XX International Sol-Gel Conference
October 25-30, 2019, St. Petersburg, Russia

Temperature-responsive behavior of POSSs containing ammonium side-chain groups

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Abstract

Most of temperature-responsive materials are organic polymers, *e.g.*, poly(*N*-isopropylacrylamide) (PNIPAM), whereas temperature-responsive oligomers are not common. In particular, to the best of our knowledge, temperature-responsive materials consisting of inorganic oligomers have not been reported. Polyhedral oligomeric silsesquioxanes (POSSs) are cage-like inorganic (siloxane) oligomers, which have thermal and chemical stabilities as inorganic compounds, as well as solubilities as organic compounds. So far, we have reported that ammonium-functionalized POSSs could be prepared by the hydrolytic condensation of amino-group-containing organotrialkoxysilanes using a superacid trifluoromethanesulfonic acid (HOTf) in higher yield with shorter reaction time.[1,2] Furthermore, the effect of the reaction solvents on the preferential formation of crystalline cage-like octamer (T_8-POSS) and amorphous cage-like decamer (T_{10}-POSS) was also investigated.[3,4]

In this study, we found that ammonium-functionalized T_8-POSS with triflate anion (OTf^-) as a counterion (**Am-T8-POSS-OTf**, Figure 1a) in water indicated temperature responsiveness. When aqueous suspension of **Am-T8-POSS-OTf** was heated to 65 °C, it became transparent. Then, when this transparent aqueous solution was cooled to 40 °C, it became turbid (Figure 2). Since these behaviors were observed even after heating and cooling repeatedly, we consider that **Am-T8-POSS-OTf** is regarded as a temperature responsive material.

For comparison, the temperature-responsive properties of ammonium-functionalized T_8-POSS with chloride anion (Cl^-) as a counterion (**Am-T8-POSS-Cl**, Figure 1b) and T_8-POSS (with OTf^- counterion) containing two ammonium groups in the repeating unit (**2Am-T8-POSS-2OTf**, Figure 1c) were also investigated in water by heating and cooling. Consequently, they were transparent at 5–90 °C (Figure 3,4), indicating no temperature responsiveness. Furthermore, when ammonium-functionalized T_{10}-POSS with OTf^- as a counterion (**Am-T10-POSS-OTf**, Figure 1d) was heated and cooled in water, it did not indicate temperature responsiveness (Figure 5).

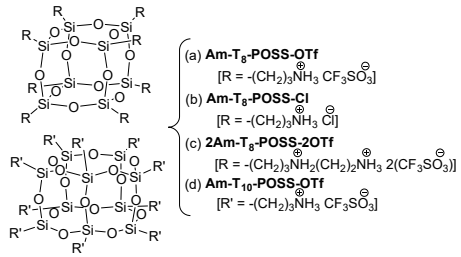

Figure 1. Structures of ammonium-functionalized POSSs.

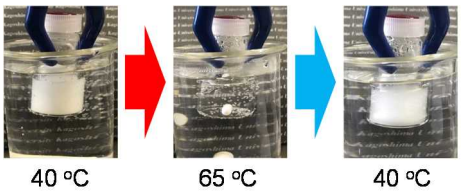

Figure 2. States of **Am-T8-POSS-OTf** in water

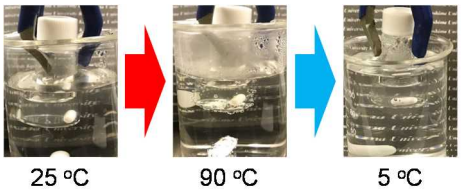

Figure 3. States of **Am-T8-POSS-Cl** in water

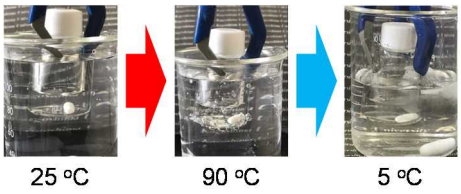

Figure 4. States of **2Am-T8-POSS-2OTf** in water

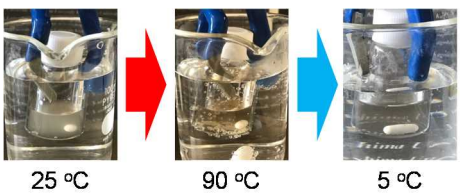

Figure 5. States of **Am-T10-POSS-OTf** in water

References

1. Y. Kaneko, M. Shoiriki, T. Mizumo, *J. Mater. Chem.*, **2012**, *22*, 14475.
2. T. Tokunaga, M. Shoiriki, T. Mizumo, Y. Kaneko, *J. Mater. Chem. C*, **2014**, *2*, 2496.
3. K. Imai, Y. Kaneko, *Inorg. Chem.*, **2017**, *56*, 4133.
4. T. Matsumoto, Y. Kaneko, *Chem. Lett.*, **2018**, *47*, 864.

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