Preparation and Characterization of Polyaminophenylsilsesquioxane Particles by Two-step Acid–Base-catalyzed Sol–Gel Process

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Spherical polyaminophenylsilsesquioxane ($H_2NC_6H_4$-$SiO_{3/2}$) particles were prepared by a two-step acid–base-catalyzed sol–gel process, and we found that the particles showed the glass transition behavior. Amino groups in the $H_2NC_6H_4$-$SiO_{3/2}$ particles were partially changed to amido ones by acetylation using acetic anhydride.

A variety of silica-based inorganic–organic hybrid particles have been prepared by the sol–gel method.[1–12] The preparation process of the particles is roughly divided into two ways. One is the surface modification of silica particles with trifunctional organoalkoxysilane,[1–3] and the other is the use of trifunctional organoalkoxysilane as a starting alkoxide,[4–12] where an organic functional group chemically bonds to a silicon atom. The particles prepared by the latter process are often referred to as polyorganosilsesquioxane ($RSiO_{3/2}$, R: organic group) particles. Among the silica-based inorganic–organic hybrid particles, the particles including amino groups have attracted considerable attention, because amino groups act as reactive sites.[1,3,4,11] As an application of amino groups, it was reported that proton-conductive membranes were obtained by the formation of ion complexes between amino groups in polyaminopropylsilsesquioxane and various kinds of acids.[13]

On the other hand, we found that polyphenylsilsesquioxane ($C_6H_5SiO_{3/2}$) particles prepared by a two-step acid–base-catalyzed sol–gel process exhibited the glass transition and that the particles were thermally softened by heating above the glass transition temperature (T_g).[12] This phenomenon can be applied to the preparation of monolithic materials. For example, $C_6H_5SiO_{3/2}$ thick films with high transparency were formed by the electrophoretic deposition of the particles and a subsequent heat treatment above T_g of the particles.[10] Moreover, $C_6H_5SiO_{3/2}$ can also be used as proton-conductive materials by incorporating sulfonic groups in phenyl groups.[14] Thus, it is expected that $C_6H_5SiO_{3/2}$-based novel materials with thermal softening behavior are obtained by incorporating organic functional groups into phenyl groups of the particles.

In the present study, polyaminophenylsilsesquioxane ($H_2NC_6H_4SiO_{3/2}$) particles have been prepared from aminophenyltrimethoxysilane ($H_2NC_6H_4Si(OCH_3)_3$). As a model reaction for further modification of the particles, acetylation of the amino groups to amido ones in the $H_2NC_6H_4SiO_{3/2}$ particles was also performed by using acetic anhydride ($(CH_3CO)_2O$).

Commercially available $H_2NC_6H_4Si(OCH_3)_3$ (mixed isomers: typically 60–70% para, 30–40% meta, Gelest, Inc.) dissolved in ethanol (EtOH) was firstly hydrolyzed with 0.01 mass % hydrochloric acid at room temperature for 3 h. Then, the resultant $H_2NC_6H_4Si(OCH_3)_3$ sol was added to 4 mass % aqueous ammonia all at once. Microparticles were formed just after the addition of the sol to the aqueous ammonia, and the sol became opaque. The sol was additionally stirred for 2 h at room temperature with the stirring rate of around 1300 rpm. The molar ratio of $H_2NC_6H_4Si(OCH_3)_3$:EtOH:H_2O (in hydrochloric acid):H_2O (in aqueous ammonia) was fixed at 1:20:20:180. The particles were collected from the sol by centrifugation and dried under vacuum.

For the acetylation of the amino groups in $H_2NC_6H_4SiO_{3/2}$ particles, the particles were dispersed in distilled water, and then $(CH_3CO)_2O$ was added to the suspension and stirred for 2 h. Two chemical equivalents of $(CH_3CO)_2O$ for one amino group in $H_2NC_6H_4SiO_{3/2}$ particles were added in the suspension. The particles were collected with a membrane filter, washed with distilled water of more than 1×10^{-3} m^3, and dried under vacuum.

Scanning electron microscopy (SEM) (JSM-5300, JEOL) was used for observation of shape and size of the particles. Fourier transform infrared (FT-IR) spectra of $H_2NC_6H_4SiO_{3/2}$ particles were obtained by the KBr pellet method using an FT-IR spectrophotometer (Spectrum GX, Perkin-Elmer). Thermal behavior of $H_2NC_6H_4SiO_{3/2}$ particles was examined from differential scanning calorimetry (DSC) curves of repeated heating and cooling runs under 20 °C/min (Pyris1 DSC, Perkin Elmer).

Figure 1 shows SEM photographs of (a) $H_2NC_6H_4SiO_{3/2}$ and (b) acetylated $H_2NC_6H_4SiO_{3/2}$ particles. Spherical $H_2NC_6H_4SiO_{3/2}$ particles with an average diameter of 1 µm are observed, and a size distribution of the particles is very narrow (Figure 1a). After acetylation (Figure 1b), no morphological change of the particles is observed in comparison with the morphology of the as-prepared particles.

Figure 2 shows FT-IR spectra of (a) $H_2NC_6H_4SiO_{3/2}$ and (b) acetylated $H_2NC_6H_4SiO_{3/2}$ particles. The spectrum of $C_6H_5SiO_{3/2}$ particles prepared from phenyltrimethoxysilane ($C_6H_5Si(OCH_3)_3$) under the same preparation condition is also shown for comparison in Figure 2c. The bands at around 1130 and 1600 cm^{-1} in all the particles are assigned to Si–O–Si and C–H (benzene ring) bonds, respectively.[15] The bands at 700 and 1430 cm^{-1} attributed to Si–C bonds are also observed in all the particles.[15] In Figures 2a and 2b, the two bands at around 1270 and 1300 cm^{-1} ascribed to C–N bonds are observed.[16] In addition, the bands at around 1580 and 1620 cm^{-1} are attributed to $-NH_3^+$ and $-NH_2$, respectively.[17] These results indicate that

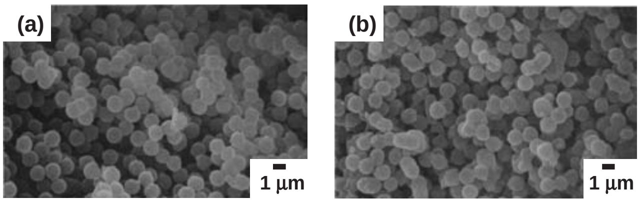

Figure 1. SEM photographs of (a) $H_2NC_6H_4SiO_{3/2}$ and (b) acetylated $H_2NC_6H_4SiO_{3/2}$ particles.

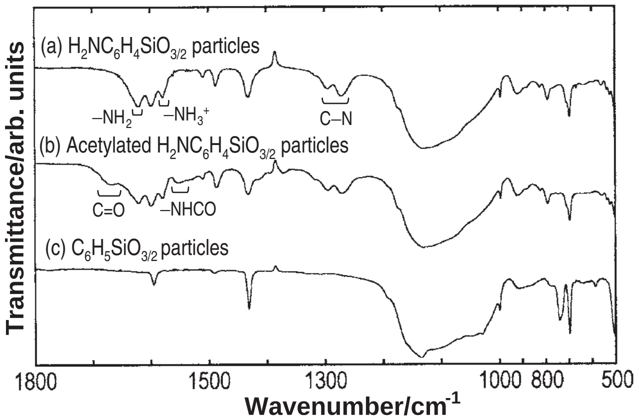

Figure 2. FT-IR spectra of (a) $H_2NC_6H_4SiO_{3/2}$ and (b) acetylated $H_2NC_6H_4SiO_{3/2}$ particles. A spectrum of pure $C_6H_5SiO_{3/2}$ particles prepared from $C_6H_5Si(OCH_3)_3$ is also shown for comparison (c).

amino groups chemically bond to phenyl groups through C–N bonds in the obtained particles and that some amino groups are protonated by residual water. Furthermore, in the acetylated $H_2NC_6H_4SiO_{3/2}$ particles (Figure 2b), new bands at around 1550 and 1670 cm^{-1} assigned to –NHCO and C=O, respectively, are observed,[16] meaning that the small amounts of amino groups are converted into amido ones. Further study of experimental conditions such as the amount of $(CH_3CO)_2O$, reaction time, and the choice of solvents is needed to increase the conversion ratio of amido groups.

Figure 3 shows DSC heating curves in the second heating run from 25 to 200 °C for (a) $H_2NC_6H_4SiO_{3/2}$ and (b) acetylated $H_2NC_6H_4SiO_{3/2}$ particles. The DSC curve for $C_6H_5SiO_{3/2}$ particles prepared from $C_6H_5Si(OCH_3)_3$ is also shown for comparison in Figure 3c. In all the particles, it is presumed that the evaporation of residual solvents such as EtOH and water occurred on the first heating process. Consequently, the same heating was carried out again after the first heating process from 25 to 200 °C. In all the particles (Figures 3a–3c), an endothermic change attributable to the glass transition is observed in the range 125–150 °C, suggesting that $C_6H_5SiO_{3/2}$ derivative particles are also thermally softened by a heat treatment above T_g, as well as pure $C_6H_5SiO_{3/2}$ particles. Actually, we confirmed that all the samples were thermally softened after the DSC measurements. These results indicate that several kinds of materials with thermal softening behavior can be prepared by incorporating organic functional groups in phenyl groups. Moreover, $H_2NC_6H_4SiO_{3/2}$ particles may be used as proton-conductive materials by reacting amino groups in the particles with acids.

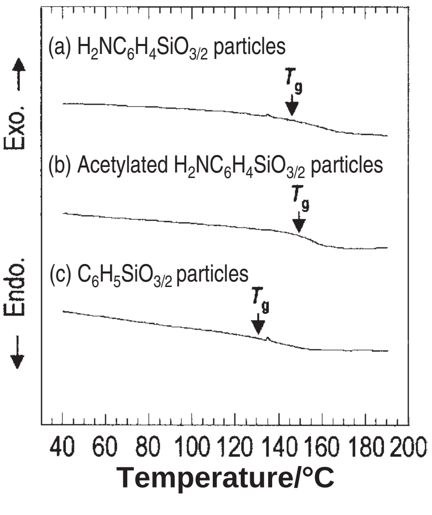

Figure 3. DSC curves in the second heating run from 25 to 200 °C at heating and cooling rate of 20 °C/min for (a) $H_2NC_6H_4SiO_{3/2}$ and (b) acetylated $H_2NC_6H_4SiO_{3/2}$ particles. A curve of pure $C_6H_5SiO_{3/2}$ particles prepared from $C_6H_5Si(OCH_3)_3$ is also shown for comparison (c).

In conclusion, we have prepared $H_2NC_6H_4SiO_{3/2}$ particles by the two-step acid–base-catalyzed sol–gel process and found that the particles exhibited the glass transition. The acetylation of the amino groups to amido ones in the $H_2NC_6H_4SiO_{3/2}$ particles was also succeeded. The success in preparing $H_2NC_6H_4SiO_{3/2}$ particles should open the door to design new inorganic–organic hybrids with thermal softening behavior.

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