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Brian M. Moore, Gregory R. Yandek, Sean M. Ramirez, Timothy S. Haddad, and Joseph M. Mabry

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Air Force Research Laboratory (AFMC)
AFRL/RZSM
9 Antares Road
Edwards AFB CA 93524-7401

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Air Force Research Laboratory (AFMC)
AFRL/RZS
5 Pollux Drive
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INFLUENCE OF PERIPHERAL ARCHITECTURE ON SYMMETRIC ARYL POLYHEDRAL OLIGOMERIC SILSESQUIOXANES (POSS)

Brian M. Moore,[1] *Gregory R. Yandek,*[1] *Sean M. Ramirez,*[2] Timothy *S. Haddad,*[2] *and Joseph M. Mabry*[1]

[1]Air Force Research Laboratory, Space & Missile Propulsion Division,
Edwards Air Force Base, CA 93524-7680
[2]ERC Inc., Air Force Research Laboratory, Space & Missile Propulsion
Division, Edwards Air Force Base, CA 93524-7680

Abstract

The synthesis of Naphthyl$_8$T$_8$ POSS has been reproduced to enable a careful examination of its properties in comparison with Phenyl$_8$T$_8$, with the overall goal of ascertaining the influence of the peripheral architecture of symmetric aryl POSS compounds on macroscopic properties. A comparison of the characteristics of Phenyl$_8$T$_8$ and 1-Naphthyl$_8$T$_8$ possessing a geometrically larger periphery has revealed that the nature of the organic moieties affects POSS packing efficiency. The differences in packing efficiencies affect both the solvent solubility and thermal characteristics of these symmetric aryl POSS compounds.

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[2]ERC Inc., Air Force Research Laboratory, Space & Missile Propulsion
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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 synthesis of a compound adhering to these criteria was reported fifty years ago, namely Naphthyl$_8$T$_8$ POSS.[6-7] The synthesis of this compound has been reproduced to enable a careful examination of its properties in comparison with Phenyl$_8$T$_8$, with the overall goal of ascertaining the influence of the peripheral architecture of symmetric aryl POSS compounds on macroscopic properties.

Experimental

Materials. Phenyl$_8$T$_8$ was synthesized following literature method.[5] All other chemicals were purchased from Aldrich. All chemicals were used without further purification unless noted otherwise. Reactions were performed under an atmosphere of dry nitrogen. Flasks were oven-dried and allowed to cool under nitrogen prior to use.

Instrumentation. ^{1}H, ^{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. 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°C/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°C/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 CuKα (λ= 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. ^{1}H NMR (CDCl$_3$, ppm) 8.46 (dd, $^{3}J_{H\text{-}H}$ 0.7, 8.4 Hz, 1H), 8.21 (dd, $^{3}J_{H\text{-}H}$ 1.2, 7.0 Hz, 1H), 8.09 (d, $^{3}J_{H\text{-}H}$ 8.3 Hz, 1H), 7.96 (d, $^{3}J_{H\text{-}H}$ 7.5 Hz, 1H), 7.70 (m, 1H), 7.59 (m, 2H). ^{13}C{^{1}H} NMR (CDCl3, ppm) 124.61, 126.53, 127.12, 127.41, 127.88, 129.34, 133.55, 134.04, 134.38, and 135.47. ^{29}Si{^{1}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).

Synthesis of 1-Naphthyl$_8$T$_8$. This compound was synthesized using a published literature method[8] to give a 52 % yield (10.9 g, 7.60 mmol). ^{29}Si NMR δ: -77.4 (s) as shown in Figure 1.

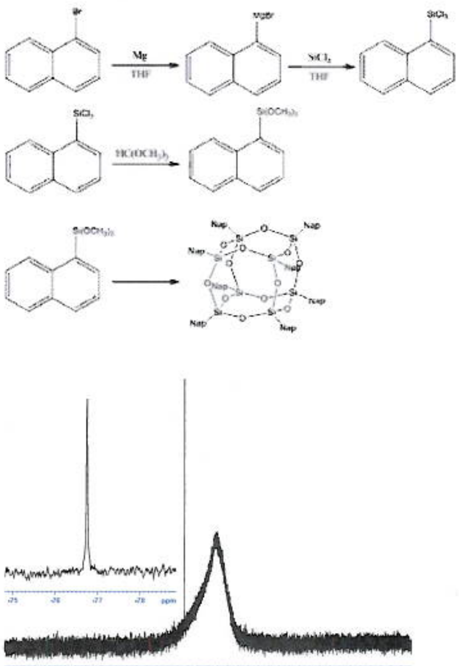

Figure 1. Reaction scheme and ^{29}Si NMR spectrum of 1-Naphthyl$_8$T$_8$.

Results and Discussion

Thermal analyses of Phenyl$_8$T$_8$ and 1-Naphthyl$_8$T$_8$ were conducted to determine any contrasts in their properties. DSC scans, as depicted in Figure 2, reveal that no melting point is detected for Phenyl$_8$T$_8$, while a sharp solid-liquid transition is seen at 350°C for 1-Naphthyl$_8$T$_8$. Analysis of powder X-ray diffraction of both materials in the region specified in Figure 3 revealed average cage centroid distances to be 10.9 Å for Phenyl$_8$T$_8$ and 11.3 Å for 1-Naphthyl$_8$T$_8$, verifying that packing efficiency is affected by peripheral geometry. Solution-grown crystals of Phenyl$_8$T$_8$ were also analyzed for a phase transition but none were detected to 500°C.

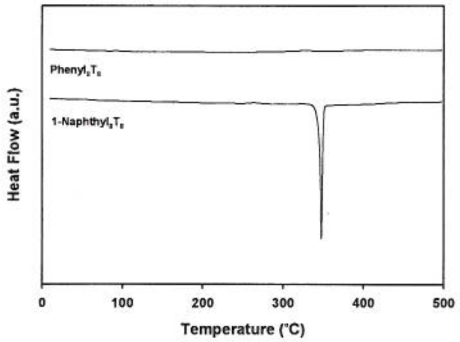

Figure 2. Differential scanning calorimetry scans of Phenyl$_8$T$_8$ and 1-Naphthyl$_8$T$_8$ POSS.

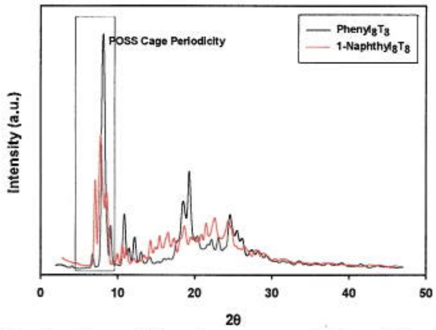

Figure 3. Powder X-ray diffraction patterns of Phenyl$_8$T$_8$ and 1-Naphthyl$_8$T$_8$. The region pertaining to POSS cage electron density periodicity is highlighted.

TGA on both materials under anaerobic and aerobic conditions also revealed contrasting thermal behavior. In both environments, Phenyl$_8$T$_8$ sublimed at the same temperatures and rates, with mass loss first appearing at 375°C followed by rapid depletion to a near zero residual mass. Anaerobic evaporative mass loss of 1-Naphthyl$_8$T$_8$ commences at approximately 400°C which is 50°C above its measured phase transition. However, the change in observed signal slope at 450°C is an indication of a secondary concomitant chemical degradation process that results in entrapment of mass due to cross-linking reactions. This secondary degradation pathway results in a thermally stable, dark char material that is a third of the material's original weight, retaining some organic character. Under aerobic conditions, the characteristic signature of evaporative loss again occurs at 400°C, however, oxidative attack of the naphthyl groups initiates at 440°C during concurrent conversion of the $SiO_{1.5}$ cage to SiO_2. Ultimately, a pure white residue was left suggesting an expected absence of any organic elements. Mass balance arithmetic on the data confirms the nature of the aforementioned loss mechanisms.

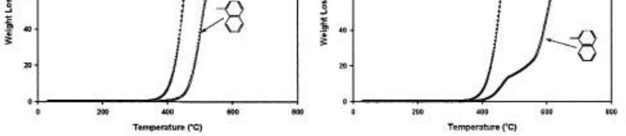

Figure 4. TGA analyses of Phenyl$_8$T$_8$ and 1-Naphthyl$_8$T$_8$ under anaerobic (left) and aerobic (right) conditions.

The solubility of Phenyl$_8$T$_8$ and 1-Naphthyl$_8$T$_8$ in various solvents was measured at room temperature. The results of this study are shown in Table 1. 1-Naphthyl$_8$T$_8$ exhibits superior solubility in three of the five chosen solvents.

Compound	**$CHCl_3$**	**THF**	**PE**	**Toluene**	**DMF**
Phenyl$_8$T$_8$	1	Insoluble	Insoluble	Insoluble	Insoluble
Naphthyl$_8$T$_8$	3	12	Insoluble	Insoluble	8

Table 1. Solubility (mg/mL) of synthesized compounds in various solvents.

Conclusions

The peripheral architecture of symmetric aryl POSS affects its macroscopic properties in the assembled state. A comparison of the characteristics of Phenyl$_8$T$_8$ and 1-Naphthyl$_8$T$_8$ possessing a geometrically larger periphery has revealed that the nature of the organic moieties affects POSS packing efficiency. The 1-Naphthyl$_8$T$_8$ average cage-to-cage centroid distance is over 1 Å greater than that of Phenyl$_8$T$_8$. This reduction in packing efficiency contributes to an improved solvent solubility. While Phenyl$_8$T$_8$ does not demonstrate a solid-liquid phase transition, 1-Naphthyl$_8$T$_8$ was observed to melt at 350°C. In terms of thermal stability, Phenyl$_8$T$_8$ sublimates rapidly to near-zero weight while 1-Naphthyl$_8$T$_8$ experiences concurrent evaporative and chemical degradation mass losses at higher temperatures than those witnessed for the former compound. Crosslinking during degradation enables the formation of a thermally stable char. Superior mass loss resistance of the 1-Naphthyl$_8$T$_8$ material could be a result of its higher molecular weight and/or short-range interactions between neighboring naphthyl groups.

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