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Recommended Citation

Son, David; Rissing, Christiana; Chen, Li; and Andersson, Theodore, "Thiol-ene Chemistry for the Synthesis and Modification of Branched Organosilicon Polymers" (2010). *Polymer Preprints 2010*, vol. 51, no. 2, p. 730.

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THIOL-ENE CHEMISTRY FOR THE SYNTHESIS AND MODIFICATION OF BRANCHED ORGANOSILICON POLYMERS

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Introduction

Thiol-ene chemistry has proved to be an extremely efficient method for the formation of sulfur-carbon bonds in both small-molecule and polymer chemistry. The favorable aspects of thiol-ene chemistry include easy initiation, high-yields, minimal product purification, and high tolerance of a variety of solvents and functional groups. Thus, thiol-ene chemistry is now routinely included in discussions of "click" chemistry.¹⁻⁵ As an extension of our work in branched organosilicon polymers, we have utilized thiol-ene chemistry for the synthesis of organosilicon-thioether dendrimers. Thiol-ene chemistry may also be used for the efficient functionalization of the dendrimer exterior, enabling tailoring of solubility properties. Herein we describe our results in this area, and also discuss the applicability of the carbosilane-thioether dendrimers for the stabilization of late transition metal nanoparticles. A possible approach to the synthesis of carbosilane-thioether hyperbranched polymers is also described.

Experimental

Carbosilane-thioether dendrimers were synthesized as recently reported.⁶ The dendrimers are described using the notation **G#-X**, where "#" represents the generation number and "X" represents the terminal functional groups. For example, **G3-OH** represents the third generation dendrimer terminated with hydroxyl groups.

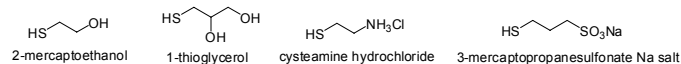
Exterior functionalization of carbosilane-thioether dendrimers. All exterior functionalizations were carried out using vinyl-terminated dendrimers as starting materials. In a typical reaction, the dendrimer and excess thiol were dissolved in a 1:1 mixture of methanol and THF. Where necessary, benzophenone was used as a photoinitiator. After irradiation with a sunlamp for 2-4 hours, the product was isolated by precipitation. In this manner, **G3-Vi** was reacted with 2-mercaptoethanol, 1-thioglycerol, cysteamine hydrochloride, and 3-mercaptopropanesulfonate sodium salt to give **G3-OH**, **G3-(OH)₂**, **G3-NH₃Cl**, and **G3-SO₃Na**, respectively. Similarly, **G4-Vi** was reacted with 1-thioglycerol and cysteamine hydrochloride to give **G4-(OH)₂** and **G4-NH₃Cl**, respectively.

Preparation of dendrimer-stabilized nanoparticles. A chloroform/methanol mixture (3:1) was used for all reactions and also as reference in UV-Vis spectroscopy measurements. In a typical reaction, either **G3-Vi** or **G4-Vi** was dissolved in the solvent system and then the metal salt was added (dendrimer:metal ratios were varied). The mixture was stirred for approximately 30 minutes and then an excess of sodium borohydride was added. The mixture was stirred for 1.5-2 hrs before UV-Vis measurements were recorded. In this fashion, copper, palladium, platinum, silver, and gold nanoparticles were prepared.

Results and Discussion

We recently reported the synthesis of carbosilane-thioether dendrimers by repetitive Grignard and thiol-ene steps.⁶ The air and moisture-stable dendrimers were obtained in good yields after precipitation. An example is shown in Figure 1.

For future applications, particularly in highly polar media, it is of interest to adjust the solubility of the dendrimers. This can be done effectively by functionalizing the dendrimer exterior using thiol-ene chemistry.^{6,7} A sampling of the thiols we used in this fashion is shown below:



A sample functionalization reaction is shown in Figure 2. The products ranged in appearance from oils to powdery solids. NMR experiments indicated that all the peripheral vinyl groups had reacted. **G3-OH** was insoluble in water but readily soluble in THF and DMSO. **G3-(OH)₂** was moderately soluble in water at room temperature and completely soluble in

hot water. **G3-NH₃Cl** was readily soluble in water at room temperature and stable in aqueous solution at temperatures up to 100°C. **G3-SO₃Na** was sufficiently soluble in water to obtain a ¹H NMR spectrum (D₂O) but overall was relatively insoluble. Like **G3-NH₃Cl**, dendrimer **G4-NH₃Cl** was also generously soluble in water. However, the solubility behavior of **G4-(OH)₂** was quite different from **G3-(OH)₂**. **G4-(OH)₂** was isolated as a tough gum that proved to be insoluble in a range of solvents we tested, including water and DMSO.

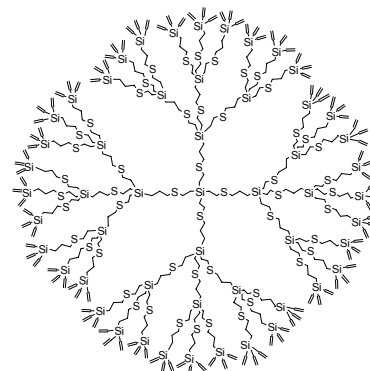


Figure 1. Third generation vinyl-terminated carbosilane-thioether dendrimer (**G3-Vi**).

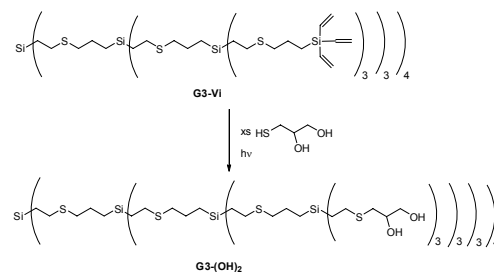


Figure 2. Example of peripheral functionalization reaction.

The vast majority of reported dendrimer-nanoparticle composites involve nitrogen-containing dendrimers such as PAMAM.⁸ This, it was of interest of us to examine the nanoparticle stabilizing characteristics of these sulfur-containing dendrimers. For example, copper nanoparticles were prepared by adding a solution of CuCl₂ to a solution of **G3-Vi** (dendrimer:Cu = 1:52), followed by addition of excess NaBH₄. This process was accompanied by a number of color changes. Addition of the copper salt solution to the colorless dendrimer solution resulted in a brown-yellow solution. Addition of the NaBH₄ resulted in a colorless solution which turned yellow, brown, and finally gray. Performing this reaction in the absence of dendrimer resulted in the formation of agglomerated copper particles.

Visible spectra of the various solutions in the Cu experiment indicated the presence of Cu nanoparticles (Figure 3). The spectrum of the reduced solution (curve marked "g3-Cu⁰") shows a plasmon absorption at 595 nm, suggesting the presence of Cu nanoparticles greater than 5 nm in size.

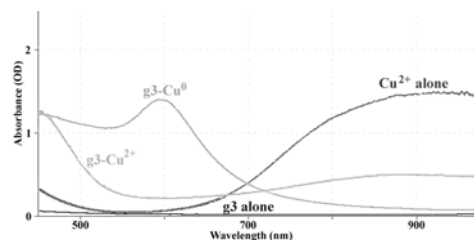
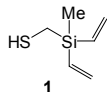


Figure 3. Visible spectra (in 3:1 chloroform:methanol) of the dendrimer solution (**g3** alone), the CuCl₂ solution (Cu²⁺ alone), the mixed dendrimer/CuCl₂ solution (**g3-Cu²⁺**), and the mixture after addition of NaBH₄ (**g3-Cu⁰**).

A current investigation in our laboratory focuses on the application of thiol-ene chemistry towards the synthesis of *hyperbranched* organosilicon polymers. While possessing many similar properties as dendrimers, hyperbranched polymers are typically prepared in a single-pot reaction, thus resulting in a much less labor-intensive synthesis as compared to dendrimers. Our initial investigations are focused on the synthesis of compound **1**, an AB₂ monomer. We have successfully synthesized small amounts of this compound, and initial results indicate that polyaddition via thiol-ene reactions does take place. Detailed results will be reported in due course.



Conclusions

Carbosilane-thioether dendrimers can be efficiently prepared using thiol-ene chemistry. Peripheral functionalization using thiol-ene chemistry is easily accomplished and results in dendrimers of varying solubility. Metal nanoparticles are formed in the presence of the dendrimers by complexing the dendrimer with the metal ion followed by reduction with NaBH₄.

Acknowledgement. The authors thank the Robert A. Welch Foundation (N-1375) and Southern Methodist University for support of this work.

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