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Preparation of Nanometer-Sized Hollow Particles by Photochemical Degradation of Polysilane Shell Cross-Linked Micelles and Reversible Encapsulation of Guest Molecules[1]

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Manipulation of the structure and composition of macromolecules at the nanometer level provides new possibilities in the application for nanomaterials.[2,3] In particular, micro- and nanometer-sized hollow particles have been the subject of intense interest in their potential application for capsules.[4] Recently, synthetic approaches with self-assembly and templating strategies have been employed for the preparation of hollow spheres.[5,6] A self-assembling process is a powerful tool for the construction of a unique macromolecular architecture.[7] In fact, being placed into a selective solvent for one of the blocks, amphiphilic block copolymers can self-assemble into polymer micelles and/or vesicles with nanometer-sized dimensions.[8] Recently, several groups reported a new method of construction of nanometer sized particle by cross-linking of the shell of polymer micelles.[9−11]

We have also succeeded in preparing shell cross-linked micelles (SCM) from diblock coplolymers of polysilanes and poly(methacrylic acid).[12] In the system, the polysilane core is surrounded by the partially cross-linked shell of poly(methacrylic acid). Since the polysilane core part can undergo photochemical degradation,[13] it is expected to provide hollow sphere particles (hollow shell cross-linked micelles, HSCM) by a photochemical process. Herein we report synthesis of nanometer-sized hollow particles derived from polysilane shell cross-linked micelles and demonstrate that the hollow particles can undergo reversible uptake of guest molecules. During our study, Wooley's group has reported hollow particles, which were called nanocages, prepared by ozonolysis of shell cross-linked micelles with poly(isoprene)-*b*-poly(acrylic acid).[14] Our system can be generated photochemically and should provide an important technique for the further application of nanoengineering.

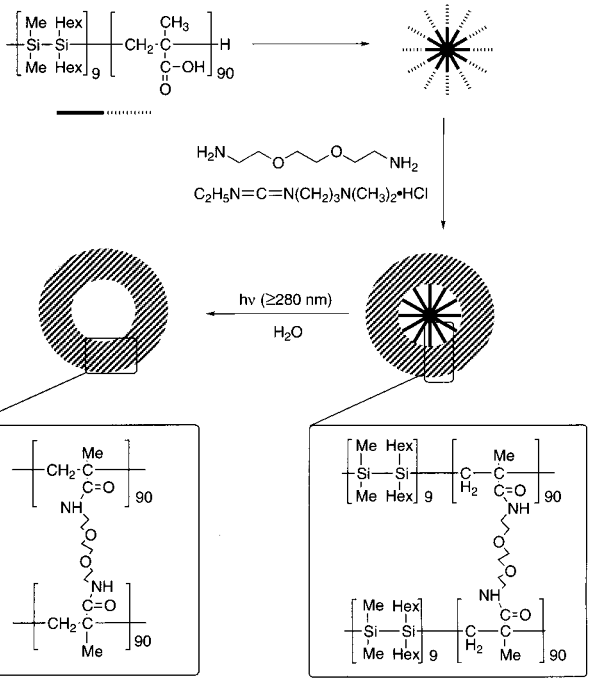

Figure 1. Schematic illustration of the synthetic pathway for hollow square particles derived from polysilane shell cross-linked micelles templates.

Poly(1,1-dimethyl-2,2-dihexyldisilene)-*b*-poly(methacrylic acid) (PMHS-*b*-PMAA) was prepared by the sequential anionic polymerization of masked disilenes[15] and trimethylsilyl methacrylate, followed by hydrolysis of the trimethylsilyl protecting group ($M_n = 9.6 \times 10^3$, $M_w/M_n = 1.3$). The composition of PMHS to PMAA, estimated by ^{1}H NMR of the block copolymer in D_2O, was 1/10. Thus, the average chemical formula of the copolymer was estimated to be $(MHS)_9$-*b*-$(MAA)_{90}$, which was evidently self-assembled in water to form polymer micelles. The formation of near-monodisperse micelles, with an intensity-averaged micelle diameter of 170 nm in water (0.2 g L^{-1}, 25 °C), was demonstrated by dynamic light scattering (DLS) studies. At this point, a rather unusually large micelle diameter of 170 nm in water should be referred. Even if the methacrylic acid units are fully stretched, the block polymer could not possibly give a spherical micelle with a diameter of 170 nm. The unusually large size of the micelles may not be explained by a simple core−shell structure of conventional micelles. Efficient packing of the rigid-rod blocks of polysilane segments should form a core domain for the polymer micelles, which could result in ordered and stable aggregates with an unusually large size.[16] At this stage, the possibility that the polymer forms vesicles instead of micelles cannot be excluded, but the formation of spherical SCMs (vide infra) supports the formation of micelles.

Then the carboxylic acid on the poly(methacrylic acid) segment of the block copolymer was subjected to the shell cross-linking reactions with 1,10-diaza-4,7-dioxadecane and 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride as schematically illustrated in Figure 1.

Finally, the polysilane core part within the shell cross-linked micelles was photodegradated (bleaching) by UV irradiation (≥280 nm) and dialysis against water produced nanometer-sized hollow particles.[17,18] In UV absorption spectra, a continuous blue shift in the absorption maximum was observed during photoirradiation (see Supporting Information), which suggests that the chain scission process of the polysilane core part within the shell cross-linked micelles did occur upon exposure.

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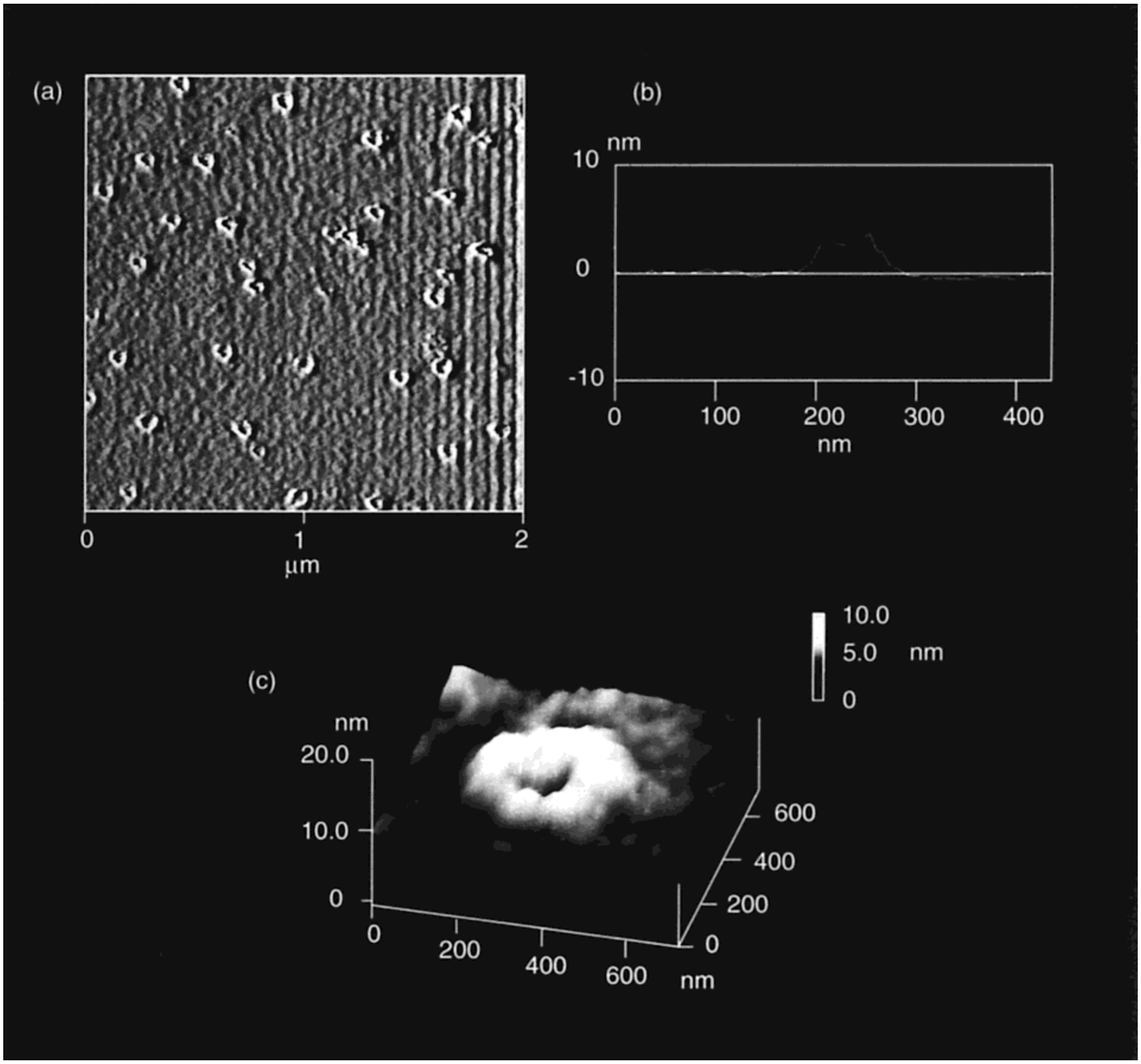

Figure 2. AFM image of (a) hollow particles on Pyrex glass plate with operating in the contact mode, (b) vertical profile of the hollow particle shown in part (a), and (c) in the tapping mode under THF wet conditions.

Some spectroscopic studies supported the formation of nanometer-sized hollow sphere particles derived from the shell cross-linked micelle templates.[19] Dynamic light scattering (DLS) studies indicated that the average hydrodynamic diameter (D_h) for the hollow particles in water was measured as about 650 nm, which was much larger than the D_h of the template shell cross-linked micelles (170 nm). The significant extent of this expansion can be explained by the swelling of the hydrophilic cross-linked poly(methacrylic acid) layer resulted in removal of the hydrophobic core. However, the diameter of the hollow particle decreased to 220 nm again in THF because of contraction of the cross-linked poly(methacrylic acid) layer under the conditions.

Images of atomic force microscopy (AFM) gave further information about the size and three-dimensional shapes of the nanometer-sized particles. Figure 2 shows AFM images of hollow particles on a Pyrex glass plate operating in the contact or tapping mode.[20] Shell cross-linked micelles appeared as clear spherical particles of about 100 nm diameter in the dry state, indicating that polysilane parts are locked into the core. However, after removal of the core within the shell cross-linked micelles, bagel (or liposome)-like objects with diameters of about 100 nm were observed as shown in Figure 2a. In vertical profiles it appears to be concave shaped, although the shells collapsed into a highly flattened form, which agrees well with their hollow-core nature (Figure 2b). The thickness of the shell is consistent with the calculated length of the cross-linked layer (ca. 30 nm). The tapping mode AFM images show clearly hollow nanospheres with diameters of about 200 nm when under the wet conditions, because the particles should be swollen to some extent under the conditions (Figure 2c).

The present system is expected to undergo encapsulation of guest molecules. Indeed, the following experiments indicate the encapsulation of 5,6-carboxyfluorescein (CF) into nanometer-sized hollow particles. A solution of the hollow shell cross-linked micelles (3 mg) and excess 5,6-carboxyfluoresce (CF) in water (10 mL) was stirred at room temperature for 4 days. After separating the complexes with CF from free dye by gel permeation chromatography with water as an eluent, fluorescence spectra of the complex were measured (3 mg/10 mL) as shown in Figure 3. Figure 3 also contains similar spectra for the SCM. The emission maximum of the entrapped dye into the shell cross-linked micelles

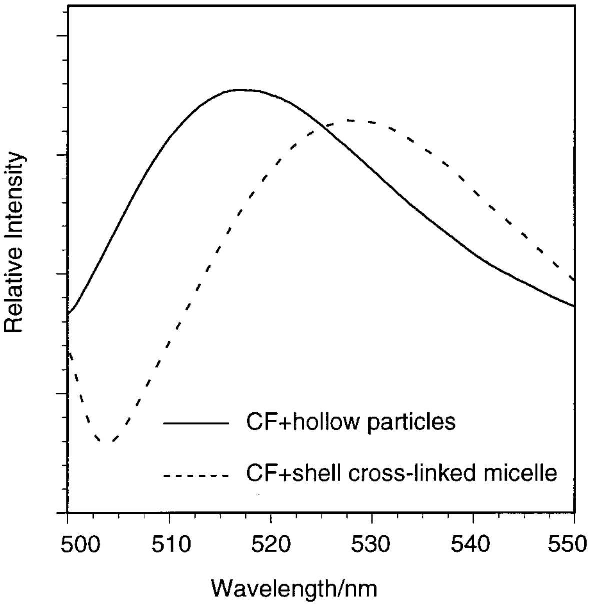

Figure 3. Fluorescence emission spectra of 5,6-carboxyfluorescein (excited at 492 nm) in hollow nanoparticles and shell cross-linked micelles in water.

is observed at 528 nm. On the contrary, a significant shift in absorption maximum is observed for the dye solubilized in the hollow particles at 518 nm, the same wavelength as that of the free dye in aqueous solution. This suggests that the dye in the hollow particles localized in an internal aqueous volume rather than in the hydrophobic domains. After dialysis against water for several days, the absorption at 518 nm disappeared gradually, indicating release of the dye (see Supporting Information).

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Supporting Information Available: UV spectral change of polysilane-incorporated shell cross-linked micelles upon photoirradiation in water (Figure 1S) and release rate of 5,6-carboxyfluorescein entrapped in hollow shell cross-linked micelles (Figure 2S) (PDF). The materials are available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Chemistry of Organosilicon Compounds 374.
(2) (a) Tomalia, *Adv. Mater.* **1994**, *6*, 529. (b) Fréchet, J. M. J. *Science* **1994**, *263*, 1710.
(3) For recent reviews on amphiphilic block polymers, see: (a) Bock, J.; Varadaraj, R.; Schulz, D. N.; Maurer, J. J. In *Macromolecular Complexes in Chemistry and Biology, Solution Properties of Hydrophobically Assosiating Water Soluble Polymers*; Doubin, P., Bock, J., Davis, R., Schulz, D. N., Thies, C., Eds.; Springer-Verlag: Berlin, 1994; p 33. (b) Tuzar, Z.; Kratochvil, P. In *Surface and Colloid Science*; Matijevic, E., Ed.; Plenum Press: New York, 1993; Vol. 15-(1).
(4) (a) Lewis, D. D. In *Biodegradable Polymers and Drug Delivery Systems*; Chansin, M., Langer, R., Eds.; Marcel Dekker: New York, 1990. (b) Lasic, D. D. *Liposomes: From Physics and Application*; Elsevier: Amsterdam, 1993. (c) Decher, G. In *Templating, Self-Assembly, and Self-Organization*; Sauvage, J.-P., Hosseini, M. W., Eds.; Pergamon: Oxford, 1996; Vol. 9, pp 507−528. (d) Chang, T. M. S. Microencapsulation (Artificial Cells). In *Polymeric Materials Encyclopedia*; Salamone, J. C., Ed.; CRC Press: New York, 1996; Vol. 6, pp 4351−4355.
(5) (a) Caruso, F.; Lichtenfeld, H.; Giersig, M.; Möhwald, H. *J. Am. Chem. Soc.* **1998**, *120*, 8523. (b) Donath, E.; Sukhorukov, G. B.; Caruso, F.; Davis, S. A.; Möhwald, H. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 2202. (c) Caruso, F.; Caruso, R.; Möhwald, H. *Science* **1998**, *282*, 1111.
(6) Wendland, M. S.; Zimmerman, S. C. *J. Am. Chem. Soc.* **1999**, *121*, 1389.
(7) (a) Lehn, J.-M. *Supermolecular Chemistry*; VCH: Weiheim, 1995. (b) Bard, A. J. *Integrated Chemical Systems*; Wiley: New York, 1995.
(8) (a) Zhang, L.; Eisenberg, A. *Science* **1995**, *268*, 1728. (b) Discher, B. M.; Won, Y.-Y.; Ege, D. S.; Lee, J. C.-M.; Bates, F. S.; Discher, D. E.; Hammer, D. A. *Science* **1999**, *284*, 1143.
(9) (a) Thurmond, K. B. II; Kowalewski, T.; Wooley, K. L. *J. Am. Chem. Soc.* **1996**, *118*, 7239. (b) Thurmond, K. B. II; Kowalewski, T.; Wooley, K. L. *J. Am. Chem. Soc.* **1997**, *119*, 6656. (c) Huang, H.; Kowalewski, T.; Remsen, E. E.; Gertzmann, R.; Wooley, K. L. *J. Am. Chem. Soc.* **1997**, *119*, 11653. (d) Wooley, K. L. *Chem. Eur. J.* **1997**, *3*, 1397.
(10) (a) Bütün, V.; Billingham, N. C.; Armes, S. P. *J. Am. Chem. Soc.* **1998**, *120*, 12135. (b) Bütün, V.; Lowe, A. B.; Billingham, N. C.; Armes, S. P. *J. Am. Chem. Soc.* **1999**, *121*, 4288.
(11) (a) Ding, J.; Liu, G. *Macromolecules* **1998**, *31*, 6554. (b) Liu, G.; Ding, J.; Stewart, S. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 835.
(12) Sanji, T.; Nakatsuka, Y.; Kitayama, F.; Sakurai, H. *Chem. Commun.* **1999**, 2201.
(13) (a) Michl, J.; Downing, J. W.; Karatsu, T.; McKinley, A. J.; Poggi, G.; Wallraff, G. M.; Sooriyakumaran, R.; Miller, R. D. *Pure. Appl. Chem.* **1988**, *60*, 959. (b) Trefonas, P.; West, R.; Miller, R. D. *J. Am. Chem. Soc.* **1985**, *107*, 2737. (c) Miyazawa, T.; Saeki, T.; Liu, C.; Kira, M. *J. Am. Chem. Soc.* **1998**, *120*, 1084.
(14) Huang, H.; Remsen, E. E.; Kowalewski, T.; Wooley, K. L. *J. Am. Chem. Soc.* **1999**, *121*, 3805.
(15) (a) Sakamoto, K.; Obata, K.; Hirata, H.; Nakajima, M.; Sakurai, H. *J. Am. Chem. Soc.* **1989**, *111*, 7641. (b) Sakamoto, K.; Yoshida, M.; Sakurai, H. *Macromolecules* **1990**, *23*, 4494.
(16) (a) Jenekhe, S. A.; Chen, X. L. *Science* **1998**, *279*, 1903. (b) Kunitake, T.; Okahata, Y.; Shimomura, M.; Yasunami, S.; Terakabe, K. *J. Am. Chem. Soc.* **1981**, *103*, 5401.
(17) A solution of the shell cross-linked micelles (47 mg) in water (10 mL) was irradiated for several minutes with a 500 W high-pressure mercury lamp equipped with selected cutoff filters ($h\nu \geq 280$ nm). After evaporating the solvent, the residual mass was washed with benzene and then transferred to a dialysis bag followed by dialysis against distilled water for 2 days. A sample of hollow particles was obtained after drying under vacuum (43 mg, 90%).
(18) Photodegradation of the polysilane core part gave linear oligosilanes with the chain length less than eight under the condition, while the final length of the oligosilane chain depends on the wavelength of the light used. Strictly speaking, the oligosilane may attach to the chain end of cross-linked poly(methacrylic acid) in the interior side of the layer.
(19) Spectral data of hollowparticles: ^{1}H NMR (D_2O, 300 MHz): δ 0.16 (brs), 0.76−1.02 (br), 1.49 (brs). ^{13}C NMR (D_2O, 75.5 MHz): δ 18.2, 39.9, 45.4, 69, 8, 126.3, 173.5. IR (KBr): 1631, 1550 (−NHC═O) cm^{-1}.
(20) Samples for AFM measurement were prepared by dipping a Pyrex glass plate, which was treated with hexamethyldisilazane, to solution of the hollow particles in THF (0.029 mg/mL) and allowing it to dry in air.

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