A Novel Method to Prepare Polysilsesquioxane Nanoparticles Possessing Bromoalkyl Groups

Yoshio Nakahara,[1] Chenghuan Ma,[2] Hiroyuki Yamamoto,[2] Fumio Oi,[2] and Keiichi Kimura*[1]
[1]*Department of Applied Chemistry, Faculty of Systems Engineering, Wakayama University,*
930 Sakae-dani, Wakayama 640-8510
[2]*Konishi Chemical IND. Co., LTD., 3-4-77 Kozaika, Wakayama 641-0007*

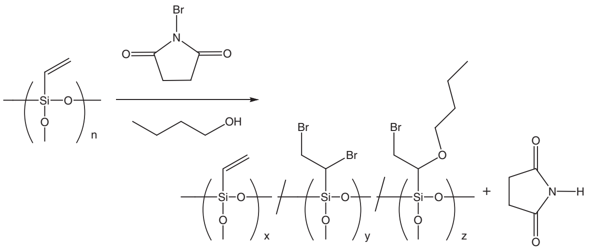
(Received May 15, 2009; CL-090481; E-mail: kkimura@sys.wakayama-u.ac.jp)

A novel method to prepare siloxane-based nanoparticles possessing bromoalkyl groups, which are reactive functional groups, by bromoalkoxylation and bromination of poly(vinylsilsesquioxane) nanoparticles using *N*-bromosuccinimide and 1-butanol was developed. No shape distortion or fusion of nanoparticles after the chemical reaction was observed by transmission electron microscopy.

Siloxane-based nanoparticles containing functional groups are of great interest because they can find applications in wide areas, such as controlled storage and release, adsorption, and catalysis. Polysilsesquioxane (PSQ) has been a promising material for preparing nanoparticles of narrow size distribution that contain a lot of functional groups because silicon atoms consisting of PSQ always have an organic group. Especially, PSQ nanoparticles possessing vinyl,[1,2] mercapto,[3–6] and amino[7–9] groups are very interesting because these functional groups are stable under normal conditions but react readily with other reactive molecules. On the other hand, there have been few reports[10] about PSQ nanoparticles possessing alkyl halides, which are applicable to Williamson etherification, cyanation, and Grignard coupling. Therefore, the development of PSQ nanoparticles possessing alkyl halides is strongly desired for preparation of important intermediates for highly functionalized siloxane-based nanomaterials.

Study of chemical reactions of poly(vinylsilsesquioxane) (PVSQ) appears in many reports.[11] Bromination and hydrobromination of PVSQ have been reported as examples of chemical reactions for introducing bromo groups. In this study, we synthesized monodisperse PVSQ nanoparticles and adopted bromoalkoxylation, in addition to bromination, using *N*-bromosuccinimide (NBS) and 1-butanol for the functionalization of PVSQ because the introduction of alkyl chains can improve the solvent dispersibility of nanoparticles. NBS is extensively used in various organic reactions as a mild bromination source, and the electrophilic bromination of alkenes proceeds via a cyclic brominium ion. When the resulting cyclic brominium ion is opened by an alcohol molecule, bromoalkoxylation proceeds. On the other hand, when the cyclic brominium ion is opened by a bromide anion, bromination proceeds. Here, we report a very convenient method to prepare PVSQ nanoparticles possessing bromoalkyl groups (Br-PVSQ) from a mixture of PVSQ nanoparticles, NBS, and 1-butanol.

The PVSQ nanoparticles were prepared by adding vinyltrimethoxysilane to an aqueous micelle solution of sodium dodecyl sulfate (SDS) with a catalytic amount of ammonia.[12] After the sol–gel reaction, a large amount of methyl ethyl ketone (MEK) was added to the aqueous solution, and then the solvents were gradually evaporated to give a MEK solution containing below 5% water. Then, precipitated SDS was removed by filteration. The mean diameter of PVSQ nanoparticles was 17 nm, determined by dynamic light scattering. The PVSQ nanoparticle can disperse in various alcoholic solvents such as ethanol, 1-butanol, and tetraethylene glycol.



Scheme 1. Synthesis of Br-PVSQ nanoparticle.

The synthesis of the Br-PVSQ nanoparticles is summarized in Scheme 1. An appropriate amount of 1-butanol was added to the MEK solution of PVSQ nanoparticles, and then only MEK was evaporated. After adding NBS to the resulting 1-butanol solution under cooling in an ice bath, the resulting mixture was stirred at 45 °C for 2 h. After cooling to room temperature, 5% aqueous sodium hydrogencarbonate solution was added to the mixture, and the Br-PVSQ nanoparticles were extracted with toluene. The purification process was only extraction, and notably no centrifugation process was needed. The toluene solution was cast on a copper grid, and the size and shape of Br-PVSQ nanoparticles were observed by transmission electron microscopy (TEM). After evaporation of toluene, the obtained white solid was characterized by FT-IR, solid-state ^{13}C NMR, elemental analysis, and thermogravimetric (TG) analysis.

FT-IR spectra of PVSQ and Br-PVSQ nanoparticles are shown in Figure 1. The large peak in the range from 1000 to 1200 cm^{-1} is assigned to the Si–O bond of the PSQ nanoparticle. The two spectra were almost the same except for some differences in the range from 2800 to 2900 cm^{-1}. The peak in this range is assigned to the C–H bond of the butoxy group. The peaks originating from the C–Br and C–O bonds were not recognized because of their overlapping with the large peak assignable to the Si–O bond. On the other hand, a peak at 1700 cm^{-1} originating from the carbonyl group of succinimide, which is a byproduct of the chemical reaction, was not detected. Figure 2 shows the solid-state ^{13}C NMR spectrum of the Br-PVSQ nanoparticles. The large *a* peak at 125–140 ppm is assigned to the unreacted vinyl group, and the *d*, *e*, and *f* peaks at 31, 19, and 14 ppm, respectively, are assigned to the alkyl chain of the butoxy group. The *b* peak is assigned to the mixture of methylene and methine groups next to the oxygen atom, and the *c* peak is

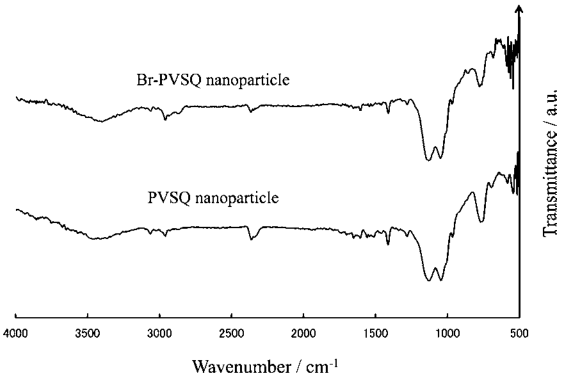


Figure 1. FT-IR spectra of PVSQ and Br-PVSQ nanoparticles in KBr pellets.

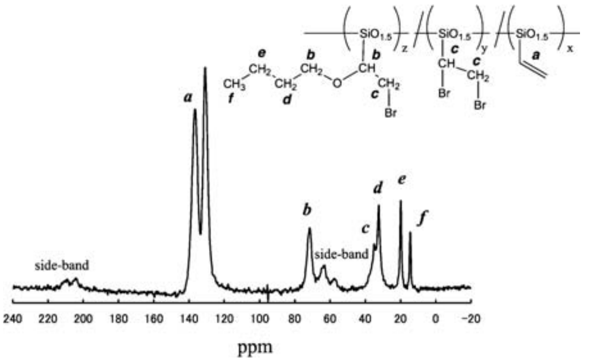


Figure 2. Solid-state ^{13}C NMR spectrum of Br-PVSQ nanoparticle.

assigned to the mixture of methylene and methine groups next to the bromo group. The peaks at 55–70 ppm and 200–215 nm are side-band peaks of the large *a* peak. In a similar way to the result of FT-IR, peaks originating from succinimide were not detected in the NMR spectrum. These results demonstrate that butoxy groups were introduced into the nanoparticle and that succinimide was completely removed in the purification process.

Next, control of the degree of Br-modification in the nanoparticles was attempted. When the chemical reaction was carried out at a molar ratio of NBS to vinyl group, 0.2, 0.5, and 1 (1-butanol exists in a large excess to both NBS and vinyl groups), the weight percents of Br were 5.1, 10.2, and 14.4, determined by elemental analysis, respectively. It was found that the larger the molar ratio of NBS to vinyl group was, the larger the weight percent of Br. The TG analyses of PVSQ and Br-PVSQ nanoparticles were made. Heating was performed in N_2 atmosphere at a rate of 10 °C min^{-1} in a range from 30 to 500 °C. In the case of the PVSQ nanoparticles, weight loss below 5% was observed. This result demonstrates that a vinyl group connected to a silicon atom is very stable on heating. On the other hand, remarkable weight loss in the range from 300 to 400 °C was observed in all cases of the Br-PVSQ nanoparticles. This phenomenon may be attributed to thermal cracking of the modified organic groups. The amount of the weight loss was dependent on the molar ratio of NBS to vinyl group in the chemical reaction. In short, the larger the molar ratio of NBS to vinyl group was, the larger the amount of the weight loss. These results show that the Br-modified amount can be controlled by the added amount of NBS with respect to vinyl groups.

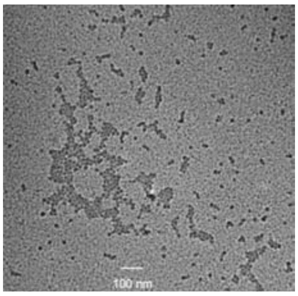


Figure 3. TEM image of Br-PVSQ nanoparticles.

Figure 3 presents the TEM image of Br-PVSQ nanoparticles. According to the chemical modification of siloxane-based nanoparticles, the chemical reaction and purification processes might transform and aggregate nanoparticles. However, in this study, monodisperse and spheral nanoparticles with about 15-nm diameter were found after the chemical reaction, and no shape distortion or fusion of nanoparticles was observed. It proves that the chemical reaction and purification processes of bromoalkoxylation and bromination using NBS were sufficiently mild to avoid the transformation and fusion of nanoparticles.

In summary, PSQ nanoparticles possessing bromoalkyl groups were synthesized under the mild synthetic conditions without distortion or fusion of nanoparticles. According to this synthetic method, the nanoparticle can be also modified by alcohol molecules, in addition to bromo groups, and, therefore, there is a possibility that functional compounds with hydroxy groups can be introduced into the PVSQ nanoparticles with ease. Further study of functionalization of bromoalkyl groups on the surface of PSQ nanoparticles is underway in our laboratory.

This study was financially supported by the Cooperation for Innovative Technology and Advanced Research in Evolutional Area (CITY AREA) program by the Ministry of Education, Culture, Sports, Science and Technology, Japan.

References

1 A. Arkhireeva, J. N. Hay, W. Oware, *J. Non-Cryst. Solids* **2005**, *351*, 1688.
2 Y. B. Kim, Y.-A. Kim, K.-S. Yoon, *Macromol. Rapid Commun.* **2006**, *27*, 1247.
3 J. Brown, R. Richer, L. Mercier, *Microporous Mesoporous Mater.* **2000**, *37*, 41.
4 S. G. Wang, J. L. Li, *Chin. Chem. Lett.* **2006**, *17*, 221.
5 J. Alauzun, A. Mehdi, C. Reye, R. J. P. Corriu, *Chem. Commun.* **2006**, 347.
6 B. Lee, Y. Kim, H. Lee, J. Yi, *Microporous Mesoporous Mater.* **2001**, *50*, 77.
7 A. van Blaaderen, A. Vrij, *J. Colloid Interface Sci.* **1993**, *156*, 1.
8 R. M. Ottenbrite, J. S. Wall, J. A. Siddiqui, *J. Am. Ceram. Soc.* **2000**, *83*, 3214.
9 B. Fei, H. Lu, R. H. Wang, J. H. Xin, *Chem. Lett.* **2006**, *35*, 622.
10 J. Ding, C. J. Hudalla, J. T. Cook, D. P. Walsh, C. E. Boissel, P. C. Iraneta, J. E. O'Gara, *Chem. Mater.* **2004**, *16*, 670.
11 R. H. Baney, M. Itoh, A. Sakakibara, T. Suzuki, *Chem. Rev.* **1995**, *95*, 1409.
12 Konishi Chemical Ind. Co., Ltd., organic-solvent dispersion of fine polysilsesquioxane particle, process for producing the same, aqueous dispersion of fine polysilsesquioxane particle, and process for producing the same, WO 2006/070846 A1, **2005**.

Published on the web (Advance View) August 1, 2009; doi:10.1246/cl.2009.876