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SHORT COMMUNICATION

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Preparation of poly(methyl methacrylate) particles by dispersion polymerization with organic peroxide in the presence of trimethylsiloxy terminated poly(dimethylsiloxane) in supercritical carbon dioxide

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Abstract Dispersion polymerizations of methyl methacrylate (MMA) were conducted with various types of organic peroxides as radical initiator in the presence of trimethylsiloxy terminated poly(dimethylsiloxane) in supercritical carbon dioxide. Micron-sized, relatively "monodisperse" poly(MMA) particles were prepared by using benzoyl peroxide.

Introduction

Recently, there is an increasing interest in carrying out chemical reactions and extractions in environmentally benign solvents such as 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. The papers describing the dispersion polymerization of vinyl monomers such as styrene (S) and methyl methacrylate (MMA) in $scCO_2$ have been published since 1994 [1–17].

DeSimone and co-workers have pioneered the preparations of polystyrene (PS) particles by dispersion polymerizations of S 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 prepared by dispersion polymerizations of MMA in $scCO_2$ with AIBN in the presences of PFOA [5–9] and PDMS-based macromonomer [3] as colloidal stabilizers. Lepilleur and Beckman [10], Yates et al. [11], Hems et al. [12] and Christian et al. [13] also prepared 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 et al. prepared PMMA particles by gamma radiation induced dispersion polymerization with different types of PDMS in $scCO_2$ [14]. In recent articles, we prepared PMMA particles by dispersion polymerization in $scCO_2$ with various types of PDMS-based polymers such as PDMS-based azoinitiator as an inistab (*ini*tiator + *stab*ilizer)

[15], aminopropyl terminated PDMS [16] and mercaptopropyl terminated PDMS as a transtab (*trans*fer agent + *stab*ilizer) [17].

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 that PDMS-based polymers are much less expensive and their solubility in conventional organic solvents makes characterizations of the products obtained easy. Up to the present, there are papers on the preparations of PS and PMMA particles by dispersion polymerizations in the presence of PDMS-based polymers in $scCO_2$ [3, 11, 14–17]. In these studies, polymer particles have not been successfully prepared by dispersion polymerization with trimethylsiloxy terminated PDMS (TS-PDMS) as a colloidal stabilizer in $scCO_2$. This seems to be based on that stabilization by physical adsorption of TS-PDMS on the particle surface was ineffective and little chemical grafting of TS-PDMS to the surface of the particles took place when AIBN was used as an initiator [3, 4, 18], because primary radicals generated by decomposition of AIBN and propagating polymer radicals, such as PS and PMMA radicals, had low ability to abstract hydrogens from methyl group of TS-PDMS. Radicals generated by decomposition of organic peroxides are known to be able to abstract hydrogens from methyl groups of TS-PDMS [19]. Using organic peroxides as radical initiators, chemical grafting of TS-PDMS to the surface of the particles should be expected to be possible.

In this article, dispersion polymerizations of MMA will be conducted with various types of organic peroxides as radical initiators in the presence of TS-PDMS for the preparation of PMMA particles in $scCO_2$.

Experimental

Materials

MMA was purified by distillation under reduced pressure in a nitrogen atmosphere. TS-PDMS with a weight-average molecular weight (M_w) of about 5,200 g/mol was used as received from Sigma-Aldrich Co.

Industrial grade CO_2, with a purity of 99.5% or more, was used. Reagent grade benzoyl peroxide (BPO) and AIBN were purified by recrystallization. Reagent grade lauroyl peroxide (LPO) and *n*-hexane were used as received from Nacalai Tesque Co. Bis(4-*t*-butylcyclohexyl)peroxy dicarbonate (p-TCP) supplied by NOF Co. was used as received. The purity of the p-TCP was 90%.

Dispersion polymerization in $scCO_2$

Dispersion polymerizations were carried out in a 10-mL stainless steel reactor, which was originally constructed in our laboratory [20]. The reactor was charged with MMA, organic peroxide, TS-PDMS and a 5/16-in-sized stainless steel ball to mix in the reactor and purged with N_2. Then the reactor was pressurized with CO_2 to 10 MPa at 25°C using a high-pressure pump (Nihon Seimitu Kagaku Co., NP-D-321J) and by shaking vigorously. The polymerizations were started by heating the mixture to desired temperature, with shaking at 60 cycles/min. After 24 h, the reactor was cooled in an ice water bath and the CO_2 was vented slowly. The prepared particles were observed with a Nikon MICROPHOT-FXA optical microscope and a Hitachi S-2500 scanning electron microscope (SEM) after centrifugal washing with *n*-hexane which is a nonsolvent for PMMA and a good solvent for PDMS [21].

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 (1,150 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 180 s at a constant acceleration voltage of 1.5 kV and at an ion beam current of 20 mA.

Results and discussion

The dispersion and precipitation polymerizations of MMA were carried out in $scCO_2$ for 24 h with different types of organic peroxides as radical initiators utilizing the 10-mL stainless steel reactor under the conditions listed in Table 1. The initiator concentration and initiation rate of radical polymerization, R_i, were kept constant. R_i is given by $f\rho_i$, where f is the initiator efficiency and ρ_i is the generation rate of radicals. The ρ_i is expressed as 2 k_d[I], where k_d is the rate coefficient for initiator decomposition, and [I] is the initiator concentration. The initiator concentration and polymerization temperature were determined on the basis of the idea described as follows. In general, dispersion polymerizations were carried out in R_i range of 10^{13} – 10^{14} mL^{-1} s^{-1} [22–24]. Guan et al. [25] reported that k_d and f values of AIBN in $scCO_2$ were, respectively, about 2.5 times lower and about 1.5 times higher than those observed in benzene at the same temperature and at atmospheric pressure because of low dielectric constant and low viscosity of $scCO_2$. In this experiment,

Table 1 Recipes for precipitation polymerization[a] and dispersion polymerizations of methyl methacrylate (MMA) with various types of initiators in the presence of trimethylsiloxy terminated poly(dimethylsiloxance) (TS-PDMS) in supercritical carbon dioxide ($scCO_2$) for 24 h at the same initiation rate of the radical polymerization ($R_i = 2\ k_d\ f[I]\ =\ 2.1 \times 10^3\ mL^{-1}\ s^{-1}$)

Ingredients						
MMA[b]	(g)	0.5	0.5	0.5	0.5	0.5
TS-PDMS[c]	(g)	–	0.05	0.05	0.05	0.05
BPO	(g)	0.0097	0.0097	–	–	–
p-TCP	(g)	–	–	0.0159	–	–
LPO	(g)	–	–	–	0.0159	–
AIBN	(g)	–	–	–	–	0.0073
Temperature	(°C)	70	70	36.7	54.6	59.9
Conversion	(%)	9	32	10	15	17

[a] 10-mL stainless steel reactor; 60 cycles/min

[b] 0.5 mol/L (5 w/v%)

[c] Weight-average molecular weight (M_w), ca. 5200; 10 wt% based on MMA

assuming that the k_d and f values of organic peroxides in $scCO_2$ have the same tendency as those of AIBN in $scCO_2$, the initiator concentration and polymerization temperature giving R_i of $2.1\times10^{13}\ mL^{-1}\ s^{-1}$ were chosen. The k_d and f values used in the calculations were $4.4\times10^{-6}\ s^{-1}$ and 1.0 for the organic peroxides, and $4.4\times10^{-6}\ s^{-1}$ and 0.9 for AIBN, respectively. These values calculated for pure $scCO_2$ may be somewhat different from those for the mixture of $scCO_2$ and MMA. Actually, there are reports that the rates of AIBN decomposition in a mixture of CO_2 and cosolvent such as tetrahydrofuran [25, 26] and methanol [27] were higher than that in pure CO_2. In calculating the k_d value in $scCO_2$ using Arrhenius equation, the activation energies of 118.7 and 126.2 kJ/mol were used for p-TCP and LPO, respectively [28]. In the case of the precipitation polymerization with BPO, PMMA was obtained as very glutinous liquid and thick irregular translucent films on the interior wall of the reactor. In the case of the dispersion polymerization with AIBN in the presence of TS-PDMS, PMMA was obtained as glutinous liquid. The conversions of the precipitation and dispersion polymerizations were gravimetrically determined to be 9% and 17%, respectively. In the cases of p-TCP and LPO in the presence of TS-PDMS, glutinous liquids were obtained, and the conversions were 10% and 15%, respectively. These results indicate that anchoring of the TS-PDMS on PMMA precipitated in the $scCO_2$ medium during the dispersion polymerization was inefficient. On the other hand, in the case of BPO in the presence of

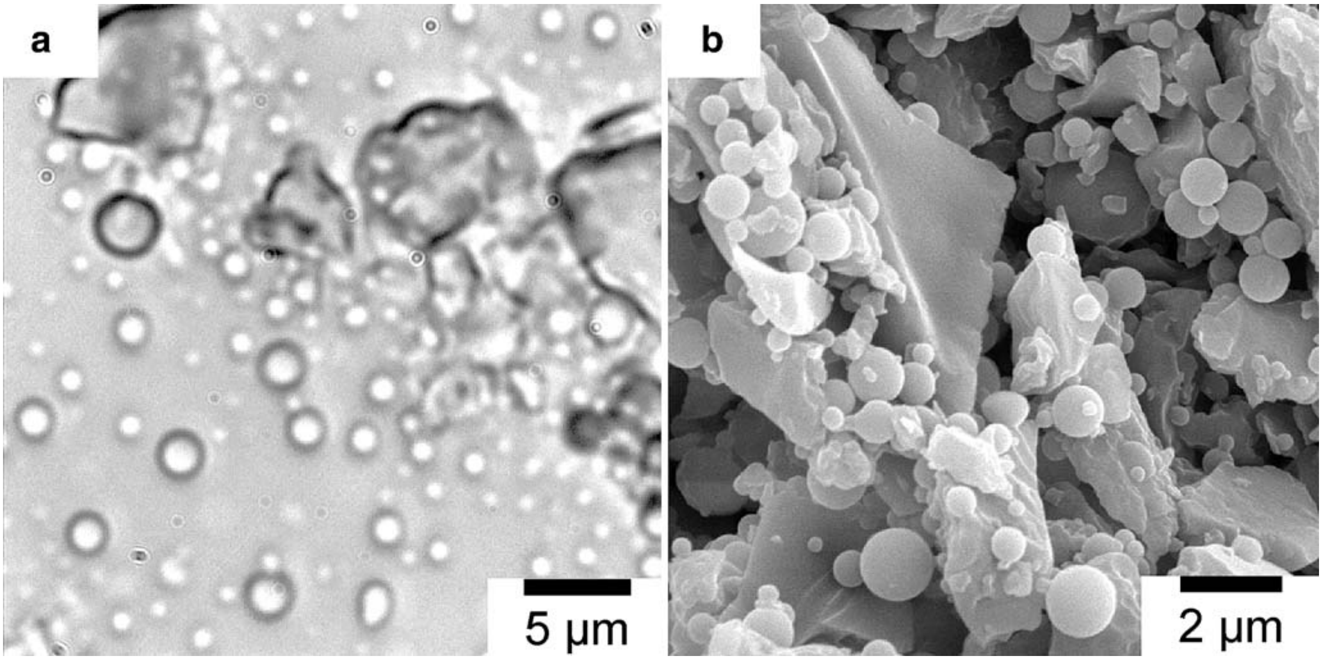
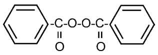
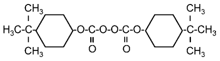
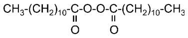
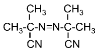


Fig. 1 An optical micrograph (**a**) and a SEM photograph (**b**) of centrifugally washed PMMA with *n*-hexane, which were prepared by dispersion polymerization of MMA with BPO (4.0 mmol/L) in the presence of TS-PDMS (10 wt% based on MMA) in $scCO_2$. In Fig. 1a, PMMA were redispersed in *n*-hexane

Table 2 Chemical formulas of benzoyl peroxide (BPO), bis(4-*t*-butylcyclohexyl)peroxy dicarbonate (p-TCP), lauroyl peroxide (LPO) and 2, 2′-azobis(isobutyronitrile) (AIBN), and their cross-liking efficiencies[a] estimated by the amount of dimers of pentadecane prepared during the decompositions of initiators in pentadecane[b]

	Chemical formulas	Cross-linking efficiencies	Temperature for decomposition (°C)
BPO		28	104.4
p-TCP		24	74.6
LPO	 CH_3-$(CH_2)_{10}$-C(=O)-O-O-C(=O)-$(CH_2)_{10}$-CH_3	8	90.8
AIBN	 CH_3-C(CH_3)(CN)-N=N-C(CH_3)(CN)-CH_3	1	93.1

[a] Percentage of the radicals used in dimerization of pentadecane

[b] Decomposition reactions were conducted for 3 h at temperature where the initiator had a half time of 15 min

Table 3 Dispersion polymerization[a] of MMA with BPO at different TS-PDMS concentrations in $scCO_2$ for 24 h at 70°C

Ingredients	TS-PDMS (wt% based on MMA)			
	10	100	200	400
MMA[b] (g)	0.5	0.5	0.5	0.5
TS-PDMS[c] (g)	0.05	0.5	1.0	2.0
BPO[d] (g)	0.0097	0.0097	0.0097	0.0097
PMMA particles[e] (wt%)	1	47	44	100

[a] 10-mL stainless steel reactor; 60 cycles/min

[b] 0.5 mol/L (5 w/v%)

[c] (M_w), ca. 5200

[d] 4.0 mmol/L; Ri (=2 $k_d f$[I]), 2.1×10^{13} mL^{-1} s^{-1}

[e] The amount of PMMA particles based on the total amount of PMMA prepared

TS-PDMS, the product was obtained as thick irregular white turbid films, and the conversion was 32%. The reason that why PMMA was obtained not as glutinous liquid but as solid films even at the conversion of 32% must be based on the extraction of most of residual MMA together with the vent of CO_2.

Figure 1 shows an optical micrograph (a) of PMMA dispersion prepared by sonication of the PMMA film in *n*-hexane, which was prepared by the dispersion polymerization with BPO initiator in $scCO_2$, after the centrifugal washing with *n*-hexane, and its SEM photograph (b). *n*-Hexane is a nonsolvent for PMMA and a good solvent for PDMS. In these photographs, many spherical PMMA particles were observed in addition to the coagulants.

Table 2 shows cross-linking efficiencies of the organic peroxides and AIBN, which were estimated by the amount of dimers of pentadecane prepared during the decompositions of the organic peroxides in pentadecane [29, 30]. BPO, p-TCP, LPO and AIBN were, respectively, decomposed for 3 h at temperatures of 104.4°C, 74.6°C, 90.8°C and 93.1°C, at which they had a half life of 15 min. The cross-linking efficiency increases with an increase of ability to abstract hydrogen [29, 30]. Assuming that these values measured for pentadecane could be applied to TS-PDMS, hydrogen abstraction from methyl groups of TS-PDMS should occur more frequently in the case of BPO than in the cases of p-TCP, LPO and AIBN. From the above consideration, it seems that some amount of PDMS-*g*-PMMA, which must work as an effective colloidal stabilizer, were generated by abstraction of hydrogens from methyl group of TS-PDMS using BPO and resulted in the production of PMMA particles. On the other hand, when p-TCP, LPO and AIBN were used, too small amount of PDMS-*g*-PMMA might be generated to prepare PMMA particles during the dispersion polymerization in $scCO_2$.

In order to generate larger amount of PDMS-*g*-PMMA, dispersion polymerizations were conducted with larger amounts of TS-PDMS under the conditions listed in Table 3. The larger the amount of TS-PDMS was loaded, the larger the amount of PMMA particles were prepared in comparison with that of PMMA films as shown in Table 3, and the degree of coagulation of the PMMA particles decreased as shown in Fig. 2.

At TS-PDMS concentration of 400 wt% based on MMA, all PMMA was obtained as particles and the conversion was 67% after the washing with *n*-hexane for the removal of excess TS-PDMS. The conversion was much higher than that in the system in which PMMA coagulants were prepared. This result was consistent

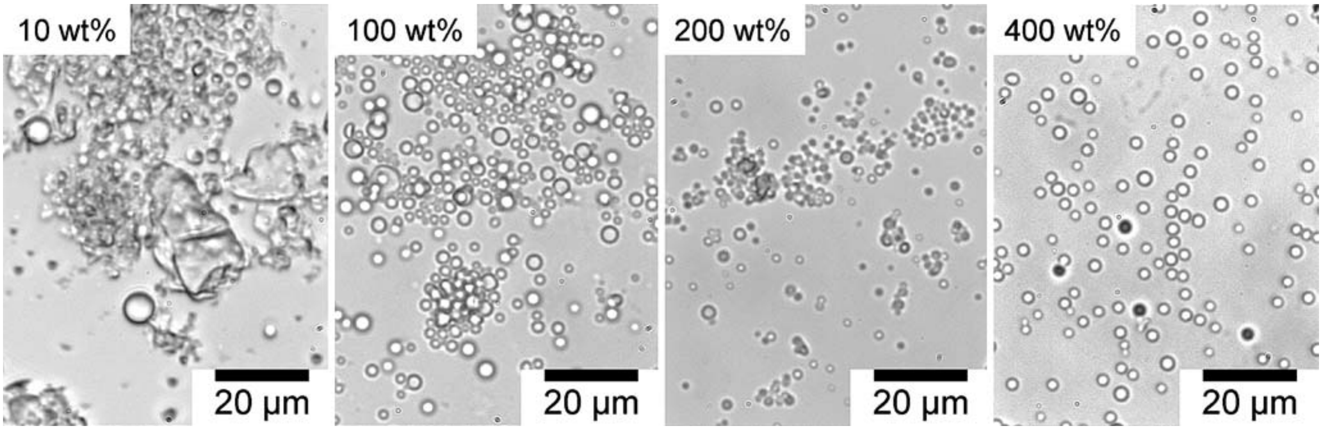
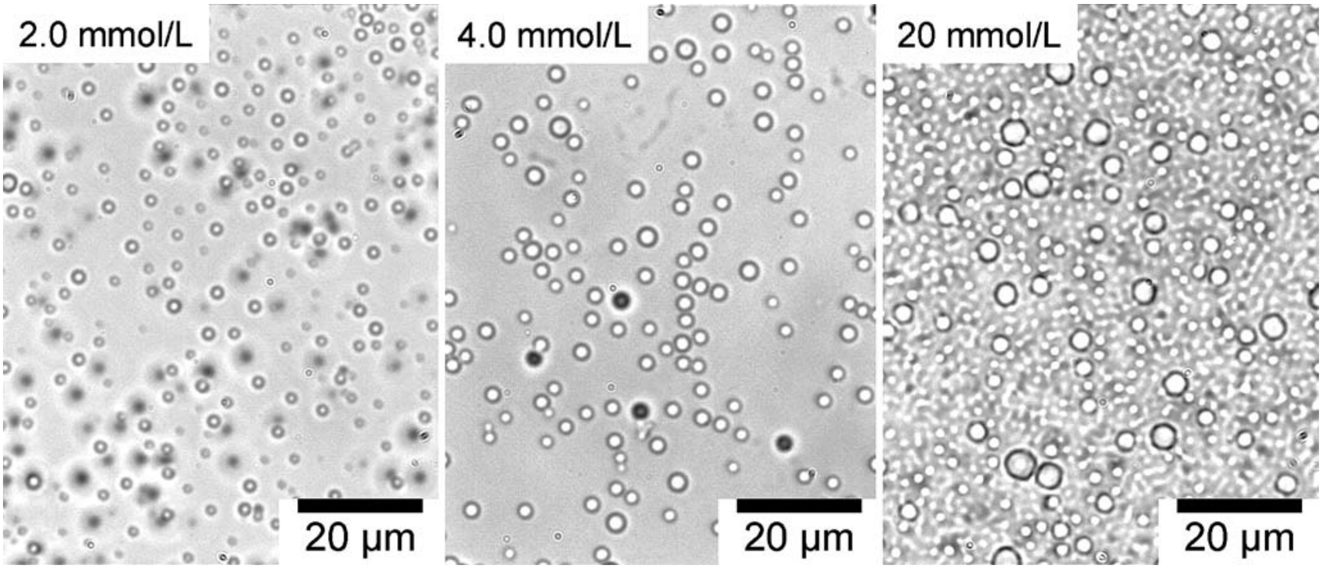


Fig. 2 Optical micrographs of *n*-hexane redispersions of centrifugally washed PMMA particles with *n*-hexane, which were prepared by dispersion polymerizations with BPO (4.0 mmol/L) at different TS-PDMS concentrations (wt% based on MMA) in $scCO_2$

with those of other dispersion polymerization systems in $scCO_2$ [1–6, 8, 12, 13, 15–17]. Even after the washing, the PMMA particles were stably dispersed in *n*-hexane. Because the solubility parameter values of both PDMS and *n*-hexane are the same, 14.9 $(MPa)^{1/2}$ [31] and *n*-hexane is a good solvent for PDMS, PDMS chains must extend into *n*-hexane medium. These suggest that PDMS component bonded at the particle surface extended into the *n*-hexane medium and worked as a colloidal stabilizer. 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), particle size distribution (D_w/ D_n) and the coefficient of variation (C_v) for the PMMA particles prepared at the TS-PDMS concentration of 400 wt% measured on the SEM photograph with image analysis software (MacScope, Mitani Co.) were 1.51 μm, 1.06% and 15%, respectively. The weight percentage of the PDMS component in the washed PMMA particles was determined to be 1.0%, from ^{1} H NMR spectra measured with a Bruker DPX250 NMR spectrometer operating at 250 MHz for proton with 200 scans. The M_w and M_w/ M_n ratio for the washed PMMA particles were, respectively, 1.0×10^5 g/mol and 3.2, which were determined from gel permeation chromatograms with tetrahydrofuran as the eluent.

Figures 3 and 4 show, respectively, optical micrographs and SEM photographs of centrifugally washed PMMA particles with *n*-hexane, which were prepared at different BPO concentrations giving R_i in the range of

Fig. 3 Optical micrographs of *n*-hexane redispersions of centrifugally washed PMMA particles with *n*-hexane, which were prepared by dispersion polymerizations at different concentrations of BPO (mmol/L) in the presence of TS-PDMS (400 wt% based on MMA) in $scCO_2$ for 24 h



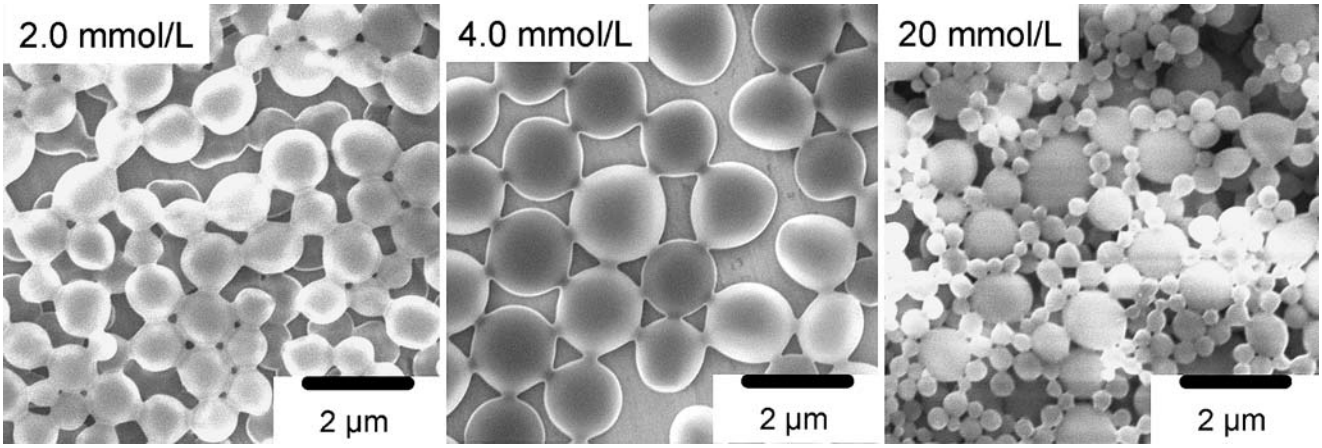


Fig. 4 SEM photographs of centrifugally washed PMMA particles with *n*-hexane, which were prepared by dispersion polymerizations at different concentrations of BPO (mmol/L) in the presence of TS-PDMS (400 wt% based on MMA) in $scCO_2$

Table 4 Dispersion polymerization[a] of MMA at different BPO concentrations in the presence of TS-PDMS in $scCO_2$ for 24 h at 70°C

Ingredients		BPO (mmol/L)		
		2.0	4.0	20.0
$R_i(=2k_d f[I])(mL^{-1}s^{-1})\times 10^{-13}$		1.1	2.1	11
MMA[b]	(g)	0.5	0.5	0.5
TS-PDMS[c]	(g)	2.0	2.0	2.0
BPO	(g)	0.0048	0.0097	0.0484

[a] 10-mL stainless steel reactor; 60 cycles/min

[b] 0.5 mol/L (5 w/v%)

[c] (M_w), ca. 5200; 400 wt% based on MMA

1.1×10^{13} –1.1×10^{14} mL^{-1} s^{-1} under the conditions listed in Table 4. In BPO concentration range of 2–20 mmol/L, all PMMA were obtained as particles. At 2.0 mmol/L, the conversion and D_n were 24% and 930 nm, respectively. At 20 mmol/L, polydisperse PMMA particles were prepared, and the conversion, D_n, $D_w/$ D_n and C_v were 67%, 465 nm, 2.80% and 59%, respectively. The conversion at 4.0 mmol/L was almost the same as that at 20 mmol/L, and it did not increase even if the polymerization time was extended to 48 h.

Figure 5 shows XPS Si_{2p} spectra before (a) and after (b) argon ion sputtering of the PMMA particles washed with *n*-hexane to remove free PDMS. In Fig. 5a, a peak due to PDMS component was observed at 103 eV, and in Fig. 5b, the peak was weakened and shifted to 101 eV after the sputtering. The intensity of Si_{2p} peak due to PDMS component was not weakened when pure PDMS-based azoinitiator (VPS-0501, Wako Pure Chemical Industries, Ltd.) was sputtered under the same conditions. These results indicate that the surfaces of the washed PMMA particles were occupied by the PDMS component that was etched by the sputtering.

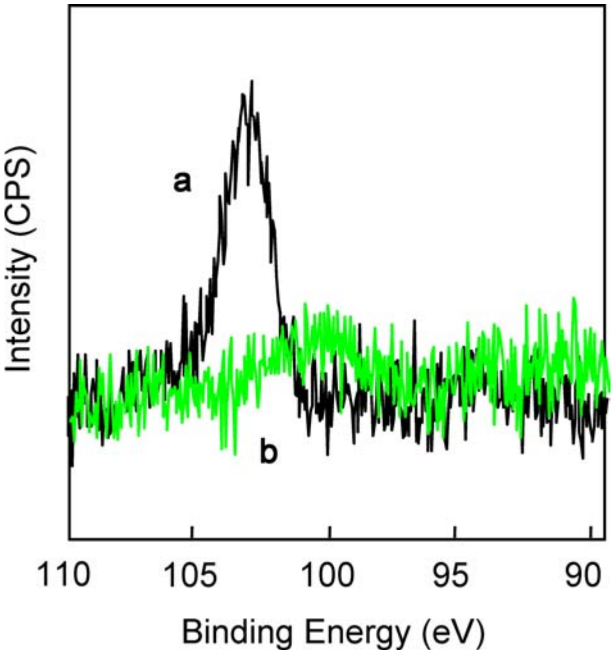


Fig. 5 XPS Si_{2p} spectra for PMMA particles, which were prepared by the dispersion polymerization with BPO (4.0 mmol/L) in the presence of TS-PDMS (400 wt% based on MMA) in $scCO_2$, before (**a**) and after (**b**) argon ion sputtering at 5.0×10^{-4} Pa for 180 s at a constant acceleration voltage of 1.5 kV and at an ion beam current of 20 mA

From the aforementioned results, it was concluded that micron-sized, relatively monodisperse PMMA particles could be prepared by the dispersion polymerization in the presence of TS-PDMS in $scCO_2$ with BPO initiator.

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