Size-Controlling Synthesis of Narrowly Distributed Particles of Methylsilsesquioxane Derivatives

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Emulsion polymerization was used to prepare methylsilsesquioxane derivatives with an average particle size of 0.2−5.0 μm and various topological morphologies. Particles with an average particle size of 0.2−2.0 μm were prepared by emulsion polymerization using close to the critical micelle concentration of a nonionic emulsifier and a small amount of sodium hydroxide as a catalyst, whereas particles with an average particle size of 2.0−5.0 μm were obtained by suspension polymerization using a small amount of sodium hydroxide as a catalyst. Aggregation between the obtained particle colloids was not observed with the addition of an anionic emulsifier to the colloid solution at the earliest point in particle growth. A nonionic or cationic emulsifier was not effective, since the adsorption or diffusion of anionic emulsifier onto the particle colloids was accelerated due to the plus ζ potential of their surfaces.

1. Introduction

Optically transparent amorphous polymeric siloxanes have been the subject of considerable interest because of their promising bulk properties, including thermal stability.[1] There has recently been tremendous interest in the area of micro- and nanostructured materials in attempts to obtain both a suitable particle size and particle shape for industrial needs.[2] We previously reported that a suitable particle shape could be obtained by topological metamorphosis, which is caused by self-assembling polymerization, from alkyltrialkoxysilanes, tetraalkoxysilanes, and dialkyldialkoxysilanes using alkali as a catalyst.[3] Furthermore, we indicated that spherical methylsilsesquioxane particles with an average diameter of 0.2−2.0 μm were prepared by emulsion polymerization using a nonionic emulsifier and a small amount of sodium hydroxide as a catalyst,[4] whereas the synthesis of spherical methylsilsesquioxane structured particles with an average diameter on a nanoscale has been reported elsewhere.[5] Silica mesopore spherical particles with a large average diameter were obtained from tetrabutoxysilane by hydrolysis and subsequent polycondensation using a large amount of quaternary ammonium salt as a catalyst and emulsifier.[6]

Sol−gel methods[7] have been applied to the polymerization of silica glass[8] or methylsilsesquioxane[9] from metal alkoxide solution, but such methods are difficult to apply to the polymerization of small particles due to the gelation of aqueous solutions of such particles. Coagulation is due to the use of a large amount of sodium hydroxide as a catalyst, since the formation of particle nuclei is not clearly distinguishable from the simultaneous growth of particle nuclei. In the use of lubricating agents for polyester film as a magnetic digital recording medium or a high-grade paintable sheet, a very narrow size distribution of the particle is required, since otherwise there would be a large reduction in recording space. Over 99.999% of such large particles should be eliminated by precision filtration. For example, particles with an average diameter or major axis of 0.5 μm need to be free from large particles with a particle size of more than 0.7 μm. To overcome this difficulty, we applied a modification of this filter method together with emulsion polymerization. Emulsion polymerization, which can easily produce a three-dimensional inorganic network at a relatively low

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(9) See for example: (a) Kimura, H. Japanese Patent Kokai-S-63-77940, 1988; *Chem. Abstr.* **1988**, *109*, 74167. (b) Kimura, H.; Takahashi, T. Japanese Patent Kokai-S-63-295637, 1988; *Chem. Abstr.* **1989**, *110*, 174011. (c) Nishida, M.; Takahashi, T.; Kimura, H. Japanese Patent Kokai-H-1-242625, 1989; *Chem. Abstr.* **1990**, *112*, 99962. (d) Terae, N.; Iguchi, Y.; Okamoto, T.; Sudo, M. Japanese Patent Kokai-H-2-209927, 1990; *Chem. Abstr.* **1991**, *114*, 43819.

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concentration of catalyst, is attractive due to its potential for use in methods for preparing these target materials. On the basis of the results, emulsion polymerization has been shown to be useful for controlling the size of small spherical particles.[4] Furthermore, a size-controlling method for the synthesis of small hollow hemispheres is needed to produce micro- and nanostructured materials.

With regard to the use of hollow hemispheres as lubricants for polyester films, these particles seem to resist release from polyester film caused by scratching of the film, compared with spherical particles. Since their concavities are filled with polyester, these particles are not easy to remove from the film.

We recently applied a combination of emulsion polymerization and topological metamorphosis to the fabrication of hollow-hemispherical particles of methylsilsesquioxane derivatives with an average particle size of 0.2−5.0 μm. In the present study, we examined the size-controlling synthesis of narrowly distributed hollow hemispheres of methylsilsesquioxane derivatives.

2. Experimental Section

2.1. General Data. The scanning electron microscopy photographs were taken by a JEOL JSM-T300 microscope. The median diameters of particles were measured on a HORIBA CAPA-700 centrifuge sedimentation particle size distributor, a HORIBA LA-700 laser-scattering particle size distributor, and a Pen Kem AcoustoPhor 8000 Particle Analyzer. The ζ potentials of concentrated colloid dispersions were estimated by a Pen Kem AcoustoPhor 8000 Particle Analyzer. The surface tensions were taken on a KYOWA CBVP surface tension meter. The IR spectra were measured by a HORIBA FT-IR spectrometer. The ^{29}Si CP/MAS NMR spectra were recorded on a JEOL LA-400 with tetramethylsilane used as an external standard.

2.2. General Method. *2.2.1. Average Diameter and Standard Deviation of Particle Size.* The particles were photographed by a JEOL scanning electron microscope JSM-T300, and 50 particles were arbitrarily selected by the photographic image. The average diameter of the selected spherical particles was measured from the photographs, whereas the average major and minor axes of selected half ball particles were calculated respectively from the photographs. The standard deviation of the particle size was estimated from the diameter or the major and minor axes of each particle.

2.2.2. Media Diameter and Distribution of Particle Size Measured by CAPA-700. The colloid dispersions were diluted by water containing 5 wt % of 10 mol adduct of nonylphenol ethylene oxide by ultrasonic frequency. The following measurements were taken by using such dispersion by means of a CAPA-700, and the density of each particle is calculated with an interpolation between methylsilsesquioxane and silica.

2.3. Materials. Methyltrimethoxysilane (MTS), tetraethoxysilane (TES), nonylphenol ethylene oxide adducts, and sodium dodecylbenzenesulfonic acid were of commercial grades and used without further purification.

Preparation of Silicone Polymer Particle 2 (as a Typical Procedure) Described in Detail. A mixture of methyltrimethoxysilane (117.1 g, 0.86 mol) and tetraethoxysilane (19.8 g, 0.095 mol) was added dropwise into a mixture of pure water (1092 mL), 48% sodium hydroxide in pure water (1.99 g), and nonylphenol ethylene oxide, 10 mol adduct (0.1365 g), over a period of 20 min, maintaining the two layers. The mixture was slowly stirred at 14 °C. After 50 min, 5% sodium dodecylbenezenesulfonic acid in pure water (8.19 g) added dropwise into reaction mixture. After aging for 10 h, separation of resulting precipitates by centrifugation, washing with pure water (200 mL), and drying for 12 h under reduced pressure (90 °C/1 Torr) afforded 53.3 g (84%) of particle **2**, empirical formula $(CH_3)_{0.9}SiO_{1.55}$ as white powder: ^{29}Si CP/MAS NMR (solid state) δ −65.7{$(CH_3)Si^*O_{3/2}$}, −56.5{$(CH_3)Si^*(OH)O_{2/2}$}, −109.6{$Si^*O_{4/2}$}, −100.3{$(HO)Si^*O_{3/2}$}; IR (KBr) 3480, 2980, 1640, 1410, 1270, 1130−1030, 910, 780 cm^{-1}; median diameter (LA-700) 0.65 μm; median diameter (CAPA-700) 0.63 μm.

Table 1. Particles 1−12 Prepared by Emulsion Polymerization under Constant Concentration of NaOH (0.087 wt %)

particle[a]	amount of MTS (mol)	amount of TES (mol)	median diameter, μm LA-700	median diameter, μm CAPA-700
1	0.96		0.65	0.64
2	0.86	0.10	0.65	0.63
3	0.76	0.19	0.65	0.58
4	0.67	0.29	0.53	0.48
5	0.57	0.38	0.23	0.36
6	0.48	0.48	0.21	0.27
7	0.96		0.41	0.40
8	0.86	0.10	0.39	0.39
9	0.76	0.19	0.37	0.33
10	0.67	0.29	0.26	0.29
11	0.57	0.38	0.22	0.23
12	0.48	0.48	0.19	0.17

[a] Particles **1−6** were prepared under constant concentration of nonionic emulsifier (0.012 wt %), whereas particle **7−12** were prepared under constant concentration of nonionic emulsifier (0.006 wt %).

Their physical properties of particles **1−12** are summarized in Table 1.

3. Results and Discussion

3.1. Synthesis. Particles formed by the polymerization of alkyltrialkoxysilanes and tetraalkoxysilanes using sodium hydroxide as a catalyst showed several exotic topological morphologies caused by topological metamorphosis. The emulsion polymerization of these particles with a small amount of sodium hydroxide as a catalyst was examined using several nonionic and/or anionic emulsifiers to control the size of the particles, whose shape was maintained with the absence of nonreversible coagulation between particles.

Scanning electron microscope photographs of particles **1**, **3**, and **5**, with an average diameter or major axis of around 0.6 μm, were obtained by emulsion polymerization, as shown in Figure 1. On the basis of these photographs, the topological shapes observed for particles with an average diameter or major axis of about 3.0 μm were maintained despite the change in particle size; the most stable particle shape maintains a balance between the internal stress and external water pressure.

Figure 1 shows scanning electron microscope photographs of particles **1**, **3**, **5**, and **9**, where the average major axis or diameter of several topological morphologies of methylsilsesquioxane derivatives reach the local minimum around the critical micelle concentration (cmc) of the emulsifier calculated from the surface tension.

Furthermore, particles with an average diameter or major axis of more than 3.0 μm should maintain their topological morphology, but the particle size distribution broadens due to the decrease in the amount of catalyst. Generally, spherical particles larger than 5.0 μm were obtained by multistage emulsion polymerization. Unfortunately, the application of multistage emulsion polymerization to nonspherical particles failed because of nonreversible coagulation between the particles. We assume that nonspherical particles increase in size as

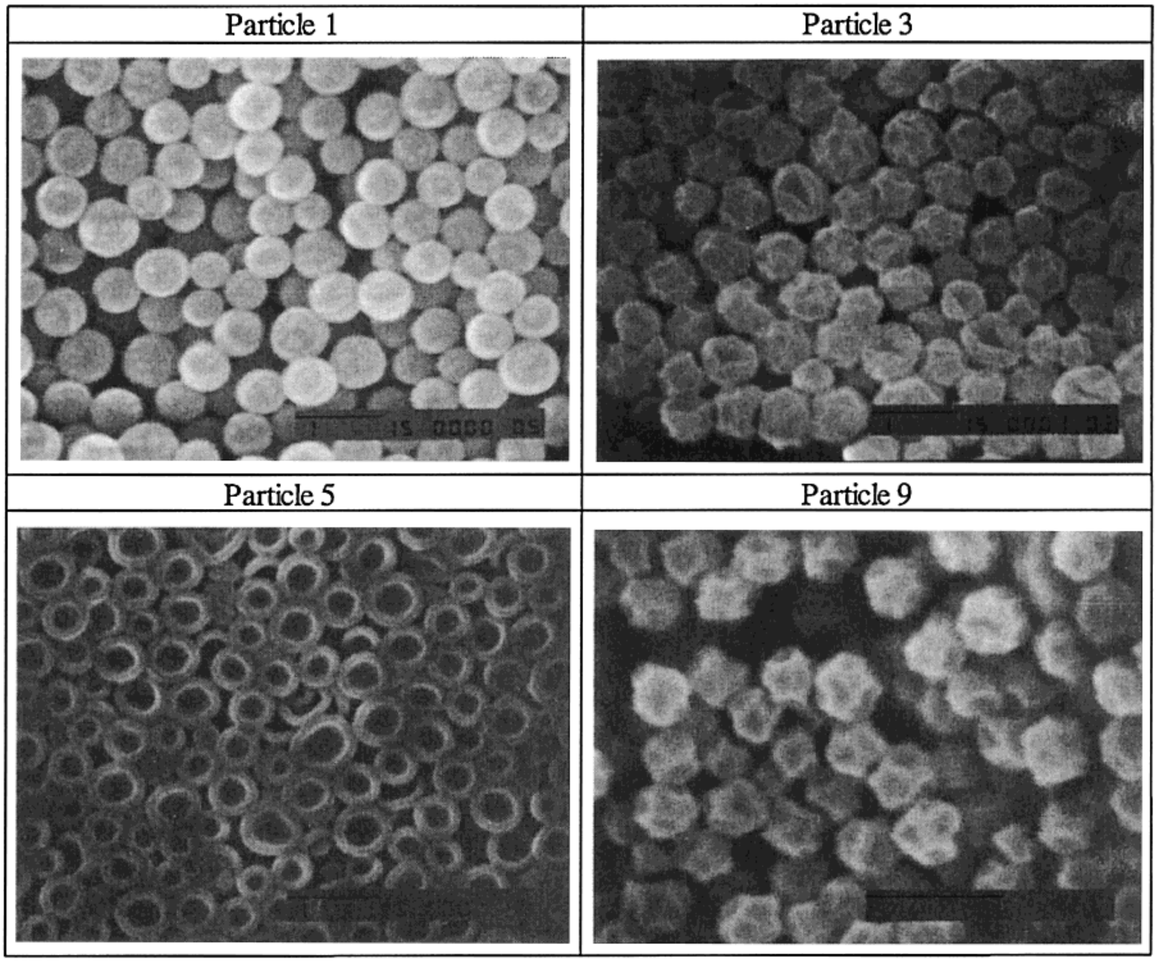

Figure 1. The photographic images of the prepared particles 1, 3, 5, and 9 by a scanning electron microscope. The bar is 1.0 μm.

the particle colloid in water expands and that topological metamorphosis by self-assembly from a heterogeneous structure to a homogeneous structure occurs in the particle colloid.

3.2. Particle Characterization. The particle size distributions and median diameters of particles **2**−**6** with an average diameter or major axis of around 0.6 μm were determined by a laser-scattering size distributor[10] and a centrifuge sedimentation particle size distributor, as shown in Figures 2 and 3.

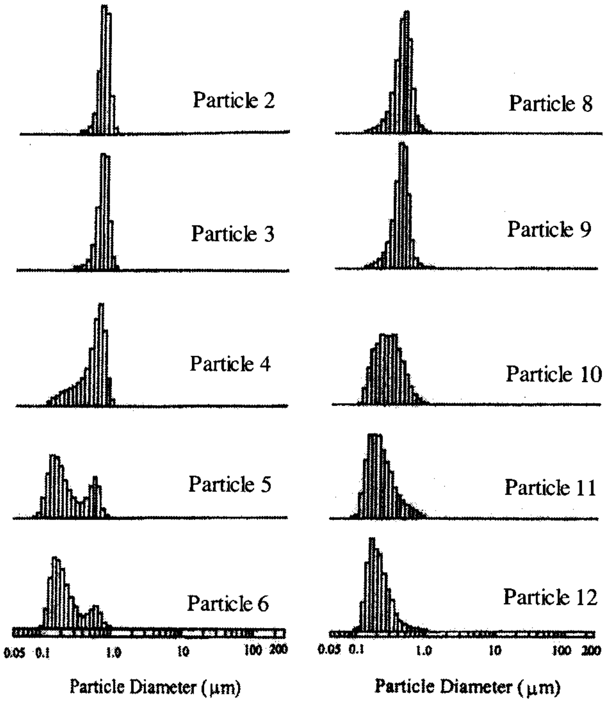

Figure 2. Particle size distribution of particles 2−6 and 8−12 measured by LA-700.

The particle size distributions of particles **2** and **3** measured by the laser-scattering size distributor (LA-700) showed a single peak in a monodispersed size distribution, whereas the particle size distribution of particles **4**−**6** showed two peaks, in contrast to the case of the same hemispherical particle with an average major axis of around 3.0 μm. These results may be due to the improved accuracy of detecting diffracted light due to the removal of extra space between counters.[11] The major- and minor-axis distributions of particles **4**−**6** occur near 0.17 μm and 0.67 μm, respectively. The histograms of the minor-axis distribution become higher as the volume described by the concavity in the hemispherical particle increases. However, the median diameter and size distribution obtained by the centrifuge sedimentation particle size distributor (CAPA-700) under the Stokes theorem is almost directly proportional to the weight of the particle.[12] The density of each

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[10] (a) Chu, B. *Laser Light Scattering*; Academic Press: New York, 1974. (b) Chu, B.; Xu, R.; Dinapoli, A. *J. Colloid Interface Sci.* **1987**, *116*, 183.

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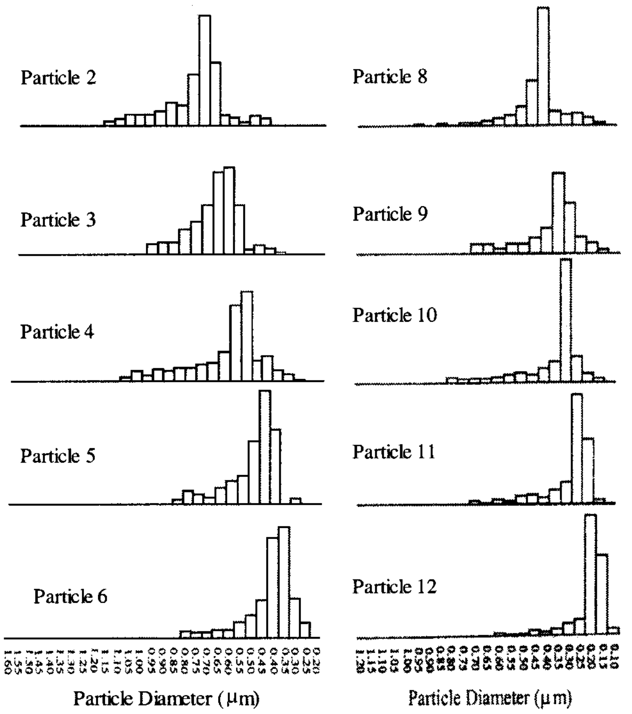

Figure 3. Particle size distribution of particles 2–6 and 8–12 measured by CAPA-700.

particle is calculated by interpolation between methylsilsesquioxane and amorphous silica. Every particle size distribution measured by the CAPA-700 showed a sharp single peak independent of the particle shape. Furthermore, the difference between the major and minor axes of particles with a hollow-hemispherical shape gradually increased as the particle size decreased. The particle shape gradually assumed the shape of a red corpuscle. The minor axis of every hollow hemisphere with an average major axis of around 3.0 μm is almost half of the major axis, whereas the minor axis of particles with a particle size of about 0.6 μm is smaller than half of the major axis. Thus, we suppose that the particle size distribution of every hollow hemisphere estimated with the LA-700 is unlikely to show a sharp peak.

The particle size distribution of methylsilsesquioxane derivative particles **8**–**12** prepared by emulsion polymerization using a cmc of nonylphenol ethylene oxide adduct as a nonionic emulsifier was measured with the LA-700 and CAPA-700 (Figures 2 and 3). The size distribution of particles **10** and **11** calculated with the LA-700 showed a single broad peak, which overlaps the monodispersed size distributions of 0.17 and 0.39 μm in detail. The peak near 0.17 μm became greater than that near 0.39 μm as the volume described by the concavity in the hemisphere increased. However, these size distributions measured by the CAPA-700 showed a single sharp peak, and the hollow-hemispherical shape caused the broad or double distribution obtained by the LA-700. The particle size distribution obtained by the CAPA-700 reflects the monodispersion of particles in the original emulsion. Accordingly, the hollow-hemispherical particle shape caused the broad or bimodal particle size distribution obtained by the LA-700.

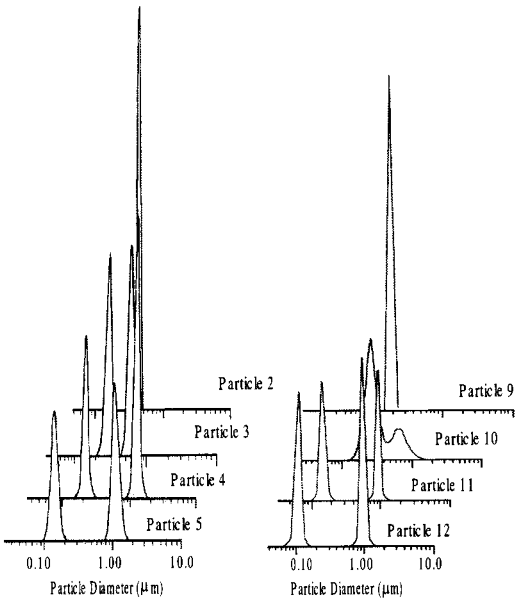

Figure 4. Particle size distribution of particles 2–5 and 9–12 measured by AcoustoPhor 8000.

These results were consistent with the particle size distribution of particles **2**–**6** and **7**–**12** obtained by acoustic attenuation spectroscopy.[13] According to the results with the laser-scattering particle size distributor, the particle size distributions of hollow hemispheres **3**, **4**, **5**, **6**, **10**, **11**, and **12** measured by acoustic attenuation spectroscopy were bimodal, as shown in Figure 4. The particle size distributions obtained for particles **4**, **5**, **6**, **11**, and **12** are clearly split into two peaks. Furthermore, the difference between the major and minor axes of particle **3** calculated from the SEM photographs was almost zero. Thus, particle **3** possessed a small concavity, but the particle size distribution showed a double peak, in contrast to the results obtained with the LA-700. However, the fitting error of this bimodal distribution was slightly different from a log-normal particle size distribution; the error is a measure of how well the predicted attenuation fits the experimental attenuation.[14,15] Particle **9**, which has the same empirical formula as particle **3**, shows a single-peak distribution by acoustic attenuation spectroscopy. Particle **9** had deep wrinkles on its surface rather than a hollow space within the particle, as shown by SEM photographs. Thus, as the volume described by the concavity in the hemisphere increases, the difference between the major and minor median axes gradually increases. The median major axes of particles **5**, **6**, **11**, and **12** are larger than the respective average major axes calculated from SEM photographs, while a reverse order is seen for the minor axes. Unfortunately, particles with an average diameter or major axis of more than 1 μm have weak scattering attenuation compared with smaller particles at frequencies below 100 MHz,[16] and the confidence of the particle size distribution decreases.

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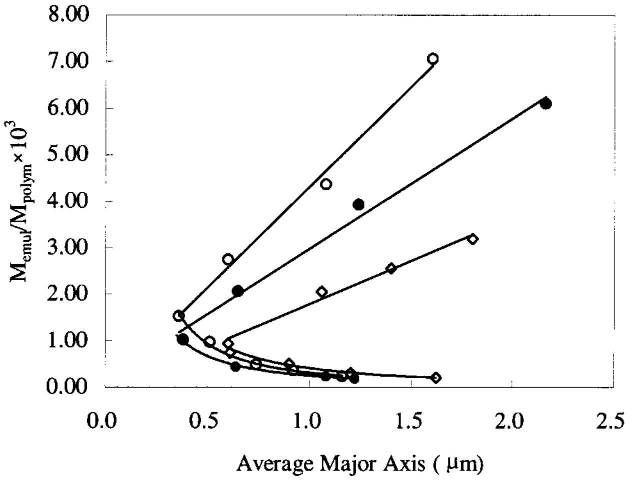

Figure 5. M_{emul}/M_{polym} dependence of the average major axis of the hemispheres, $(CH_3)_{0.7}SiO_{1.65}$, prepared by emulsion polymerization. The average major axis was calculated from SEM photographs: (◇)NP-8, (●) NP-10, and (○) NP-14.

The polymerization of particles with a uniform particle size was accomplished by the formation of particle nuclei that was clearly distinct from the subsequent growth of each particle nucleus, since the formation of particle nuclei within a narrow range of a high concentration of silicone monomer should occur with a decrease in the catalyst concentration.

3.3. Effect of Nonionic Emulsifier. Figure 5 shows the relationship between M_{emul}/M_{polym} of nonylphenol (NP) ethylene oxide adducts as an emulsifier to polymer and the size of hemispherical particles with an empirical formula of $(CH_3)_{0.7}SiO_{1.65}$.

The average major axis of the hemispherical particles reaches a local minimum around the critical micelle concentration (cmc) of the emulsifier calculated from the surface tension, and the particle size ranges from 0.2 to 2.0 μm below and above cmc. The relation between M_{emul}/M_{polym} and average major axis (D_{major}) for $M_{emul}/M_{polym} \geq 0.001$ is linear, as shown in Figure 5. Finally, the particle size is close to the size of the particles obtained by suspension polymerization using the same amount of catalyst as the amount of the emulsifier increases. Below the cmc of the emulsifier, if M_{polym}/M_{emul} is plotted against the average major axis of the hemispherical particles, there is also a linear correlation between M_{polym}/M_{emul} and D_{major}, as shown in Figure 6.

3.4. Idea Micelle Model of Particle Nuclei. Recently, a quantitative relation between particle size and the amount of an emulsifier was investigated using the polymerization of styrene in three-component cationic microemulsions.[17] For the model system of styrene μ-spheres using a cationic emulsifier, the following relations between the average radius and the fleet ratio were applied. Antonietti proposed an idealized micelle structure, whose average diameter D consists of an inner oil core surrounded by a spherical shell of emulsifier with average thickness b.[18] A more realistic model which makes the emulsifier chain partly penetrate into the polymer matrix was also evaluated.[19] This simple structural model was extended from styrene nanospheres to methylsilsesquioxane nanospheres.[5]

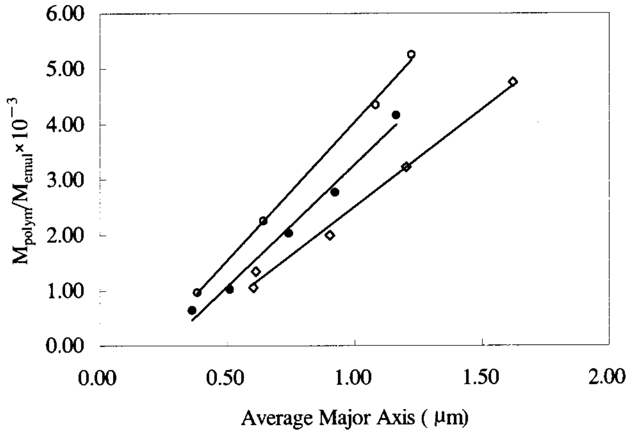

Figure 6. Plot of M_{polym}/M_{emul} versus the average major axis (D_{major}), where D_{major} was calculated from SEM photographs. The lines represent a least-squares fitting: (◇) NP-8, (●) NP-10, and (○) NP-14.

We investigate whether we will expand the relation between M_{polym}/M_{emul} and the major axis to submicrohemispheres of methylsilsesquioxane derivatives. Below the cmc of the emulsifier, the relation between M_{polym}/M_{emul} and average major axis (D_{major}) is linear, in agreement with eq 2, as shown in Figure 6. Thus, the described polymerization for submicrohemispheres of methylsilsesquioxane is phenomenologically similar to polymerization in nanospheres. If all particle nuclei grow into particles of the same size, this theory should be valid.[5,20] Since the polymerization of particles with a uniform particle size is accomplished by the formation of particle nuclei that is clearly distinct from the subsequent growth of each particle nucleus, this calculation will nicely fit the experimental data.

Above the cmc of the emulsifier, at very large M_{emul}/M_{polym} values, such an excess of emulsifier is not

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(18) Antonietti proposed an idealized micelle structure; the weight ratio of emulsifier to polymer, M_{emul}/M_{polym}, is compared with the spherical diameter D calculated using the model. Eventually, the spherical diameter D emerges from eq 1 as

$$\frac{M_{emul}}{M_{polym}} = \frac{\rho_{emul}}{\rho_{polym}}\,\frac{{}^{1}/_{6}\pi D^3 - {}^{4}/_{3}\pi(D/2 - b)^3}{{}^{4}/_{3}\pi(D/2 - b)^3} \doteqdot \frac{D^3}{8(D/2 - b)^3} - 1$$

$$D \doteqdot 2b\left(1 - \left(1 + \frac{M_{emul}}{M_{polym}}\right)^{-1/3}\right)^{-1} \tag{1}$$

See: (a) Antonietti, M.; Bremser, W.; Schmidt, M. *Macromolecules* **1990**, *23*, 3796. (b) Antonietti, M.; Bremser, W.; Muschenborn, D.; Rosenauer, C.; Schupp, B.; Schmidt, M. *Macromolecules* **1991**, *24*, 6636.

(19) This calculation from the more realistic model finally arrives at

$$\frac{M_{polym}}{M_{emul}} = \frac{N_A\rho_{polym}}{6W_{emul}}a_0 D - C \tag{2}$$

where N_A is Avogadro's number, W_{emul} is the molecular weight of the emulsifier, ρ_{polym} is the particle density in solution, and a_0 is the calculated headgroup area per emulsifier. The constant C depends on the contribution of the headgroup of the emulsifier to the hydrodynamic radius. From the molecular weight of emulsifier W_{emul} and the density of dry polymer ρ_{polym}, we were able to obtain each a_0 from the slope estimated by least-squares fitting. See: (a) Wu, C. *Macromolecules* **1994**, *27*, 298. (b) Wu, C. *Macromolecules* **1994**, *27*, 7099.

(20) Baumann, F.; Deubzer, B.; Geck, M.; Dauth, J.; Schmidt, M. *Macromolecules* **1997**, *30*, 7568.

Table 2. Average Diameter (*D*) and Average Major Axis (D_{major}) of Methylsilsesquioxane Derivatives Obtained by Emulsion Polymerization

particle	empirical formula	emulsifier	$M_{\mathrm{emul}}/M_{\mathrm{polym}} \times 10^3$	$M_{\mathrm{polym}}/M_{\mathrm{emul}} \times 10^{-3}$	D or D_{major} (μm)
2	$(CH_3)_{0.9}SiO_{1.55}$	NP-10	2.07	0.48	0.65
3	$(CH_3)_{0.8}SiO_{1.60}$	NP-10	2.07	0.48	0.66
4	$(CH_3)_{0.7}SiO_{1.65}$	NP-10	2.07	0.48	0.64
5	$(CH_3)_{0.6}SiO_{1.70}$	NP-10	2.07	0.48	0.63
6	$(CH_3)_{0.5}SiO_{1.75}$	NP-10	2.07	0.48	0.63
8	$(CH_3)_{0.9}SiO_{1.55}$	NP-10	1.10	1.82	0.38
9	$(CH_3)_{0.8}SiO_{1.60}$	NP-10	1.10	1.82	0.38
10	$(CH_3)_{0.7}SiO_{1.65}$	NP-10	1.10	1.82	0.37
11	$(CH_3)_{0.6}SiO_{1.70}$	NP-10	1.10	1.82	0.38
12	$(CH_3)_{0.5}SiO_{1.75}$	NP-10	1.10	1.82	0.38

[a] D and D_{major} are the average diameter or major axis estimated from SEM photographs.

accounted for in the model calculation discussed above, and therefore the linear relationship between D_{major} and $M_{\mathrm{polym}}/M_{\mathrm{emul}}$ breaks down, as in the case of methylsilsesquioxane nanoparticles.[5] However, if $M_{\mathrm{emul}}/M_{\mathrm{polym}}$ is plotted against the average major axis of the hemispherical particles, a linear dependence for $M_{\mathrm{emul}}/M_{\mathrm{polym}} \geq 0.001$ is observed, as shown in Figure 5. Critical examination of these results raises two important possibilities regarding the ideal model:

1. In the ideal model of an associated micelle, are the roles of polymer and emulsifier reversed? The silicone monomer seems to act as an emulsifier-like reagent, since it has hydrophobic Si−CH$_3$ (or Si−OR) and hydrophilic Si−O$^-$ groups. As a result, silicone monomers surround the free spherical micelle of emulsifier. There was a linear correlation between $M_{\mathrm{emul}}/M_{\mathrm{polym}}$ and the average major axis of the hemispherical particles, in agreement with

$$\frac{M_{\mathrm{emul}}}{M_{\mathrm{polym}}} = \frac{N_{\mathrm{A}}\rho_{\mathrm{emul}}}{6W_{\mathrm{polym}}} a_0\, D_{\mathrm{major}} - C \qquad (3)$$

2. We assumed that homomicelles in the solution could not take part in the formation of the core−shell model above the cmc of the emulsifier. Thus, the amount of the free emulsifier decreases as formation of the homomicelle increases. As a result, there was also a linear correlation between $M_{\mathrm{emul}}/M_{\mathrm{polym}}$ and the average major axis of the hemispherical particles.

Finally, the particle size is close to the size of the particles obtained by suspension polymerization using the same amount of catalyst as the amount of the emulsifier increases. Together with this phenomenon, our results from further investigation support the second assumption. The hollow hemispheres and spheres of methylsilsesquioxane derivatives show the same behavior as hemispherical particles with an empirical formula of $(CH_3)_{0.7}SiO_{1.65}$ (Table 2), and we did not consider the swelling effect of the three-dimensional inorganic network due to an increase in the $SiO_{4/2}$ segment of the particles.[3,20]

3.5. Effect of Anionic Emulsifier. As with a nonionic emulsifier, emulsion polymerization using close to the cmc of the anionic emulsifier of sodium dodecylbenzene sulfonic acid gave methylsilsesquioxane particles with a local minimum of particle size. Hollow hemispheres were not obtained by this emulsion polymerization.

Table 3. ζ Potential and Median Particle Size of Each Particle Calculated by Acoustic Attenuation Spectroscopy

			acoustic spectroscopy	
particle	empirical formula	ζ potential (mV)	median diameter (μm)	disperse form
1	$(CH_3)_{1.0}SiO_{1.50}$	20.31	0.49	monodisperse
2	$(CH_3)_{0.9}SiO_{1.55}$	11.48	0.49	monodisperse
3	$(CH_3)_{0.8}SiO_{1.60}$	23.47	0.59, 0.29	bimodaldisperse
4	$(CH_3)_{0.7}SiO_{1.65}$	25.10	1.21, 0.21	bimodaldisperse
5	$(CH_3)_{0.6}SiO_{1.70}$	25.56	1.15, 0.15	bimodaldisperse
6	$(CH_3)_{0.5}SiO_{1.75}$	28.11	1.08, 0.18	bimodaldisperse
7	$(CH_3)_{1.0}SiO_{1.50}$	16.55	0.50	monodisperse
8	$(CH_3)_{0.9}SiO_{1.55}$	11.43	0.48	monodisperse
9	$(CH_3)_{0.8}SiO_{1.60}$	15.89	0.48	monodisperse
10	$(CH_3)_{0.7}SiO_{1.65}$	15.70	0.65, 0.27	bimodaldisperse
11	$(CH_3)_{0.6}SiO_{1.70}$	17.86	1.04, 0.17	bimodaldisperse
12	$(CH_3)_{0.5}SiO_{1.75}$	26.99	1.11, 0.14	bimodaldisperse

To explain these complicated results, we attempted to measure the ζ potential of each particle colloid obtained by emulsion polymerization. The ζ potential of each particle colloid was obtained by measuring the attenuation of a sound wave as it passed through the particles over a wide range of ultrasonic frequencies, as summarized in Table 3.[22]

On the basis of the results summarized in Table 3, the surface potential of these particles is positive under alkaline conditions, in contrast to the potential on a silica particle. Thus, the particle surface was surrounded by methyl groups, and the methyl group contributed to the plus ζ potential. The silicone monomers that surround emulsifier micelles seem to have their hydrophilic group in the water phase while the hydrophobic alkyl group is buried in the colloid. The silicone monomer micelle developed by suspension polymerization is phenomenologically similar. In the progression from silicone monomer micelle to particle colloid, the number of methyl groups on the particle colloid surface increase as the number of hydroxyl groups on its surface decreases.[21] The minus potential of an anionic emulsifier is not stable on the surface of a particle nucleus colloid, since the ζ potential of a particle nucleus colloid of methylsilsesquioxane derivatives is almost positive. Moreover, the diffusion of silicone monomers to the particle nucleus was hindered by the minus potential of anionic emulsifiers due to the minus potential of silicone monomers, especially $SiO_4{}^{4-}$ monomer.

3.6. Characterization of Particle Colloids. Table 3 shows that the surface potential of these particles is positive under alkaline conditions and that a particle with an empirical formula of $(CH_3)_{0.9}SiO_{1.55}$ is unstable at the particle surface potential. Furthermore, our previous report indicated that a spherical particle of $(CH_3)_{0.9}SiO_{1.55}$ was metastable because of its heterogeneous structure.[3]

The aggregation of particle colloids, which were obtained by emulsion polymerization, proceeded early in the growth of the particle. To prevent such aggregation, we examined a method for facile polymerization together with the factors that contributed to aggregation.

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An embryonic colloid with a very small particle size probably has a minus electron potential due to the abundance of hydroxyl groups on its surface. However, the surface potential of the particle colloid changes from minus to plus due to surface methyl groups, which increase in number with an increase in particle size throughout the subsequent growth process from particle nucleus to particle. We assumed that the plus ζ potential of particle nucleus colloids accelerated the approach and adsorption of anionic emulsifiers by an electronic effect, in contrast to cationic and nonionic emulsifiers, and that anionic emulsifiers on the colloid surface acted as an active surface agent. To prevent aggregation between particles without a change in particle size, we tried adding emulsifiers to the particle colloid as soon as the particle nuclei were completely formed, and we were able to improve the stability of the particle colloid. The results obtained based on the ζ potential of particle colloids were consistent with experimental data that the aggregation between particles detected by a filtration method using a pore filter was prevented by anionic emulsifiers, but not cationic or nonionic emulsifiers.

However, the electronic repulsion between particle colloids must be considered to achieve the permanent stability of particle colloids without aggregation between particles. According to DLVO theory, aggregation between particles can be determined by the sum of electron repulsion and the London–van der Waals attractive force.[23,24] Thus, the aggregation of particle colloids depends on the ζ potential in the colloid, and slow aggregation should result from a ζ potential below the Brownian movement (kT) of the particle.[25] On the basis of the results of the ζ potential, even if the average diameter or major axis of these particles is more than 5.0 μm, the particle colloid solution seems to be permanently stable with a ζ potential over 25 mV. However, it is possible that over 99.999% of the large particles are eliminated by filtration, since these colloid solutions were stable, albeit temporarily.

4. Conclusion

Several topological morphologies were observed with the emulsion polymerization of methylsilsesquioxane derivatives with an average particle size of 0.2–2.0 μm. Aggregation between these particle colloids was not observed in a monodisperse emulsion. In the case of methylsilsesquioxane derivatives with an average particle size of 2.0–5.0 μm, a monodisperse colloid solution was obtained by the combination of suspension and emulsion polymerization. Aggregation between these colloids was not observed in these colloid solutions because of the slow progress of the reaction with a small amount of catalyst.

The stability of these colloid emulsions was examined by measuring their surface ζ potential. On the basis of these results, these colloid solutions seem to be stable, albeit temporarily. Hence, it is possible that over 99.999% of the relatively large particles in the colloid solution are removed by filtration.

The median diameter was measured by several particle size distributors, and that detected by the static laser-scattering method was closest to the average particle size estimated by SEM photographs. However, the particle size distribution calculated by acoustic attenuation spectroscopy was sensitive to the concavity in the hollow hemisphere, and the aggregation between particle colloids was accurately detected by the centrifuge sedimentation particle distributor.

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