

Preparation and Isolation of Cage-like Oligosilsesquioxane (POSS) Containing Carboxyl Side-chain Groups

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Abstract

Silsesquioxanes (SQs) have attracted much attention in the research fields of materials science. Since SQs contain siloxane bond frameworks and the various organic side-chain groups, they indicate high thermal stabilities and the remarkable compatibilities with organic materials such as polymers. In particular, soluble SQ compounds containing reactive side-chain groups can afford the hybrid materials connected with organic materials by covalent bond. Among these reactive-group-containing SQs, there are only a few synthetic examples of SQs with acidic groups, such as carboxyl side-chain groups, because carboxyl-group-containing organotrialkoxysilanes as starting materials are unstable. So far, as a few examples of soluble carboxyl-group-containing SQs, we have reported the preparation of rod-like polySQs by the hydrolytic condensation of 2-cyanoethyltriethoxysilane using aqueous NaOH¹⁾ and the modification reaction of amino-group-containing rod-like polySQs with succinic anhydride.²⁾ On the other hand, to obtain a cage-like oligoSQ (POSS) containing such side-chain groups, it is necessary the modification reaction.^{3), 4)}

In this study, to obtain a POSS containing carboxyl side-chain groups by hydrolytic condensation method, we investigated the reaction of 3-(triethoxysilyl)propyl succinic anhydride (TESPSA) using aqueous tetra-*n*-butylammonium hydroxide ((*n*-Bu)₄N·OH) as a catalyst. Then, POSS octamer (T₈-POSS) was isolated by treatment with clay mineral.

The preparation of SQs containing carboxyl side-chain groups was performed by the following procedure: (*n*-Bu)₄N·OH was added to TESPSA with stirring and this solution was further stirred for 2 h at room temperature. Then, the solution was heated (*ca.* 50-60°C) in an open system until the solvent was completely evaporated. After the resulting crude product was maintained at 100°C for *ca.* 2 h, acetone was added to this product at room temperature. Then, this solution including (*n*-Bu)₄N·OH was neutralized by adding aqueous HCl and this solution was evaporated. After acetone was added again to the resulting product, soluble-part was isolated by filtration and this solution was evaporated. Then, the resulting solid product was washed with chloroform and dried under reduced pressure to yield SQ containing carboxyl side-chain groups (Scheme 1a). The ²⁹Si NMR spectrum of the product in DMSO-*d*₆ indicated that the product was a mixture of POSSs as main products and SQs of unknown structures as minor products.

Therefore, we investigated the isolation of T₈-POSS by adsorption/desorption to a clay mineral. This was performed by the following procedure: After the SQ mixture obtained by the aforementioned procedure and Montmorillonite as a clay mineral were mixed in water, the resulting suspension was stirred at room temperature and the insoluble-part was collected by filtration. Then, acetone was added to the resulting solid product and the acetone-soluble-part was corrected by filtration. Finally, the resulting solution was evaporated and dried under reduced pressure to obtain the product (Scheme 1b). It was confirmed that the product was only T₈-POSS by the ²⁹Si NMR spectrum.

References

- 1) H. Toyodome, Y. Kaneko, K. Shikinaka, and N. Iyi, *Polymer*, **53**, 6021 (2012).
- 2) Y. Kaneko and N. Iyi, *Z. Kristallogr.*, **222**, 656 (2007).
- 3) K. Tanaka, F. Ishiguro, and Y. Chujo, *J. Am. Chem. Soc.*, **132**, 17649 (2010).
- 4) A. Boulanger, G. Gracy, N. Bibent, S. Devautour-Viont, S. Clément, and A. Mehdi., *Eur. J. Inorg. Chem.*, 143 (2012).

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