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Influence of Peripheral Architecture on the Properties of Aryl Polyhedral Oligomeric Silsesquioxanes (POSS)

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Abstract

The peripheral architecture of Aryl Polyhedral Oligomeric Silsesquioxanes (POSS) plays a significant role in observed macroscopic properties including phase transitions, thermal stability, and solubility. A relationship between these properties and POSS packing efficiency is offered, providing evidence that peripheral interactions require consideration in resolving the observed phenomena. These interactions further assume a pivotal role in determining POSS phase behavior in host materials such as low molecular weight solvents and polymers. The findings reported herein will improve the efficacy of designing POSS molecules for the purposes of fabricating multifunctional polymer matrix composites and protective barrier coatings for organic materials.

Introduction

Polyhedral Oligomeric Silsesquioxanes (POSS) are nanostructured materials featuring an inorganic core and an organic periphery. The utility of POSS has been demonstrated in a breadth of applications including nanomedicine,¹ optoelectronics,² and polymer enhancement,³ to name a few. The foundation of the latter is the ability to tailor the POSS periphery to achieve optimal states in polymer hosts with respect to desired properties. Design parameters of the periphery include size, reactivity, symmetry, and electronic character, all of which influence not only interactions with a host but the properties of POSS in the monolithic, assembled state.

POSS molecules featuring a non-reactive periphery offer some advantages as drop-in additives for commercial thermoplastics through conventional compounding methods as well as thermosets without the necessity of considering stoichiometry, incomplete consumption of reactive groups, and embrittlement due to excessive cross-linking. The majority of inert POSS materials feature an aliphatic periphery demonstrating low melting points due to weak molecular interactions.⁴ This characteristic permits the thermodynamics of mixing to affect dispersion outcome. However, aliphatic moieties do not promote POSS solubility in high performance, aromatic polymers. State-of-the-art aryl POSS materials possess symmetric phenyl peripheral architectures that interact strongly with those of adjacent molecules, translating to the macroscale as crystalline powders having high binding energies. As a result, these powders demonstrate either no or exceedingly high solid-liquid transition temperatures thus compromising use of polymer melt blending techniques. Furthermore, they are also resistant to solvation. Due to these characteristics, effective dispersion of these compounds has proven difficult.

Recently, we reported a new class of POSS materials that are peripherally asymmetric to circumvent this challenge.⁵ These compounds have demonstrated enhanced solubility in low molecular weight solvents and high performance polymers without conciliating absolute peripheral aromaticity. An alternative approach is to increase the size of the aryl groups while maintaining peripheral symmetry with the expectation that molecular interactions will be similarly affected. The goal of this work is to develop an understanding of the effects of peripheral architecture on the macroscopic properties of aryl functionalized POSS, specifically focusing on thermal properties such as phase transitions and thermal stability in relation to POSS packing efficiency in the assembled state.

Experimental

Materials. $\text{Ph}_7\text{Si}_7\text{O}_9(\text{OH})_3$ was obtained from Hybrid Plastics, while other silicon-containing organic compounds were purchased from Gelest. All other chemicals were purchased from Aldrich and were used without further purification unless otherwise noted. Reactions were performed under an atmosphere of dry nitrogen. Flasks were oven-dried and allowed to cool under nitrogen prior to use.

Instrumentation. ^1H , ^{13}C , and ^{29}Si NMR spectra were obtained on Bruker 300-MHz and 400-MHz spectrometers using 5 mm o.d. tubes. Sample concentrations were approx. 10% (w/v) in CDCl_3 and were referenced to internal solvent. A 15 sec delay was used to acquire ^{29}Si NMR spectra. Combustion analysis was performed by Atlantic Microlab, Inc. Non-isothermal differential scanning calorimetry (DSC) was performed on a TA Instruments Q200 under a nitrogen purge of 50 mL/min and a scan rate of $10^\circ\text{C}/\text{minute}$. Thermal gravimetric analysis (TGA) was conducted using a TA Instruments Q5000 under nitrogen and air atmospheres at a purge rate of 30 mL/minute and a scan rate of $10^\circ\text{C}/\text{minute}$. For x-ray diffraction, powder samples were loaded into 1 mm diameter quartz capillary tube (Mark-Röhrchen) for measurement. Powder diffraction for each compound was collected at $T=273.0$ (K) using a Kusing Bruker 3-circle, SMARTAPEX CCD with c -axis fixed at 54.748, running on SMART V 5.625 program (Bruker AXS: Madison, 2001). Graphite monochromated $\text{CuK}\alpha$ ($\lambda=1.54179$ Å) radiation was employed for data collection, which was analyzed using XRD2 Eval (Bruker APEX 2).

Synthesis of 1-naphthyltrichlorosilane. Under a dry nitrogen atmosphere, a solution of 1-bromonaphthalene (27.7 g, 0.134 mol) in THF (175 mL) was added slowly to a suspension of magnesium turnings (3.9 g, 0.16 mol) in THF (15 mL) that had previously been activated with an iodine crystal. After cooling to room temperature, the Grignard reagent was added *via* canula to a THF solution of SiCl_4 (25.1 g, 0.148 mol) and stirred overnight. The mixture was evaporated to dryness, extracted with hexane, and filtered to remove MgBrCl . The hexane-soluble 1-naphthyltrichlorosilane was distilled at 120°C under dynamic vacuum to provide a 67% yield (23.6 g, 0.0902 mol) of product. ^1H NMR (CDCl_3 , ppm) 8.46 (dd, $^3J_{\text{H-H}}$ 0.7, 8.4 Hz, 1H), 8.21 (dd, $^3J_{\text{H-H}}$ 1.2, 7.0 Hz, 1H), 8.09 (d, $^3J_{\text{H-H}}$ 8.3 Hz, 1H), 7.96 (d, $^3J_{\text{H-H}}$ 7.5 Hz, 1H), 7.70 (m, 1H), 7.59 (m, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , ppm) 124.61, 126.53, 127.12, 127.41, 127.88, 129.34, 133.55, 134.04, 134.38, and 135.47. $^{29}\text{Si}\{^1\text{H}\}$ (CDCl_3 , ppm) -0.50 (s).

Synthesis of 1-Naphthyltrimethoxysilane. Under a dry nitrogen atmosphere, trimethylorthoformate, (173.6 g, 1.64 mol), was added slowly to neat 1-naphthyltrichlorosilane (34.5 g, 0.132 mol). The solution was refluxed at 106°C for 40 hours. The 1-naphthyltrimethoxysilane was isolated by fractional distillation at 130°C under dynamic vacuum to give an 89 % yield (29.1 g, 0.117 mol) of product. ^{29}Si NMR δ : -52.7 (s).

General synthesis of Aryl Corner-Capped-(Phenyl)T8 POSS compounds: 1-naphthyl(Ph) $_7\text{Si}_8\text{O}_{12}$ (3). Under a dry nitrogen atmosphere, $(\text{Ph})_7\text{Si}_7\text{O}_9(\text{OH})_3$ (19.7 g, 0.021 mol) was dissolved in THF (150 mL). To this a solution of 1-naphthyltrichlorosilane (5.6 g, 0.022 mol) in THF (50 mL) was added slowly. To this a dilute triethylamine (6.8 g, 0.068 mol) solution in THF (100 mL) was added over a 90 minute period under vigorous stirring and the reaction was allowed to proceed overnight. The solution was then filtered and the volume reduced under dynamic vacuum. Ether was then added and an aqueous workup was performed. The solution was again reduced under vacuum and the remaining oil was dissolved in THF. The solution was precipitated in methanol and then filtered to produce a 95% yield (21.0 g, 0.20 mol). ^1H NMR (CDCl_3 , ppm) 8.51 (m, 1H - nap), 8.04 (dd, J 1.3, 6.8 Hz, 1H - nap), 7.98 (d, J 8.3 Hz, 1H - nap), 7.81 (m, 15H - nap/ph), 7.36 (m, 24H - nap/ph). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , ppm) 124.84 (CH - nap), 125.73 (CH - nap), 126.50 (CH - nap), 127.85, 127.88, 127.90 (3:1:3, CH - ph), 128.26 (C - nap), 128.36 (CH - nap), 128.64 (CH - nap), 130.05, 130.15, 130.19 (3:1:3, C - ph), 130.77, 130.80, 130.82 (3:1:3, CH - ph), 131.50 (CH - nap), 133.16 (C - nap), 134.19, 134.22, 134.23 (3:1:3, CH - ph), 135.36 (CH - nap), and 136.45 (C - nap). $^{29}\text{Si}\{^1\text{H}\}$ (CDCl_3 , ppm) -77.37, -78.05, -78.14, and -78.17 (1:3:1:3). Elemental Anal. (Calcd): C, 57.68 (57.64); H, 3.81 (3.91).

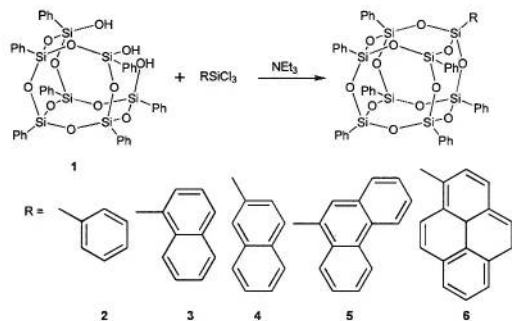


Figure 1. General synthesis method and numbering assignments for Aryl Corner-Capped-(Phenyl)₇T₈ POSS.

Synthesis of Symmetric Aryl T₈ POSS Compounds. 1-Naphthyl₈T₈ was synthesized using a published literature method, WO 01/10871 A1, to give a 52 % yield (10.9 g, 7.60 mmol). ²⁹Si NMR δ: -77.4 (s). Benzyl₈T₈ and Phenethyl₈T₈ were also synthesized according to previously reported literature methods. The chemical structures and numbering assignments are depicted in Figure 2.

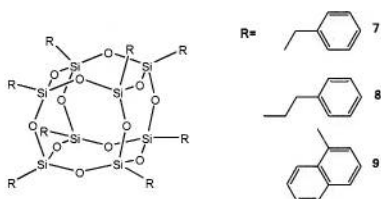


Figure 2. Numbering assignments for symmetric Aryl₈T₈ POSS compounds.

Results and Discussion

Thermal analyses of all Aryl POSS compounds were conducted to determine any contrasts in their properties. TGA results are shown in Figures 3 and 4 for symmetric and asymmetric POSS compounds, respectively. For the symmetric compounds, under anaerobic conditions (A), mass loss proceeds by sublimation for **2** and by evaporation for **7-9** above their observed melting points. In aerobic conditions, **2** again undergoes sublimation at equivalent temperatures, however, **7** and **8** begin losing mass at relatively low temperature due to peroxidation and subsequent crosslinking of the aliphatic spacers between the POSS cages and the peripheral phenyl groups. **9**, on the other hand, exhibits good thermal stability undergoing evaporation and degradation simultaneously.

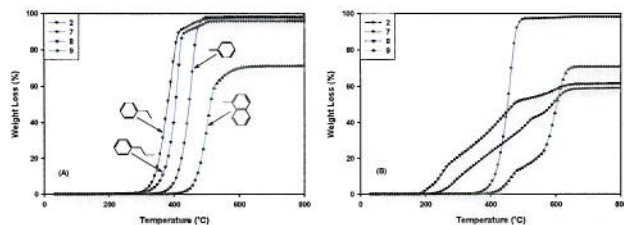


Figure 3. TGA analysis of symmetric Aryl POSS compounds in (A) nitrogen and (B) air.

For the asymmetric compounds, mass loss proceeds by sublimation initially, characterized by a steep change in the mass loss profile, followed by more gradual chemical degradation mechanisms. The extent of sublimation is dependent on POSS packing efficiency determined from powder x-ray diffraction, where extent of loss correlates with increasing average cage-to-cage distance. In air, chemical degradation occurs at earlier temperatures due to oxidation.

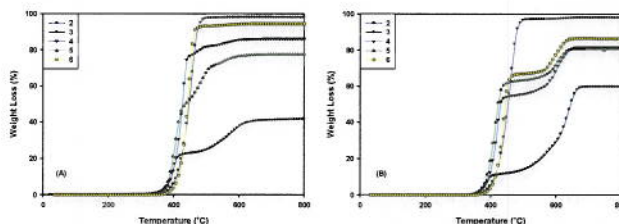


Figure 4. TGA analysis of asymmetric Aryl POSS compounds in (A) nitrogen and (B) air.

Conclusions

The peripheral architecture of Aryl POSS affects its macroscopic properties in the assembled state. A comparison of thermal stabilities has revealed that under anaerobic conditions, symmetric Aryl POSS evaporates above its melting point according to molecular weight. In the case of **2**, sublimation is prevalent independent of atmosphere. In aerobic conditions, on the other hand, aliphatic spacers are prone to peroxidation reactions that facilitate crosslinking resulting in higher mass char residues. Asymmetric Aryl POSS compounds lose mass through a combination of sublimation and chemical degradation at elevated temperature. Extent of sublimation is directly dependent on average cage-to-cage distance which is a measure of POSS packing efficiency.

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