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Effect of reaction temperatures/pressures/times on the structures of ammonium-functionalized POSSs prepared using a superacid catalyst

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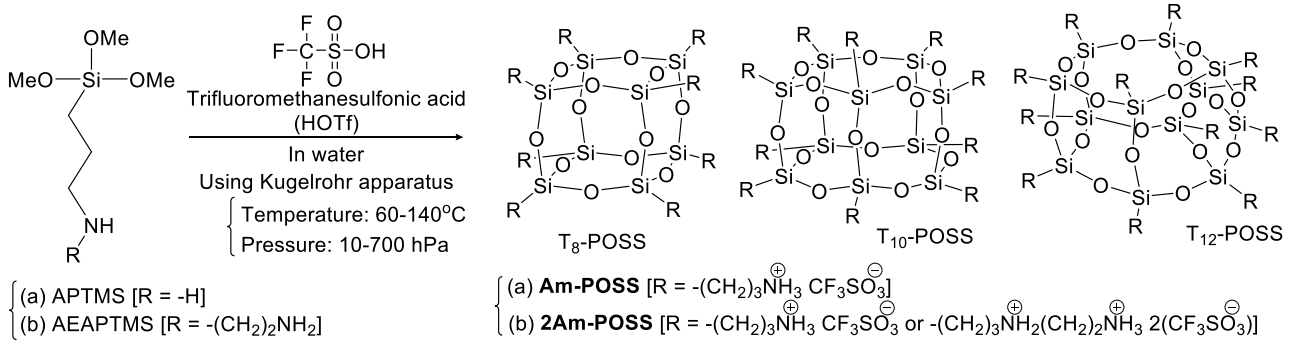
Abstract

Polyhedral oligomeric silsesquioxanes (POSSs) containing reactive groups, such as amino (ammonium) groups, have attracted much attention because they allowed to hybridize with organic compounds by covalent bonds. In ammonium-functionalized POSSs, a highly symmetrical POSS octamer (T_8-POSS) was preferentially prepared,[1] whereas the preparation of large-sized POSSs, *e.g.*, POSS decamer (T_{10}-POSS) and POSS dodecamer (T_{12}-POSS), was limited. So far, it has been reported that POSS mixture with a high proportion of T_{10}-POSS was prepared by rearrangement reaction from T_8-POSS.[2] On the other hand, there have been no reports regarding the preferential preparation of large-sized POSSs containing ammonium side-chain groups from amino-group-containing organotrialkoxysilanes (silane coupling agents) by hydrolytic condensation.

Recently, we have found that ammonium-functionalized POSSs were easily prepared in higher yield with a shorter reaction time by the hydrolytic condensation of 3-aminopropyltrimethoxysilane (APTMS)[3] and 3-(2-aminoethylamino)propyltrimethoxysilane (AEAPTMS),[4] respectively, using a superacid trifluoromethane- sulfonic acid (HOTf) as a catalyst in water by heating in an open system at *ca.* 50–60°C until the solvent completely evaporated. In addition, we also found that size of POSSs could be controlled by changing the reaction solvents, *i.e.*, the main products were T_8-POSS in water and T_{10}-POSS in 1-hexanol, respectively.[5] However, there are still many unclear points on the correlation between POSS sizes and reaction conditions.

In this study, hydrolytic condensation of APTMS and AEAPTMS was performed using HOTf aqueous solution as a catalyst and a solvent at various temperatures, pressures, and times using a Kugelrohr apparatus (Scheme 1). Consequently, a POSS mixture with a high proportion of T_8-POSS was obtained under the conditions of a pressure of 10 hPa and temperatures of 60, 80, 100, 120, and 140°C on the Kugelrohr apparatus. Under these reaction conditions, the solvent was distilled off and the reaction was completed within 2.5 h. On the other hand, when the reactions were performed under the conditions at temperatures of 120 and 140°C and pressure of 700 hPa on the Kugelrohr apparatus, the proportion of T_{10}-POSS in the POSS mixture increased. Under these reaction conditions, it took relatively long time (*ca.* 4.0–6.0 h) to distill off the solvent and complete the reactions. These results indicate that T_{10}-POSS is easy to form by the distilling off the solvent at higher temperatures taking longer times. Based on the above results, T_{10}-POSS is expected to be thermodynamically more stable than T_8-POSS.



Scheme 1. Preparation of (a) **Am-POSS** and (b) **2Am-POSS** by hydrolytic condensation of APTMS and AEAPTMS, respectively, using HOTf aqueous solution under the following conditions: temperatures and pressures of Kugelrohr apparatus were ranges of 60–140°C and 10–700 hPa, respectively.

References

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