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A Novel Linear Titanium(IV)-POSS Coordination Polymer

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During the past two decades, research in the area of polyhedral oligomeric silsesquioxanes (POSS) chemistry has developed along two major lines: (i) the use of POSS in the preparation of nanostructured organic−inorganic hybrids with enhanced physical and thermal properties[1−3] and (ii) the preparation of polyhedral oligomeric metallasilsesquioxanes (POMSS), some that were structural or functional models of industrially important silica supported metal catalysts.[4,5] A third area of POSS research that has seen minor progress during this same time period is the synthesis and characterization of metal-POSS coordination polymers, where the coordination bond is part of the polymer backbone.[6−9] One reason for the slow development of this research area has been the lack of an appropriate POSS starting material that lends itself to function as both a molecular linker and a ditopic chelating ligand. Recently, however, the synthesis of the sodium salt of the tetrasilanol phenyl POSS has been published,[10,11] and the protonated version (**1**) has become commercially available. We considered **1** to be an appropriate starting material for the preparation of metal-POSS coordination polymers and report here the synthesis and characterization of the first coordination polymer containing **1** as the linkers and titanium(IV) atoms as the nodes.

Titanium(IV) isopropoxide (**2**) has been used to prepare cleanly titanium(IV)-containing POMSS in high yields.[4,12] Therefore, under a nitrogen atmosphere, we reacted **2** with a dilute THF solution containing a stoichiometric amount of **1**. The dilute conditions were used to promote the formation of a linear polymer. After stirring for ca. 19 h, **3** had precipitated and was collected by filtration, rinsed twice with anhydrous THF, and dried at room temperature under reduced pressure (76.6% yield, Figure 1).

Even at elevated temperatures, **3** was sparingly soluble or insoluble in common organic solvents; therefore, most characterizations were performed using solid-state methods. Results of powder X-ray diffraction (XRD) and polarized optical microscopy of **3** (Figure 2) were consistent with a crystalline solid. This suggested the molecular architecture of **3** was linear-like rather than network-like. Its surface composition was measured by X-ray photoelectron spectroscopy (XPS) and was found to contain titanium in the +4 oxidation state. Its atomic distribution was measured as follows: 67.8% carbon, 10.1% silicon, 21.0% oxygen, and 1.11% titanium. Assuming all of the carbon, silicon, and oxygen atoms originated from **1**, the predicted Si/C ratio would be 8:48, whereas the Si/O ratio would be 8:14. The experimental Si/C ratio was calculated to be 7.15:48, whereas the experimental Si/O ratio was 6.73:14. The elemental analysis of

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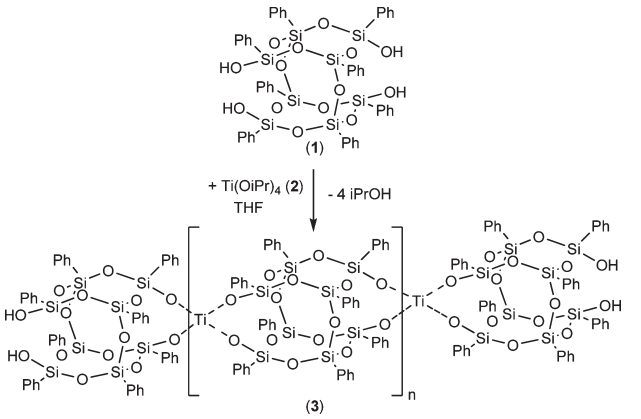

Figure 1. Phenyl POSS tetrasilanol (**1**) reacts with titanium(IV) isopropoxide (**2**) to form a coordination polymer (**3**).

3 was also consistent with all carbon and hydrogen originating from **1** (theoretical: C, 51.78%; H, 3.630%. experimental: C, 50.15%; H, 3.707%). Although the carbon percentage was slightly lower than the theoretical value, we would have expected higher experimental carbon and hydrogen percentages if isopropxide or THF were present in **3**. The slightly low percentage of carbon detected may be the result of the formation of silicon carbides during the combustion analysis.

The solid-state ^{13}C cross-polarization magic angle spinning (CPMAS) NMR spectra for both **1** and **3** were very similar, showing broad resonances from 133.3 to 127.2 ppm in each spectrum. These peaks were characteristic for aromatic carbons and thus were assigned to the phenyl substitutents of the POSS.[13] Other than spinning side bands, no other peaks were observed in the solid-state ^{13}C CPMAS spectrum of **3**. This suggested that within the detection limits of the experiment, all of the carbon in **3** originated from the phenyl substitutents in **1**, and no other carbon-containing molecules, such as isopropoxide or THF, were present.

The solid-state ^{29}Si spectrum of **1** had two broad resonances at −80.8 and −70.5 ppm (Figure 3, top). Silicon sites were designated following the conventional notation, where T^n = R-Si-$(OR')_3$ and *n* was the number of bridging oxygen atoms.[14] A T^3 type peak at −80.8 ppm corresponded to the four internal silicons in the POSS cage, each with three bridging oxygens and one phenyl substitutent. The second peak at −70.5 ppm was attributed to the four T^2 type silicons with two bridging oxygens, one phenyl substitutent, and one hydroxide.[15] After deconvolution of the two peaks, the integration confirmed a 1:1 ratio between the two types of silicons, which was consistent with the structure of **1**. The solid-state ^{29}Si NMR spectrum of **3** also had two resonances: a large T^3 peak at −79.1 ppm and a much smaller T^2 peak at −70.2 ppm (Figure 3, bottom). The smaller T^2 resonance was consistent with silanol silicons on the end of the polymer chain and had a chemical shift similar to that of the corresponding silicons in **1**, whereas the large T^3 resonance corresponded to the remaining internal silicons within the coordination polymer. Resonances for the T^3 silicons bridging to titanium likely overlap with resonances because of silicons bridging to only other silicons, which produced the large broad peak at −79.1 ppm. This was consistent with previous ^{29}Si NMR studies on metal-POSS compounds that had reported the silicon resonances of Si−O−Si and Si−O−M within a few ppm of each other.[8,12,16]

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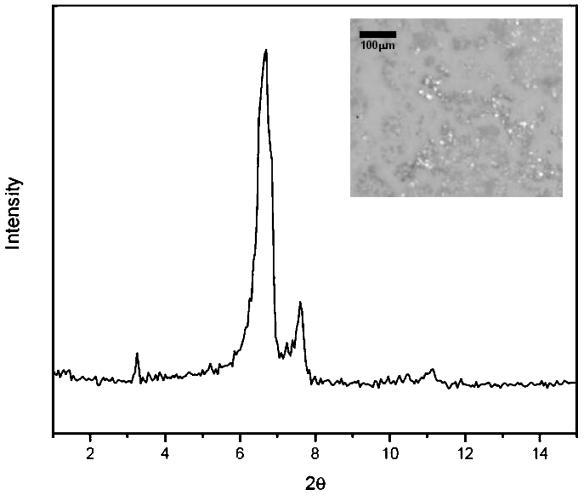

Figure 2. Powder XRD of **3**. Inert: polarized optical microscopy of **3**, where scale bar represents 100 μm.

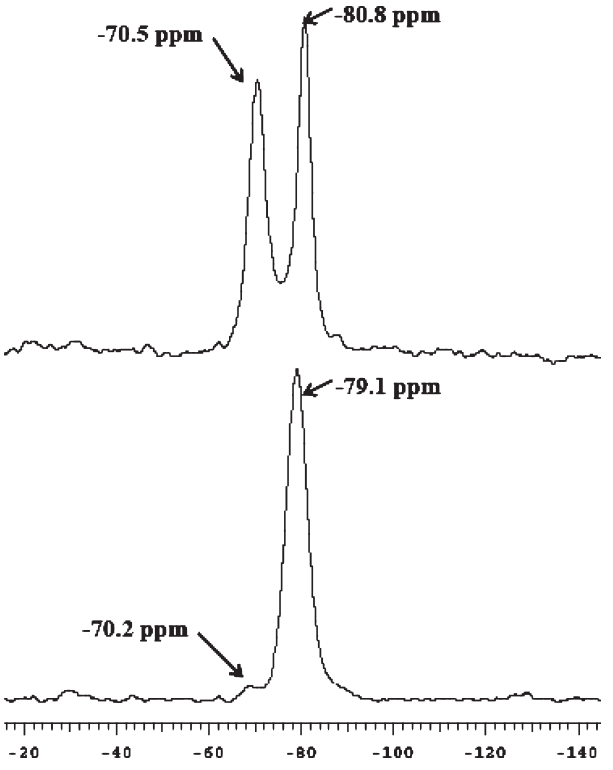

Figure 3. Solid-state ^{29}Si NMR of **1** (top) and **3** (bottom). The small peaks at approximately −30 and −130 ppm are spinning sidebands.

Solid-state NMR spectroscopy was an appropriate method to ascertain the degree of polymerization of these coordination polymers because of its nondestructive nature and the limited solubility of **3**. To obtain accurate integration, a standard inversion−recovery experiment was run on **1** to determine T_1 values. It was assumed that **3**, because it is a polymer, will have shorter T_1 values than that of **1**, and values determined for **1** served as the upper limit for **3**. T_1 analysis of **1** gave an approximate T_1 for both sites of 58 s. Thus, ^{29}Si NMR spectra of **3** were acquired with a pulse delay of 300 s, and proton decoupling was applied during acquisition only. Standard integration of the two resonances was not possible because of their significant overlap. Therefore, deconvolution analysis was performed. Deconvolution of the two peaks gave approximately a 90:1 integrated ratio between the T^3 and T^2 silicon resonances.

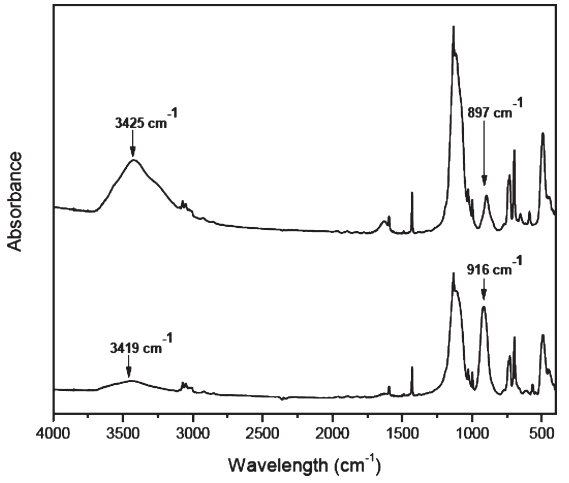

Figure 4. Infrared spectral data of **1** (top) and **3** (bottom).

On the basis of these results, we concluded that the estimated number averaged degree of polymerization was 40.

The infrared (IR) spectrum of **1** was compared with that of **3** (Figure 4). The majority of the bands in the two spectra were identical. Both showed the same peaks between 2900 and 3100 cm^{-1} indicative of phenyl substitutents on the POSS[17,18] as well as a very intense band at 1132 cm^{-1} characteristic of a mixture of Si−O stretching and Si−O−Si, O−Si−O bending vibrations attributed to the POSS cage.[19] The broad −OH peak at ∼3400 cm^{-1} was present in both, but in **3**, it was significantly less intense relative to the other bands in the spectrum. Also, the Si−O−H peak at 897 cm^{-1} in **1** has been replaced with a larger peak at 916 cm^{-1} due to the presence of a Si−O−Ti vibration.[20] Also, the IR of **3** did not exhibit any peaks that would be consistent with the presence of isoproxide or THF. The combined IR data supported the fact that **3** was a titanium-POSS coordination polymer with phenyl-POSS silanol end groups.

Although **3** was insoluble in almost all solvents tested, enough dissolved in acetone for analysis by MALDI-TOF mass spectroscopy in a 9-nitroanthracene matrix. Four major fragments at 5562.03 m/z, 4449.51 m/z, 3335.73 m/z, and 2223.26 m/z were detected under positive ion conditions. These were consistent with small oligomers having the general formula $((C_6H_5)_8Si_8O_{14}Ti)_n$ (n = 5, 4, 3, 2) with all four species having lost three or four H^+. The calculated isotopic distribution for each oligomer gave 100% intensity values of 5562.02 m/z, 4449.01 m/z, 3336.00 m/z, and 2223.00 m/z, which matched very well with the experimental data. Negative ion conditions produced four fragments at 5521.83 m/z, 4409.86 m/z, 3295.93 m/z, and 2182.24 m/z. These corresponded with oligomers of the general formula $((C_6H_5)_8Si_8O_{14})_n(Ti)_{n-1}$ (n = 5, 4, 3, 2) with all four species having gained four or five H^+. Once again, the calculated isotopic distribution for each oligomer gave 100% intensity values that agreed with the experimental data: 5522.13 m/z, 4410.13 m/z, 3296.11 m/z, and 2182.10 m/z. The detection of low-molecular-weight oligomers in the MALDI-TOF mass spectrum of **3** was consistent with a polydisperse polymer where the higher molecular weight chains (n > 5) were insoluble in acetone, whereas the lower molecular weight chains (n = 2 to 5) were soluble and thus detectable by mass spectroscopy.

In summary, the powder XRD and polarized optical microscopy of **3** confirmed its crystalline nature, which was consistent with a chain-like architecture rather than a network-like amorphous material. The quantitative solid-state ^{29}Si NMR of **3** also illustrated that this chain-like POSS containing coordination polymer with silanol end groups had an estimated number-average degree of polymerization of 40. The elemental analysis,

solid-state ^{13}C CPMAS NMR, and IR data suggested that the phenyl substitutents from the POSS are the only source of carbon in **3**, and neither isopropoxide nor THF were present. In addition, XPS established the presence of both titanium(IV) and POSS in **3**, whereas IR and MALDI-TOF mass spectrometry supported the existence of Ti−O−Si linkages. Although the full crystal structure was not yet obtained, this current data confirmed that **3** was most likely a linear titanium(IV)-POSS coordination polymer. The fact that **1** reacted with a metal ion to form a polymer leads us to believe that **3** was the first in a potentially large number of new POSS-containing coordination polymers that will be prepared from **1**, many of which could have potentially interesting physical and chemical properties.

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Supporting Information Available: The detailed experimental procedure, elemental analysis, XPS data, and MALDI-TOF mass spectrometry data for **3** and the powder XRD of **3** with **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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