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Preparation of soluble polysilsesquioxane containing macrocyclic structure by sol-gel reaction and metal ions capture

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Abstract

Polymers containing macrocyclic structures, that can capture atoms or molecules depending on the ring size and the functional groups, are expected as metal scavengers and stationary phases for chromatographic separation. However, only a few studies regarding the preparation of such polymers containing macrocyclic structure.[1] On the other hand, silsesquioxanes (SQs) have attracted much attention in the fields of organic-inorganic hybrid materials because they are inorganic materials indicating remarkable compatibility with organic compounds such as polymers, in addition to exhibiting superior thermal, mechanical, and chemical stabilities due to siloxane (Si-O-Si) bond frameworks. However, the regularly structured soluble polySQs (PSQs) have only been obtained in limited cases.[2,3] In this study, we found that soluble PSQ containing macrocyclic structure (PSQ-MC) was successfully prepared by the hydrolytic condensation of dual-site silane coupling agent, bis{3-[3-(trimethoxysilyl)propylthio]propyl}phthalate (BTPP),[4] using HCl as a catalyst in ethyl acetate/acetone mixed solvent. In addition, we investigated the capture of metal ions using PSQ-MC.

PSQ-MC was prepared by the following procedures: Acetone solution of HCl was added to BTPP in ethyl acetate with stirring at room temperature and this solution was further stirred for 24 h. Then, the solution was heated (*ca*. 50 °C) in an open system until the solvent was completely evaporated (Scheme 1). After the product was dissolved in ethyl acetate, the solution was added to toluene. Then, the toluene-insoluble part was recovered by decantation to remove the low molecular weight components. PSQ-MC was soluble in organic solvents, such as DMSO, acetone, ethyl acetate, and chloroform. ^{1}H NMR spectrum of PSQ-MC exhibited the peaks corresponding to the side chain structure of the polymer. The weight average molecular weight of PSQ-MC estimated by GPC was *ca*. 3.8×10^4. Solid-state ^{29}Si NMR spectrum exhibited broad peaks in the T^3 and T^2 regions. Their integral ratio was *ca*. 1:1, which exhibited the presence of large amount of silanol (Si-OH) groups in the product. Because PSQ-MC was soluble polymer with high molecular weight, we assume that this PSQ is not a polymer with random structure. Conversely, ladder-like PSQs are generally known as soluble PSQ. However, since PSQ-MC contained a large amount of silanol groups, it seems that the present PSQ is not ladder-like PSQ, which has only a small amount of silanol groups. Detailed studies on its structure are now in progress.

Furthermore, we investigated the capture of Pd ions using PSQ-MC. $PdCl_2$ was dissolved in HCl aq. and this solution was added to chloroform solution of PSQ-MC. Then, this mixture was stirred for 30 min. Consequently, we visually confirmed that chloroform layer was colored. EDX pattern of the solid product obtained by drying the chloroform layer exhibited the peaks assigned to Pd. Therefore, PSQ-MC has the capability to capture Pd ions.

References

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