 12 and 14 carbon atoms may result in compounds with greater hexadecane contact angles than FD, which would, therefore, be more oleophobic than currently available.

Also, nano-scale roughness is observed in FD but not in the fluorohexyl POSS indicating that increased chain length not only lowers surface energy but increases the nano-scale roughness.[4] This could be another factor in the increased contact angle and could be used as a variable in wetting properties.

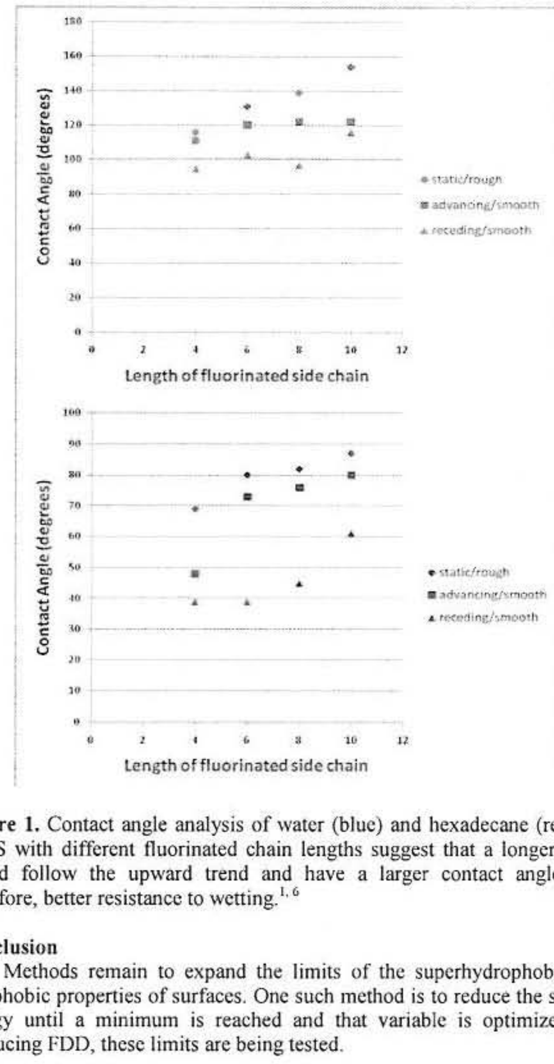

Figure 1. Contact angle analysis of water (blue) and hexadecane (red) for POSS with different fluorinated chain lengths suggest that a longer chain would follow the upward trend and have a larger contact angle and, therefore, better resistance to wetting.[1, 6]

Conclusion

Methods remain to expand the limits of the superhydrophobic and oleophobic properties of surfaces. One such method is to reduce the surface energy until a minimum is reached and that variable is optimized. By producing FDD, these limits are being tested.

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