J|A|C|S
COMMUNICATIONS

Photodeformable Spherical Hybrid Nanoparticles

Lihua Zhao,[†] Douglas A. Loy,[‡] and Kenneth J. Shea*,[†]

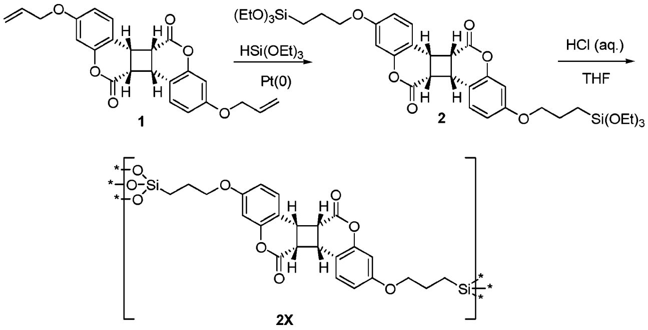
Department of Chemistry, University of California, Irvine, Irvine, California 92697, and Department of Material Science and Engineering and Department of Chemistry, University of Arizona, Tucson, Arizona 85721-0012

Received August 19, 2006; Revised Manuscript Received October 2, 2006 ; E-mail: kjshea@uci.edu

Bridged polysilsesquioxanes (BPs) are a family of hybrid organic−inorganic materials formed by sol−gel polymerization from molecular building blocks that incorporate a variable organic fragment and two or more polymerizable trifunctional silyl groups.[1] The organic fragment has been used to modulate the chemical, optical, and bulk physical properties such as porosity, modulus, and nonlinear optical response in the resultant xerogels.[2,3] More recently through a judicious choice of the bridging organic fragment or by the addition of surfactants to the sol−gel polymerization, hybrid materials with mesostructure have been produced.[4] In consideration of the potential applications of these materials, it would be highly desirable to control the shape and size of these materials. Here we report the first synthesis of BP spherical nanoparticles. In addition to shape control, these nanoparticles incorporate a photolabile organic fragment as bridging group. The photoresponsive organic fragments permit the nanoparticles to be deformed and eventually "melted" by UV irradiation. The spherical nanoparticles are prepared by a simple template-free sol−gel method.

The photoresponsive fragment of the sol−gel polymerizable monomer is derived from a photodimer of a derivative of 7-hydroxycoumarin, a common natural product. Coumarin photodimerization has been studied in homogeneous solution, in organized media and in polymers.[5] When covalently bound in polymers or inorganic materials, photoinduced dimerization can result in cross-linking or aggregation.[6−8] On the other hand, the incorporation of *coumarin photodimer* as structural units in polymers and network materials would provide for photoinduced bond cleavage that could be used to alter the physical, optical, and mechanical properties of the material. There are, however, relatively few reports of coumarin photodimers used as building blocks for polymers or materials.[9,10] Reasons for this can be attributed in part to the chemical lability of some known photodimers.[10,11] After screening the isomeric photodimers of 7-allyloxycoumarin, we established that the syn-head-to-tail (syn-ht) photodimer **1** exhibited greater chemical stability than its regio- and stereoisomers. The syn-ht-7-allyloxycoumarin dimer (**1**) was elaborated to a sol−gel processable monomer, the bistriethoxysilyl derivative **2**, by hydrosilylation. Monomer **2** was polymerized under acidic sol−gel conditions (Scheme 1). Unlike many bridged-bistriethoxysilane monomers,[12] gelation took more than 2 days even at relatively high concentration (1 M in THF). The slow gelation gives some indication that intramolecular (and/or bimolecular) cyclization,[13] perhaps a consequence of the unique "U" shape of **2**, may be taking place during sol−gel polymerization. The slow air-dried monolithic xerogel **2X** was coarsely ground and dried under vacuum (100 °C). The glassy materials are hard, brittle, and thermally robust; the onset of weight loss occurs at approximately 300 °C. FT-IR analysis (lactone diagnostic: ∼1750 cm^{-1}, Figure S1a) establishes that the bislactone substructure of the coumarin dimer remains intact in the dried xerogel **2X**. Analysis of the nitrogen absorportion isotherm showed that the xerogel **2X** is nonporous indicating a relatively compliant network that collapses during drying.

Scheme 1. Synthesis of Syn-Head-to-Tail(ht)-Coumarin Dimer **2** and Bridged Polysilsesquioxane **2X**



Interestingly, electron microscopy images of the powder of **2X** (Figure 1a) showed that the material appeared to consist of aggregates of spherical particles. This was confirmed when particles of **2X** were sonicated in water. Subsequent examination by SEM microscopy revealed a collection of spherical nanoparticles in the 50−100 nm range (Figure 1b and 1c). Since no detergents or templates were employed, these particles were formed by spontaneous self-assembly of monomer **2** or oligomers/macromolecules formed from the monomer under the sol−gel conditions. The detailed mechanism of their formation is under investigation. This

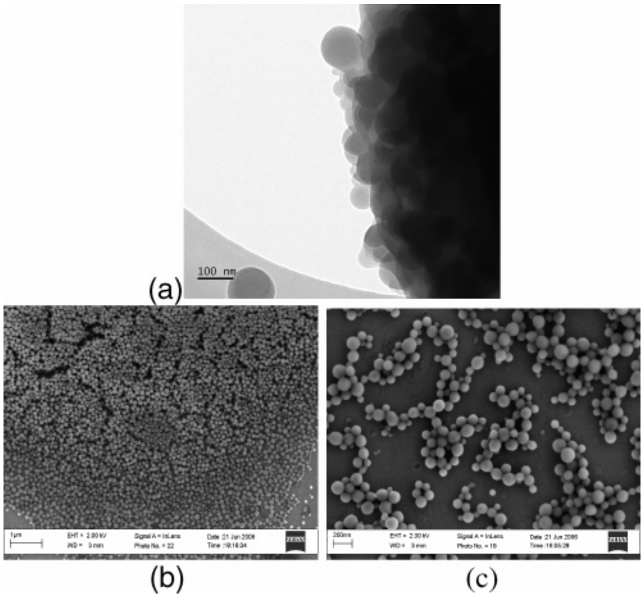


Figure 1. TEM image (a) of the powder of xerogel **2X** and SEM images (b and c with different magnifications) of spherical nanoparticles of **2X**.

[†] University of California, Irvine.
[‡] University of Arizona.

10.1021/ja066047n CCC: $33.50 © 2006 American Chemical Society

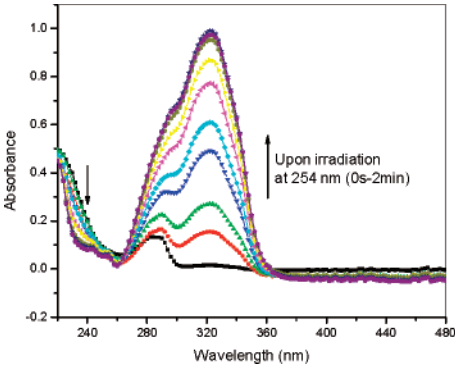
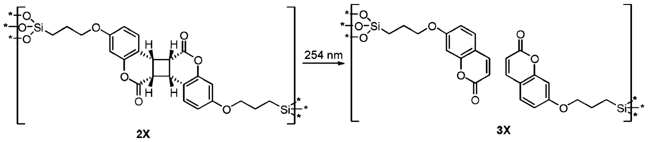


Figure 2. UV spectral changes of THF solution of nanoparticles of syn-ht-coumarin dimer bridged polysilsesquioxane **2X** during photoirradiation by a UV light with the wavelength of 254 nm.

Scheme 2. Photocleavage of Bridged Polysilsesquioxane **2X**



represents the first synthesis of uniform spherical bridged polysilsesquioxane nanoparticles. High-resolution TEM images (Figure S2a, Supporting Information) and the electron diffraction pattern (Figure S2b) of individual nanoparticles indicate that the material is amorphous, with no evidence of phase separation of organic and inorganic domains at a length scale of ~10 Å.

The photoresponse of the spherical nanoparticles of **2X** was probed by irradiating a clear dilute suspension in THF with a UV light (254 nm). The absorbance change of the suspension was monitored by UV−vis spectroscopy (Figure 2). The absorbance at 322 nm increases during irradiation, consistent with photoinduced cleavage of the photodimer to produce a pair of 7-alkyloxy coumarin fragments **3X** (Scheme 2). FT-IR analysis also showed a new absorption at 1735 cm^{-1} confirming the assignment (Figure S1b). Materials prepared with this monomer are hard, brittle, glassy substances. Remarkably, direct irradiation of the nanoparticles of **2X** resulted in their deformation. We were able to follow this by SEM which revealed a progressive deformation and eventual “melting” upon UV irradiation for several minutes with a simple hand held black light lamp (Figure 3). This hard−soft transformation is analogous to photochemically annealing by cleavage of the coumarin dimer cross-links in the silsesquioxane network.

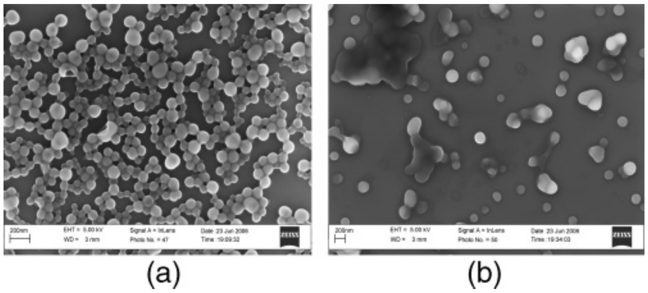


Figure 3. SEM images of nanoparticles irradiated by 254 nm UV light for 1 min (a) and 10 min (b).

In conclusion, we report the first synthesis of spherical nanoparitcles of a bridged polysilsesquioxane. Their spontaneous formation may result from the unique shape of the monomer. If this proves to be correct, it can lead to a more general paradigm for the control of particle shape by the rational design of molecular building blocks for bridged polysilsesquioxanes. These hybrid nanoparticles incorporate a photoresponsive fragment, the syn-ht-7-substituted coumarin dimer. Photocleavage of these bridged dimers results in “softening” and deformation of nanoparticles by direct irradiation with a UV light (254 nm). Future efforts will focus on the detailed mechanism of nanoparticle formation and applications of these materials for photoinduced delivery systems and in photomechanical devices.

Acknowledgment. Support of this research was funded in part from the Division of Graduate Research at the University of California, Irvine. Lihua Zhao thanks Lawrence Livermore National Laboratory for a graduate fellowship. We thank Miss Mariya Khiterer for her assistance with SEM and Dr. Wen-An Chiou and Mr. Li-Chung Lai for their assistance with TEM.

Supporting Information Available: Experimental details, FT-IR data, high-resolution TEM image, and the electron diffraction pattern. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Loy, D. A.; Shea, K. J. *Chem. Rev.* **1995**, *95*, 1431−1442. (b) Shea, K. J.; Loy, D. A. *Chem. Mater.* **2001**, *13*, 3306−3319. (c) Shea, K. J.; Moreau, J.; Loy, D. A.; Corriu, R. J. P.; Boury, B. In *Functional Hybrid Materials;* Gomez-Romero, P., Sanchez, C., Eds.; Wiley-VCH: Weinheim, Germany, 2004; p 50−85.
(2) Hoffmann, F.; Cornelius, M.; Morell, J.; Froba, M. *Angew. Chem., Int. Ed.* **2006**, *45*, 3216−3251.
(3) (a) Sanchez, C.; Julian, B.; Belleville, P.; Popall, M. *J. Mater. Chem.* **2005**, *15*, 3559−3592. (b) Gomez-Romero, P., Sanchez, C., Eds. *Functional Hybrid Materials*; Wiley-VCH: Weinheim, Germany, 2004. (c) Landskron, K.; Ozin, G. A. *Angew. Chem., Int. Ed.* **2005**, *44*, 2107−2109.
(4) (a) Landskron, K.; Ozin, G. A., *Science* **2004**, *306*, 1529−1532. (b) Hoffmann, F.; Cornelius, M.; Morell, J.; Froba, M. *J. Nanosci. Nanotechnol.* **2006**, *6*, 265−288.
(5) Trenor, S. R.; Shultz, A. R.; Love, B. J.; Long, T. E. *Chem. Rev.* **2004**, *104*, 3059−3077.
(6) (a) Fujiwara, M.; Shiokawa, K.; Kawasaki, N.; Tanaka, Y. *Adv. Funct. Mater.* **2003**, *13*, 371−376. (b) Mal, N. K.; Fujiwara, M.; Tanaka, Y. *Nature* **2003**, *421*, 350−353.
(7) Chen, Y.; Hong, R. T. *J. Polym. Sci., Part A: Polym. Chem.* **1997**, *35*, 2999−3008.
(8) Schadt, M.; Seiberle, H.; Schuster, A. *Nature* **1996**, *381*, 212−215.
(9) (a) Chen, Y.; Chen, K. H. *J. Polym. Sci., Part A: Polym. Chem.* **1997**, *35*, 613−624. (b) Saigo, K.; Shiwaku, T.; Hayashi, K.; Fujioka, K.; Sukegawa, M.; Chen, Y.; Yonezawa, N.; Hasegawa, M.; Hashimoto, T. *Macromolecules* **1990**, *23*, 2830−2836.
(10) Saigo, K.; Nakamura, M.; Suzuki, Y.; Fang, L.; Hasegawa, M. *Macromolecules* **1990**, *23*, 3722−3729.
(11) Yu, X.; Scheller, D.; Rademacher, O.; Wolff, T. *J. Org. Chem.* **2003**, *68*, 7386−7399.
(12) Shea, K. J.; Loy, D. A. *Acc. Chem. Res.* **2001**, *34*, 707−716.
(13) Loy, D. A.; Carpenter, J. P.; Myers, S. A.; Assink, R. A.; Small, J. H.; Greaves, J.; Shea, K. J. *J. Am. Chem. Soc.* **1996**, *118*, 8501−8502.

JA066047N