

Preparation of Nano-Particles of Poly(phenylsilsesquioxane)s by Emulsion Polycondensation of Phenylsilanetriol Formed in Aqueous Solution

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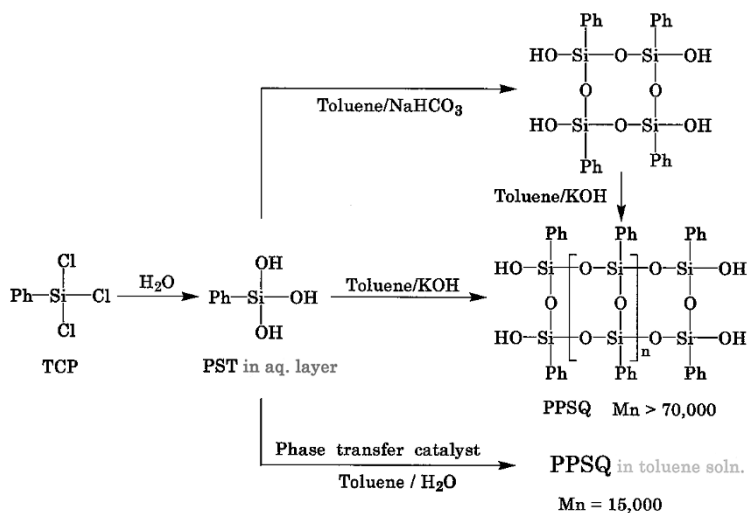
ABSTRACT: Spherical nano-particles of Poly(phenylsilsesquioxane) (PPSQ) were prepared by emulsion polymerization of phenylsilanetriol (PST) that had been formed in aqueous solution after hydrolysis of trichlorophenylsilane (TCP). The average size of the resultant particles was controlled from 30 nm to 110 nm in diameter by changing the amount of the emulsifier added to the solution. The PPSQ forming the particles was low molecular weight oligomer, consisting of silanol groups that can be utilized as functional groups for further chemical modification.

KEY WORDS Poly(phenylsilsesquioxane) / Nano-Particle / Emulsion Polymerization / Trichlorophenylsilane /

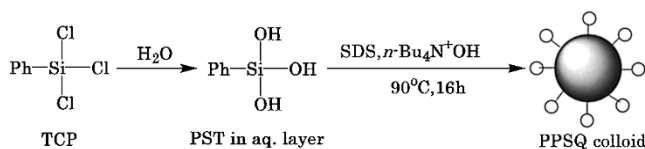
Poly(phenylsilsesquioxane) (PPSQ) is one of the most extensively investigated polymers of silsesquioxane and has been convinced to have wide application because of their supreme thermal and electrical properties.^{1,2} In 1960, Brown *et al.* first reported that the hydrolytic polycondensation of phenyltrichlorosilane (TCP) gave a PPSQ with ladder structure.³ Its structure confirmation and formation mechanism, however, has ever since been controversial among the researchers in this field. In the general synthetic method for PPSQ, TCP is hydrolyzed in aqueous/organic bilayer system, and the resultant hydrolysate is extracted into the organic layer and subjected to the alkali-catalyzed dehydrative polycondensation in organic solvent such as toluene. Recently, we have shown that the hydrolysate extracted in the organic layer consists of oligomers of phenylsilanetriol (PST) that is the primary hydrolysis product. The monomeric PST is highly soluble in aqueous media and resides in the aqueous

layer. We have also shown that PPSQ with a highly ordered ladder structure can be obtained when the monomeric PST isolated from the aqueous layer is subjected to the KOH-catalyzed polycondensation in refluxing toluene.^{4,5} Furthermore, we synthesized a tetracyclo(phenylsilsesquioxane) (T₄) by the oligomerization of PST by the catalysis of a weak base, NaHCO₃, and then polymerized it by the KOH-catalyzed polycondensation in toluene to obtain the ladder PPSQ.⁶ More recently, we conducted the polycondensation of PST in a refluxing toluene/water bilayer system added with a phase transfer catalyst to obtain PPSQ in high yield (Scheme 1) without passing the isolation step of PST and its oligomers.⁷

With increasing interest in designing micro- and nano-structured materials, many attempts have been made to obtain nano-particles with suitable shapes.^{8,9} Minami *et al.*, for example, prepared PPSQ particles from organoalkoxysilane by using the sol-gel technique



Scheme 1. Preparation of PPSQ by dehydrative polycondensation of PST formed from TCP.



Scheme 2. Preparation of nano-particles of PPSQ from PST in aqueous solution.

and used them for preparing PPSQ thick films on a glass substrate for application to micro-optic devices.¹⁰ However, the PPSQ particles prepared thus far were mainly of micron-size with a wide size distribution, and no report has appeared on the preparation of nano-particles of PPSQ.

The present study discloses the first preparation of PPSQ nano-particles by emulsion polymerization of PST formed in the aqueous layer. The reaction is conducted in the presence of emulsifier (Scheme 2) with which the size-control of the PPSQ particles can be possible.

EXPERIMENTAL

Materials

TCP, sodium dodecyl sulfate (SDS), and tetra-*n*-butylammonium hydroxide (TBAH, 40% in water) were supplied by Tokyo Kasei Kogyo Co., Ltd. (Tokyo) and used without purification. Toluene was distilled over sodium metal before use.

Measurements

Transmission electron microscopy (TEM) was performed on a JEOL TEM-2010/SP electron microscope operated at an acceleration voltage of 200 kV. Using the TEM photographs of the particles, the average diameter and its standard deviation were determined for the arbitrarily selected fifty images. Dynamic light scattering (DLS) was measured on an Otsuka Electronics DLS-7100 instrument using helium-neon ion laser with a wavelength of 632.8 nm. The scattering data were analyzed according to the cumulant method. ²⁹Si NMR spectra were measured at 99.3 MHz on a Bruker ARX-500 spectrometer in CDCl₃ with tetramethylsilane (TMS) as the external standard. The number- (*M_n*) and weight-average (*M_w*) molecular weights were determined by gel permeation chromatography (GPC). The analyzer was composed of a Shimadzu LC-10A pump, a Shodex RI SE-31RI detector, and a Shimadzu C-R7A Chromatopac data processor. A combination of two polystyrene gel columns of Toso TSK gel G4000H₈ and G2500H₈ were used with chloroform as the eluent at 35°C. The molecular weight was calibrated according to polystyrene standards.

Hydrolysis of TCP

A solution of TCP (4.3 g) in toluene (100 mL) was added dropwise to a water (500 mL) under vigorous agitation at 0°C for a period of 1 h. After the addition, the mixture was kept stirred at the same temperature for 15 min, and the aqueous layer was separated from the toluene layer. Then, the pH of the aqueous layer was adjusted to 7.0 with a saturated solution of NaHCO₃. The finally obtained aqueous layer (560 mL in volume) contained 3.2 g of PST (90% yield), as estimated from the amount of the oligomeric hydrolysate isolated from the toluene layer.

Preparation of PPSQ Particles

An aliquot (100 mL) of the aqueous solution of PST obtained above was added with SDS (0–3.0 wt% relative to the water) and stirred vigorously at 0–10°C for 10 min. A small amount of TBAH (0.7 mol% relative to the PST) was added to it as a phase transfer catalyst, and the solution was heated at 90°C for 16 h with stirring to obtain a homogeneous colloidal solution of PPSQ that was almost transparent. For isolating the product, the solution was frozen in a freezer at –18°C overnight and defrosted at room temperature. The white powders, having resulted in the aqueous solution, were filtered, washed with water, and dried thoroughly in vacuo (60% yield).

RESULTS AND DISCUSSION

Effect of Emulsifier on the Formation of PPSQ Particles

We showed in our former papers⁴ that the hydrolysis of TCP in toluene/water bilayer system yields PST as well as a small amount of its primary condensates (dimer, trimer, and tetramer) in the aqueous layer. Neutralization of this aqueous layer undergoes slow dehydrative condensation of PST at room temperature to make the oligomers precipitating out from the solution. In the present study, we put an anionic emulsifier into the neutralized aqueous layer to conduct the emulsion polycondensation of PST in the aqueous medium. SDS was first examined because it is a typical emulsifier that has often been adopted in this type of reactions, finding out that it was quite effective as the emulsifier in the present polymerization.

When the emulsion polymerization was conducted at 90°C for 16 h with 0.5–3.0 wt% of SDS relative to the amount of PST involved in the aqueous solution, a transparent colloidal dispersion was formed without coagulation occurring. When the aqueous PST solution was directly heated at the same reaction conditions without the emulsifier added, rapid coagulation was induced. Therefore, addition of the emulsifier was

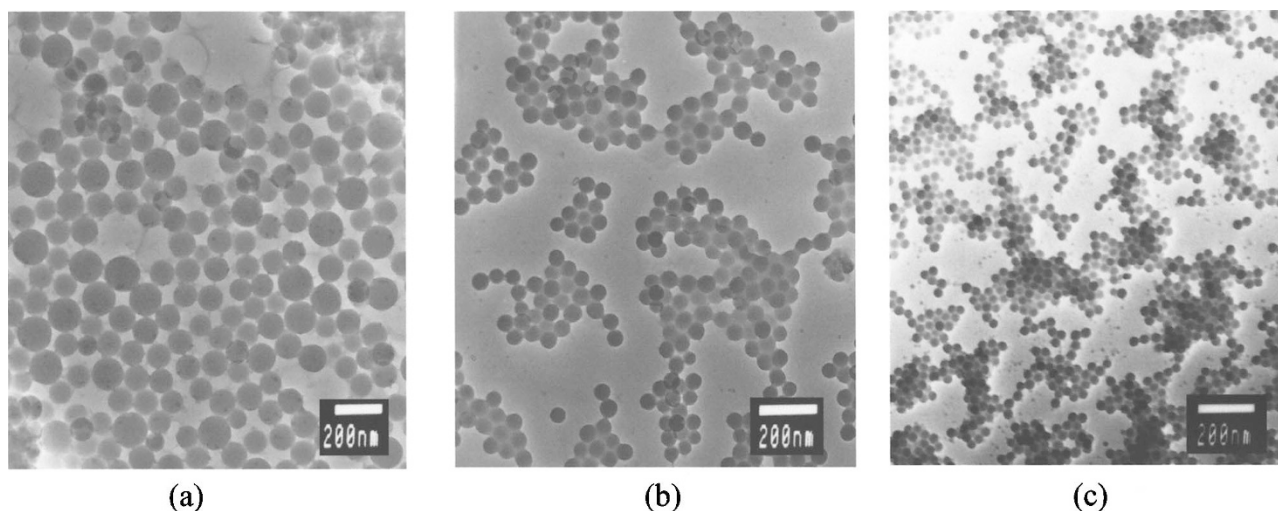


Figure 1. TEM of the PPSQ particles prepared at 90° in the presence of (a) 0.5, (b) 1.0, and (c) 2.0 wt% of SDS.

Table I. The particle sizes of PPQS measured by TEM and DLS

| Concentration of SDS wt% | TEM | | DLS | |
|--------------------------------|------------------------|--------------------------|------------------------|--------------------------|
| | Average diameter nm | Standard deviation nm | Average diameter nm | Standard deviation nm |
| 0.5 | 110 | 14.4 | 114 | 19.0 |
| 1.0 | 57 | 3.3 | 59 | 11.1 |
| 2.0 | 31 | 2.1 | 49 | 13.1 |

known to be effective for the colloidal formation from PST. Figure 1 shows the TEM photographs of the particles obtained with different amounts of SDS (0.5–2.0 wt%). It is known that strictly spherical particles having nanometer size have been produced in each case and that the size distribution is narrow. With 3.0 wt% of SDS, however, no particle image was observed, probably because the polycondensate of PST had been well solubilized or emulsified in the solution. Table I summarizes the average diameters of the spherical particles obtained for the three cases. It is shown that the particle diameter decreases from 110 nm to 31 nm with increasing amount of SDS from 0.5 wt% to 2.0 wt%. The size distribution of the particles also decreases with the increased SDS concentration, as evidenced by the standard deviation (14.4–2.1 nm). These results indicate that the number and size of the particles can be controlled by the amount of emulsifier added to the aqueous PST solution. Although the particle size may also depend on other factors, *e.g.*, the initial concentration of PST, the effect of the emulsifier amount is to be crucial.

Figure 2 shows the DLS histograms of the resultant colloidal dispersions. The average diameters of the particles are determined to be 114, 59, and 49 nm for the dispersions containing 0.5, 1.0, and 2.0 wt% of SDS, respectively. The larger sizes compared with those observed by TEM photographs can be attributed to the surface solvation and surfactant accumulation. The histogram shifts to the smaller diameter region with in-

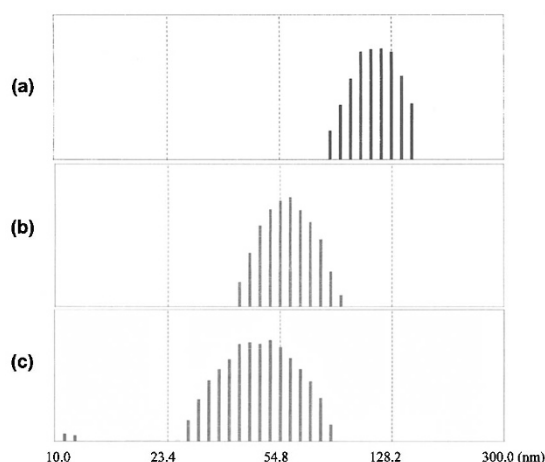


Figure 2. DLS histograms of colloidal PPSQ prepared at 90° C in the presence of (a) 0.5, (b) 1.0, and (c) 2.0 wt% SDS.

creasing amount of SDS, being in agreement with the TEM results.

Structure of the Particle Polymer

The particles obtained above were coagulated by freezing the aqueous dispersion and isolated as powder. Figure 3 shows the TEM photograph of the PPSQ powder dispersed in 1.0 wt% aqueous ammonium solution. It is apparent that the original spherical particles were retained as the primary grains and coagulated in part into the larger secondary grains. The resultant powders were soluble in common organic solvents such as chloroform, toluene, tetrahydrofuran, etc. Figure 4 shows

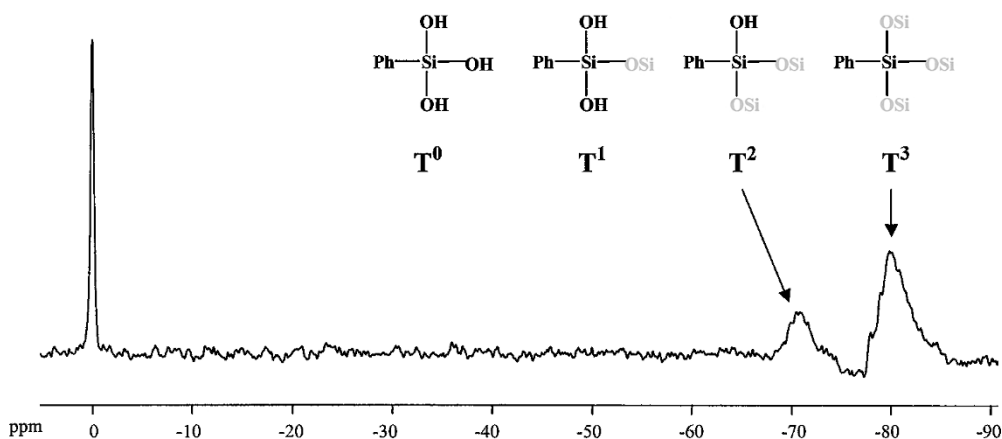


Figure 4. A typical 99.3 MHz ^{29}Si NMR spectrum of the particle polymer isolated by freezing (in CDCl_3).

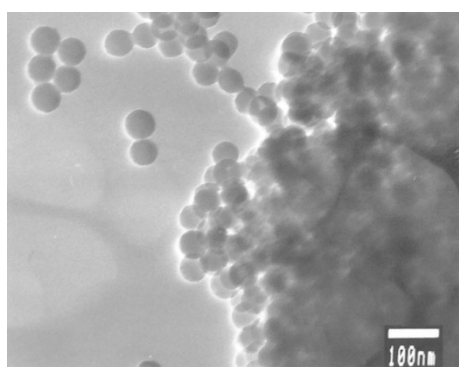


Figure 3. A typical TEM photograph of the particles isolated by freezing method.

a typical 99.3 MHz ^{29}Si NMR spectrum of the isolated product. A broad signal due to the T^2 units is exhibited at $\delta -71$ ppm in addition to the signal due to T^3 units at $\delta -80$ ppm. Here, T^i ($i = 0-3$) denotes the specimen that has i siloxane bonds and $(3-i)$ siloxyl groups with one phenyl side group. This result indicates that the particle polymer is PPSQ containing many silanol groups in the T^2 units with least formation of the ladder structure consisting of the T^3 units.

Figure 5 shows typical GPC curves of the particle polymers isolated by the freezing method. Each of the curves has a small sharp peak around 700 Da in molecular weight that is attributable to the cyclic tetramer T_4 as noted before.⁶ The main peak of the curves shifts to the region with higher molecular weight for the polymer prepared with smaller amount of emulsifier. The polymer prepared with 1.0 wt% of SDS shows a bimodal peak having fractions with both higher ($M_n = 4400$ Da) and lower ($M_n = 1800$ Da) molecular weights, while the polymers prepared with 0.5 and 2.0 wt% of SDS show a unimodal main peak centered at a similar molecular weight ($M_n = 2900-3000$ Da). Since the GPC curvature reflects the hydrodynamic volume of the sample polymer, it cannot tell the exact molecular weight of PPQS containing many silanol

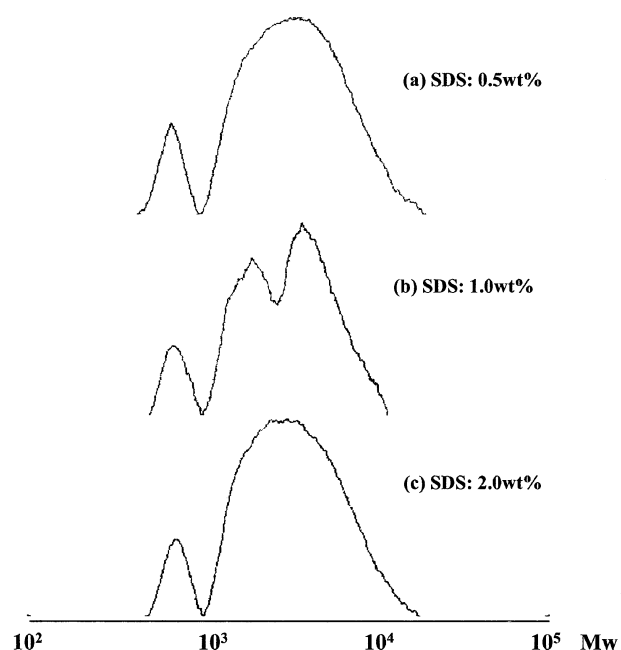


Figure 5. GPC curves of the particle polymers prepared at different conditions.

groups. The different GPC curves for the three products may be attributed to the difference in T^2/T^3 ratio in the products that would sensitively fluctuate depending on their formation and isolation conditions. It is therefore concluded here that PPSQ prepared in the aqueous medium is a low molecular weight oligomer.

The above data combined indicate that the PPSQ particles prepared by the polycondensation of PST should have an oligomeric structure with many siloxyl groups. The molecular weight of the PPSQ may be increased by annealing, while the siloxyl groups can be utilized as functional groups for further chemical modification.

CONCLUSION

The spherical nano-particles of PPSQ could be obtained by emulsion polymerization of PST that was

formed in the aqueous layer by the hydrolysis of TCP. The average size of the resultant particles could be controlled from 30 nm to 110 nm in diameter by changing the amount of the added emulsifier. When coagulated by the freezing method, the particles were isolated as white powder in which the original nano-particles were retained as the primary grain. The PPSQ nano-particles can be combined with the ordinary organic polymer dispersions for making different kinds of organic/inorganic nano-hybrid materials.

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