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ORIGINAL CONTRIBUTION

Synthesis of polyhedral particles by dispersion polymerization in supercritical carbon dioxide

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Abstract The novel synthesis of polyhedral particles was attained by the dispersion polymerization of styrene in supercritical carbon dioxide using a polydimethylsiloxane-based macroazoinitiator as a precursor of the surfactant. The macroazoinitiator, VPS-1001, composed of poly(dimethylsiloxane) and 6-8 molecules of the azo groups served as a precursor of the surfactant for the dispersion polymerization by azobisisobutylonitrile as an initiator to produce 0.8-4 μm polyhedral particles. The size of the particles decreased as a result of increasing the VPS-1001 concentration. Too high a concentration of VPS-1001 caused coagulation of the particles. A decrease in the temperature increased the particle size and size distribution, while a decrease in the pressure produced particles with nonspecific shapes. An increase in the stirring rotation speed tended to increase the size and size distribution. However, too high a speed of rotation also caused coagulation of the particles.

Keywords Polyhedral particles · Dispersion polymerization · Supercritical carbon · Dioxide · Macroazoinitiator · A precursor of surfactant · Polystyrene · Azobisisobutylonitrile

Introduction

Nonspherical particles have characteristics not found in spherical particles. The physical properties of nonspherical particles play a significant role in powder technologies. For instance, the shape of the particles has an influence on the drag coefficient [1–4], coaxial jet, swirling flow [5], packing properties [6], shear flow behavior, and paint-brushing viscosity [7]. The research concerning the influences of the particle shape has been performed for spheroids, disks, cylinders, ice crystals [4], needles [6], and lobed particles [7]. The nonspherical particles are often prepared by heterogeneous polymerizations such as emulsion polymerization and dispersion polymerization. In particular, seeded emulsion and dispersion polymerizations produced many nonspherical particles with unique shapes; i.e., golf ball-like [8], octopus ocellatus-like [9], snowman-like [10, 11], raspberry-like [12], confetti-like [13], disk-like [14], and void-containing [15]. All these particles are composite particles consisting of two polymer components. Li and coworkers reported the preparation of polyhedral particles through biphasic concentrated emulsion polymerization in an aqueous solution [16].

A novel preparation of polyhedral particles was determined by the dispersion polymerization of styrene in supercritical carbon dioxide ($scCO_2$) using a poly(dimethylsiloxane)-based macroazoinitiator as a precursor of the surfactant. Part of this work has already been reported [17]. The heterogeneous polymerizations in $scCO_2$ including dispersion polymerization, emulsion polymerization, and suspension polymerization have environmental benefits for simplification of the drying process, reduction in waste water, and no use of organic solvents. These polymerizations in $scCO_2$ commonly produce spherical particles due to the use of fluorinated polymer surfactants [18, 19] and a poly(dimethylsiloxane) (PDMS) macromonomer [20]. This paper describes the preparation of polyhedral particles by the dispersion polymerization of styrene in $scCO_2$ and the effects of the temperature, pressure, and

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rotation speed of stirring on the shape and size of the particles.

Experimental

Instrumentation The size exclusion chromatography (SEC) was performed using a Tosoh GPC-8020 instrument equipped with a DP-8020 dual pump, a CO-8020 column oven, and a RI-8020 refractometer. Two polystyrene gel columns, Tosoh TSK G2000H_{XL} and G4000H_{XL}, were used with tetrahydrofuran as the eluent at 40 °C. The scanning electron microscopy (SEM) measurements were made using a JEOL JSM-6300 electron microscope.

Materials The poly(dimethylsiloxane)-based macroazoinitiator, VPS-1001 (Mn=70,000–90,000, Mn of a PDMS block=10,000, azo content=0.09 mmol/g) was obtained from Wako Pure Chemical Industries [17]. Styrene was washed with aqueous alkaline solution and water and distilled under reduced pressure over calcium hydride. The styrene was deoxygenated by bubbling nitrogen at room temperature for 15 min. Azobisisobutylonitrile (AIBN) was recrystallized in methanol. 4-Methoxy-2,2,6,6-tetramethylpiperidine-1-oxy (MTEMPO) was prepared as reported previously [21]. Industrial-grade CO_2 with a purity of 99.5% or higher was purchased from Sanyo Shoji.

Dispersion polymerization of styrene in scCO$_2$ The polymerization was conducted in CO_2 in a 10-mL high-pressure view cell equipped with tempered glass windows which permit visual observation of the reaction mixture. The reactor was purged with a flow of nitrogen prior to the addition of the following reaction mixture. VPS-1001 (25 mg, 1.25 wt%) dissolved in deoxygenated styrene (2.00 g, 19.2 mmol) and AIBN (95 mg, 3 mol%) were placed in the reactor and were purged with a flow of nitrogen again. A Nihon Seimitsu Kagaku NP-D-321 personal pump equipped with an Eyela CCA-1110 cooler was used to pressurize the reactor with CO_2 to ~180 bar at 35 °C, and the reaction mixture was heated to 65 °C. The pressure was reached to ~350 bar at 65 °C. The remaining CO_2 was added to the system until the pressure was reached to 400 bar. Once the final conditions were obtained, the reaction was allowed to proceed with stirring for 24 h. At the end of the reaction, the vessel was cooled to room temperature. The CO_2 was slowly vented from the cell through a pressure letdown valve to a 500-mL Erlenmeyer flask in order to collect any polymer that sprayed out during the venting process. The polymer product was removed from the reaction vessel. The remaining polymer in the vessel was dissolved in dichloromethane and was evaporated, then dried in vacuo for several hours. Polystyrene particles (1.86 g) were obtained. The yield of the polymer was determined gravimetrically.

Reaction of VPS-1001 with 4-methoxy-2,2,6,6-tetramethylpiperidine-1-oxyl in scCO$_2$ VPS-1001 (100 mg, the azo content=9×10^{-3} mmol) and MTEMPO (17 mg, 0.0914 mmol) dissolved in deoxygenated benzene (2.2 mL) were placed in the reactor purged with a flow of nitrogen. Liquefied CO_2 was added to the reactor to 90 bar, and the reaction mixture was heated to 65 °C. The pressure was reached to ~306 bar at 65 °C. The remaining CO_2 was added to the system until the pressure was reached to 400 bar. Once the final conditions were obtained, the reaction was allowed to proceed with stirring for 24 h. At the end of the reaction, the vessel was cooled to room temperature. The CO_2 was slowly vented from the cell through a pressure letdown valve to a 500-mL Erlenmeyer flask in order to collect any product that sprayed out during the venting process. The product in the vessel was dissolved in dichloromethane and was evaporated, then dried in vacuo for several hours. The product (110 mg) was obtained.

Cloud point measurement The cloud point measurement was performed with a variable volume view cell [22] for the PDMS fragments obtained by the reaction of VPS-1001 and MTEMPO in the presence of benzene at 65 °C at 400 bar for 24 h. The measurement was carried out for the PDMS fragments in the presence of MTEMPO and the benzene without isolation of the PDMS fragments from the cell. The cloud point was defined as the point at which the contents of the cell turned opaque, indicating precipitation of the polymer from solution.

SEM measurement The polystyrene particles were put on a carbon adhesive tape and were subjected to SEM measurement after coated with Pt.

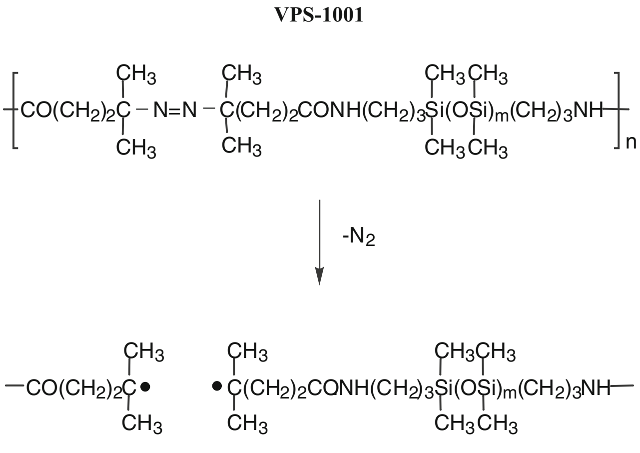


Fig. 1 The VPS-1001 macroazoinitiator

Table 1 Dispersion polymerization of styrene by VPS-1001 and AIBN in $scCO_2$

VPS-1001 (wt%)	Yield (%)	M_n	M_w/M_n	D_n (μm)	D_w/D_n[a]	Particle shape
0.625	89	5900	2.48	3.96	2.84	Spherical
1.25	92	6580	2.45	2.06	2.37	Spherical
2.50	90	7060	2.25	1.06	2.60	Spherical
5.00	86	7140	2.17	1.02	1.20	Spherical
7.50	82	7670	2.01	1.09	2.16	Coagulated

[AIBN]=3 mol%, temperature=65 °C, initial pressure=400 bar, stirring rotation speed=300 rpm, time=24 h

[a] [23]

Results and discussion

VPS-1001 itself serves as an initiator for radical polymerization, since it contains the azo groups that produce radical species (Fig. 1). The polymerization of styrene was performed in $scCO_2$ by VPS-1001 as an initiator to produce a polymer in only 20% yield. The polymerization was carried out using 5 wt% of VPS-1001 under the conditions of 65 °C, 400 bar, and 300 rpm for 24 h. Most of the styrene remained as a monomer. The molecular weight and molecular weight distribution of the resulting polymer were Mn=53,000 and Mw/Mn=3.24, respectively, based on SEC. It was considered that this molecular weight of the resulting polymer was attributed to that of VPS-1001, when it was taken into account that the molecular weight of VPS-

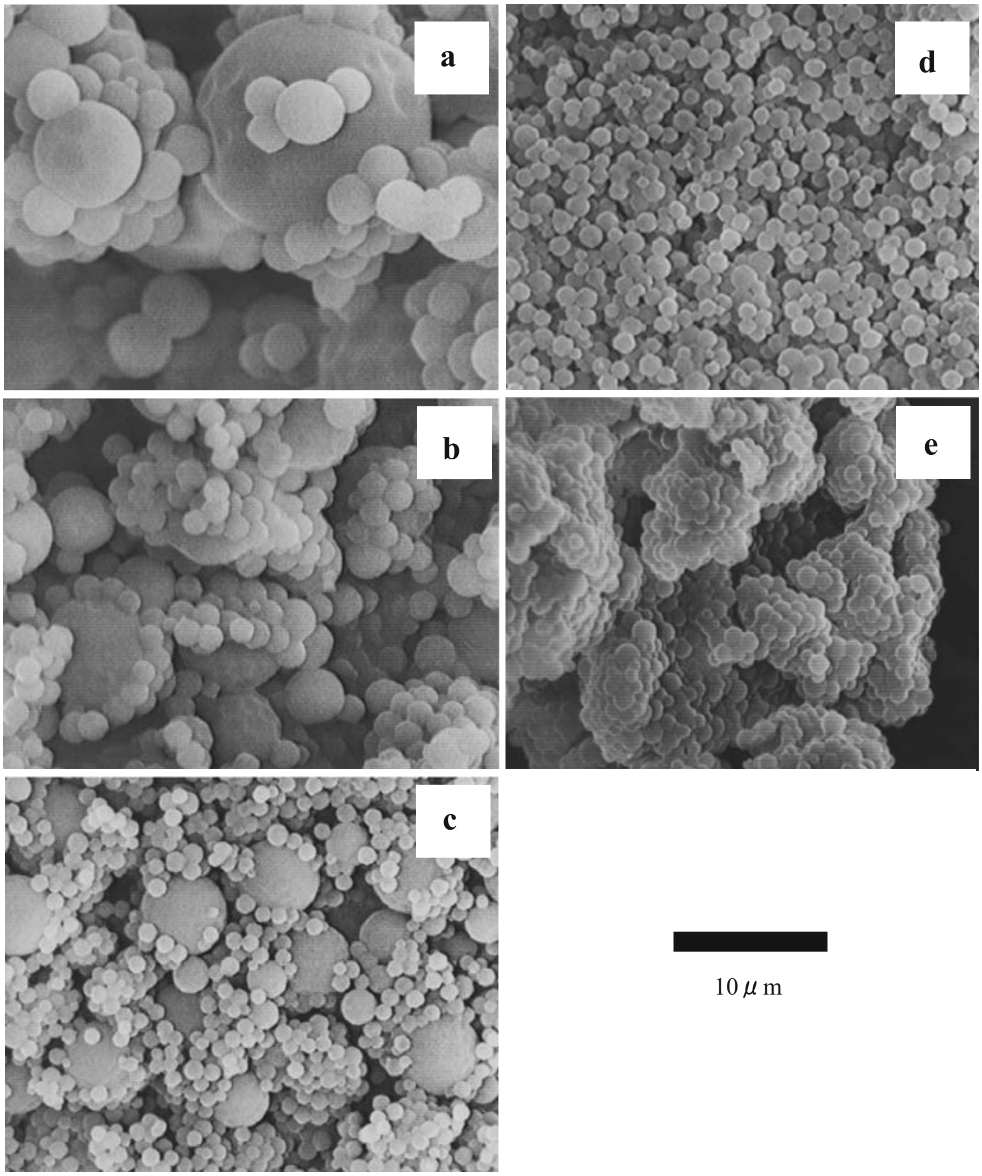


Fig. 2 SEM images of the polystyrene obtained by the polymerization at **a** 0.625, **b** 1.25, **c** 2.50, **d** 5.00, and **e** 7.50 wt% of the VPS-1001 concentrations

1001 was estimated to be Mn=52,200 by SEC based on polystyrene standards.

The polymerization by AIBN (3 mol% to styrene) instead of VPS-1001 provided an oligomer in 54% yield. The molecular weight and its distribution of the oligomer were Mn=3,210 and Mw/Mn=1.46, respectively. The formation of the low molecular weight product was due to the precipitation of the product during the polymerization. The faster polymerization by AIBN than VPS-1001 is based on the difference in the concentration of the azo group; only 4.09×10^{-3} mol% of the azo groups was contained in the polymerization by VPS-1001, whereas the azo concentration was 3 mol% of that by AIBN. The products obtained by the polymerizations using VPS-1001 and AIBN both had nonspecific shapes based on the SEM observations.

In order to accelerate the polymerization and avoid the precipitation of the product polymer, the polymerization was performed in the presence of both VPS-1001 and AIBN. The polymerization was carried out at 65 °C, 400 bar, and 300 rpm for 24 h. The results are listed in Table 1. The yields were attained over 85%, independent of the VPS-1001 concentration. The molecular weight increased with an increase in the concentration of VPS-1001, whereas the molecular weight distribution decreased with it. The particle size and size distribution of the polystyrene decreased with an increase in the VPS-1001 concentration. Figure 2 shows the SEM images of the particles. It was observed that the size distribution decreased with an increase in the VPS-1001 concentration. However, the high concentration over 5 wt% of VPS-1001 caused coagulation of the particles. The magnification of the SEM images revealed that the particles had polyhedral shapes. Figure 3 shows the magnification of the SEM images for the polystyrenes obtained at 1.25 and 5.00 wt% of the VPS-1001 concentration. For the 1.25-wt% sample, each face of the polyhedral particle is observed as a mark where the small particle attached to the large particle was separated from it.

In order to explore the cause of the polyhedron formation, the decomposition of VPS-1001 was investigated. It was considered that VPS-1001 produced a block copolymer consisting of PDMS and polystyrene, because a PDMS homopolymer did not served as a surfactant for the dispersion polymerization of styrene in $scCO_2$ [17]. For the purpose of the determination of the PDMS block length, VPS-1001 was heated in $scCO_2$ at 65 °C, 400 bar, and 300 rpm for 24 h in the presence of MTEMPO as a scavenger of the initiator radicals generated from VPS-1001 and benzene instead of styrene. SEC demonstrated that the average molecular weight of VPS-1001 decreased from Mn=52,200 to 26,700. Only one azo group among six to eight azo groups per molecule of VPS-1001 produced the initiator radicals. On the other hand, the molecular weight distribution of VPS-1001 increased from Mw/Mn=2.15 to 9.79. This great increase in the molecular weight distribution suggests that the scission of the VPS-1001 chains occurred on the different azo groups, resulting in the formation of block copolymers with different PDMS chain lengths (Fig. 4). When the VPS-1001 concentration was low, the block copolymers with different PDMS blocks should stabilize the polystyrene particles, causing the broad distribution of the particle size. At the high concentration, the copolymers with longer PDMS blocks may predominantly stabilize the particles because of their higher stabilizing ability than the shorter one, resulting in the formation of the particles with the lower distribution. The polyhedral shapes were considered to result from the firm cohesion of the particles by low glass temperature of the PDMS blocks when the pressure was released. This is because the coagulated particles obtained at 7.5 wt% of the VPS-1001 concentration were spherical rather than polyhedral.

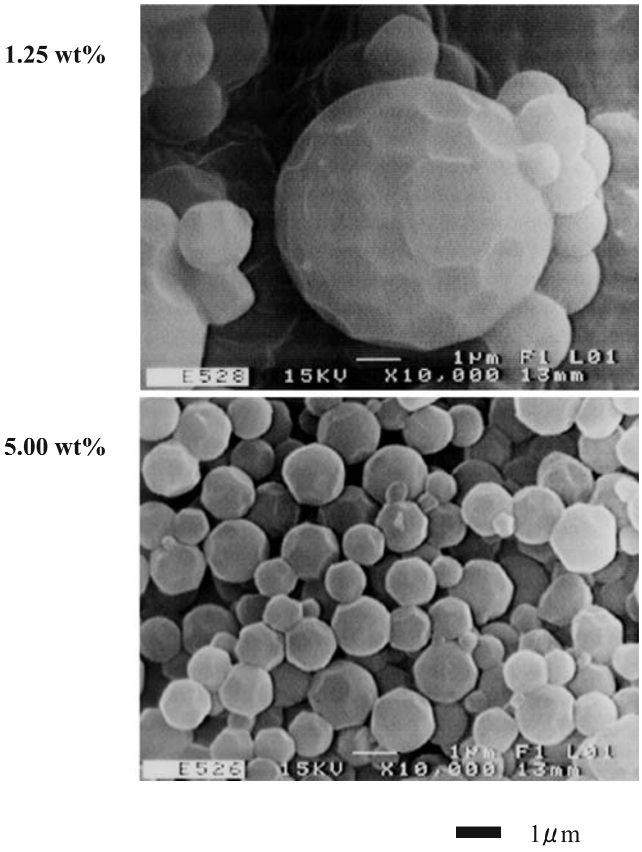
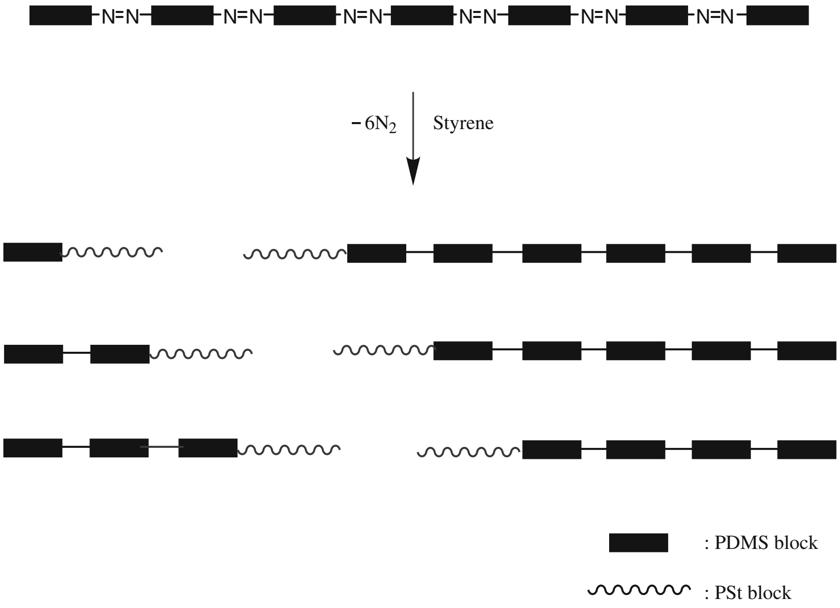


Fig. 3 The magnification of the SEM images for the polystyrenes obtained at 1.25 and 5.00 wt% of the VPS-1001 concentrations

The polymerization was explored in more detail concerning the polymerization time, temperature, pressure, and rotation speed of stirring. Figure 5 shows the variability in the yield, molar ratio of the styrene unit to the

Fig. 4 The scission of the VPS-1001 chain



dimethylsiloxane unit (St/DMS) in the resulting polymer, coupled with the molecular weight of the polymer and its distribution versus the polymerization time. They all increased with time. In particular, the yield and the St/DMS ratio showed a good correlation. It was found that the yield, coupled with the molecular weight and its distribution, was dependent on the polymerization temperature. The results on the polymerization performed at 45, 55, and 65 °C are shown in Table 2. As a result of the decreasing temperature, the yield decreased due to a decrease in the rate of the polymerization. On the other hand, the molecular weight and molecular weight distribution increased with the decrease in the temperature. The particle size and its distribution also increased with the decrease in it. These increases in the particle size and its distribution should be attributed to the increases in the molecular weight and molecular weight distribution of the polystyrene. It is clear that the formation of the larger particle is not based on the solubility of the polystyrene because the CO_2 density dominating the solubility increases with the decrease in the temperature. Figure 6 shows the SEM images of the

Fig. 5 The variability in the yield, St/DMS ratio, molecular weight of the polymer, and its distribution versus the polymerization time. [VPS-1001]= 5.00 wt%, [AIBN]=3 mol%, 65 °C, 400 bar, 300 rpm, and 24 h

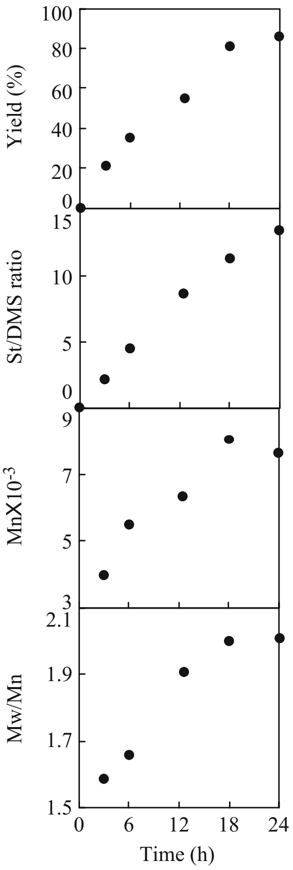


Table 2 Temperature dependence on polymerization of styrene by VPS-1001 and AIBN in $scCO_2$

Temperature (°C)	CO_2 density (g/mL)	Yield (%)	M_n	M_w/M_n	D_n (μm)	D_w/D_n[a]	Particle shape
45	0.941	54	24400	5.19	–[b]	–[b]	Nonspherical
55	0.908	79	16300	2.71	1.34	2.45	Spherical
65	0.870	86	7140	2.17	1.02	1.20	Spherical

[VPS-1001]=5 wt%, [AIBN]=3 mol%, initial pressure=400 bar, stirring rotation speed=300 rpm, time=24 h

[a] [23]

[b] Could not estimated

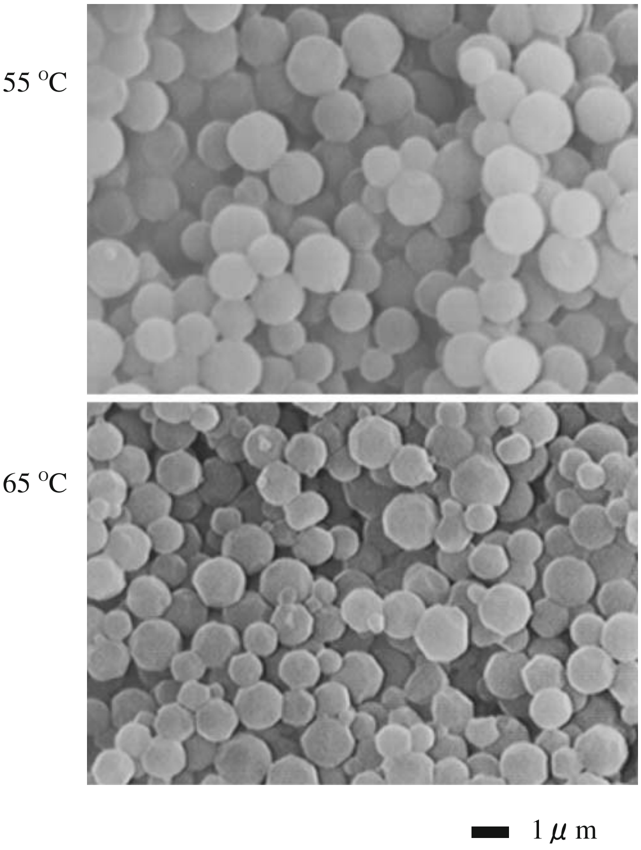


Fig. 6 SEM images of the polystyrene obtained by the polymerization at 55 and 65 °C

particles obtained at 55 and 65 °C. The sample prepared at 45 °C was nonspecific due to the low conversion. The particles obtained at 55 °C showed spherical-like polyhedral compared to that at 65 °C. It may be accounted for by the fact that the PDMS blocks covering the particles are less mobile and cohesive at the lower temperature.

The pressure also affected the shape of the particles. The results of the polymerization performed at different pressures are shown in Table 3. As the pressure decreased, the yield and molecular weight of the particles decreased. The very broad molecular weight distribution for the 200-bar sample was due to the fact that the precipitation polymerization proceeded at this pressure. Consequently, the 200-bar sample showed a nonspecific shape. The 300-bar sample was also nonspecific in spite of the fact that the dispersion polymerization proceeded, although some spherical particles were confirmed in the SEM image (Fig. 7). It was revealed that the difference in the polymerization based on the pressure was attributed to the solubility of the VPS-1001 surfactant. The solubility of VPS-1001 was explored by the measurement of the cloud point for the PDMS fragments to form the PDMS blocks of the block copolymer surfactant. The PDMS fragments were obtained by the reaction of VPS-1001 and MTEMPO in the presence of benzene at 65 °C at 400 bar for 24 h. The PDMS fragments had the cloud point at 280 bar at 65 °C. At 200 bar, the PDMS blocks were insoluble in $scCO_2$, causing the precipitation polymerization. The PDMS blocks did not sufficiently stabilize the polystyrene particles at 300 bar. Those served as surfactants at the much higher

Table 3 Pressure dependence on polymerization of styrene by VPS-1001 and AIBN in $scCO_2$

Pressure (bar)	CO_2 density (g/mL)	Yield (%)	M_n	M_w/M_n	D_n (μm)	D_w/D_n[a]	Particle shape
200	0.694	60	3770	10.15	–[b]	–[b]	Nonspherical
300	0.812	63	4020	1.83	–[b]	–[b]	Nonspherical
400	0.870	86	7140	2.17	1.02	1.20	Spherical

[VPS-1001]=5 wt%, [AIBN]=3 mol%, temperature=65 °C, stirring rotation speed=300 rpm, time=24 h

[a] [23]

[b] Could not estimated

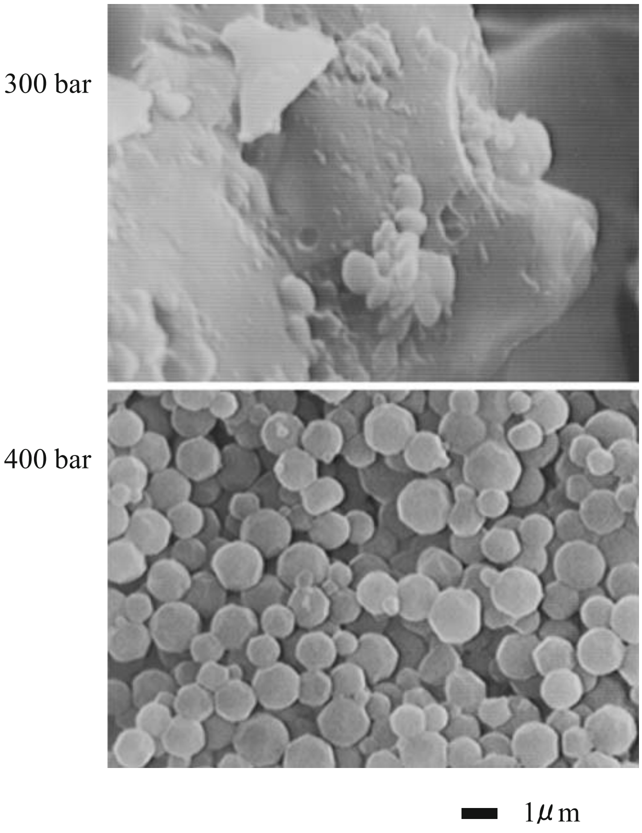


Fig. 7 SEM images of the polystyrene obtained by the polymerization at 300 and 400 bar

pressure than the cloud point to produce the polyhedral particles.

The effect of the rotation speed of stirring on the particles was explored at 300, 700, and 1,000 rps. These results are summarized in Table 4. The rotation speed made a slight difference in the yield, molecular weight, and molecular weight distribution, while it had an effect on the particle size and its distribution. As a result of increasing the rotation speed from 300 to 700 rps, the particle size increased. However, an increase in the speed from 700 to 1,000 rps decreased the particle size. The size distribution increased with an increase in the rotation speed. The SEM observations revealed that the particles were not stabilized enough at 1,000 rps. Figure 8 shows the SEM images of the particles obtained at each rotation speed. The particles were coagulated at 1,000 rpm. The particles were not stabilized enough at 1,000 rpm due to a very weak force of the surfactant. It was deduced that the rotation speed of stirring had an influence on the stabilization of the particles by the surfactant, resulting in changes in the particle shape and the size.

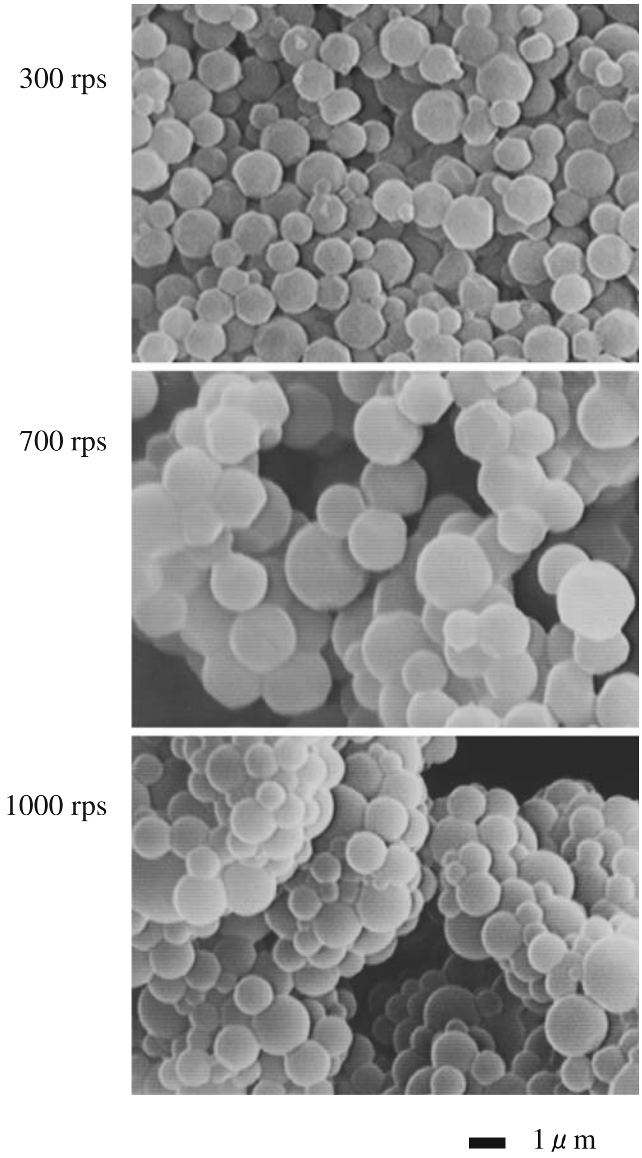


Fig. 8 SEM images of the polystyrene obtained by the polymerization at 300, 700, and 1,000 rps

Conclusion

The synthesis of polyhedral particles was attained by the dispersion polymerization of styrene in $scCO_2$ using the PDMS-based macroazoinitiator as a precursor of the surfactant and AIBN as an initiator. The shape of the particles, coupled with the particle size and size distribution, was dependent on the VPS-1001 concentration, temperature, pressure, and rotation speed of stirring. As a result of increasing the VPS-1001 concentration, the particle size decreased. However, too high a concentration of VPS-1001 caused the coagulation of the particles. The temperature increased the molecular weight and molecular weight distribution, resulting in the formation of the large particles with the broad distribution. The pressure varied the solubility of the surfactant which changed the particle shape and size. The rotation speed had an influence on the stabilization of the particles by the surfactant. The formation of the polyhedral particles was considered to result from the firm cohesion of the particles based on the low glass temperature of the PDMS blocks when the pressure was released. This study clarified the effects of the physical conditions of the polymerization on the shape, size, and size distribution of the polyhedral particles.

Table 4 Dependence of rotation speed of stirring on polymerization of styrene by VPS-1001 and AIBN in $scCO_2$

Rotation speed (rpm)	Yield (%)	M_n	M_w/M_n	D_n (μm)	D_w/D_n[a]	Particle shape
300	86	7140	2.17	1.02	1.20	Spherical
700	85	7990	2.04	1.65	1.99	Spherical
1,000	92	8470	1.96	1.13	2.70	Coagulated

[VPS-1001]=5 wt%, [AIBN]=3 mol%, temperature=65 °C, initial pressure=400 bar, time=24 h

[a] [23]

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