# Formation of Stable Nanoparticles of Poly(phenyl/methylsilsesquioxane) in Aqueous Solution

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ABSTRACT:    Nanoparticles of poly(phenyl/methylsilsesquioxane) (PPMSQ) were prepared by emulsion polymerization of the co-hydrolysate that had been formed from a mixture of trichlorophenylsilane (TCP) and trichloromethylsilane (TCM) in aqueous solution. The average size of the resultant particles was controlled from 30 to 250 nm in diameter by changing the initial concentration of the co-hydrolysate and the amount of the emulsifier added. The PPMSQ formed from the hydrolysate of TCP/TCM had a high cross-linking density, being insoluble and stable in nature. The ^{1}H NMR spectrum of the co-hydrolysate revealed that both the primary hydrolysates of TCP and TCM are involved in the fast co-polycondensation to afford meta-stable water-soluble oligomers having many silanol groups. These oligomers are allowed to react with each other to form the nanoparticles with the aid of emulsifier.
KEY WORDS    Polysilsesquioxane / Nanoparticles / Emulsion Polymerization / Trichlorophenylsilane / Trichloromethylsilane /

Polysilsesquioxanes (PSQ) with the formula of $(RSiO_{3/2})_n$ are a family of silicone compounds having outstanding thermal stability and good electric insulating properies.[1—3] In general, PSQ can be obtained by the hydrolytic polycondensation of trifunctional monomers, $RSiX_3$, where X can be a halide, an alkoxide, or a carboxylate. Their typical examples are poly(phenylsilsesquioxane) (PPSQ) and poly(methylsilsesquioxane) (PMSQ) that are synthesized from phenyltrichlorosilane (TCP)[4] and methyltrichlorosilane (TCM),[5] respectively. Recently, we reported that the hydrolysis of TCP in an aqueous/organic bilayer system produces monomeric phenylsilanetriol (PST) in the aqueous layer and that the KOH-catalyzed polycondensation of this PST in refluxing toluene gives rise to PPSQ with highly ordered ladder structure.[6,7] More recently, we conducted the polycondensation of the TCP hydrolysate in a refluxing toluene/water bilayer system with the aid of a phase transfer catalyst to obtain PPSQ in high yield without passing the isolation step of the TCP hydrolysate.[8] We also disclosed the preparation of nanoparticles of PPSQ having an average diameter of 30–110 nm by conducting the emulsion polymerization of the TCP hydrolysate after the addition of an emulsifier.[9] This was the first success in preparing the nanoparticles of PSQ.

With increasing interest in designing micro- and nano-structured materials for industrial needs, many attempts have been made to obtain particles with suitable size and shape.[10,11] Minami *et al.*, for example, prepared PPSQ particles with an average diameter of 0.2–1.0 μm and a relatively wide size distribution from organoalkoxysilane. They used these microparticles for preparing the thick films of PPSQ and applied as micro-optical devices.[12] Nota *et al.* prepared the PMSQ particles with an average diameter of 0.2–5.0 μm by emulsion polymerization of organoalkoxysilane.[13,14] Our former success in preparing the PPSQ nanoparticles has opened a new option in designing the nano-structured materials.

The present study discloses the preparation of nanoparticles of poly(phenyl/methylsilsesquioxane) (PPMSQ) that are more stable than the PPSQ particles mentioned above. Those particles can readily be prepared by emulsion polymerization of the co-hydrolysate that is formed by the hydrolysis of a mixture of TCP and TCM (Scheme 1). The average diameter of these nanoparticles can be controlled precisely from 30 to 250 nm. The formation mechanism of the co-hydrolysate of the TCP/TCM mixture and PPMSQ is also described in detail.

## EXPERIMENTAL

### Materials

TCP, TCM, sodium dodecyl sulfate (SDS) were supplied by Tokyo Kasei Kogyo Ltd. (Tokyo) and used without purification. Toluene was distilled over sodium metal before use. PMSQ as a model compound was prepared by hydrolytic polycondensation of TCM in an aqueous solution at room temperature, and the product obtained as gel was dried *in vacuo* at 90°C for 3.5 h.
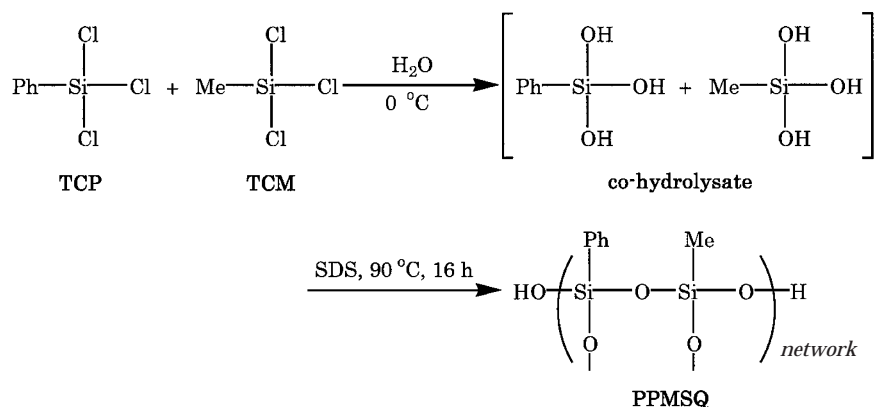
**Scheme 1.** Preparation of PPMSQ *via* co-hydrolysis of TCP and TCM.

*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 of the particles. 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. 500 MHz $^1$H NMR spectra were measured on a Bruker ARX-500 spectrometer in deuterium oxide (D$_2$O) containing sodium 3-(trimethylsilyl)propanesulfonate (DSS) as the internal reference. Transmission FT-IR spectra were recorded on a Shimadzu FTIR-8200pc infrared spectrophotometer in the wave-number range from 4000 to 500 cm$^{-1}$. X-Ray photoelectron spectra (XPS) were obtained with a JOEL JPS-9010MC/SP photoelectron spectrometer with MgKa source excitation (10.0 kV). Thermogravimetry (TG) was done on a Shimadzu TGA 2950 thermogravimetric analyzer under 10°C min$^{-1}$.

*Hydrolysis of TCP/TCM*

A mixed solution of TCP (4.3 g, 20.2 mmol) and TCM (3.1 g, 20.2 mmol) 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 NaHCO$_3$. The finally obtained aqueous layer (614 mL in volume) contained 4.2 g of the hydrolysate of TCP/TCM (*ca.* 90% yield), as estimated from the amount of the hydrolysate isolated from the toluene layer. At different TCP/TCM molar ratios the identical hydrolysis was performed to obtain the corresponding hydrolysates.

*Preparation of PPMSQ Particles*

An aliquot (150 mL) of the aqueous solution of the hydrolysate of TCP/TCM obtained above was added with SDS (0.5–3.0 wt% relative to the water) and stirred vigorously at 0–10 °C for 10 min, and the solution was heated at 90 °C for 16 h with stirring to obtain a homogeneous colloidal solution of PPMSQ that was almost transparent. For isolating the polymeric 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 thoroughly with distilled water, and dried *in vacuo* (80% yield).
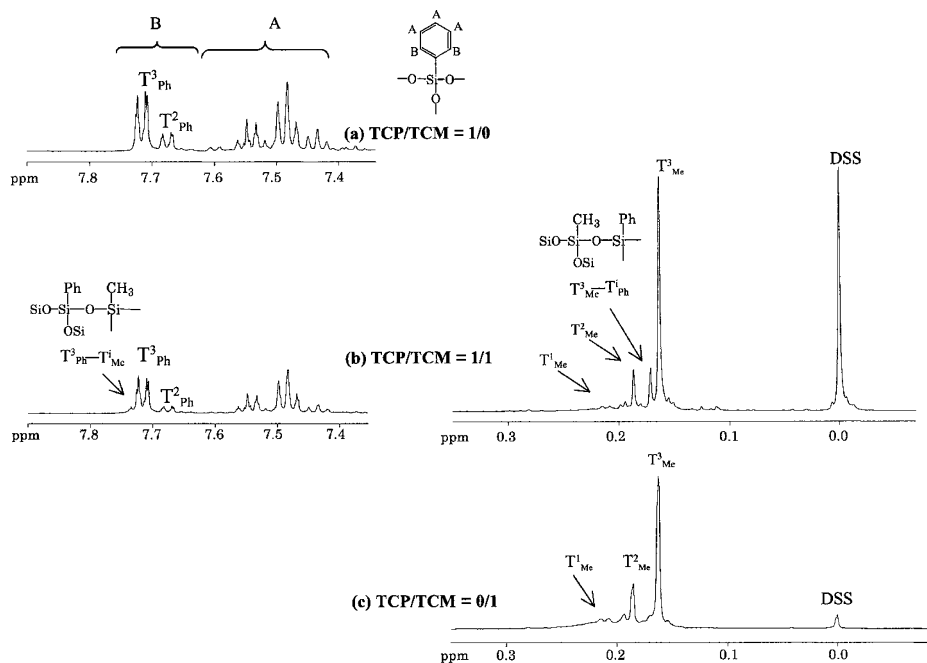
*$^1$H NMR Analysis of the Hydrolysate of TCP/TCM*

A mixture of TCP (0.043 g, 0.20 mmol) and TCM (0.031 g, 0.20 mmol) (TCP/TCM = 1/1) dissolved in toluene (2 mL) was hydrolyzed in D$_2$O (10 mL) as above. The D$_2$O layer whose pH was adjusted to 7.0 with a saturated NaHCO$_3$ in D$_2$O was directly subjected to the 500 MHz $^1$H NMR spectroscopy. At different TCP/TCM ratios, the identical reaction and analysis were done likewise.

## RESULTS AND DISCUSSION

*Formation of the TCP/TCM co-Hydrolysate*

As we reported previously, the well-controlled hydrolysis of TCP in the toluene/water bilayer system produces a water-soluble PST oligomer in the aqueous layer with a slight formation of oligomeric PPSQ.[7] The identical hydrolysis of TCM, on the other hand, leads to the formation of gel in the aqueous layer and oligomeric PMSQ in the organic layer, and no hydrolysis product is isolated from the aqueous layer.[15] This may be because methylsilanetriol (MST) formed from TCM as the primary hydrolysate is so unstable as to incur the spontaneous intermolecular polycondensation by the silanol coupling. In the present study, a mixture

**Figure 1.** 500 MHz $^1$H NMR spectra of the hydrolysates of (a) TCP, (b) 1:1 mixture of TCP/TCM, and (c) TCM in D$_2$O.

of TCP and TCM was subjected to the co-hydrolysis with the identical conditions. As a result, we discovered that the main hydrolysis product was retained in the aqueous layer in a yield of *ca.* 90% if the TCM ratio was less than 50% relative to the total amount of TCP and TCM. With the increased TCM ratio above 50%, an insoluble product precipitated out from the reaction system probably because of the gellation of the MST and its oligomers. The water-soluble nature of the hydrolysate obtained from the mixture with less than 50% of TCM suggests that it should be siloxyl-containing monomeric or oligomeric silsesquioxanes comprising the $T_X^1$ and $T_X^2$ units. Here, $T_X^i$ (i = 0–3) denotes the specimen that has i siloxane bonds and (3–i) siloxyl groups with one side organic group: X = Me or Ph, depending on the substituent. In the present hydrolysis a highly diluted monomer concentration was used to prevent the silanol coupling of the hydrolysates. Even with this condition, the hydrolysis of the TCM-rich mixtures resulted in the gellation, and accordingly the TCM ratio was set below 50%.

For direct analysis of the hydrolysate formed in the aqueous solution, the hydrolysis of the TCP/TCM mixture was conducted in D$_2$O under a highly diluted concentration (0.04 mmol mL$^{-1}$) where the hydrolysate was retained in the aqueous layer with little gellation occurring even in the hydrolysis of sole TCM. Then, the resulting aqueous layer was directly subjected to the 500 MHz $^1$H NMR spectroscopy. Figure 1 shows typical spectra of the hydrolysates of TCP (1a), the 1/1 mixture of TCP/TCM (1b), and TCM (1c). It is known that the signals around 7.4–7.8 ppm and 0.1–0.3 ppm

are attributed to the Ph–Si and Me–Si groups, respectively, and their integral ratio in Figure 1b is compatible with that calculated from the initial TCP/TCM ratio. The TCP hydrolysate shows complex phenyl protons around 7.66–7.75 ppm. According to the former study,[6] the two signals at $\delta$ 7.72 and 7.68 ppm are reasonably attributed to the symmetric ortho protons in the phenyl groups of $T_{Ph}^3$ and $T_{Ph}^2$, respectively. The presence of $T_{Ph}^3$ and $T_{Ph}^2$ suggests that the primary hydrolysate PST underwent silanol coupling to produce oligomers during the hydrolysis and the following neutralization. The unit ratio of $T_{Ph}^3$ calculated from their integral ratio was 75%. Similarly, the TCM hydrolysate shows the methyl signals due to the $T_{Me}^3$, $T_{Me}^2$, and $T_{Me}^1$ around 0.16, 0.19, and 0.21 ppm, respectively, indicating that the oligocondensation occurred. The $T_{Me}^3$ unit ratio was calculated to be 60% from its integral ratio. The co-hydrolysate of TCP and TCM, on the other hand, shows the new signals at 0.17 and 7.74 ppm corresponding to the $T_{Me}^3$ and $T_{Ph}^3$ bonding with different species ($T_{Ph}^i$–$T_{Me}^i$), respectively, in addition to the signals due to both methyl and phenyl protons of the ordinary homo units ($T_{Ph}^i$–$T_{Ph}^i$ or $T_{Me}^i$–$T_{Me}^i$). The signal integration revealed that the total ratio of $T_{Ph}^3$ was 83% and that the ratio of the $T_{Ph}^3$ connecting with $T_{Me}^i$ was 18% of the whole $T_{Ph}^3$. Likewise, the total ratio of $T_{Me}^3$ was 76% while the ratio of the $T_{Me}^3$ bonding with $T_{Ph}^1$ was 16% of the whole $T_{Me}^3$. It is accordingly concluded that the silanol coupling is driven in higher degree in the co-hydrolysis system and that the co-condensation of the both TCP and TCM hydrolysates is induced to form the oligomer of PPMSQ in the hydrolysis stage.

(a)        (b)        (c)        (d)
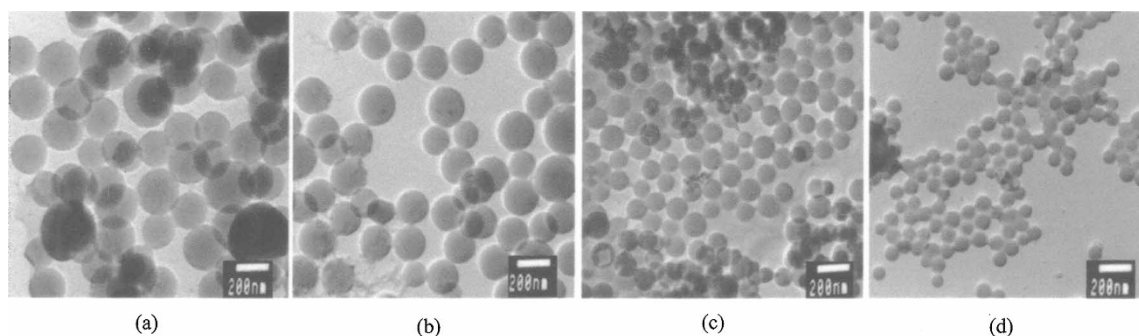
**Figure 2.** TEM of the PPMSQ particles prepared at 90 °C in the presence of (a) 0.5, (b) 1.0, (c) 2.0, and (d) 3.0 wt% of SDS (at 59 mM in the concentration of the co-hydrolysate).

**Table I.** Size data for the PPMSQ particles determined by TEM and DLS

| Run no. | Co-hydrolysate[a] (mM) | SDS (wt%) | TEM Average diameter (nm) | TEM Standard deviation (nm) | DLS Average diameter (nm) | DLS Standard deviation (nm) |
|---|---|---|---|---|---|---|
| 1 | | 0.5 | 244 | 34.4 | 252 | 57.6 |
| 2 | 59 | 1.0 | 206 | 29.0 | 195 | 50.2 |
| 3 | | 2.0 | 127 | 17.8 | 143 | 36.2 |
| 4 | | 3.0 | 96 | 13.5 | 119 | 35.9 |
| 5 | | 0.5 | 77 | 10.8 | 93 | 17.7 |
| 6 | 29 | 1.0 | 52 | 7.3 | 66 | 16.7 |
| 7 | | 2.0 | 38 | 5.4 | 54 | 13.4 |
| 8 | | 3.0 | 36 | 5.0 | 45 | 11.5 |

[a]Hydrolysis of a 1:1 mixture of TCP and TCM.

It is also known that the hydrolysate in the aqueous solution has mainly the $T^3$ structure with many silanol groups around it.

*Effect of Emulsifier on the Formation of PPMSQ Particles*

Into the neutralized aqueous layer obtained after the hydrolysis of TCP/TCM, we put an anionic emulsifier to conduct the emulsion polycondensation of the co-hydrolysate in the aqueous medium. SDS was first examined as an anionic emulsifier that had been found out to be quite effective for obtaining the PPSQ nanoparticles.[9] In fact, 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 the aqueous medium, a transparent colloidal dispersion was formed without coagulation occurring. When the aqueous layer was directly heated at the same conditions without the emulsifier added, rapid coagulation was induced. Therefore, addition of the emulsifier was known to be effective for the colloidal formation from the co-hydrolysate.

Figure 2 shows the TEM photographs of the particles obtained after the emulsion polymerization with different amounts of SDS (0.5–3.0 wt%) at a constant TCP/TCM ratio in feed (50/50) and at a concentration of the co-hydrolysate(59 mM). It is known that strictly spherical particles having sub-micron size have been produced in each case and that the size distribution is narrow. Table I (Run no. 1–4) summarizes the average diameters of the spherical particles obtained for the four cases with different concentrations of SDS. It is shown that the particle diameter decreases from 244 nm to 96 nm with increasing amount of SDS from 0.5 wt% to 3.0 wt%. As evidenced by the standard deviation (34.4–13.5 nm), the size distribution of the particles also decreases with the increased SDS concentration. These results indicate that the number and the size of the particles can be controlled by the amount of emulsifier added to the aqueous solution of the co-hydrolysate.

Figure 3 shows the DLS histograms of the same dispersions. The average diameters of the particles are determined to be 252, 195, 143, and 119 nm for the dispersions containing 0.5, 1.0, 2.0, and 3.0 wt% of SDS, respectively. The different sizes compared with those observed by TEM photographs can be attributed to the surface solvation and surfactant accumulation in the dispersion state. The histogram shifts to the smaller diameter region with increasing amount of SDS, being in agreement with the TEM results.

For studying the effect of initial concentration of the co-hydrolysate on the formation of the particles, we performed the emulsion polymerization at a half concentration of the co-hydrolysate with different amounts of SDS (0.5–3.0%). The TEM photographs and the size data of the resultant particles are shown in Figure 4 and

Table I (Run no. 5–8), respectively. It is clear that the particle size decreases at the lower initial concentration of the co-hydrolysate. With increased emulsifier, the nanoparticles (< 100 nm) with narrow size distribution can be obtained successfully.

*Structure and Properties of the Particle Polymer*

The nanoparticles obtained were successfully coagulated to be isolated as powders by the freezing technique. The isolated PPMSQ powders were re-dispersed in aqueous solution with ultrasonic wave applied. A typical TEM photograph of the re-dispersed powders is shown in Figure 5. Apparently, the original spherical particles are retained as the primary grains though coagulated in part into the larger secondary grains. The resultant powders were insoluble in common organic solvents such as chloroform, toluene, acetone, methyl isobutyl ketone (MIBK), etc. that are the good solvent of PPSQ. It is therefore suggested that the PPMSQ synthesized by this condition is crosslinked.

Figure 6 shows the FT-IR spectra of the isolated PPMSQ (b, c) and PPSQ (a) particles, as compared with the spectrum of the PMSQ (d) that was formed as the gel by the hydrolysis of TCM. In the PPMSQ both absorptions of Si–Ph ($1430 \, cm^{-1}$) and Si–CH$_3$ groups ($1300 \, cm^{-1}$) are exhibited, and the absorption of Si–CH$_3$ group increases with increasing TCM ratio in the feed.

Table II shows the XPS results of the PPSQ and PPMSQ particles as compared with those of the ordinary colloidal silica with no organic substituent. The Si/O atomic ratios of PPMSQ prepared from TCP/TCM = 50/50, 75/25, and 100/0 (PPSQ only) are 1/2.6, 1/2.5, and 1/3.5, respectively. Since these ratios are larger than the ratio of the colloidal silica (1/2.4), the PPMSQ and PPSQ particles should contain a large number of silanol groups in the surface. The number of silanol groups is larger in the PPSQ surface than in the PPMSQ surface because of the enhanced polycondensation of the less stable TCM hydrolysate. On the other hand, the Ph/Me substituent ratios in the particle surface, calculated from the Si/C ratios, are 1/2.3 and 1/1 for the particles prepared with the TCP/TCM ratios of 50/50 and 75/25, respectively. It is therefore suggested that the more hydrophilic $T_{Me}^i$ should occupy
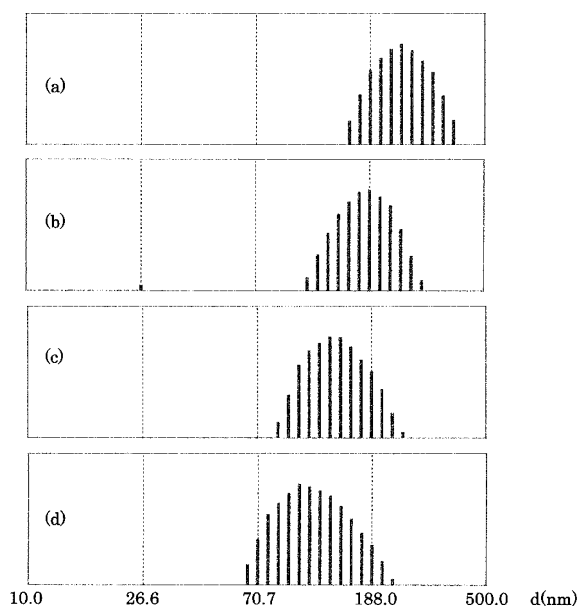


**Figure 3.** DLS histograms of the colloidal PPMSQ prepared at 90 °C in the presence of (a) 0.5, (b) 1.0, (c) 2.0, and (d) 3.0 wt% SDS (at 59 mM in the concentration of the co-hydrolysate).
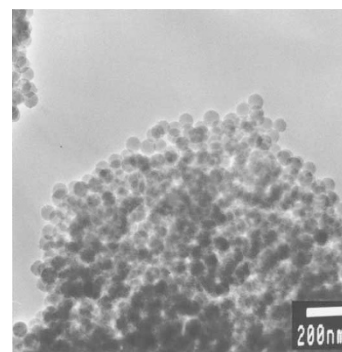


**Figure 5.** A typical TEM photograph of the PPMSQ particles isolated by freezing method (the original sample: Run no.4 in Table I).
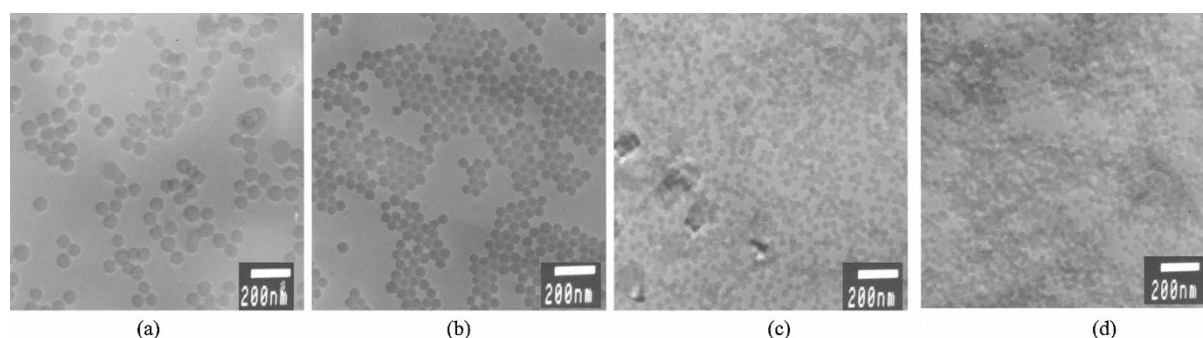


**Figure 4.** TEM of the PPMSQ particles prepared at a low concentration (29 mM) of the co-hydrolysate in the presence of (a) 0.5, (b) 1.0, (c) 2.0, and (d) 3.0 wt% of SDS.
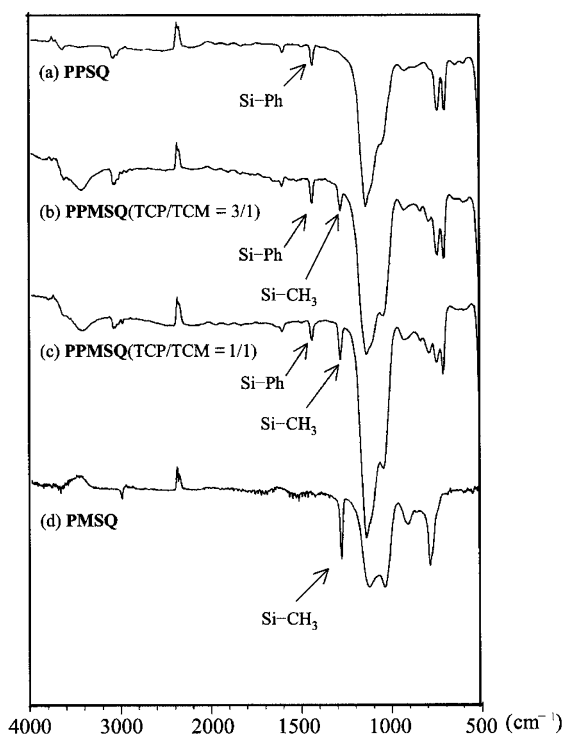
**Figure 6.** FT-IR spectra of PPSQ, PMSQ, and PPMSQ prepared at different initial TCP/TCM ratio.

**Table II.** Surface atomic ratios of colloidal silica, PPMSQ and PPSQ as analyzed by XPS

| Sample | Si | O | C | Ph/Me |
|---|---|---|---|---|
| Colloidal silica | 1 | 2.4 | 0.1 | – |
| PPMSQ (TCP/TCM = 50/50) | 1 | 2.6 | 2.5 | 30/70 |
| PPMSQ (TCP/TCM = 75/25) | 1 | 2.5 | 3.5 | 50/50 |
| PPSQ (TCP/TCM = 100/0) | 1 | 3.5 | 6.4 | – |

the surface of the particles in higher degree than the hydrophobic $T^i_{Ph}$ at the polycondensation.

Figure 7 shows typical TG curves of PPMSQ and PPSQ particles as compared with the curve of PMSQ gel. The initial decomposition temperature of the PPMSQ particles (b, c) in air is higher than that of the PMSQ gel (a) and PPSQ particles (d), indicating that the PPMSQ particles should have high cross-linking density and accordingly higher stability. On the other hand, the weight loss of the PPMSQ particles (b, c) at high temperature (~700 °C) decreases with increasing the initial TCM ratio in the feed.

## CONCLUSIONS

The spherical nano-to-submicron particles of PPMSQ could be obtained by emulsion polymerization of the co-hydrolysate of TCP and TCM that had been formed in the aqueous layer. The average diameter of the resultant particles could be controlled from 30 nm to 250 nm by changing the amount of
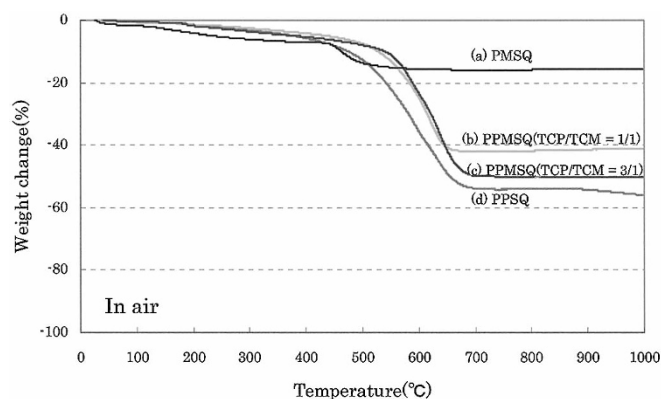


**Figure 7.** TG curves of the PPSQ particles, PPMSQ particles, and PMSQ gel measured in air.

the added emulsifier and the concentration of the co-hydrolysate. When coagulated by the freezing method, the particles were isolated as white powders in which the original particles were retained as the primary grains. The copolymerization between the TCM and TCP hydrolysates was confirmed by the ^{1}H NMR spectrum of the co-hydrolysates. The XPS and TG analyses revealed that the PPMSQ particles have a high cross-linking density with many siloxyl groups in the surface.

## REFERENCES

1. R. H. Baney, M. Itoh, A. Sakakibara, and T. Suzuki, *Chem. Rev.*, **95**, 1409 (1995).
2. L. A. S. D. Prado, E. Radovanovic, H. O. Pastore, I. V. P. Yoshida, and I. L. Torriani, *J. Polym. Sci., Part A: Polym. Chem.*, **38**, 1580 (2000).
3. C. Liu, P. Xie, D. Dai, R. Zhang, C. Zhu, and C. Wang, *Polym. Adv. Technol.*, **12**, 626 (2001).
4. J. F. Brown, J. J. H. Vogt, J. A. Katchman, J. W. Eustance, K. M. Kiser, and K. W. Krantz, *J. Am. Chem. Soc.*, **82**, 6194 (1960).
5. a) T. Suminoe, Y. Matsumura, and O. Tomomitsu, Japanese Patent Kokoku-S-60-17214, 1985. [Kokai-S-53-88099, 1978] b) T. Suminoe, Y. Matsumura, and O. Tomomitsu, *Chem. Abstr.* **89**, 180824, (1978).
6. E.-C. Lee and Y. Kimura, *Polym. J.*, **29**, 678 (1997).
7. E.-C. Lee and Y. Kimura, *Polym. J.*, **30**, 234 (1998).
8. C. Ma and Y. Kimura, *Kobunshi Ronbunshu*, **58**, 319 (2001).
9. C. Ma and Y. Kimura, *Polym. J.*, **34**, 709 (2002).
10. C. R. Martin, *Science.*, **266**, 1961 (1994).
11. K. Asao, H. Ohnishi, and H. Morita, *Kobunshi Ronbunshu*, **57**, 271 (2000).
12. A. Matsuda, T. Sasaki, K. Hasegawa, M. Tatsumisago, and T. Minami, *J. Ceram. Soc. Jpn.*, **108**, 830 (2000).
13. I. Noda, T. Kamoto, and M. Yamada, *Chem. Mater.*, **12**, 1708 (2000).
14. I. Noda, M. Isikawa, M. Yamawaki, and Y. Sasaki, *Inorg. Chim. Acta.*, **263**, 149 (1997).
15. M. Itoh, *Kobunshi*, **47**, 899 (1998).