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ORIGINAL CONTRIBUTION

Syuji Fujii
Hideto Minami
Masayoshi Okubo

Production of poly(methyl methacrylate) particles by dispersion polymerization with mercaptopropyl terminated poly (dimethylsiloxane) stabilizer in supercritical carbon dioxide

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S. Fujii · M. Okubo (✉)
Division of Molecular Science, Graduate School of Science and Technology,
Kobe University, 657–8501 Kobe, Japan
E-mail: okubo@cx.kobe-u.ac.jp
Tel.: +81-78-803-6161
Fax: +81-78-803-6161

H. Minami · M. Okubo
Department of Chemical Science and Engineering, Faculty of Engineering,
Kobe University, 657–8501 Kobe, Japan

Abstract Poly(methyl methacrylate) (PMMA) particles were produced by dispersion polymerization of methyl methacrylate in the presence of mercaptopropyl terminated poly(dimethylsiloxane) (MP-PDMS) in supercritical carbon dioxide at about 30 MPa for 24 h at 65 °C. The particle diameter could be controlled in a size range of submicron to micron by varying MP-PDMS concentration. The MP-PDMS worked as not only a chain *tran*sfer agent but also a colloidal *stab*ilizer, which was named "*transtab*."

Keywords Supercritical carbon dioxide · Mercaptopropyl terminated poly(dimethylsiloxane) · Dispersion polymerization · Particle · Poly(methyl methacrylate)

Introduction

Up to the present, some polymer industries, (e.g., paint, textile, and cosmetic industries) have used large amounts of volatile organic compounds to prepare polymer molecules and to apply them as a medium. However, because of environmental problems, the use of environmentally favorable media is desirable. Water is one of the environmentally sound media. There are a number of reports on radical polymerizations in aqueous and alcohol/water media: emulsion, dispersion, and suspension polymerizations.

Recently, in addition to water, there has been increasing interest in supercritical carbon dioxide ($scCO_2$). The use of $scCO_2$ as a medium for polymerizations has several potential advantages: low cost, no toxicity, eases of medium removal and recycling, and marked variations of solubility power, viscosity, and polarity by relatively small changes in temperature and pressure without altering medium composition. Papers describing the dispersion polymerization of vinyl monomers such as styrene and methyl methacrylate (MMA) in $scCO_2$ have been published in recent years [1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14].

DeSimone and coworkers have pioneered the production of polystyrene (PS) particles by dispersion polymerizations of styrene in $scCO_2$ with 2,2'-azobis(isobutyronitrile) (AIBN) in the presences of PS-*b*-poly(1,1-dihydroperfluorooctyl acrylate) (PFOA) [1], PFOA [2], poly(dimethylsiloxane) (PDMS)-based macromonomer [3], and PS-*b*-PDMS [4] as colloidal stabilizers. Moreover, they reported that poly(MMA) (PMMA) particles were produced by dispersion polymerizations of MMA in $scCO_2$ with AIBN in the presence of PFOA [5, 6, 7, 8, 9] and PDMS-based macromonomer [3] as colloidal stabilizers. Lepilleur and

Beckman [10], Yates and coworkers [11], Hems and coworkers [12], and Christian and coworkers [13] also produced PMMA particles in $scCO_2$ with AIBN using poly(MMA-*co*-hydroxyethyl methacrylate)-*g*-poly(perfluoropropylene oxide), PDMS-*b*-poly(methacrylic acid), PMMA-*b*-poly(fluoroalkyl methacrylate) and carboxylic terminated perfluoropolyether, respectively. Caputo and coworkers produced PMMA particles by gamma radiation induced dispersion polymerization with different types of PDMS in $scCO_2$ [14].

In recent articles, we have described the production of PMMA particles by dispersion polymerizations in $scCO_2$ with PDMS-based azoinitiator as an inistab (an *ini*tiator + a colloidal *stab*ilizer) [15] and aminopropyl terminated PDMS [16]. In these ways, since some amorphous fluorinated and PDMS-based polymers have been identified as being soluble in CO_2 or CO_2-philic, they have been used as colloidal stabilizers in the dispersion polymerization in $scCO_2$. In general, PDMS-based polymers may have advantages over fluorinated polymers from the viewpoints of price and their solubility in conventional organic solvents, which makes it easier to characterize the products obtained.

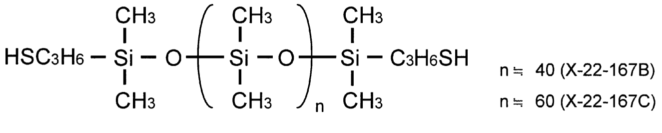
Mercaptopropyl terminated PDMS (MP-PDMS) consists of PDMS unit and mercaptopropyl group that should work as a chain transfer agent in radical polymerizations. PDMS-*b*-PMMA, which must be generated by a chain transfer reaction during a dispersion polymerization of MMA in $scCO_2$, should work as a colloidal stabilizer. MP-PDMS is commercially available and is much less expensive in comparison with general colloidal stabilizers used in $scCO_2$. Taking the industrialization into consideration, it will be advantageous to use MP-PDMS as a colloidal stabilizer in $scCO_2$.

In this article, we describe the production of PMMA particles by dispersion polymerization of MMA in $scCO_2$ with AIBN in the presence of MP-PDMS as a colloidal stabilizer.

Experimental

Materials

MMA was purified by distillation under reduced pressure in a nitrogen atmosphere. Reagent grade AIBN was purified by recrystallization. Two kinds of MP-PDMSs (X-22–167B and X-22–167C) supplied by Shin-Etsu Chemical Co. were used as received. The chemical formulae are given in Scheme 1.



$$HSC_3H_6-\overset{CH_3}{\underset{CH_3}{Si}}-O\left(\overset{CH_3}{\underset{CH_3}{Si}}-O\right)_n\overset{CH_3}{\underset{CH_3}{Si}}-C_3H_6SH$$

Scheme 1

The number-average molecular weights (M_n) of X-22–167B and X-22–167C are 3340 and 4820 g/mol, respectively [17]. Hereafter, these MP-PDMSs were defined as MP-PDMS3340 and MP-PDMS4820, respectively. Trimethylsiloxy terminated PDMS (TS-PDMS) with a weight-average molecular weight (M_w) of 5200 g/mol was used as received from Sigma Aldrich. Industrial grade CO_2, with a purity of 99.5% or more, was used. Guaranteed reagent *n*-hexane and chloroform were used as received from Nacalai Tesque. Sodium dodecyl sulfate (SDS) was used as received from Wako Pure Chemical Industries.

Dispersion polymerization in $scCO_2$

Dispersion polymerizations were carried out in 10-mL and 25-mL stainless steel reactors, which were originally constructed in our laboratory [18], under the conditions listed in Tables 1 and 2. Each reactor was charged with MMA, AIBN, MP-PDMS, and a 5/16-inch-sized stainless steel ball for the 10-mL reactor or a magnetic stir bar for the 25-mL reactor to mix in the reactors, and purged with N_2. Then, the reactors were pressurized with CO_2 to 10 MPa at 25 °C using a high-pressure pump (Nihon Seimitu Kagaku, NP-D-321 J) and shaking vigorously. The polymerizations were started

Table 1 Recipes for precipitation polymerization[a] of methyl methacrylate (MMA) with 2,2'-azobis(isobutyronitrile) (AIBN) and dispersion polymerizations[a] of MMA with AIBN in the presences of trimethylsiloxy terminated poly(dimethylsiloxane) (TS-PDMS[b]) and two kinds of mercaptopropyl terminated poly(dimethylsiloxane) (MP-PDMS[c,d]) in supercritical carbon dioxide (scCO2) in 10-mL high-pressure reactors with a stainless steel ball

Ingredients	(g)			
MMA[e]	2.0	2.0	2.0	2.0
AIBN[f]	0.01	0.01	0.01	0.01
TS-PDMS[b]	–	0.2	–	–
MP-PDMS3340[c]	–	–	0.2	–
MP-PDMS4820[d]	–	–	–	0.2

[a] ca. 30 MPa, 65 °C, 60 cycles/min, 24 h
[b] Number-average molecular weight (Mn) 5200 g/mol
[c] *M*n 3340 g/mol
[d] *M*n 4820 g/mol
[e] 2.0 mol/L (20 w/v%)
[f] Ri ($=2k_d f[I]$), 5.1×10^{13} mL^{-1} s^{-1}; k_d 7.7×10^{-6} s^{-1}; f 0.9

Table 2 Recipes for dispersion polymerizations of MMA with AIBN at different MPPDMS4820 concentrations in $scCO_2$ in the 10-mL high-pressure reactors[a] with the stainless steel ball and in a 25-mL high-pressure reactor[b] with a magnetic stir bar

Ingredients	MP-PDMS4820 concentration (wt% based on MMA)					
	0.5[a] (g)	2.5[a]	5.0[a]	10[a]	25[a]	10[b]
MMA[c]	2.0	2.0	2.0	2.0	2.0	5.0
AIBN[d]	0.01	0.01	0.01	0.01	0.01	0.025
MP-PDMS4820	0.01	0.05	0.1	0.2	0.5	0.5

[a] ca. 30 MPa, 65 °C, 60 cycles/min, 24 h
[b] ca. 30 MPa, 65 °C, 420 rpm, 24 h
[c] 2.0 mol/L (20 w/v%)
[d] Ri (= $2k_d f[I]$), 5.1×10^{13} mL^{-1} s^{-1}; k_d 7.7×10^{-6} s^{-1}; f 0.9

by heating the mixture to 65 °C, at which the pressure in the reactor reached about 30 MPa, with shaking at 60 cycles/min for the 10-mL reactor or with stirring at 420 rpm for the 25-mL reactor. After 24 h, the reactors were cooled in an ice water bath and the CO_2 was vented slowly. The polymerizations of MMA with AIBN initiator were conducted in a similar way in the absence/presence of TS-PDMS. The particles produced were observed with a Hitachi S-2460 N scanning electron microscope (SEM) after centrifugal washing with *n*-hexane which is a non-solvent for PMMA and a good solvent for PDMS [19].

X-ray photoelectron spectroscopy

The polymer composition of the particle surface was estimated by X-ray photoelectron spectroscopy (XPS) with a Shimadzu ESCA-3400 electron spectrometer using magnesium Kα radiation (1150 eV) at a potential of 8 kV and an X-ray current of 30 mA. The dried particles were spread at the surface of an indium plate with a spatula. Argon ion sputtering was conducted at 5.0×10^{-4} Pa for 150 s at a constant acceleration voltage of 1.5 kV and at an ion beam current of 20 mA.

Extraction of PDMS component

A chloroform (1.6 g) solution, in which PMMA particles (100 mg) produced in $scCO_2$ were dissolved, was emulsified in water (20 g) dissolving SDS (10 mg) using an ultrasonic homogenizer (US-300T, Nihonseiki Kaisha, Tokyo, Japan) in a glass cylindrical reactor, and then the chloroform was gradually released by evaporation from the emulsion under stirring at room temperature for 48 h. After three centrifugal washings with distilled water, the particles were dried and were redispersed in *n*-hexane. Then extraction of the PDMS component from the particles was conducted under stirring at room temperature for 2 weeks. After the extraction, the amount of PDMS component in the particles was determined using ^{1}H NMR. Extraction of PDMS component from the particles, which was made of the mixture of MP-PDMS4820 and PMMA homopolymer produced by solution polymerization in toluene, was conducted in the same way.

Results and discussion

The precipitation and dispersion polymerizations of MMA were carried out in $scCO_2$ at about 30 MPa for 24 h at 65 °C utilizing the 10-mL stainless steel reactor under the conditions listed in Table 1. The AIBN concentration giving R_i of 5.1×10^{13} mL^{-1} s^{-1} was chosen on the basis of the idea referred to in previous articles [15, 16].

Figure 1 shows PMMA produced by the precipitation and dispersion polymerizations with AIBN in $scCO_2$ after centrifugal washing with *n*-hexane, which is a good solvent for PDMS. In the case of the precipitation polymerization (Fig. 1a), PMMA was obtained as thick irregular translucent films on the interior wall of the reactor. In the presence of MP-PDMS3340 (Fig. 1c), the product was a thick irregular white PMMA film. In this case, the length of PDMS unit may be too small to stabilize PMMA particles. On the other hand, in the presence of MP-PDMS4820 (Fig. 1d), the product was obtained as non-spherical PMMA particles and thick irregular white PMMA films, and the conversion was gravimetrically determined to be 83%. Even after the washing, the PMMA particles were stably dispersed in *n*-hexane, which suggests that the PDMS component in the MP-PDMS bonded at the particle surface extended into the *n*-hexane medium and worked as a colloidal stabilizer. Because the solubility parameter values of both PDMS and *n*-hexane are the same value, 14.9 (MPa)$^{1/2}$ [19], PDMS chains must extend into the *n*-hexane medium. Since the PDMS component is CO_2-philic, it should effectively operate as a colloidal protective layer to disperse the PMMA particles stably in $scCO_2$ medium during the dispersion polymerization. The number-average diameter (D_n) and the coefficient of variation (C_v) for the washed PMMA particles measured on the SEM photograph with image analysis software (MacScope, Mitani) were 1.71 μm and 33%, respectively. The weight percentage of the PDMS component in the washed PMMA particles was determined to be 0.9%, from ^{1}H NMR spectra measured with a Bruker DPX250 NMR spectrometer operating at 250 MHz for proton with 200 scans. The M_n and M_w/M_n ratio for the washed PMMA particles were, respectively, 1.5×10^5 g/mol and 2.2, which were determined from gel perme-

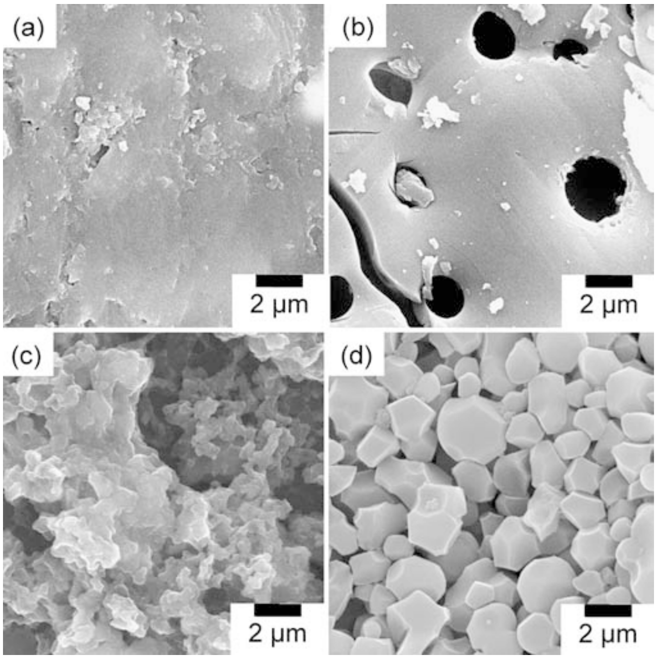


Fig. 1a–d Scanning electron microscope (SEM) photographs of poly(methyl methacrylate) (PMMA) particles produced by precipitation polymerization with 2,2'-azobis(isobutyronitrile) (AIBN) (**a**) and by dispersion polymerizations of methyl methacrylate (MMA) with AIBN in the presence of trimethylsiloxy terminated poly(dimethylsiloxane) (**b**) and two kinds of mercaptopropyl terminated poly(dimethylsiloxane) (MP-PDMS) [M_n3340 g/mol (**c**); 4820 g/mol (**d**)] in supercritical carbon dioxide ($scCO_2$) in 10-mL high-pressure reactors after a centrifugal washing with *n*-hexane

ation chromatograms with tetrahydrofuran as the eluent. In the case of TS-PDMS (Fig. 1b), which had a similar molecular weight (M_w, 5200 g/mol) to that of MP-PDMS4820, PMMA was obtained as thick irregular translucent films on the interior wall of the reactor. This result indicates that anchoring of the TS-PDMS at the surface of the PMMA particle generated was inefficient. Chain transfer constants (C_s) to 3-(3-mercaptopropyl)siloxane and dodecamethyl pentasiloxane, which could be thought to be model reagents of MP-PDMS and TS-PDMS, respectively, in radical polymerization of MMA at 79.5 °C were 1.28×10^{-1} and 1.45×10^{-5}, respectively [19]. C_s value of 3-(3-mercaptopropyl)siloxane was four orders of magnitude higher than that of dodecamethyl pentasiloxane. There were reports that in the presence of TS-PDMS, PMMA and PS particles were not obtained by dispersion polymerization with AIBN in $scCO_2$ [3, 4] nor in heptane [20]. That is, in these polymerization systems, the TS-PDMS did not operate as an effective colloidal stabilizer, because it did not occupy their particle surfaces by chemical grafting or physical adsorption. On the other hand, in the case of the MP-PDMS, based on the large C_s value, it is expected that PDMS-*g*-PMMA will be generated by the chain transfer reaction to terminal mercaptopropyl group of the MP-PDMS during the dispersion polymerization of MMA and the block copolymer should work as an effective colloidal stabilizer in $scCO_2$.

In order to check whether MP-PDMS molecules, which were free in *n*-hexane and adsorbed physically on the PMMA particles, were washed away by the above centrifugal washing with *n*-hexane, the amount of PDMS in the PMMA particles produced in the presence of MP-PDMS4820 was measured using ^{1}H NMR after ten centrifugal washings with *n*-hexane for a mixture of *n*-hexane (25 g), MP-PDMS4820 (1 g), and the PMMA particles already washed (100 mg). The mixture was kept for 24 h at room temperature before the washing. The weight percentage of the PDMS component in the PMMA particles after the ten washings was consistent with that of the washed PMMA particles before the mixing with the MP-PDMS. This indicates that the MP-PDMS molecules, which were free and adsorbed physically, were washed away by the washing. In the following procedures, the dispersion polymerizations were carried out in the presence of MP-PDMS4820.

Figure 2 shows XPS Si_{2p} spectra of the washed PMMA particles before (a) and after (b) argon ion sputtering. A peak due to the PDMS component was observed at 103 eV before the sputtering, and was weakened and shifted to 102 eV after the sputtering. It was confirmed that the intensity of Si_{2p} peak due to the PDMS component was not weakened when pure PDMS-based azoinitiator (VPS-0501, Wako Pure Chemical Industries) was sputtered under the same conditions. The peak shift should be due to the chemical change of the PDMS component by the argon ion sputtering. These results indicate that the PDMS component mainly existed at the surfaces of the washed PMMA particles.

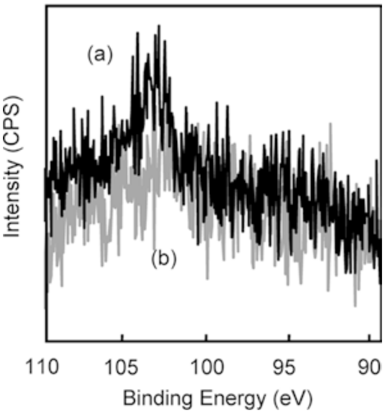


Fig. 2 X-ray photoelectron spectroscope Si_{2p} spectra of PMMA particles produced by the dispersion polymerization with AIBN in the presence of MP-PDMS with M_n of 4820 g/mol (MP-PDMS4820) in $scCO_2$ in the 10-mL high-pressure reactor after the centrifugal washing with *n*-hexane, before (*a*) and after (*b*) argon ion sputtering at 5.0×10^{-4} Pa for 150 s at a constant acceleration voltage of 1.5 kV and at an ion beam current of 20 mA

Figure 3 shows SEM photographs of PMMA particles produced at different MP-PDMS4820 concentrations (wt% based on MMA) under the conditions listed in Table 2. At 0.5 wt%, all PMMA was obtained as a thick irregular white film. At 2.5–25 wt%, non-spherical PMMA particles and white PMMA films were prepared, and the particle diameter decreased from micron to submicron with an increase in the MP-PDMS4820 concentration. At 25 wt%, the weight percentage of the PDMS component in the particles after the washing was determined to be 1.6 wt%, which was a larger value than that at 10 wt%. In order to check whether or not PDMS-*b*-PMMA was generated by a chain transfer reaction during the dispersion polymerization, an extraction experiment was conducted. To minimize experimental error, the PMMA particles produced at the MP-PDMS4820 concentration of 25 wt% were used. The amount of the PDMS component in the PMMA particles was not changed much before and after the extraction with *n*-hexane, which is a non-solvent for PMMA and a good solvent for PDMS [19], whereas that in the particles made of the mixture of MP-PDMS4820 and PMMA prepared by solution polymerization in toluene decreased to the experimental error level by the extraction. These results show that the PDMS component in the PMMA particles produced in $scCO_2$ was not due to MP-PDMS4820 included inside the particles but to PDMS-*b*-PMMA generated by the chain transfer reaction during the dispersion polymerization. Thus, the

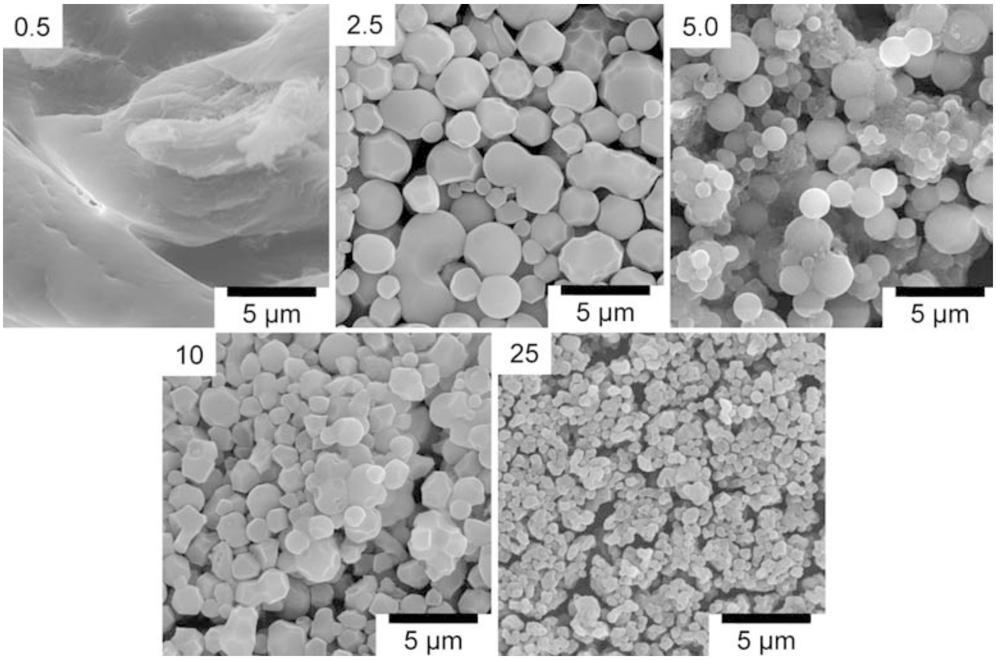


Fig. 3 SEM photographs of PMMA particles produced by the dispersion polymerization with AIBN at different MP-PDMS4820 concentrations (wt% based on MMA) in $scCO_2$ in the 10-mL high-pressure reactors after the centrifugal washing with *n*-hexane

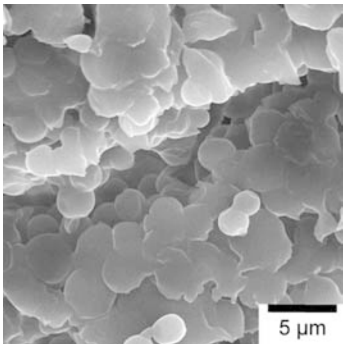


Fig. 4 SEM photograph of a section of a thick irregular white PMMA film produced by the dispersion polymerization with AIBN at MP-PDMS4820 concentration of 10 wt% based on MMA in $scCO_2$ in the 10-mL stainless steel high-pressure reactor after the centrifugal washing with *n*-hexane

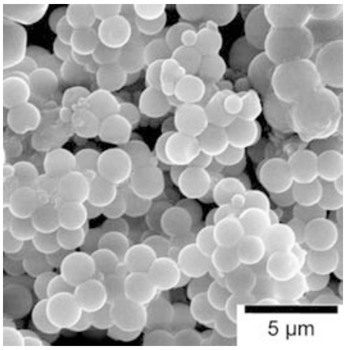


Fig. 5 SEM photograph of PMMA particles produced by dispersion polymerization with AIBN at MP-PDMS4820 concentration of 10 wt% based on MMA in $scCO_2$ in the 25-mL high-pressure reactor after the centrifugal washing with *n*-hexane

MP-PDMS had two functions in the polymerization: a chain transfer agent and a colloidal stabilizer. Hereafter, it is called "transtab" (a *tran*sfer agent and a colloidal *stab*ilizer).

Figure 4 shows a SEM photograph of a section of the thick irregular white PMMA film produced by the dispersion polymerization at the MP-PDMS4820 concentration of 10 wt%. The film seems to be formed by coagulation of the particles. Because PMMA is highly plasticized by CO_2, glass transition temperature (T_g) of PMMA particles is lowered in $scCO_2$ [21, 22, 23, 24]. Fehrenbacher and coworkers reported that PMMA film sorbed 28 vol% of CO_2 based on the volume of PMMA film in $scCO_2$ at 59.8 °C and 29.9 MPa [25]. Assuming that the density of PMMA and CO_2 in PMMA are, respectively, estimated to be 1.19 [19] and 1.0 g mL^{-1} [25, 26], the weight ratio of $PMMA/CO_2$ in the $scCO_2$ is calculated to be 1/0.24. Condo and coworkers predicted that T_g of PMMA, which sorbed about 25 wt% of CO_2 based on the weight of PMMA, might be reduced to about –25 °C [21]. From the above data and the prediction, it should be considered that T_g of PMMA particles in $scCO_2$ at 65 °C and 30 MPa was reduced near –25 °C. This value may be somewhat different from the actual value in the dispersion polymerization system, because the PMMA particles contains MMA in addition to CO_2 during the dispersion polymerization. Considering that the density of CO_2-sorbed PMMA particles in the $scCO_2$ (1.15 g mL^{-1})

should be larger than that of $scCO_2$ (0.85 g mL^{-1}) at 60 °C and 32.9 MPa, micron-sized, CO_2-sorbed PMMA particles in the $scCO_2$ should sediment by the end of the dispersion polymerization without efficient stirring. In the dispersion polymerization of MMA in the 10-mL reactor with the stainless steel ball, the efficiency of stirring may be low [18] and the CO_2-sorbed PMMA particles, whose T_g might be near – 25 °C, seem to sediment, which results in deformation of PMMA particles and formation of the thick irregular white PMMA film. The formation of the PMMA film must be promoted by rolling of the stainless steel ball on the sedimented PMMA particles.

To improve the efficiency of stirring, the 25-mL high-pressure reactor, which has higher efficiency of stirring in comparison with 10-mL reactor [18], was used. In this reactor, the stirring was conducted with the magnetic stir bar. Utilizing the 25-mL high-pressure reactor, PMMA was almost obtained as a free-flowing white powder under the conditions shown in Table 2, and it was confirmed that spherical PMMA particles were produced as shown in Fig. 5. The conversion was determined to be 82%, which was almost the same value as that obtained utilizing the 10-mL high-pressure reactor. D_n and C_v of the washed PMMA particles were 2.37 μm and 16%, respectively, and the diameter became larger and the C_v value was decreased by increasing of the stirring efficiency. The weight percentage of the PDMS component in the washed PMMA particles was determined to be 2.9%, which corresponds to 24 wt% of the total amount of MP-PDMS4820 put in the polymerization system. The M_w and M_w/M_n ratio for the washed PMMA particles were, respectively, 2.5×10^5 g/mol and 2.5.

From the above results, it is concluded that submicron-sized to micron-sized PMMA particles could be produced by the dispersion polymerization of MMA in $scCO_2$ with AIBN in the presence of MP-PDMS as a transtab.

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