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Synthesis and Characterization of an Isocyanate Functionalized Polyhedral Oligosilsesquioxane and the Subsequent Formation of an Organic−Inorganic Hybrid Polyurethane

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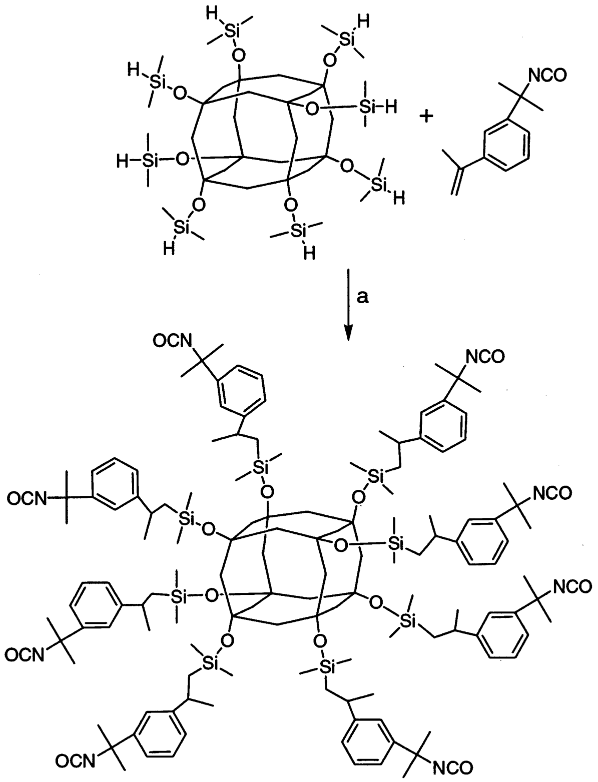
The term silsesquioxane is used to denote materials containing, on average, one silicon atom bound to one and a half oxygen atoms and one R group (where R may be a range of organofunctional groups) and having the general formula $[RSiO_{3/2}]_n$ (n is an even integer ≥ 4). These materials have received an increasing amount of interest since their first synthesis in 1946.[1] Silsesquioxanes exist in a variety of structures from random polymers to more ordered arrangements,[2,3] but the polyhedral oligosilsesquioxanes (POSS) with their unique cagelike structures and nanoscale dimensions are of particular interest. The Si_8O_{12} core can have a wide variety of functional groups attached to each vertex of the core, leading to its use in a variety of different applications.[4]

The inorganic nature and multiple reactive functionalities of POSS make these compounds ideal for their use in the construction of organic−inorganic hybrid nanomaterials. Hybrids may be produced by blending POSS into a polymer matrix, by covalently bonding POSS into a polymer backbone, or by using POSS as a pendant group of a polymer. Using POSS as a pendant group of a linear polymer gives a linear organic−inorganic hybrid. This is generally achieved by forming a POSS macromer possessing a single polymerizable functional group with the remaining vertices having inert organic groups. The macromer is then copolymerized with a suitable monomer, yielding the desired organic−inorganic hybrid material. Hybrids produced using this methodology include polysiloxane,[5] poly(methyl methacrylate),[6] poly(4-methyl styrene),[7,8] epoxy,[9,10] polynorbornene,[11,12] and polyurethane.[13] Incorporation of POSS as a pendant group of a linear polymer increases oxygen permeability and glass transition and degradation temperatures, while reducing flammability, density, and viscosity.

POSS may also be used as a nanocross-linker in polymeric systems. This is accomplished through the functionalization of POSS with eight identical groups that may be reacted to form materials with a high cross-link density. Functional groups that have been employed in the preparation of cross-linked hybrid materials are epoxy,[14−17] amine,[18,19] methacryloyl,[20] vinyl,[21] alkyl halide,[22] and hydrido.[21]

We report here the synthesis of a new type of POSS macromer with eight reactive isocyanate groups suitable for the synthesis of hybrid organic−inorganic urethane nanomaterials (Scheme 1). The macromer has also been used to synthesize the first cross-linked polyurethane with discrete POSS molecules dispersed within the polymer matrix. The POSS-isocyanate is also suitable for synthesis of other compounds such as organic−inorganic dendritic materials or star polymers, work which is currently being pursued.

Scheme 1. Synthesis of $Q_8M_8^{TMI}$ [a]



[a] The core shown in the diagram represents the Si_8O_{12} structure of the POSS. Conditions: (a) THF, Karstedt's catalyst, reflux for 2 days. See the Supporting Information for reaction details.

Unlike most other isocyanates, m-isopropenyl-α,α′-dimethylbenzyl isocyanate (m-TMI) is known to undergo hydrosilylation with Si−H bonds quantitatively yielding only the β-addition product, and without any competing reaction of the isocyanate group.[23,24] The exclusively β addition product and lack of any side reaction make this isocyanate an ideal candidate for the functionalization of the cubic hydrido functional POSS, octakis(dimethylsiloxy)octasilsesquioxane ($Q_8M_8^H$). To date, the complete functionalization of a cubic POSS molecule with eight isocyanate groups has not been reported. Octafunctionalization of POSS with isocyanate groups is desirable due the high reactivity and versatility the groups offer, for the synthesis of a wide range of hybrid materials.

Initial attempts to obtain octakis[m-isopropenyl-α,α′-dimethylbenzyl isocyanatodimethylsiloxy]octasilsesquioxane $Q_8M_8^{TMI}$ using dry toluene as the solvent afforded a product with incomplete substitution of starting compound $Q_8M_8^H$, as determined by a peak in the ^{1}H NMR of the product at $\delta = 4.7$ ppm attributed to residual

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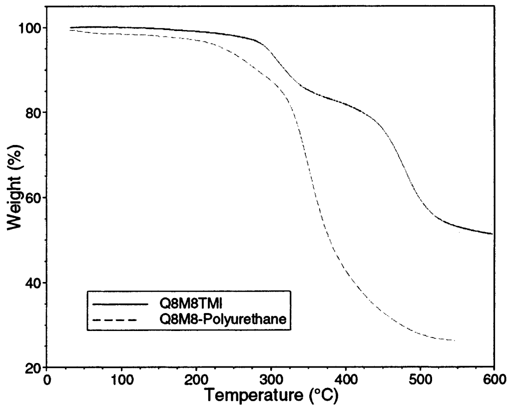

Figure 1. TGA of $Q_8M_8^{TMI}$ and Q_8M_8 nanocomposite polyurethane.

Si−H groups. Increased reaction time, temperature, and catalyst concentration did not enable the reaction to go to completion.

In an effort to obtain complete substitution, dry tetrahydrofuran was used as a solvent for the reaction. The reaction using Karstedt's catalyst[25] was refluxed for 2 days, after which no remaining Si−H bonds were observed by ^{1}H NMR. Solvent and excess TMI were removed under high vacuum, affording a slightly cloudy, viscous oil. Analysis by ^{1}H and ^{13}C NMR displayed peaks consistent with the desired product. ^{29}Si NMR analysis displayed a singlet at $\delta = 12.2$, corresponding to the M-type silicon, and another singlet at $\delta = -109.6$, corresponding to the Q-type silicon of the POSS core. The presence of only two singlets in the ^{29}Si NMR confirms that the cubic structure of POSS has remained intact during the reaction. A minor peak was observed at $\delta = 7.4$, which is attributed to the α hydrosilylation product. FT-IR and microchemical analysis provided further confirmation of the complete reaction of TMI with $Q_8M_8^H$.

Thermogravimetric analysis of the product under nitrogen displayed two weight losses (Figure 1). The first loss of 15.1% beginning at 253 °C was attributed to cleavage of the peripheral arms attached to the POSS core, whereas the second weight loss beginning at 383 °C can be attributed to breaking down of the core Si−O structure.

An organic−inorganic hybrid polyurethane was also synthesized to demonstrate the suitability of the $Q_8M_8^{TMI}$ macromer for synthesis of these types of materials. Poly(ethylene glycol) with a narrow average molecular weight of 600 was used as the organic tether. $Q_8M_8^{TMI}$ and a slight excess of PEG-600 were dissolved in dry THF, and 20 μL of dibutyltin dilaurate catalyst was added to the mixture. The solution was poured onto a Teflon dish and placed in a desiccator in an oven at 80 °C for 10 h. After such time, the THF had evaporated off, leaving behind a clear elastomer.

Analysis by photoacoustic FT-IR and near-IR spectroscopy confirmed the complete reaction of isocyanate groups ($\nu_{NCO} = 2262$ cm^{-1}) with the hydroxyl groups of the PEG-600 forming urethane linkages ($\nu_{NHCO} = 3330$, 1728 cm^{-1}). Some residual hydroxyl groups, believed to result from the residual moisture inherent to PEG-600 starting material, were observed as a broad peak at $\nu = 3300$ cm^{-1} in the FT-IR. CP-MAS ^{29}Si NMR of the elastomer displayed two peaks consistent with the two types of silicon present in the hybrid. A peak due to the M-type silicon of the POSS core is observed at $\delta = 12.2$ ppm, and another peak due to the Q-type silicon of the core is observed at $\delta = -109$ ppm, thereby confirming the POSS core has remained intact during the reaction with PEG-600.

Thermogravimetric analysis of the hybrid displays a broad weight loss beginning at 190 °C due the cleavage of urethane linkages, followed by decomposition of the core itself (Figure 1).

We have studied the synthesis of a new type of functionalized POSS. The hydrosilylation of octakis(hydridodimethylsiloxy)-octasilsesquioxane with *m*-isopropenyl-α,α′-dimethylbenzyl isocyanate (*m*-TMI) in THF with Karstedt's catalyst was shown to be free from side reactions. An organic−inorganic hybrid polyurethane was then synthesized using the POSS macromer as a nanocross-linker.

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Supporting Information Available: Experimental procedures and NMR data (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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