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博士論文

Studies on Production of Polymer Particles in Supercritical Carbon Dioxide

超臨界二酸化炭素を重合媒体とする高分子微粒子の作製に関する研究

２００３年１月

神戸大学大学院自然科学研究科

藤井　秀司

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Contents

General 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 [1, 2] on polymerizations in aqueous and alcohol/water media: emulsion, dispersion, suspension and miniemulsion polymerizations.

Recently, in addition to water, there have been increasing interests in supercritical carbon dioxide ($scCO_2$). Carbon dioxide (CO_2) is naturally occurring and readily available. Sources of CO_2 include both abundant natural reservoirs and recycled CO_2 which is recovered from the exhaust streams of power plants and industrial plants which produce ammonia, ethanol, ethyl-

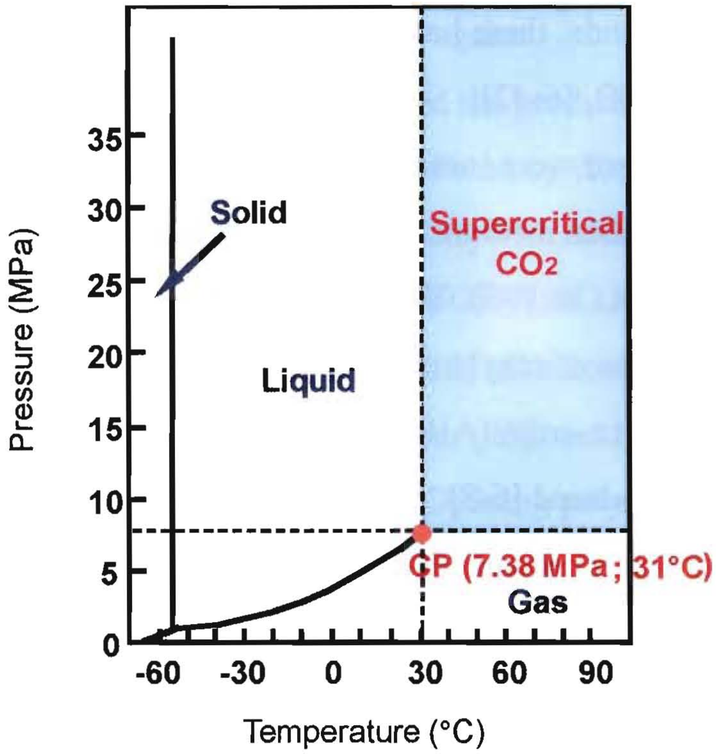

Figure 1 A pressure-temperature diagram for CO_2

ene oxide, and hydrogen [3]. Additionally, CO_2 has an easily accessible critical point with a T_c of 31.1°C and a P_c of 7.38 MPa [4] as shown in Fig. 1. The use of $scCO_2$ as a medium for polymerizations has several potential advantages: low cost, no toxicity, and marked variations of solubility power, viscosity and polarity by relatively small changes in temperature and pressure without altering the composition of the medium. Moreover, the use of $scCO_2$ eliminates the need for energy intensive drying processes; the polymers produced in $scCO_2$ are obtained completely in dry state only by venting to remove the CO_2. This should be especially advantageous for polymers which are not heat-stable to be dried. Furthermore, the use of $scCO_2$ makes possible the effective use of a greenhouse gas. Since 1751, roughly 277 billion tons of carbon have been released to the atmosphere from the consumption of fossil fuels and cement production [5], and a proposal to reduce greenhouse gasses was presented at the United Nations meeting in Kyoto. From the above backgrounds, there have been increasing interests in conducting polymerization in CO_2 [6-42].

In the 1960s, there were initial breakthroughs in the use of compressed CO_2 as a polymerization medium, especially in cationic and radical precipitation polymerizations. In 1968, Hagiwara and coworkers conducted precipitation polymerization of ethylene in CO_2 using either gammma radiation or 2,2'-azobis(isobutyronitrile) (AIBN) initiation, and indicated that polyethylene powder was produced [6-8]. Also in 1968, a French Patent issued to the Sumitomo Chemical Company disclosed the precipitation polymerization of several vinyl monomers in CO_2 [9]. The United States version of this patent was issued in 1970, when Fukui and coworkers published results for the precipitation polymerization of several vinyl monomers such as vinyl chloride, styrene (S), acrylonitrile (AN), acrylic acid and vinyl acetate in liquid CO_2 or $scCO_2$ [10]. In 1960, Biddulph and Plesch conducted cationic precipitation polymerization of isobutylene in liquid CO_2 [11]. In the late 1960s, Yokota and coworkers conducted cationic precipitation polymerization of formaldehyde in liquid CO_2 or $scCO_2$ [12-14]. The patent issued in 1970 included the polymerization of ethyl vinyl ether in liquid CO_2 [10]. These studies on polymerizations in CO_2 in 1960s were followed by very little activity in the 1970s and 1980s. In 1990s, however, there have been an increasing number of research in this area [15-42]. The next breakthrough in the use of CO_2 as a polymerization medium was realized when some amorphous fluorinated and PDMS-based polymers were identified as being soluble in CO_2 or CO_2-philic at easily attainable temperatures ($T < 100°C$) and pressures ($P < 35$ MPa). This realization opened up research area of production of polymer particles by dispersion and inverse emulsion polymerizations in CO_2, and precipitation polymerization in CO_2 drew attentions again.

DeSimone and coworkers have pioneered the productions of poly(methyl methacrylate) (PMMA) particles were produced by dispersion polymerizations of methyl methacrylate (MMA) in $scCO_2$ with AIBN in the presence of poly(1,1-dihydroperfluorooctyl acrylate) (PFOA) [18-22] and poly(dimethylsiloxane) (PDMS)-based macromonomer [23] as colloidal stabilizers. Lepilleur and Beckman [24], Yates and coworkers [25], and Hems and coworkers [26] also produced PMMA particles in $scCO_2$ using poly(MMA-*co*-hydroxyethyl methacrylate)-*g*-poly(perfluoropropylene oxide), PDMS-*b*-poly(methacrylic acid), and PMMA-*b*-poly(fluoroalkyl methacrylate) as colloidal stabilizers, respectively. Caputo and coworkers produced PMMA particles in the presence of different types of PDMS by gamma radiation in-duced dispersion polymerization of MMA in $scCO_2$ [27]. Moreover, DeSimone and coworkers reported that polystyrene (PS) particles were produced by dispersion polymerizations of S in $scCO_2$ with AIBN in the presence of PDMS-based macromonomer [23], PFOA [28], PS-*b*-PDMS [29], PS-*b*-PFOA [30], and random copolymers containing a fluorinated acrylate [31] as colloidal stabilizers. And they reported that poly(vinyl acetate) [32], polyacrylonitrile (PAN) [33], poly(2-hydroxyethyl methacrylate) [34] and poly(glycidyl methacrylate) [35] particles were also produced by dispersion polymerizations in $scCO_2$ with AIBN in the presences of various CO_2-soluble or CO_2-philic stabilizers such as FOA, PDMS-based macromonomer, PS-*b*-PDMS and PS-*b*-PFOA. Berger and coworkers produced poly(vinylpyrrolidone) particles in $scCO_2$ in the presence of PS-*b*-PDMS [36]. Additionally, there are some reports on productions of polymer particles by dispersion polymerization using other polymerization methods as well as conventional radical polymerization.

Clark and coworkers produced PS particles by cationic dispersion polymerization in liquid CO_2 [37]. Xia and coworkers reported that PMMA particles were produced by atom transfer radical dispersion polymerization of MMA in $scCO_2$ in the presence of PFOA [38].

In addition to the dispersion polymerization, recently, Romack and coworkers, and Cooper and coworkers succeeded in producing poly(acrylic acid) [39] and polydivinylbenzene [40, 41] particles by precipitation polymerizations without any stabilizers in $scCO_2$ with AIBN, respectively.

Furthermore, Adamsky and Beckman conducted inverse emulsion polymerization of acrylamide in $scCO_2$ [42].

The production of polymer particles in $scCO_2$ is of interest from academic and industrial viewpoints. Furthermore, despite the fact that the use of $scCO_2$ to produce polymer particles in $scCO_2$ have been expected to be advantageous and an increasing number of studies in the research area have been conducted, the production of polymer particles in $scCO_2$ has been remained a technical challenge, and it is desirable to widen the conditions for producing polymer particles by polymerizations in $scCO_2$.

The aims of this doctoral dissertation are: i) construction of high-pressure reactors, ii) production of polymer particles by dispersion and precipitation polymerizations in $scCO_2$ utilizing the reactors, and iii) characterization of the polymer particles produced by a wide range of methods from the viewpoint of polymer colloid chemistry. This thesis consists of following two parts which have been subdivided to seven chapters to fullfil the above aims.

PART I concerns construction and development of high-pressure reactors for the production of polymer particles in $scCO_2$.

This part contains 1 chapter. In **Chapter 1**, design, construction and development of small-scale high-pressure reactors for the production of polymer particles in $scCO_2$ were conducted, because of the background that there have been few reports describing the design and construction of high-pressure reactors for the purpose in detail, at this stage. The effects of the types of reactors on the polymer produced were also investigated.

PART II concerns the productions of polymer particles by dispersion and precipitation polymerizations in $scCO_2$.

This part contains six chapters. Chapters 2-5 concern the productions of PMMA particles by dispersion polymerizations with various types of PDMS-based polymers as colloidal stabilizers in $scCO_2$. 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. However, limited types of PDMS-based polymers have been used as colloidal stabilizers in $scCO_2$. In **Chapter 2**, dispersion polymerizations of MMA were conducted with different types of organic peroxides as initiators in the presence of trimethylsiloxy terminated PDMS stabilizers. And the effect of the type of organic peroxides on the production of PMMA particles was discussed. In **Chapter 3**, the production of PMMA particles by dispersion polymerization with mercaptopropyl terminated PDMS stabilizer was presented. In **Chapter 4**, the production of PMMA particles by dispersion polymerization with PDMS-based azoinitiator was presented. In **Chapter 5**, the production of the PMMA particles by dispersion polymerization with aminopropyl terminated PDMS stabilizer was presented. Chapters 6 and 7 concern the productions of polymer particles with clean surfaces by precipitation polymerization without any colloidal stabilizers in $scCO_2$. In dispersion polymerization, colloidal stabilizers are generally expensive (especially in the case of fluorinated polymer) or difficult to synthesize, and moreover, some stabilizers remain adsorbed or grafted on particle surfaces and those may operate as impurities in some applications. It is likely that some kinds of monomers could be obtained as polymer particles by precipitation polymerization in $scCO_2$, but there have been limited number of papers concerning the production of polymer particles by precipitation polymerization in $scCO_2$ from the viewpoint of polymer colloid chemistry until now. From such a background, it seems to be worthwhile discussing the precipitation polymerizations in $scCO_2$. In **Chapter 6**, production of polydivinylbiphenyl particles by precipitation polymerization in $scCO_2$ was presented. In **Chapter 7**, production of PAN particles by precipitation polymerization of AN in $scCO_2$ was presented. The particles produced in this study were characterized by a wide range of methods.

It is to be mentioned that the productions of polymer particles in $scCO_2$ were studied from the viewpoint of polymer colloid chemistry. The author reports the work titled as "Studies on production of polymer particles in $scCO_2$".

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PART I

Design and Construction of Small-scale High-pressure Reactors for Polymerization in Supercritical Carbon Dioxide

Chapter 1

Design and construction of small-scale high-pressure reactors for polymerization in supercritical carbon dioxide

1.1 Introduction

Recently, there is 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 the composition of the medium. The productions of polymer particles in $scCO_2$ have been, actively, reported by some research groups since 1994 as described in general introduction [1-3]. In these studies, various types high-pressure reactors were utilized in order to conduct polymerizations in $scCO_2$. Adamsky and Beckman used a 50-mL high-pressure reactor equipped with a blade stirrer and aligned sapphire windows [4]. DeSimone and coworkers used 10-mL and 25-mL high-pressure view cells with magnetic stir bars [5,6]. In addition to the high-pressure reactors for polymerizations in $scCO_2$, a high-pressure variable volume view cell was used for phase equilibria measurements [6].

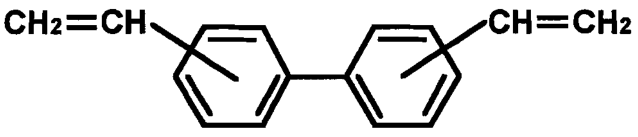
However, at this stage, since there have been few reports describing the design and construction of high-pressure reactors for the productions of polymer particles in $scCO_2$ in detail, we have originally constructed two types of small-scale high-pressure reactors for the productions of polymer particles in scCO$_2$. In addition to these reactors, a commercially available 90-mL high-pressure reactor equipped with sapphire windows and a rotary impeller was purchased and developed by ourselves for the purpose.

As the first chapter of the doctoral dissertation, design and construction of the two small-scale high-pressure reactors will be reported, and effects of the reactors, including 90-mL reactor, on the productions of polymer particles in scCO$_2$ will be reported.

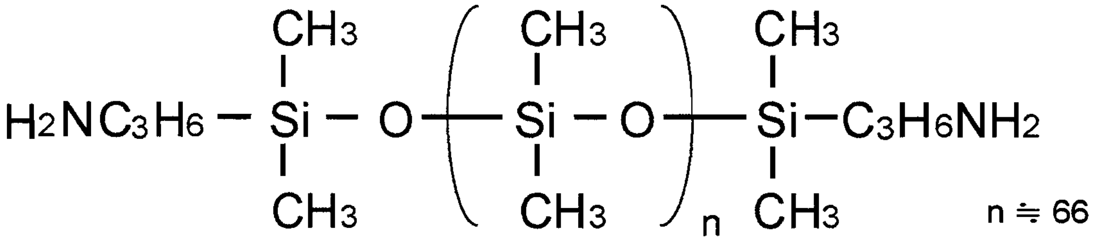
1.2 Experimental

1.2.1 Materials

Methyl methacrylate (MMA) was purified by distillation under reduced pressure in a nitrogen atmosphere. Divinylbiphenyl (DVBP), whose formula is given in Scheme 1, was supplied by Nippon Steel Chemical Co., and the purity was 51.7% [7]. DVBP was washed with 1 N NaOH aqueous solution and deionized water to remove polymerization inhibitors before use. Acrylonitrile (AN) was purified by inhibitor remover (Aldrich Co., AL-154) before use. Reagent grade 2,2'-azobis(isobutyronitrile) (AIBN) was purified by recrystallization. Aminopropyl terminated poly(dimethylsiloxane) (AP-PDMS) (Silaplane FM-3321), supplied by Chisso Co., was used as received. The chemical formula is given in Scheme 2. The number-average molecular



Scheme 1 A chemical formula of DVBP



$$H_2NC_3H_6-\overset{CH_3}{\underset{CH_3}{Si}}-O\left(\overset{CH_3}{\underset{CH_3}{Si}}-O\right)_n\overset{CH_3}{\underset{CH_3}{Si}}-C_3H_6NH_2 \qquad n \fallingdotseq 66$$

Scheme 2 A chemical formula of AP-PDMS

weight was about 5000. Poly(dimethylsiloxane) (PDMS)-based azoinitiator (VPS-0501), commercially supplied by Wako Pure Chemical Industries was used as received. Industrial grade CO_2, with a purity of 99.5% or more, was used. Guaranteed reagent *n*-hexane was used as received from Nacalai Tesque Co. Oil-soluble dye (Oil Blue) was used as received.

1.2.2 Procedure for polymerizations in $scCO_2$

Polymerizations were carried out in the high-pressure reactors. The reactors were charged with monomer, initiator and colloidal stabilizer (if included), and air was purged with CO_2 or N_2. Then, the reactors were filled with liquid CO_2 with shaking and the pressure was brought to about 10 MPa at 25°C using a syringe pump (Nihon Seimitsu Kagaku Co., NP-D-321J). The polymerizations were started by heating the reactors to desired temperature. After the polymerizations, the reactors were cooled in an ice water bath and the CO_2 was vented slowly. The particles produced were observed with a Hitachi S-2460N scanning electron microscope (SEM).

1.2.3 Estimation of efficiency of stirring

Blue-colored *n*-hexane containing Oil Blue (200 μL) was gently injected into 25-mL glass tubular reactor or 30-mL glass cylindrical reactor, in which pure colorless and transparent *n*-hexane was filled in advance, and the time for the blue-colored solution to become wholly homogeneous with stirring was measured. Each stirring was conducted under similar conditions to those of actual polymerizations. *n*-Hexane was used in place of scCO$_2$ because it has similar characteristics to scCO$_2$: low polarizability, low solubility parameter and relatively low viscosity [8]. The 25 mL- and 30 mL- glass reactors had similar shapes to the 10 mL and 25 mL high-pressure reactors, in which the stirring was conducted with a stainless steel ball and a magnetic stir bar, respectively.

1.3 Results and discussion

1.3.1 Construction of small-scale high-pressure stainless steel reactors

Two types of small-scale tubular reactors were manufactured by way of trial. Each reactor was mainly composed of a valve, an original condenser and a reactor body, and all metal parts are fabricated of commercial SUS 316 stainless steel, which is relatively resistant to corrosion, and these parts were purchased from Osaka valve fitting Co. The condenser was originally developed in our laboratory for cooling a pipe line down to about 5°C (under the critical temperature of CO$_2$, 31°C) and preventing the polymerization in the pipe line. Without the condenser, the pipe line and the needle valve were clogged up with polymer generated. It was difficult to wash away the polymer, which should lead to the parts of the reactor (e.g., the valves and swagelok ferrules) being damaged. This simple structure made it possible to construct the reactor inexpensively and conveniently. These small-scale reactors were easier to check the leak of CO$_2$ prior to the polymerizations because of their small number of joint points in comparison with 90-mL reactor.

1.3.1.1 10-mL tubular reactor

Figure 1 shows an optical photograph of the 10-mL high-pressure stainless steel tubular reactor. The reactor consists of a swagelok needle valve with a metal stem (SS-1RS4) (1), the condenser (2), a swagelok 1/4 inch union (SS-400-6) (3), a bent stainless steel tube which had 1/4-inch diameter, 0.049-inch wall thickness and 1.97-inch length (4), a swagelok reducing union (SS-810-6-4) (5), a stainless steel tube which had 1/2-inch diameter, 0.065-inch wall thickness and 5.3-inch length (6), and a 1/2-inch swagelok cap (SS-810-C) (7). Stirring was conducted by shaking with a 5/16-inch stainless steel ball (8) in the reactor. This reactor withstood the pressure up to 33 MPa and the temperature up to 204°C.

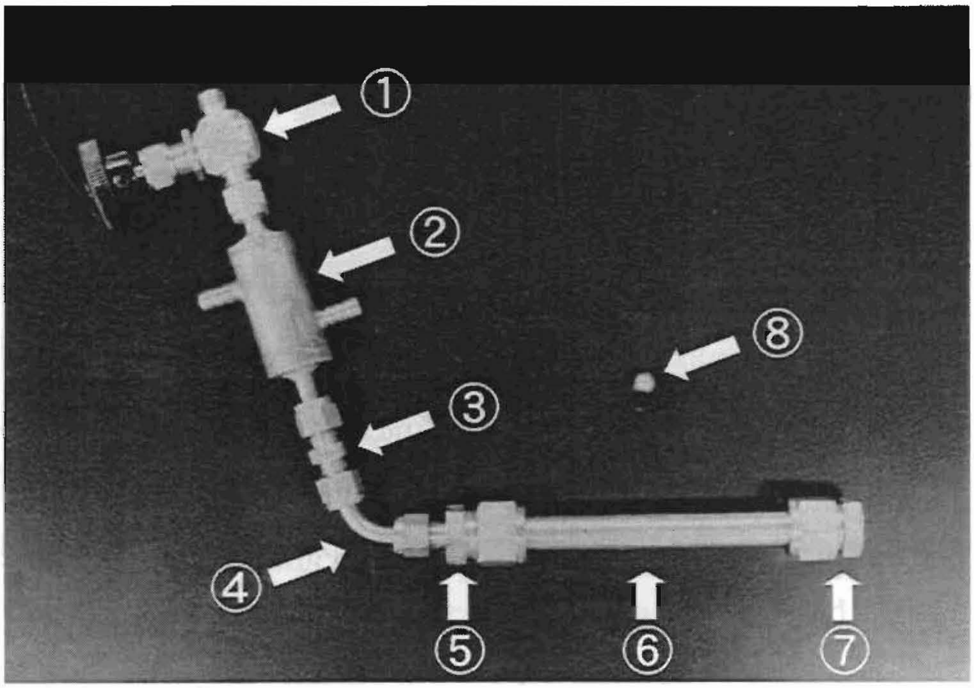


Figure 1 An optical photograph of the 10-mL high-pressure stainless steel tubular reactor for polymerizations in supercritical carbon dioxide ($scCO_2$) (type of stirring, the stainless steel ball)

1.3.1.2 25-mL tubular reactor

Figure 2 shows an optical photograph of the 25-mL high-pressure stainless steel tubular reactor. The reactor consisted of a 1/4 inch swagelok needle valve (SS-1RS4) (1), the original condenser (2), a swagelok reducing union (SS-1610-6-4) (3), a stainless steel tube which had 1-inch diameter, 0.12-inch wall thickness and 3.02-inch length (4), and a 1-inch swagelok cap (SS-1610-C) (5). Stirring was conducted with a magnetic stir bar (6). This reactor withstood the pressure up to 30 MPa and the temperature up to 204°C.

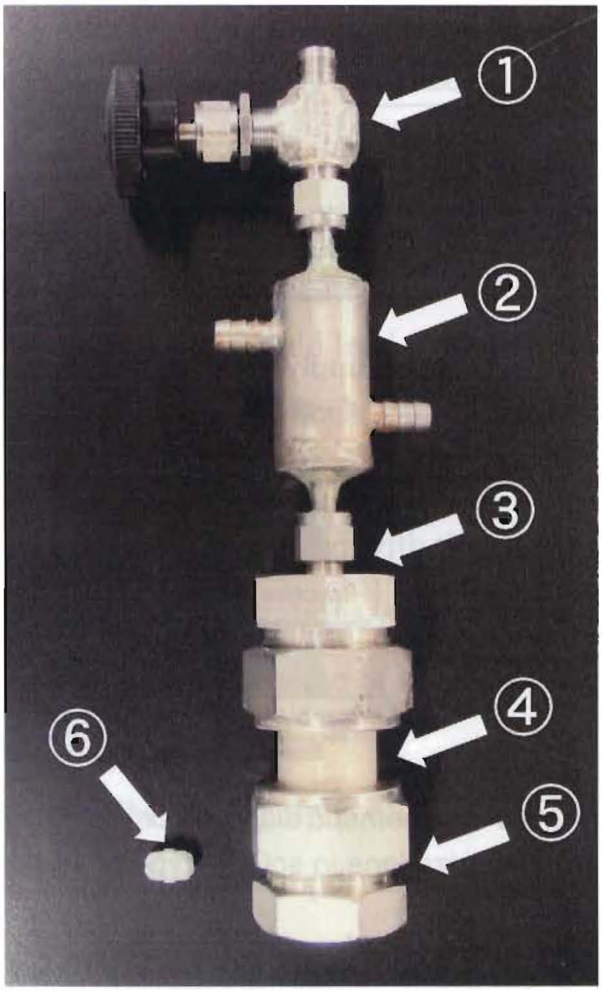


Figure 2 An optical photograph of the 25-mL high-pressure stainless steel tubular reactor for polymerizations in $scCO_2$ (type of stirring, the magnetic stir bar)

1.3.1.3 Development of a 90-mL reactor

A 90-mL reactor, which was purchased from Taiatsu Techno Co., was developed to the suitable reactor for polymerization in $scCO_2$. For example, all the pipe lines were equipped with the original condensers, and the pipe line between the syringe pump and the reactor was equipped with a one-way valve to prevent diffusion of monomer and polymer into the syringe pump from occurring. A schematic diagram of the 90-mL high-pressure reactor is shown in Fig. 3. The reactor consisted of a reactor lid (1), a reactor body (2) with sapphire windows for observation of the inside (3), and the rotary impeller for stirring (4). The reactor had four stainless steel pipe lines,

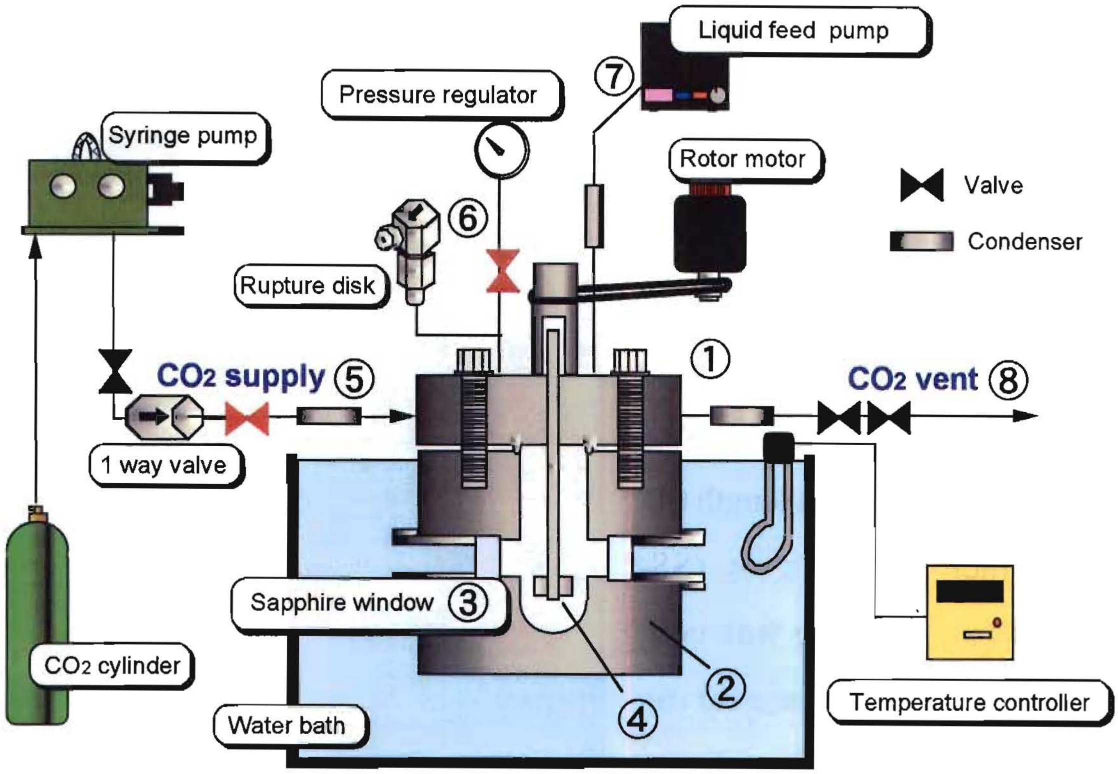


Figure 3 A schematic diagram for the 90-mL high-pressure stainless steel reactor for polymerizations in $scCO_2$ (type of stirring, the rotary impeller)

which had condensers, connected to the reactor lid: CO_2 feed pipe line (5), the pipe line leading to a pressure gauge (6), liquid feed pipe line (7) and CO_2 vent pipe line (8). This reactor withstood the pressure up to 35 MPa and the temperature up to 100°C.

1.3.2 Dispersion and precipitation polymerizations in $scCO_2$

In general, emulsion, dispersion and suspension polymerizations in usual media such as aqueous, alcohol/water and conventional organic media, the sealed tubular reactors are not filled with reaction mixtures and stirring are usually conducted by simple shakes. However, when $scCO_2$ was used as a medium, it is difficult to mix in the reactor by a simple shake because the reactor was filled with the reaction mixture. In the precipitation polymerization of DVBP in scCO$_2$ utilizing the 10-mL high-pressure stainless steel tubular reactor as shown in Fig. 1 with a simple shake, PDVBP was mainly obtained as irregular blocks. This result should be due to incomplete mixing during the polymerization. In order to mix in the 10-mL high-pressure reactor, the stainless steel ball was put into the reactor and the reactor was shaken. With shaking, the stainless steel ball moved in the reactor, which should lead to the stirring. As shown in Table 1, the time which was needed to obtain a homogeneous blue solution was shortened by the presence of the stainless steel ball. This result indicates that the efficiency of stirring was improved with the stainless steel ball. The precipitation and dispersion polymerizations were carried out under the conditions as shown in Table 2. These are some of the many recipes that we have prepared.

Figures 4, 5, and 6 show optical and SEM photographs of PDVBP, PAN and PMMA produced by precipitation and dispersion polymerizations, respectively, in scCO$_2$ utilizing the 10-mL high-pressure tubular reactor with the stainless steel ball. A free flowing white PDVBP powder was successfully obtained by the precipitation polymerization of DVBP in scCO$_2$, and the

Table 1 Times[a] which it took for blue-colored *n*-hexane containing Oil Blue[b] (200 μL) to diffuse homogeneously in transparent *n*-hexane medium by different types of stirring in glass reactors

	25 mL[c]		30 mL[d]
	Without stainless ball	With stainless ball	Magnetic stir bar
Time (s)	> 300	35	8

[a] Determined with the naked eye
[b] Oil-soluble blue-coloured dye
[c] 25 mL-glass reactor; 60 cycles/min; 2-cm strokes, shaken horizontally
[d] 30 mL-glass reactor; 420 rpm

Table 2 Recipes for the productions of PDVBP, PAN and PMMA particles by precipitation and dispersion polymerizations in $scCO_2$[a] with AIBN utilizing the 10-mL high-pressure stainless steel tubular reactor (type of stirring, the stainless steel ball)

Ingredients		Precipitation polymerization		Dispersion polymerization
DVBP[b]	(g)	2.0	—	—
AN[c]	(g)	—	2.0	—
MMA[d]	(g)	—	—	2.0
AP-PDMS[e]	(g)	—	—	0.2
AIBN[f]	(mg)	15	5	10

[a] ca. 30 MPa; 65°C; 24 h; 60 cycles/min; 2-cm strokes, shaken horizontally
[b] 1.0 mol/L (20 w/v%)
[c] 3.8 mol/L (20 w/v%)
[d] 2.0 mol/L (20 w/v%)
[e] M_n, ca. 5000
[f] R_i (= $2kdf[I]$), 10^{13} ~10^{14} mL^{-1} s^{-1}; kd, 7.7 x 10^{-5} s^{-1}; f, 0.9

Abbreviations: PDVBP, polydivinylbiphenyl; PAN, polyacrylonitrile; PMMA, poly(methyl methacrylate); DVBP, divinylbiphenyl; AN, acrylonitrile; MMA, methyl methacrylate; AIBN, 2,2'-azobis(isobutyronitrile); AP-PDMS, aminopropyl terminated poly(dimethylsiloxane)

conversion was gravimetrically determined to be 90%. In Fig. 4b, it was confirmed that PDVBP was obtained as particles. By the precipitation polymerization of AN in $scCO_2$, a free-flowing white PAN powder, which consisted of micron-sized, relatively monodisperse particles, was also obtained as shown in Fig 5b. The details about production of the PDVBP and PAN particles will be discussed in Chapters 6 and 7, respectively. By the dispersion polymerization of MMA, a free flowing PMMA powder and hard PMMA blocks were obtained at the same time (see Fig. 6a), and the conversion of MMA was determined to be 82%. The number average diameter (D_n) and the coefficient of variation (C_v) of the PMMA particles measured on the SEM photograph (Fig. 6b) with image analysis software (MacScope, Mitani Co.) were 565 nm and 61%, respectively. Judging from a SEM photograph of a section of a PMMA block shown in Fig. 6c, the blocks seems to be formed by coagulation of the particles. It is well known that PMMA was highly plasti-

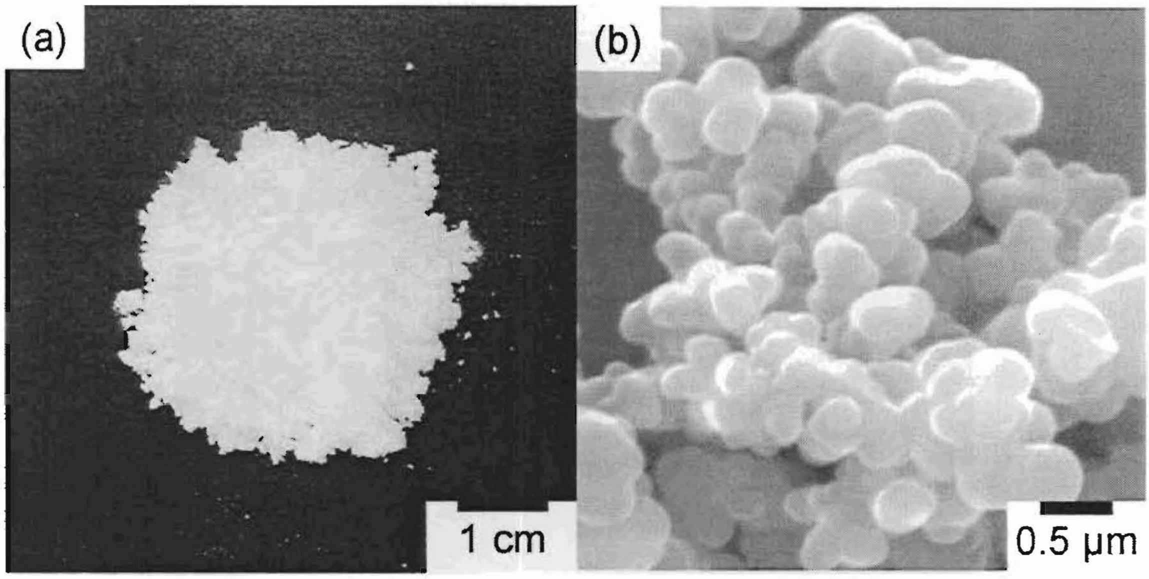


Figure 4 An optical (a) and a scanning electron microscope (SEM) (b) photographs of polydivinylbiphenyl produced by the precipitation polymerization in scCO$_2$ utilizing the 10-mL high-pressure stainless steel tubular reactor (type of stirring, the stainless steel ball)

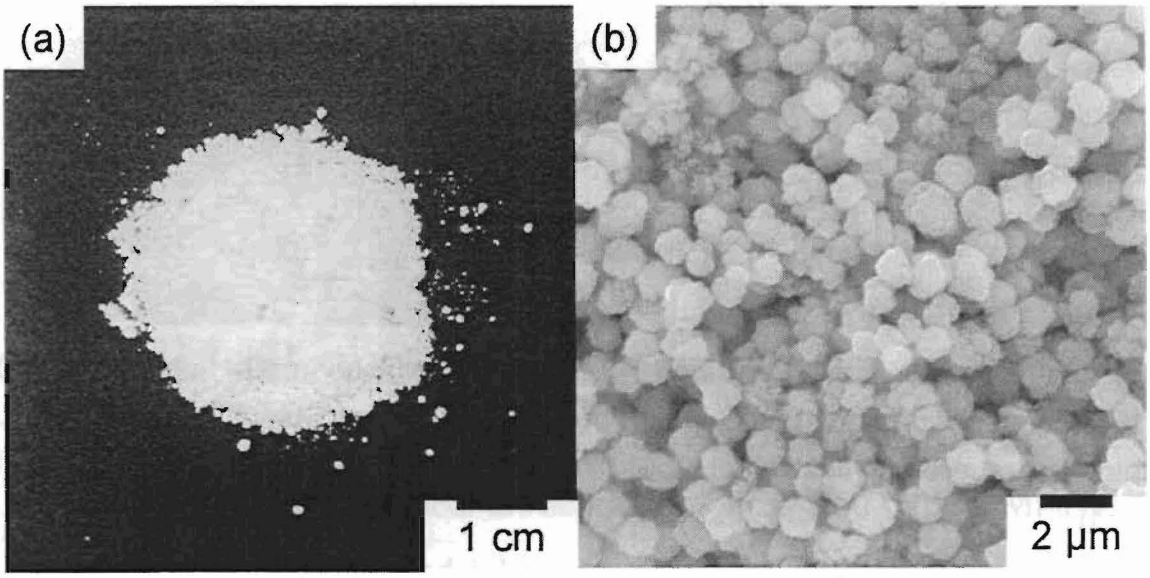


Figure 5 An optical (a) and a SEM (b) photographs of polyacrylonitrile produced by the precipitation polymerization in scCO$_2$ utilizing the 10-mL high-pressure stainless steel tubular reactor (type of stirring, the stainless steel ball)

cized by CO$_2$, which resulted in the lowering of glass transition temperature (T_g) of PMMA [9-12]. Fehrenbacher and coworkers indicated that PMMA film sorbed 28 vol% of CO$_2$ based on the volume of PMMA film in scCO$_2$ at

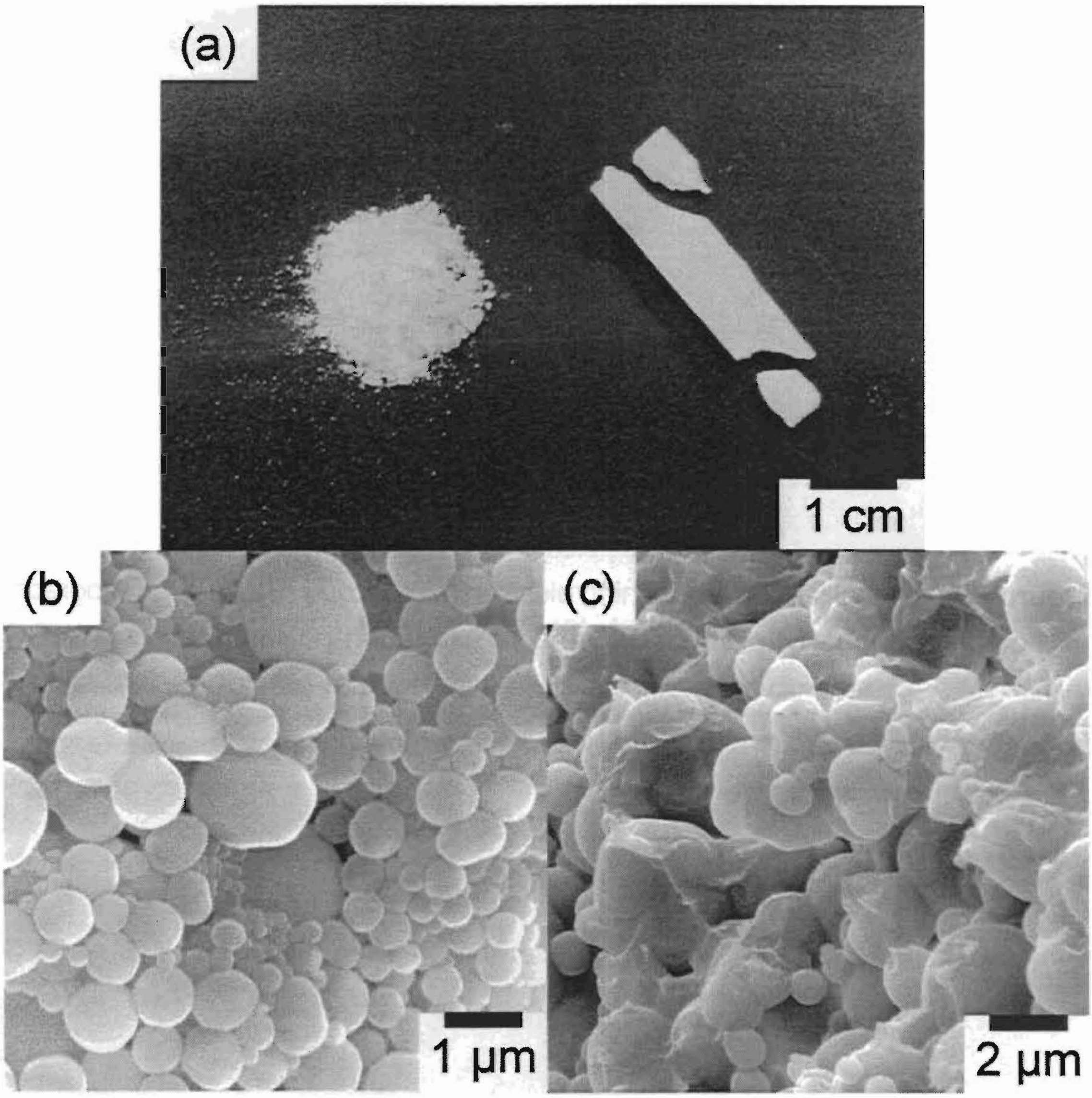


Figure 6 An optical (a) and SEM photographs of poly(methyl methacrylate) (PMMA) produced by the dispersion polymerization in $scCO_2$ utilizing the 10-mL high-pressuere stainless steel tubular reactor (type of stirring, the stainless steel ball)

59.8°C and 29.9 MPa [13]. Assuming that the density of CO_2 in PMMA is estimated to be 1.0 g mL^{-1} [13,14], the weight ratio of PMMA/CO_2 in the $scCO_2$ is calculated to be 1/0.28. Johnston and coworkers predicted that T_g of PMMA, which sorbed about 25 wt% of CO_2 based on the weight of PMMA, might be down to about –25°C [9]. From the above data and the prediction, it should be thought that T_g of PMMA particles in $scCO_2$ at 65°C and 30 MPa

Table 3 A recipe for the production of PMMA particles by dispersion polymerization of MMA in scCO$_2$[a] with AIBN in the presence of AP-PDMS[b] utilizing the 25-mL high-pressure stainless steel tubular reactor (type of stirring, the magnetic stir bar)

Ingredients		
MMA[c]	(g)	5.0
AP-PDMS[b]	(g)	0.5
AIBN[d]	(g)	0.025

[a] ca. 30 MPa; 65°C; 24 h; 420 rpm

[b] M_n, ca. 5000

[c] 2.0 mol/L (20 w/v%)

[d] R_i (= $2kdf[I]$), 5.0 x 10^{13} mL^{-1} s^{-1}; kd, 7.7 x 10^{-5} s^{-1}; f, 0.9

Abbreviations: PMMA, poly(methyl methacrylate); MMA, methyl methacrylate; AIBN, 2,2'-azobis(isobutyronitrile); AP-PDMS, aminopropyl terminated poly(dimethylsiloxane)

was down near –25°C. Sedimentation distance of 1-μm CO$_2$-sorbed PMMA particle in scCO$_2$ (PMMA/CO$_2$ weight ratio, 1/0.28) for 24 h should be calculated to be 188 mm utilizing the Stokes equation, and the distance of the particle by Brownian motion in the scCO$_2$ should be calculated to be 1.1 mm utilizing the Einstein-Stokes equation. In the calculations of these distances, the following values were used: the densities of scCO$_2$ (60°C, 32.9 MPa) and PMMA, 0.85 g mL^{-1} [15] and 1.19 g mL^{-1} [16], respectively; coefficient of viscosity of scCO$_2$ (77°C, 30 MPa), 0.075 x 10^{-3} kg m s^{-1} [17]; Avogadro's number, 6.02 x 10^{23} mol^{-1}; gravitational acceleration, 9.81 m s^{-2}. The calculated distances mean that CO$_2$-sorbed, micron-sized PMMA particles in the scCO$_2$ should sediment by the end of the dispersion polymerization without stirring. In the dispersion polymerization of MMA utilizing the 10-mL reac-

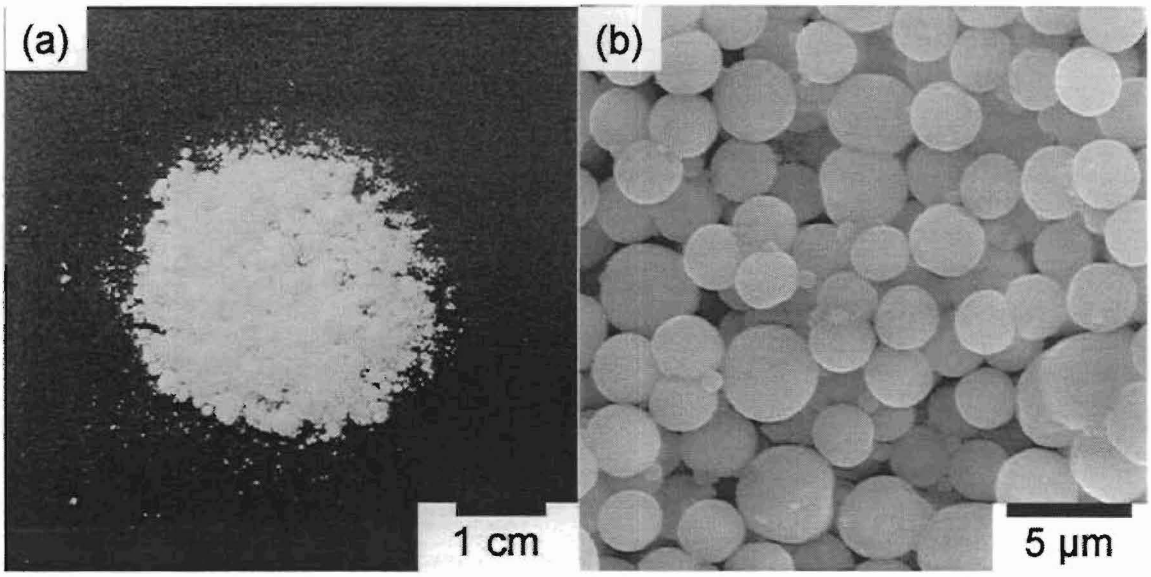


Figure 7 An optical (a) and a SEM (b) photographs of PMMA produced by the dispersion polymerization in $scCO_2$ utilizing the 25-mL high-pressure stainless steel tubular reactor (type of stirring, the magnetic stir bar)

tor with the stainless steel ball, the efficiency of stirring may be still low and the CO_2-sorbed PMMA particles, whose T_g might be near –25°C (further below –25°C if there were MMA and CO_2 in PMMA particles), seem to sediment and coalesce, which results in the hard blocks. The formation of the hard PMMA blocks must be promoted by rolling of the stainless steel ball on the sedimented PMMA particles. In the precipitation polymerization of DVBP in $scCO_2$, the PDVBP particles produced should not be highly swollen by CO_2 and DVBP because of high cross-linking, and the PAN particles should not be also highly swollen by CO_2 [18] and AN [16]. It should not lead to coalescence that PDVBP and PAN particles were not swollen with CO_2 and monomers and the particles were rigid during the precipitation polymerizations in $scCO_2$.

To improve the efficiency of stirring, the 25-mL high-pressure reactor as shown in Fig. 2 was designed and constructed. In this reactor, the stirring

Table 4 A recipe for the production of PMMA particles by dispersion polymerization of MMA with PDMS-based azoinitiator in scCO$_2$[a] utilizing the 90-mL stainless steel reactor (type of stirring, rotary impeller)

Ingredients		
MMA[b]	(g)	18
PDMS-based azoinitiator[c]	(g)	9.1

[a] 30 MPa; 65°C; 200 rpm; 24 h

[b] 2.0 mol/L (20 w/v%)

[c] The concentration of azo-group in PDMS-based azoinitiator, 20 mmol/L; R_i (= 2 k_d f [I]), 3.7 x 10^{13} mL^{-1} s^{-1}

Abbreviations: PMMA, poly(methyl methacrylate); MMA, methyl methacrylate; PDMS, poly(dimethylsiloxane)

was conducted with a magnetic stir bar. As shown in Table 1, the time needed to obtain the homogeneous Oil Blue solution was shorter in the magnetic stirrer system than in the stainless steel ball system. Utilizing the 25-mL high-pressure reactor, PMMA was obtained completely as a free flowing white powder as shown in Fig. 7a under the conditions shown in Table 3. The conversion was determined to be 96%, which was higher value in comparison with that obtained utilizing the 10-mL high-pressure reactor. In Fig. 7b, it was confirmed that PMMA particles resulted, and D_n and C_v of the PMMA particles after five times centrifugal washing with *n*-hexane were 2.89 μm and 30%, respectively. The diameter became larger and the monodispersity of PMMA particles was improved by increasing of the stirring efficiency. The details about production of the PMMA particles will be discussed in

Chapter 5.

The schematic diagram of the 90-mL high-pressure reactor equipped with the sapphire windows and the rotary impeller is shown in Fig. 3. One of the advantages of this reactor was that the inside of the reactor could be observed through the windows. Another advantage was that some liquids could be pumped into the reactor against high pressure (~30 MPa) utilizing the liquid feed pump. Utilizing this reactor, we succeeded in producing submicron-sized PMMA particles as shown in Fig. 8 with PDMS-based azoinitiator in $scCO_2$ under the conditions shown in Table 4, which will be discussed in detail in Chapter 4. Before the polymerization, it could be confirmed that the reaction mixture was homogeneous through the sapphire windows with a white light at the opposite side. After 1 h, a red color was observed, which is thought to be due to the scattering of transmitted light by the growing polymer particles. After the polymerization, light could not be transmitted and a white powder was observed through the windows. The conversion was determined to be 87% by weight analysis. D_n and C_v of the PMMA particles after the centrifugal washing with *n*-hexane were 210 nm and 15.5%, respectively.

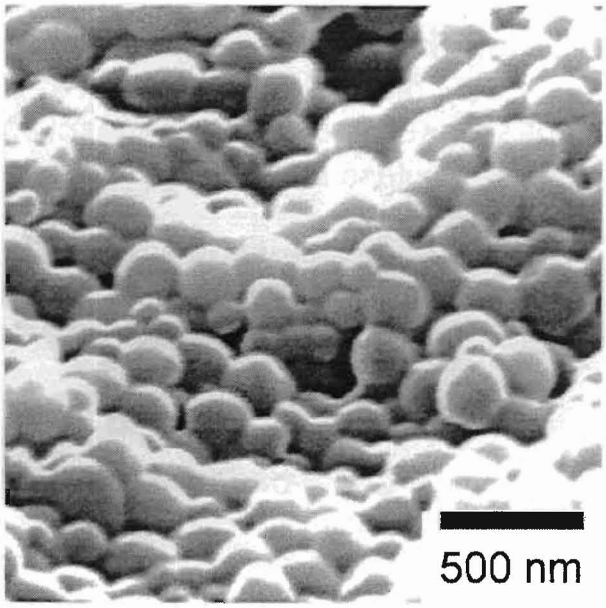


Figure 8 A SEM photograph of PMMA produced by the dispersion polymerization in $scCO_2$ utilizing the 90-mL high-pressure stainless steel tubular reactor (type of stirring, the rotary impeller)

1.4 Conclusions

The small scale high-pressure reactors for productions of polymer particles in scCO$_2$ were successfully designed and constructed. Utilizing these reactors, PMMA particles and PDVBP particles were produced by dispersion polymerization and precipitation polymerization in scCO$_2$, respectively.

1.5 References

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PART II

Production of Polymer Particles by Polymerization in Supercritical Carbon Dioxide

Chapter 2

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

2.1 Introduction

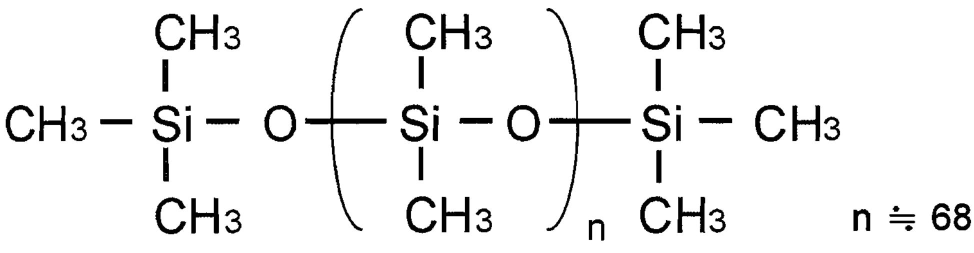
Supercritical carbon dioxide ($scCO_2$) is rapidly becoming an attractive alternative to liquid solvents traditionally used in separations, coating applications and polymerizations, since it is an environmentally benign medium. And there has been increasing interest in producing polymer particles in $scCO_2$ [1-14]. Since some amorphous fluorinated and poly(dimethylsiloxane) (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, and up to the present, there are a few papers on productions of polymer particles such as polystyrene (PS) and poly(methyl methacrylate) (PMMA) particles by dispersion polymerization in the presences of PDMS-based polymers in $scCO_2$ [3, 4, 11, 14]. There are a few papers on dispersion polymerization of vinyl monomers such as methyl methacrylate (MMA) and styrene in the presence of trimethylsiloxy terminated PDMS (TS-PDMS), however, at this stage polymer particles have not been produced in the presence of TS-PDMS as a colloidal stabilizer in scCO$_2$, as far as the author is aware. This should be because 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 2,2'-azobis(isobutyronitrile) (AIBN) was used as an initiator [3, 4]. From these results, it should be indicated that primary radicals generated by decomposition of AIBN and propagating polymer radicals, such as PS and PMMA radicals, had low ability to abstract hydrogens from siloxane methylene group of TS-PDMS [15]. Using organic peroxide as a radical initiator, which should be able to abstract hydrogens from siloxane methylene groups of TS-PDMS, chemical grafting of TS-PDMS to the surface of the particles should be expected to be possible.

In this chapter, dispersion polymerizations of MMA will be conducted with various types of organic peroxides as radical initiators in the presence of TS-PDMS in scCO$_2$, and PMMA particles will be produced.

2.2 Experimental

2.2.1 Materials

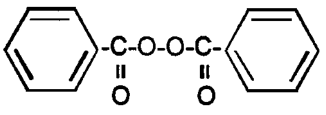
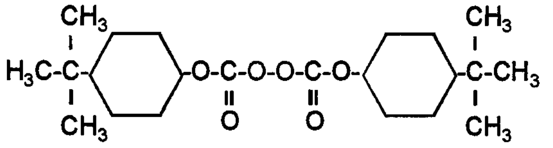
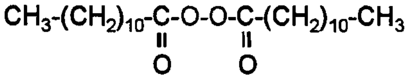
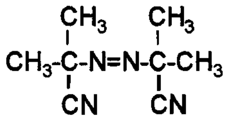
MMA was purified by distillation under reduced pressure in a nitrogen atmosphere. TS-PDMS with a weight-average molecular weight (M_w) of about



$$CH_3-\underset{CH_3}{\overset{CH_3}{Si}}-O\left(\underset{CH_3}{\overset{CH_3}{Si}}-O\right)_n\underset{CH_3}{\overset{CH_3}{Si}}-CH_3 \qquad n \fallingdotseq 68$$

Scheme 1 A chemical formula of TS-PDMS

Table 1 Chemical formulas of initiators used in this study (BPO, p-TCP, LPO and AIBN), and their cross-linking efficiencies a) estimated by the amount of dimers of pentadecane produced during the decompositions of initiators in pentadecane b)

	Chemical formulas	Cross-linking efficiencies
BPO		28
p-TCP		24
LPO	 $CH_3-(CH_2)_{10}-\underset{\underset{O}{\Vert}}{C}-O-O-\underset{\underset{O}{\Vert}}{C}-(CH_2)_{10}-CH_3$	8
AIBN	 $CH_3-\overset{\overset{CH_3}{\vert}}{\underset{\underset{CN}{\vert}}{C}}-N=N-\overset{\overset{CH_3}{\vert}}{\underset{\underset{CN}{\vert}}{C}}-CH_3$	1

a) Percentage of the radicals used in dimerization of pentadecane
b) The temperature for decomposition was set at which the initiator had a half time of 15 min.

Abbreviations: BPO, benzoyl peroxide; p-TCP; bis(4-*t*-butylcyclohexyl)peroxy dicarbonate; LPO, lauroyl peroxide; AIBN, 2,2'-azobis(isobutyronitrile)

5200 g/mol was used as received from Sigma-Aldrich Co. The chemical formula is given in Scheme 1. 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%. The chemical formulas of initiators used in this study are given in Table 1.

2.2.2 Dispersion polymerization in $scCO_2$

Dispersion polymerizations were carried out in a 10-mL stainless steel reactor as described in Chapter 1, under the conditions listed in Tables 2, 3 and 4. The reactor was charged with MMA, organic peroxide, TS-PDMS, and a 5/

16-inch-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 Seimitsu Kagaku. Co., NP-D-321J) and shaking vigorously. The polymerizations were started by heating the mixture to desired temperature, with shaking at 60 cycles/min. After 24 h, the reactors were cooled in an ice water bath and the CO_2 was vented slowly. The particles produced 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 [16].

2.2.3 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 180 sec at a constant acceleration voltage of 1.5 kV and at an ion beam current of 20 mA.

2.3 Results and discussion

The dispersion and precipitation polymerizations of MMA were carried out, in $scCO_2$ for 24 h with different types of initiators utilizing the 10-mL stainless steel reactor under the conditions listed in Table 2. The initiator concentration and polymerization temperature were determined on the basis of the idea described as follows. Initiation rate of radical polymerization, R_i, is

Table 2 Recipes for the productions of PMMA particles by precipitation polymerization[a] of MMA with BPO and dispersion polymerizations[a] of MMA with various types of initiators in the presence of TS-PDMS[b] in $scCO_2$

Ingredients						
MMA[c]	(g)	0.5	0.5	0.5	0.5	0.5
TS-PDMS[b]	(g)	0.05	0.05	0.05	0.05	——
BPO[d]	(g)	0.0097	——	——	——	0.0097
p-TCP[e]	(g)	——	0.0159	——	——	——
LPO[f]	(g)	——	——	0.0159	——	——
AIBN[g]	(g)	——	——	——	0.0073	——

[a] 10-mL stainless steel reactor; 60 cycles/min; 24 h
[b] Weight-average molecular weight (M_w), ca. 5200; 10 wt% based on MMA
[c] 0.5 mol/L (5 w/v%)
[d] 4.0 mmol/L; R_i (= $2k_d f[I]$), 2.1 x 10^{13} mL^{-1} s^{-1}; 70.0°C
[e] 4.0 mmol/L; R_i (= $2k_d f[I]$), 2.1 x 10^{13} mL^{-1} s^{-1}; 36.7°C
[f] 4.0 mmol/L; R_i (= $2k_d f[I]$), 2.1 x 10^{13} mL^{-1} s^{-1}; 54.6°C
[g] 4.4 mmol/L; R_i (= $2k_d f[I]$), 2.1 x 10^{13} mL^{-1} s^{-1}; 59.9°C

Abbreviations: PMMA, poly(methyl methacrylate); MMA, methyl methacrylate; TS-PDMS, trimethylsiloxy terminated poly(dimethylsiloxane); BPO, benzoyl peroxide; p-TCP; bis(4-*t*-butylcyclohexyl)peroxy dicarbonate; LPO, lauroyl peroxide; AIBN, 2,2'-azobis(isobutyronitrile)

given by $R_i = f\rho_i$, where f is the initiator efficiency and ρ_i is the generation rate of radicals. The ρ_i is expressed as $2k_d[I]$, where k_d is the rate coefficient for initiator decomposition, and [I] is the initiator concentration. In general, dispersion polymerizations were carried out in R_i range of 10^{13}-10^{14} mL^{-1} s^{-1} [17-19]. Guan and coworkers [20] 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, 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 x 10^{13} $mL^{-1}s^{-1}$ were chosen. The k_d and f values used in the calculations were 4.4 x 10^{-6} s^{-1} and 1.0 for the organic peroxides, and 4.4 x 10^{-6} s^{-1} and 0.9 for AIBN, respectively.

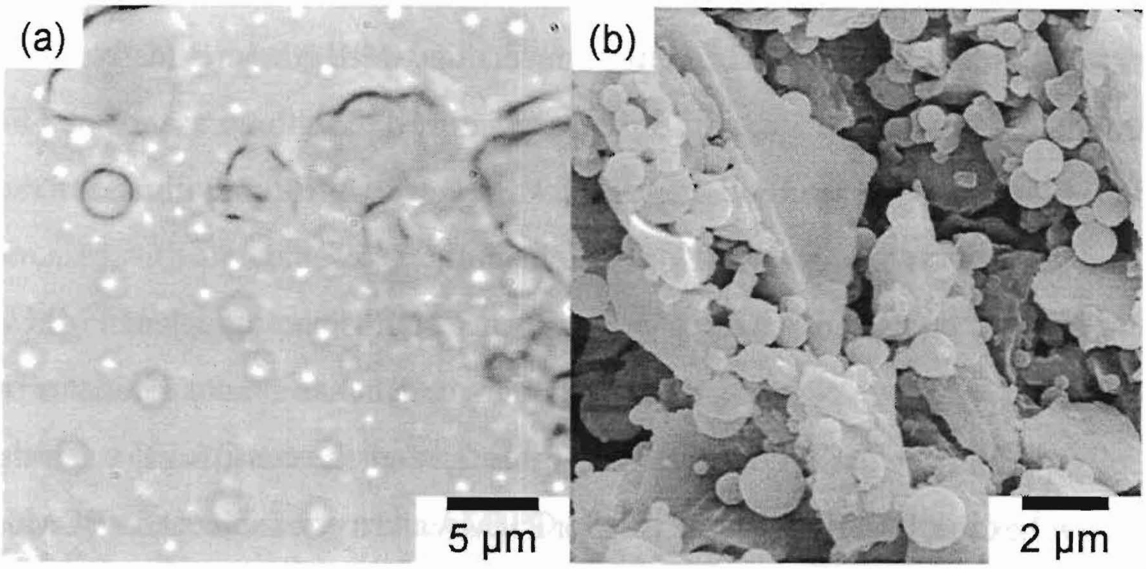


Figure 1 An optical micrograph (a) and a scanning electron microscope (SEM) photograph (b) of poly(methyl methacrylate) (PMMA) particles produced by the dispersion polymerization of methyl methacrylate (MMA) with benzoyl peroxide (BPO) (4.0 mmol/L) in supercritical carbon dioxide (scCO$_2$) for 24 h in the presence of trimethylsiloxy terminated poly(dimethylsiloxane) (TS-PDMS) (10 wt% based on MMA). PMMA particles were redispersed in *n*-hexane.

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 (THF) [21] and methanol [22] 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 [23]. In the case of the precipitation polymerization with BPO and the dispersion polymerization with AIBN in the presence of TS-PDMS, PMMA were obtained as very glutinous liquids and solids on the interior wall of the reactor. For the mixture of AIBN and TS-PDMS system, this result indicated that anchoring of the TS-PDMS at the surface of the PMMA particle generated was inefficient. Using p-TCP and LPO in the presence of TS-PDMS, glutinous liquids were obtained, and the conversions were gravimetrically determined to be 10 and 15%, respectively. Using BPO in the presence of TS-PDMS, the product was obtained as thick irregular white turbid films, and the conversion was gravimetrically determined to be 46%.

Figure 1 shows an optical micrograph and a SEM photograph of PMMA produced by the dispersion polymerization with BPO as a radical initiator in $scCO_2$ under the conditions listed in Table 2, after the centrifugal washing with *n*-hexane, which is a nonsolvent for PMMA and a good solvent for PDMS. When PMMA produced was put into *n*-hexane and sonicated, transparent medium became translucent, which should indicate the production of PMMA particles. As shown in Fig. 1, actually, PMMA particles were produced in addition to the coagulants.

In Table 1, cross-linking efficiency values of organic peroxides (BPO, p-

Table 3 Recipes for the productions of PMMA particles by dispersion polymerization(a) of MMA with BPO at different TS-PDMS(b) concentrations (wt% based on MMA) in $scCO_2$

Ingredients		TS-PDMS concentrations (wt% based on MMA)			
		10	100	200	400
MMA(c)	(g)	0.5	0.5	0.5	0.5
TS-PDMS(b)	(g)	0.05	0.5	1.0	2.0
BPO(d)	(g)	0.0097	0.0097	0.0097	0.0097

(a) 70°C; 10-mL stainless steel reactor; 60 cycles/min; 24 h
(b) M_w, ca. 5200
(c) 0.5 mol/L (5 w/v%)
(d) 4.0 mmol/L; R_i (= $2k_d f[I]$), 2.1×10^{13} mL^{-1} s^{-1}

Abbreviations: PMMA, poly(methyl methacrylate); MMA, methyl methacrylate; BPO, benzoyl peroxide; TS-PDMS, trimethylsiloxy terminated poly(dimethylsiloxane)

TCP and LPO) and AIBN, which were estimated by the amount of dimmers of pentadecane produced during the decompositions of organic peroxides in pentadecane [24, 25] were shown. The cross-linking efficiency value increases with an increase of ability to abstract hydrogen. Assuming that these values measured for pentadecane could be applied to TS-PDMS, hydrogen abstraction from siloxane methylene groups should occur more frequently in the case of BPO than in the cases of p-TCP, LPO and AIBN due to the higher cross-linking efficiency value of BPO. From the above consideration, it could be thought that some amount of PDMS-*g*-PMMA were generated by abstraction of hydrogens from siloxane methylene group using BPO and they worked as an effective colloidal stabilizer, which leads to the production of PMMA particles. When p-TCP, LPO and AIBN were used, too small amount of PDMS-*g*-PMMA should be generated to produce PMMA particles during the dispersion polymerization in scCO$_2$.

In order to generate more PDMS-*g*-PMMA, the concentration of TS-PDMS was increased and dispersion polymerizations were conducted under the conditions listed in Table 3. The larger the amount of TS-PDMS was loaded, the larger the amount of PMMA particles were produced, 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 gravimetrically determined to be 67% after the washing with *n*-hexane for the removal of excess TS-PDMS. It was indicated that the conversion in the system, in which PMMA particles were efficiently produced, was higher than that in the system in which PMMA coagulants were produced. Even after the washing, the PMMA particles were stably dispersed in *n*-hexane, which suggested that PDMS component bonded

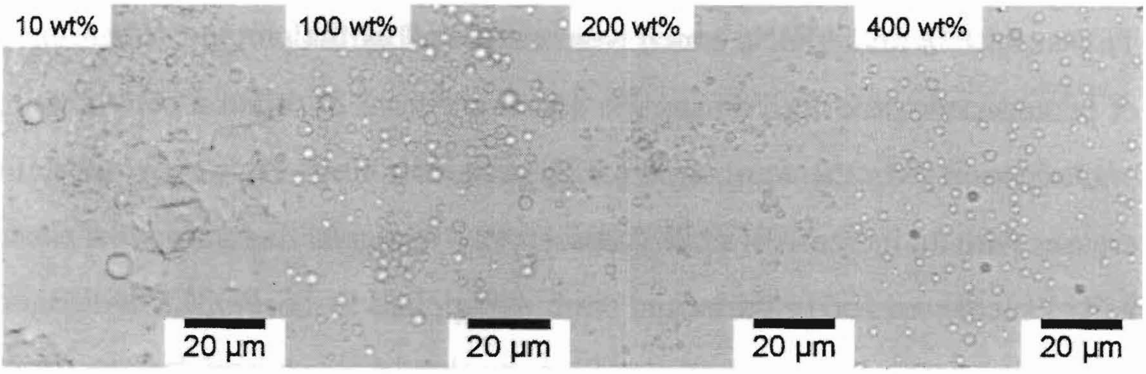


Figure 2 Optical micrographs of PMMA particles produced by dispersion polymerizations of MMA in $scCO_2$ with BPO (4.0 mmol/L) at different TS-PDMS concentrations (wt% based on MMA). PMMA particles were redispersed in *n*-hexane.

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 $(MPa)^{1/2}$ [16], and *n*-hexane is a good solvent for PDMS, PDMS chains must extend into *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), particle size distribution (D_w/D_n) and the coefficient of variation (C_v) for the PMMA particles produced at 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 M_w and M_w/M_n ratio for the washed PMMA particles were, respectively, 1.0 x 10^5 g/mol and 3.2, which were determined from gel permeation chromatogram with THF as the eluent. The weight percentage of the PDMS component in the washed PMMA particles was determined to be 1.0%, from ^1H NMR spectrum measured with a Bruker DPX250 NMR spectrometer operating at 250 MHz for proton with 200 scans.

Table 4 Recipes for the productions of PMMA particles by dispersion polymerization[a] of MMA at different BPO concentrations (mmol/L) in the presence of TS-PDMS[b] in $scCO_2$

Ingredients		BPO (mmol/L)		
		2.0[d]	4.0[e]	20.0[f]
MMA[c]	(g)	0.5	0.5	0.5
TS-PDMS[b]	(g)	2.0	2.0	2.0
BPO	(g)	0.0048	0.0097	0.0484

[a] ca. 30 MPa; 70°C; 10-mL stainless steel reactor; 60 cycles/min; 24 h
[b] M_w, ca. 5200; 400 wt% based on MMA
[c] 0.5 mol/L (5 w/v%)
[d] R_i (= $2k_d f[I]$), 1.1 x 10^{13} mL^{-1} s^{-1}
[e] R_i (= $2k_d f[I]$), 2.1 x 10^{13} mL^{-1} s^{-1}
[f] R_i (= $2k_d f[I]$), 1.1 x 10^{14} mL^{-1} s^{-1}

Abbreviations: PMMA, poly(methyl methacrylate); MMA, methyl methacrylate; BPO, benzoyl peroxide; TS-PDMS, trimethylsiloxy terminated poly(dimethylsiloxane)

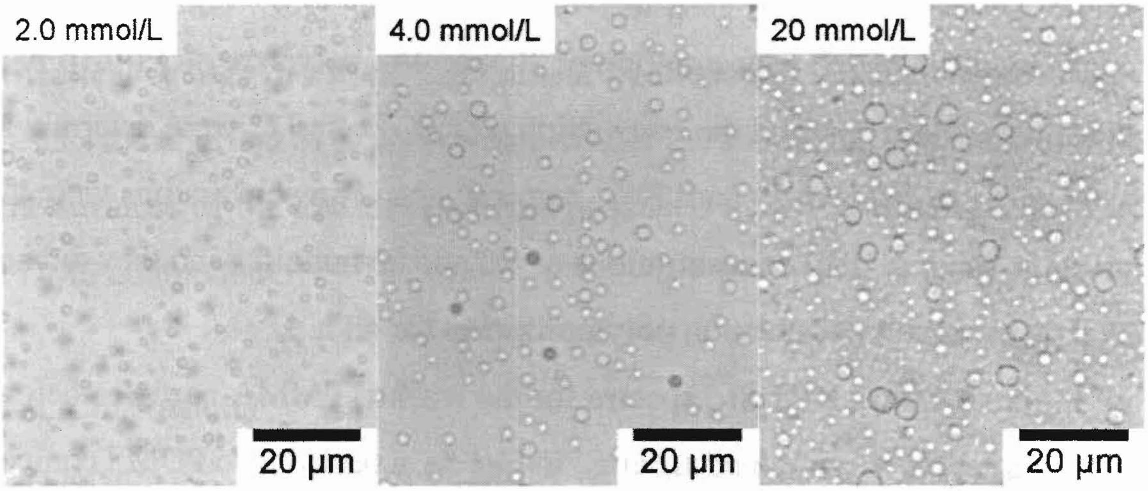


Figure 3 Optical micrographs of PMMA particles produced by dispersion polymerizations of MMA in $scCO_2$ at different concentrations of BPO (mmol/L) in the presence of TS-PDMS (400 wt% based on MMA). PMMA particles were redispersed in *n*-hexane.

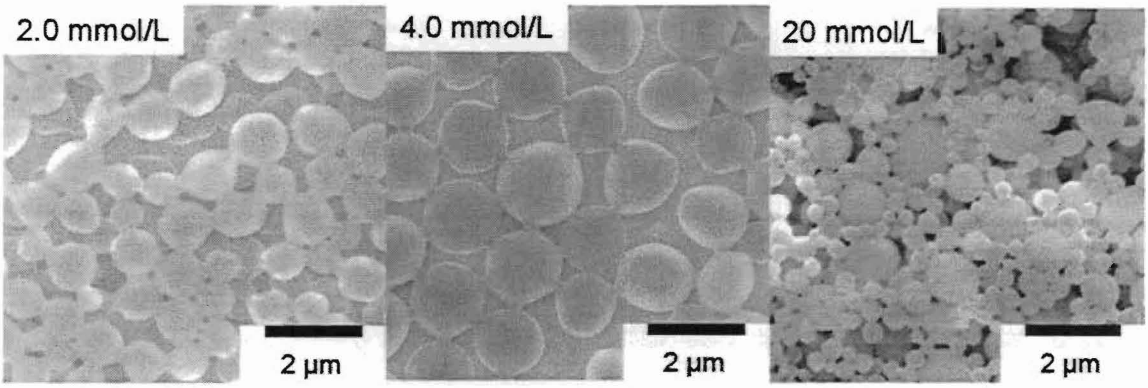


Figure 4 SEM photographs of PMMA particles produced by dispersion polymerizations of MMA in $scCO_2$ at different concentrations of BPO (mmol/L) in the presence of TS-PDMS (400 wt% based on MMA)

Figures 3 and 4 show optical micrographs and SEM photographs of PMMA particles produced at different BPO concentrations giving R_i in the range of 1.1×10^{13} - 1.1×10^{14} mL^{-1} s^{-1} under the conditions listed in Table 4. In Fig. 3, PMMA particles redispersed in *n*-hexane after the centrifugal washing with *n*-hexane were observed with optical microscope. At every BPO concentration, all PMMA were obtained as particles. At BPO concentration of 2.0 mmol/L, the conversion and D_n were determined to be 24% and 930 nm, respectively. At BPO concentration of 20 mmol/L, polydisperse PMMA particles were observed, and the conversion, D_n, D_w/D_n and C_v were determined to be 67%, 465 nm, 2.80 and 59%, respectively. The conversions were almost the same at BPO concentrations of 4.0 and 20 mmol/L, and they did not change even in the dispersion polymerization for 48 h.

Figure 5 shows XPS Si_{2p} spectra for the washed PMMA particles before (a) and after (b) argon ion sputtering. 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. It has been confirmed that the intensity of Si_{2p} peak due to PDMS component was not weakened when pure PDMS-

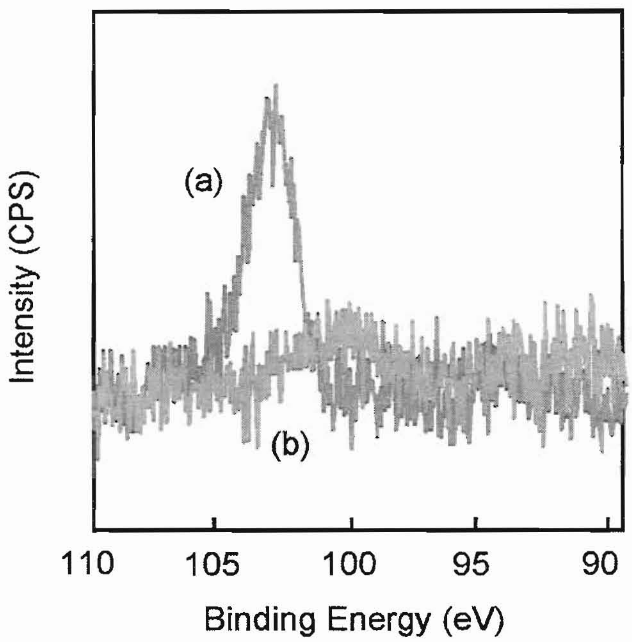


Figure 5 XPS Si_{2p} spectra for PMMA particles produced by the dispersion polymerization of MMA in $scCO_2$ with BPO (4.0 mmol/L) in the presence of TS-PDMS (400 wt% based on MMA) before (a) and after (b) argon ion sputtering at 5.0×10^{-4} Pa for 180 sec at constant acceleration voltage of 1.5 kV and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

based azoinitiator (VPS-0501, Wako Pure Chemical Industries, Ltd.) was sputtered under the same conditions. The peak shift should be due to the chemical change of PDMS component by the argon ion sputtering. These results indicate that Si atom was etched after the sputtering, which means that the surfaces of the PMMA particles produced in $scCO_2$ were occupied by PDMS component.

2.4 Conclusions

Dispersion polymerizations of MMA were conducted with various types of organic peroxides as radical initiators in the presence of TS-PDMS stabilizer in $scCO_2$. Using BPO as radical initiator, micron-sized, relatively monodisperse PMMA particles were produced.

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Chapter 3

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

3.1 Introduction

Supercritical carbon dioxide ($scCO_2$) possesses interesting solvent properties which have been applied to a range of separation and extraction processes, as well as organic reactions and polymerizations [1-5]. There has been increasing interest in conducting dispersion polymerization in $scCO_2$ and stabilizers have been developed which are effective in $scCO_2$. Up to present, some fluorinated polymers and poly(dimethylsiloxane)-based polymers have been identified as being soluble in CO_2 [4, 5]. In Chapter 2, the author succeeded in producing poly(methyl methacrylate) (PMMA) particles by dispersion polymerization of methyl methacrylate (MMA) in the presence of trimethylsiloxy terminated PDMS with benzoyl peroxide as an initiator in $scCO_2$.

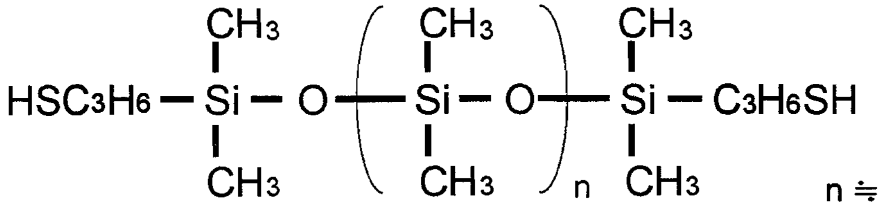
Mercaptopropyl terminated PDMS (MP-PDMS), whose formula is given in Scheme 1, consists of PDMS unit, which is CO_2-philic, and mercaptopropyl group, which should work as a chain transfer agent in radical polymerizations. It should be expected that PDMS-*b*-PMMA is generated by a chain transfer reaction during a dispersion polymerization of MMA in $scCO_2$ and that it should work as a colloidal stabilizer. MP-PDMS is commercially available and is much less expensive (ca. 130 euro/kg [6]) in comparison with general colloidal stabilizers used in scCO$_2$ (e.g., ca. 330 euro/450 g for the carboxylic terminated perfluoropolyether [7], ca. 120 euro/50 g for the PDMS macromonomer [8]). Taking the industrialization into consideration, it will be advantageous to use MP-PDMS as a colloidal stabilizer in scCO$_2$.

In this chapter, PMMA particles will be produced by dispersion polymerization of MMA in scCO$_2$ with 2,2'-azobis(isobutyronitrile) (AIBN) in the presence of MP-PDMS as a colloidal stabilizer.

3.2 Experimental

3.2.1 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 formulas are given in Scheme 1. The number-average molecular weights (M_n) of X-22-167B and X-22-167C are about 3340 and 4820 g/mol, respectively [6]. Trimethylsiloxy terminated PDMS (TS-PDMS) with a weight-average molecular weight (M_w) of about 5200 g/mol was used as received from Sigma-Aldrich Co. Industrial grade CO$_2$, with a purity of 99.5% or more, was used. Guaranteed reagent *n*-hex-



$$HSC_3H_6-Si(CH_3)_2-O-\left(Si(CH_3)_2-O\right)_n-Si(CH_3)_2-C_3H_6SH$$

n ≒ 40 (X-22-167B)
n ≒ 60 (X-22-167C)

Scheme 1 Chemical formulas of MP-PDMS

Table 1 Recipes for the productions of PMMA particles by precipitation polymerization[a)] of MMA with AIBN and dispersion polymerizations[a)] of MMA with AIBN in the presence of TS-PDMS[b)] or MP- PDMS[c),d)] in $scCO_2$

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

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

Abbreviations: PMMA, poly(methyl methacrylate); MMA, methyl methacrylate; AIBN, 2,2'-azobis(isobutyronitrile); TS-PDMS, trimethylsiloxy terminated poly(dimethylsiloxane); MP-PDMS, mercaptopropyl terminated poly(dimethylsiloxane)

ane and chloroform were used as received from Nacalai Tesque Co. Sodium dodecyl sulfate (SDS) was used as received from Wako Pure Chemical Industries, Ltd.

3.2.2 Dispersion polymerization in $scCO_2$

Dispersion polymerizations were carried out in 10-mL and 25-mL stainless steel reactors as described in Chapter 1, under the conditions listed in Tables 1, 2 and 3. 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 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 shaking vigorously. The polymerizations were started 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 reactor was cooled in an ice water bath and the CO$_2$ was vented slowly. Polymerizations of MMA with AIBN initiator in the absence/presence of TS-PDMS were conducted in a similar way. The particles produced were observed with a Hitachi S-2460N scanning electron microscope (SEM) after centrifugal washing with *n*-hexane which is a nonsolvent for PMMA and a good solvent for PDMS [9].

3.2.3 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 sec at a constant acceleration voltage of 1.5 kV and at an ion beam current of 20 mA.

3.2.4 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 a SDS aqueous medium (20 g) using an ultrasonic homogenizer 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 times centrifugal washing with a distilled water, the particles were dried and were redispersed in *n*-hexane, and then extraction of 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-PDMS (M_n, about 4820 g/mol) and PMMA homopolymer produced by solution polymerization with AIBN in toluene, was conducted in the same way.

3.3 Results and discussion

Chain transfer constants (C_s) to dodecamethyl pentasiloxane and 3-(3-mercaptopropyl)siloxane, which could be thought to be model reagents of TS-PDMS and MP-PDMS, respectively, in radical polymerization of MMA at 79.5°C were 1.45×10^{-5} and 1.28×10^{-1}, respectively [9]. C_s value of 3-(3-mercaptopropyl)siloxane was four orders of magnitude higher than that of dodecamethyl pentasiloxane. In the presence of TS-PDMS, PMMA and PS particles could not be obtained by dispersion polymerization with AIBN in $scCO_2$ [10, 11] and in heptane [12]. In these polymerization systems, the TS-PDMS could not be attached to PMMA and PS particles by chemical grafting and physical adsorption, which should not lead to TS-PDMS being an effective colloidal stabilizer. In the case of MP-PDMS, based on the large C_s value, it should be expected that PDMS-*g*-PMMA will be generated by the chain transfer reaction to terminal mercaptopropyl group of MP-PDMS during the dispersion polymerization of MMA and should work as an effective colloidal stabilizer in $scCO_2$.

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 was determined on the basis of the idea described as follows. Initiation rate of radical polymerization, R_i, is given by $R_i = f\rho_i$, where f is the initiator efficiency and ρ_i is the generation rate of radicals. The ρ_i is expressed as $2k_d[I]$, where k_d is the rate coefficient for initiator decomposition, and [I] is the initiator concentration. In general, dispersion polymerizations were carried out in R_i range of 10^{13}-10^{14} mL^{-1} s^{-1} [13-15]. Guan and coworkers 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$_2$ [16]. In this experiment, the AIBN concentration giving R_i of 5.1 x 10^{13} mL^{-1}s^{-1} was chosen. The k_d and f values used in the calculation were 7.7 x 10^{-6} s^{-1} and 0.9, 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 (THF) [17] and methanol [18] were higher than that in pure CO$_2$.

Figure 1 shows PMMA produced by the precipitation and dispersion polymerizations with AIBN in scCO$_2$ after the centrifugal washings. In the latter polymerizations, TS-PDMS and MP-PDMS were used as colloidal stabilizer. In the cases of the precipitation polymerization (Fig. 1a) and the dispersion polymerization with the TS-PDMS (Fig. 1b), PMMA were 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. In the presence of MP-PDMS (M_n, about 3340 g/mol), the product was a thick irregular white PMMA film and the irregular structure was observed in Fig. 1c. In the presence of MP-PDMS

(M_n, about 4820 g/mol), the product was obtained as nonspherical PMMA particles as shown in Fig. 1d and a thick irregular white PMMA film, and the conversion was gravimetrically determined to be 83%. Even after the washing, the PMMA particles were stably dispersed in *n*-hexane, which suggested that 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 $(MPa)^{1/2}$ [21], and *n*-hexane is a good solvent for PDMS, PDMS chains must extend into *n*-hexane medium. Since the PDMS compo-

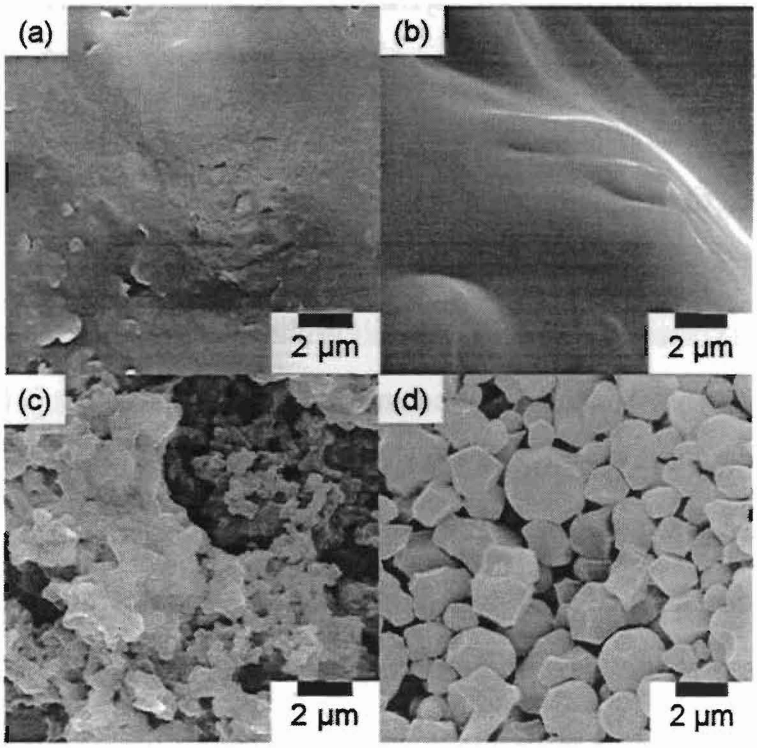


Figure 1 Scanning electron microscope (SEM) photographs of poly(methyl methacrylate) (PMMA) particles produced by the precipitation polymerization of methyl methacrylate (MMA) with 2,2'-azobis(isobutyronitrile) (AIBN) (a) or the dispersion polymerizations of MMA with AIBN in the presence of trimethylsiloxy terminated poly(dimethylsiloxane) (b) or mercaptopropyl terminated poly(dimethylsiloxane) (MP-PDMS) [M_n (g/mol): (c) ca. 3340; (d) ca. 4820] in $scCO_2$ utilizing the 10-mL high-pressure reactor after a centrifugal washing with *n*-hexane

nent 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 Co.) were 1.71 μm and 33%, respectively. The M_n and M_w/M_n ratio for the washed PMMA particles were, respectively, 1.5 x 10^5 g/mol and 2.2, which were determined from gel permeation chromatograms with THF as the eluent. 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. In order to check whether MP-PDMS, which were free and adsorbed physically on the PMMA particles, was washed away by the centrifugal washing, ten times washing of the mixture of MP-PDMS (1 g) and the washed PMMA particles (100 mg) with *n*-hexane was conducted, furthermore. The weight percentage of the PDMS component in the mixture of MP-PDMS and the PMMA particles after the ten times washing with *n*-hexane was consistent with that of the washed PMMA particles before the mixing with MP-PDMS. It was likely that MP-PDMS which were free and adsorbed physically was washed away by the washing and that PDMS component in the particles after the washing was due to PDMS-*g*-PMMA generated during the dispersion polymerization.

These results indicate that MP-PDMS had two functions: a chain transfer agent and a colloidal stabilizer. Hereafter, it is called "transtab" (transfer agent and stabilizer). In following, the dispersion polymerizations were carried out in the presence of MP-PDMS (M_n, about 4820 g/mol) as a transtab.

Figure 2 shows XPS Si_{2p} spectra for the washed PMMA particles before

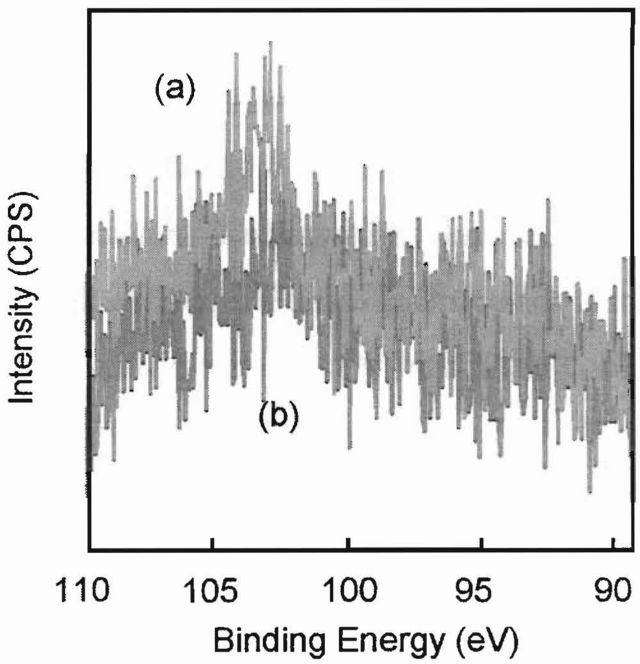


Figure 2 X-ray photoelectron spectroscopy Si_{2p} spectra for PMMA particles produced by the dispersion polymerization of MMA with AIBN in the presence of MP-PDMS (M_n, ca. 4820 g/mol) in $scCO_2$ utilizing the 10-mL high-pressure reactor after the centrifugal washing with *n*-hexane, before (a) and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

(a) and after (b) argon ion sputtering. A peak due to 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 PDMS component was not weakened when pure PDMS-based azoinitiator (VPS-0501, Wako Pure Chemical Industries, Ltd.) was sputtered under the same conditions. The peak shift should be due to the chemical change of PDMS component by the argon ion sputtering. These results indicate that the surfaces of the washed PMMA particles were occupied by PDMS component.

Figure 3 shows SEM photographs of PMMA particles produced at different MP-PDMS (M_n, about 4820 g/mol) concentrations (wt% based on MMA)

Table 2 Recipes for the productions of PMMA particles by the dispersion polymerization[a)] of MMA with AIBN in the presence of MP-PDMS (M_n, ca. 4820 g/mol) in $scCO_2$

Ingredients		0.5	2.5	5.0	10	25
MMA[b)]	(g)	2.0	2.0	2.0	2.0	2.0
AIBN[c)]	(g)	0.01	0.01	0.01	0.01	0.01
MP-PDMS	(g)	0.01	0.05	0.1	0.2	0.5

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

Abbreviations: PMMA, poly(methyl methacrylate); MMA, methyl methacrylate; AIBN, 2,2'-azobis(isobutyronitrile); MP-PDMS, mercaptopropyl terminated poly(dimethylsiloxane)

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%, nonspherical PMMA particles and white PMMA films were prepared, and the particle diameter decreased from micronsize to submicronsize with an increase in the transtab concentration. At 25 wt%, the weight percentage of PDMS component in the particles after the washing was determined to be 1.6 wt%, which was larger value than that of 10 wt%. To minimize experimental error, the PMMA particles produced at the transtab concentration of 25 wt% was used for the extraction experiment. The amount of PDMS component in the PMMA particles was not changed before and after the extraction with *n*-hexane, whereas for the particles of the mixture of MP-PDMS and PMMA homopolymer, the amount of PDMS component decreased to the experimental error level after the extraction. These results showed that PDMS component in PMMA particles produced in $scCO_2$ was due to PDMS-*g*-PMMA generated by the chain transfer reaction during the dispersion polymerization.

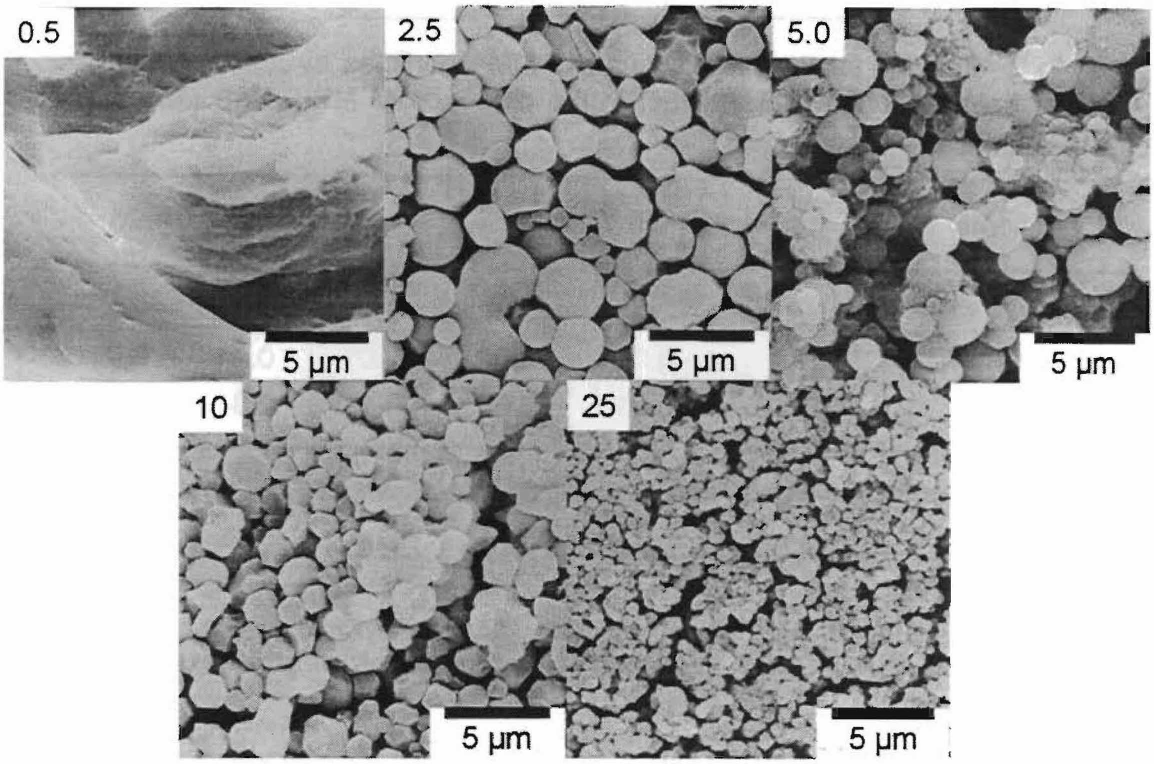


Figure 3 SEM photographs of PMMA particles produced by the dispersion polymerization of MMA with AIBN at different MP-PDMS (M_n, ca. 4820 g/mol) concentrations (wt% based on MMA) in $scCO_2$ utilizing the 10-mL high-pressure reactor after the centrifugal washing with *n*-hexane

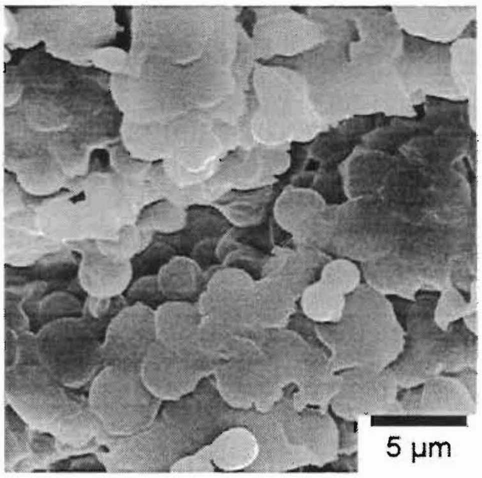


Figure 4 A SEM photograph of a section of a thick irregular white PMMA film produced by the dispersion polymerization of MMA with AIBN at MP-PDMS (M_n, ca. 4820 g/mol) concentration of 10 wt% based on MMA in $scCO_2$ utilizing the 10-mL stainless steel high-pressure reactor after the centrifugal washing with *n*-hexane

Figure 4 shows a SEM photograph of a section of the thick irregular white PMMA film produced by the dispersion polymerization at the MP-PDMS (M_n, about 4820 g/mol) concentration of 10 wt%. The film seems to be formed by coagulation of the particles. It is well known that PMMA was highly plasticized by CO_2, which resulted in the lowering of glass transition temperature (T_g) of PMMA [19-22]. Fehrenbacher and coworkers indicated 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 [23]. Assuming that the density of CO_2 in PMMA is estimated to be 1.0 g mL^{-1} [23, 24], the weight ratio of PMMA/CO_2 in the $scCO_2$ is calculated to be 1/0.28. 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 down to about –25°C [19]. From the above data and the prediction, it should be thought that T_g of PMMA particles in $scCO_2$ at 65°C and 30 MPa was down near –25°C. Sedimentation distance of 1-μm-sized CO_2-sorbed PMMA particle in $scCO_2$ (PMMA/CO_2 weight ratio, 1/0.28) for 24 h should be calculated to be 188 mm utilizing the Stokes equation, and the distance for the particle to move by Brownian motion in the $scCO_2$ should be calculated to be 1.1 mm utilizing the Einstein-Stokes equation. In the calculations of these distances, the following values were used: the densities of $scCO_2$ (60°C, 32.9 MPa) and PMMA, 0.85 g mL^{-1} [25] and 1.19 g mL^{-1} [9], respectively; coefficient of viscosity of $scCO_2$ (77°C, 30 MPa), 0.075×10^{-3} kg m s^{-1} [26]; Avogadro's number, 6.02×10^{23} mol^{-1}; gravitational acceleration, 9.81 m s^{-2}. The calculated distances mean that micron-sized, CO_2-sorbed PMMA particles in the $scCO_2$ should sediment by the end of the dispersion polymerization without stirring. In the dispersion polymerization of MMA utilizing the 10-mL reactor with the stainless steel ball, the efficiency of stir-

Table 3 A recipe for the production of PMMA particles by dispersion polymerization[a] of MMA with AIBN in the presence of MP-PDMS (*Mn*, ca. 4820 g/mol) in $scCO_2$

Ingredients		
MMA[b]	(g)	5.0
AIBN[c]	(g)	0.025
MP-PDMS	(g)	0.5

[a] ca. 30 MPa; 65°C; 25-mL stainless steel reactor 420 rpm; 24 h

[b] 2.0 mol/L (20 w/v%)

[c] R_i (= $2k_d f$[I]), 5.0×10^{13} mL^{-1} s^{-1}; k_d, 7.7×10^{-6} s^{-1}; *f*, 0.9

Abbreviations: PMMA, poly(methyl methacrylate); MMA, methyl methacrylate; AIBN, 2,2'-azobis(isobutyronitrile); MP-PDMS, mercaptopropyl terminated poly(dimethylsiloxane)

ring may be low as described in Chapter 1, and the CO_2-sorbed PMMA particles, whose T_g might be near –25°C (further below –25°C if there were MMA and CO_2 in PMMA particles), seem to sediment, which results in deformation of PMMA particles and formation of the thick irregular white PMMA film. The deformation of PMMA particles and 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 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 3, and it was confirmed that spherical PMMA particles resulted as shown in Fig. 5. The

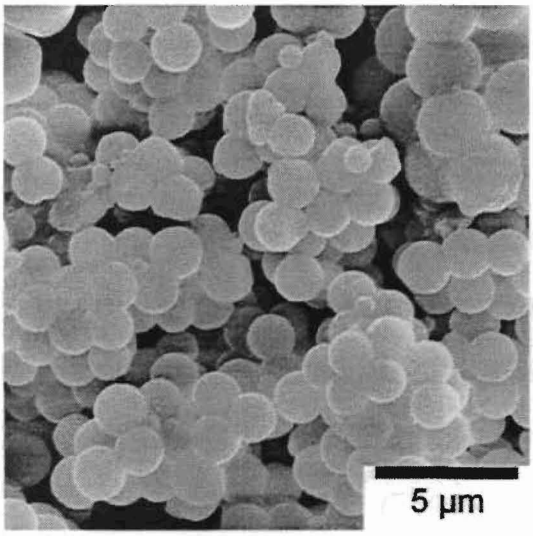


Figure 5 A SEM photograph of PMMA particles produced by dispersion polymerization of MMA with AIBN at MP-PDMS (M_n, ca. 4820 g/mol) concentration of 10 wt% based on MMA in $scCO_2$ utilizing the 25-mL high-pressure reactor after the centrifugal washing with *n*-hexane

conversion was determined to be 82%, which was almost the same value in comparison with that obtained utilizing the 10-mL high-pressure reactor. 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, and the weight percentage of the PDMS component in the PMMA particles after the washing was determined to be 2.9%. D_n and C_v of the PMMA particles after the washing were 2.37 μm and 16%, respectively. The diameter became larger and the monodispersity of the PMMA particles was improved by increasing of the stirring efficiency.

3.4 Conclusions

PMMA particles were produced by dispersion polymerization of MMA in the presence of MP-PDMS in $scCO_2$ at about 30 MPa for 24 h at 65°C. The particle diameter could be controlled in a range of submicron to micron by varying MP-PDMS concentration. The MP-PDMS worked as not only a chain transfer agent but also a colloidal stabilizer, which was named "tran stab".

3.5 References

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Chapter 4

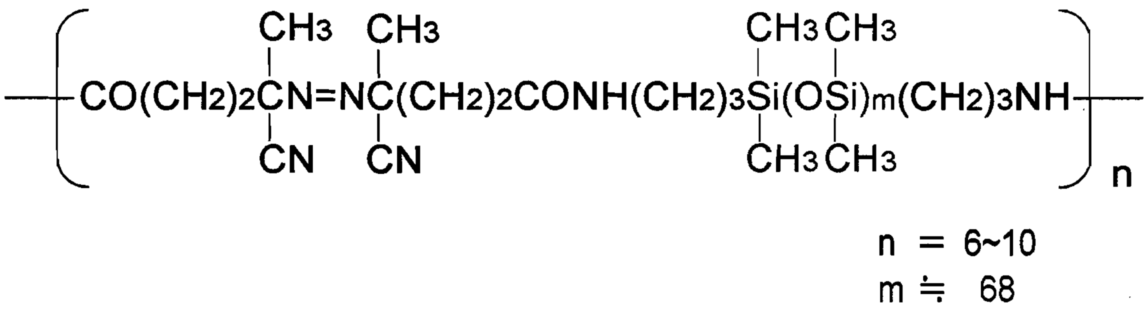
Production of poly(methyl methacrylate) particles by dispersion polymerization with poly(dimethylsiloxane)-based azoinitiator in supercritical carbon dioxide

4.1 Introduction

Dispersion polymerization is a valuable method for the production of polymer particles in the size range submicronsize to micronsize. In the dispersion polymerization, a colloidal stabilizer is used to stabilize the product as a polymer colloid, and their architectures include homopolymer as well as block, graft, or random copolymers and copolymerizable stabilizers [1-3]. In the dispersion polymerization in supercritical carbon dioxide ($scCO_2$), various types of colloidal stabilizers described above have been also used [4]. For example, recently, Shaffer and coworkers conducted dispersion polymerization of methyl methacrylate (MMA) in the presence of poly(dimethylsiloxane) (PDMS)-based macromonomer with 2,2'-azobis(isobutyronitrile) (AIBN) in $scCO_2$, and succeeded in producing poly(methyl methacrylate) (PMMA) particles [5]. In this polymerization system, PDMS-based macromonomer copolymerized with MMA, and worked as a colloidal stabilizer in $scCO_2$. In Chapters 2 and 3, it has been shown that trimethylsiloxy terminated PDMS and mercaptopropyl terminated PDMS (transtab) can be covalently bonded at the surface of PMMA particles and can be used as colloidal stabilizers in $scCO_2$, respectively.

PDMS-based azoinitiator, whose formula is given in Scheme 1, has azo-groups and PDMS units, and this macroinitiator is expected to work not only as an initiator but also as a colloidal stabilizer.

In this chapter, submicron- to micron-sized PMMA particles will be produced by the dispersion polymerizations of MMA in $scCO_2$ with PDMS-based azoinitiator in the absence of colloidal stabilizer.



$$-\left[CO(CH_2)_2\underset{CN}{\overset{CH_3}{C}}N{=}N\underset{CN}{\overset{CH_3}{C}}(CH_2)_2CONH(CH_2)_3\underset{CH_3}{\overset{CH_3}{Si}}(O\underset{CH_3}{\overset{CH_3}{Si}})_m(CH_2)_3NH\right]_n-$$

$n = 6\sim10$

$m \fallingdotseq 68$

Scheme 1 A chemical formula of PDMS-based azoinitiator (VPS-0501)

4.2 Experimental

4.2.1 Materials

MMA was purified by distillation under reduced pressure in a nitrogen atmosphere. Reagent grade AIBN was purified by recrystallization. PDMS-based azoinitiator (VPS-0501), commercially supplied by Wako Pure Chemical Industries was used as received. The number-average molecular weight is in the range of about 3×10^4 - 5×10^4 g/mol. Industrial grade CO_2, with a purity of 99.5% or more, was used as received from Kobe Sanso Co. Guaranteed reagent *n*-hexane was used as received from Nacalai Tesque Co. Trimethylsiloxy terminated PDMS (TS-PDMS) with weight-average molecular weight (M_w) of about 5200 g/mol was used as received from Sigma-Aldrich Co. Commercial grade sorbitan monooleate nonionic emulsifier (Rheodol SP-O10, Kao Co.) and oxyethylene oxypropylene block copolymer

(Pronon#201, NOF Co.) were used as received.

4.2.2 Dispersion polymerization in $scCO_2$

Polymerizations were carried out in a 90-mL stainless steel reactor, equipped with sapphire windows for observation of the inside, as described in Chapter 1. The reactor was charged with MMA and VPS-0501, and purged with CO_2, and then pressurized with CO_2 to 10 MPa using high pressure pump (Nihon Seimitu Kagaku. Co., NP-D-321J) at room temperature with stirring at 750 rpm using a rotary impeller stirrer to mix in the reactor. It was confirmed with naked eyes through the sapphire windows that the CO_2 solution was homogeneous. The polymerization was started by heating the mixture to 65°C, at which the pressure in the reactor was adjusted to 30 MPa by adding CO_2 with stirring at 200 rpm. The internal pressure decreased somewhat during the polymerization, which should be due to the decrease of the volume with the conversion of MMA to PMMA. After 24 h, the reactor was cooled to room temperature and the CO_2 was vented slowly. The polymerizations of MMA (18.0 g) with either AIBN (0.295 g) or the mixture of AIBN (0.295 g) and the TS-PDMS (9.07 g) were conducted in a similar way. The produced particles were observed with a Hitachi S-2500 scanning electron microscope (SEM).

4.2.3 X-ray photoelectron spectroscopy (XPS)

XPS data in Fig. 4 were obtained with a Kratos XSAM-800 apparatus using magnesium Kα radiation (1253.6 eV) at a potential of 12.5 kV and an X-ray current of 12 mA. The pressure in the measurement chamber was about 2.0×10^{-7} Torr. A Digital Equipment Corporation DS-800 computer system was used for spectrometer control and data handling. XPS data in Fig. 5 were obtained 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. Argon ion sputtering was conducted at 5.0 x 10^{-4} Pa for 200 sec at a constant acceleration voltage of 1.5 kV and at an ion beam current of 20 mA. Dried particles were stored under reduced pressure by continuous operation of a diffusion pump just before XPS measurement. The dried particles were spread on an indium plate with a spatula.

4.3 Results and discussion

Dispersion polymerization of MMA (18.0 g) was carried out with VPS-0501 initiator (9.07 g) in $scCO_2$ at 30 MPa for 24 h at 65°C in the 90-mL stainless steel reactor. Where, the VPS-0501 concentration was determined on the basis of the idea described below. In radical polymerization, initiation rate of polymerization, R_i, is given by $R_i = f\rho_i$, where f is the initiator efficiency and ρ_i is the generation rate of radicals. The ρ_i is expressed as $2k_d[I]$, where k_d is the rate coefficient for initiator decomposition, and [I] is the initiator concentration. In general, dispersion polymerizations were carried out in R_i range of 10^{13}-10^{14} mL^{-1} s^{-1} [6-8]. DeSimone and coworkers 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 $scCO_2$ [9]. Assuming that k_d value of VPS-0501 is equal to that of 4,4'-azobis(4-cyanopentanoic acid) [10], the f value of VPS-0501 is 0.24 [11], and these k_d and f values of VPS-0501 in $scCO_2$ have the same tendency as those of AIBN in $scCO_2$ described above, the VPS-0501 concentration giving R_i of

3.7 x 10^{13} $mL^{-1}s^{-1}$ was determined. This value calculated for pure $scCO_2$ may be somewhat different from that for the mixture of $scCO_2$ and MMA in the polymerization system. Actually, there are reports that the rates of AIBN decomposition in a mixture of CO_2 and cosolvent such as tetrahydrofuran (THF) [9] and methanol [12] were higher than in pure CO_2.

Figure 1 shows optical photographs of the state of the reaction mixture as observed through the sapphire windows during the dispersion polymerization with VPS-0501 in $scCO_2$. Before the polymerization, it could be confirmed that the mixture was homogeneous. After about 1 h, a red color, which should be due to the scattering of transmitted light by the growing polymer particles, was observed. After the polymerization, light could not be transmitted. The conversion of MMA was determined to be 87% with a gravimetrical method.

Figure 2 shows SEM photographs of produced PMMA particles, before (a) and after (b) centrifugal washing with *n*-hexane, which is a nonsolvent for PMMA and a good solvent for VPS-0501. The boundary among the particles was not clear before the washing, whereas it was clearly distinguished after

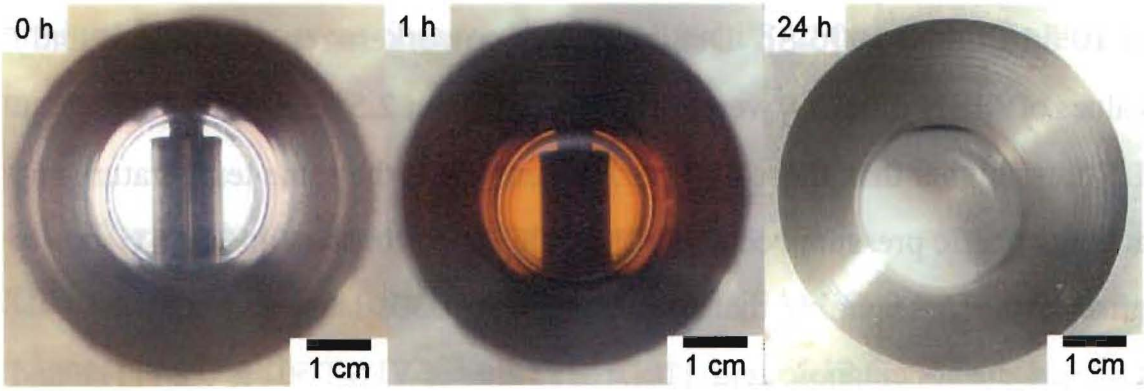


Figure 1 Optical photographs of the state of the reaction mixture as observed through the sapphire windows during the dispersion polymerization of methyl methacrylate (MMA) with VPS-0501 in supercritical carbon dioxide ($scCO_2$)

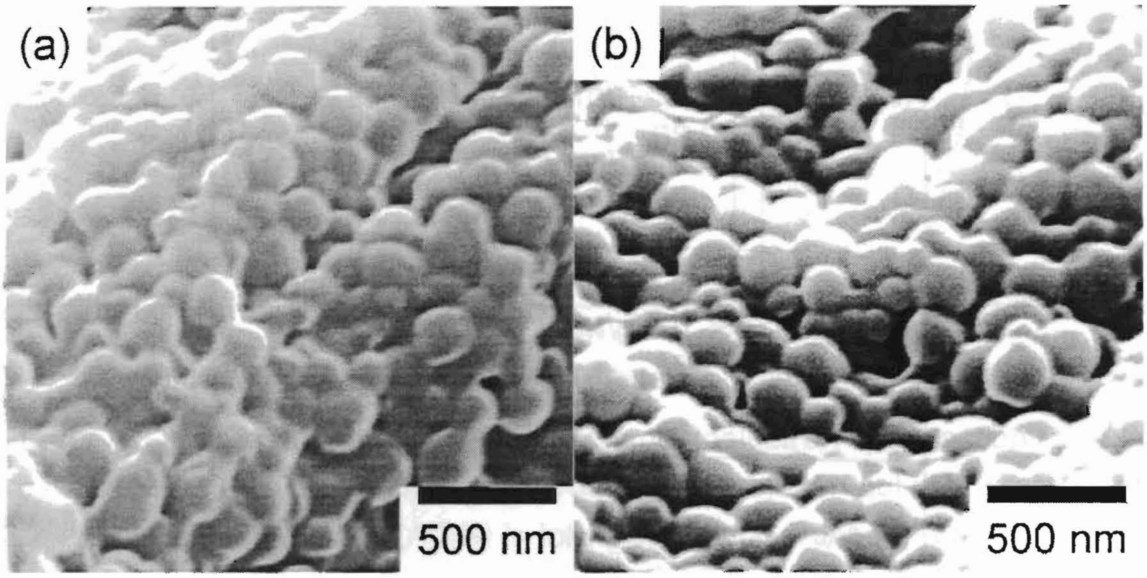


Figure 2 Scanning electron microscope (SEM) photographs of poly(methyl methacrylate) (PMMA) particles produced by the dispersion polymerization of MMA with VPS-0501 in $scCO_2$ before (a) and after (b) centrifugal washing with *n*-hexane

the washing. Free PDMS generated by complete decomposition of VPS-0501, and undecomposed and partially decomposed VPS-0501 should be removed by the washing. The washed product was a free-flowing white powder, though the original product before the washing was tacky solid, which should be due to the existences of excessive free PDMS and undecomposed and partially decomposed VPS-0501. The number-average diameter (D_n) and the coefficient of variation (C_v) for the washed PMMA particles measured with image analysis software for Macintosh (Mac Scope, Mitani Co.) were, respectively, 210 nm and 15.5%. The weight percentage of PDMS component in the washed PMMA particles was determined to be 15% from ^{1}H NMR spectrum measured with a Bruker DPX250 NMR spectrometer operating at 250 MHz for proton with 200 scans. When AIBN was used as initiator in place of VPS-0501 with or without TS-PDMS, prepared PMMA was not particles but a thick irregular film on the interior walls and the sapphire win-

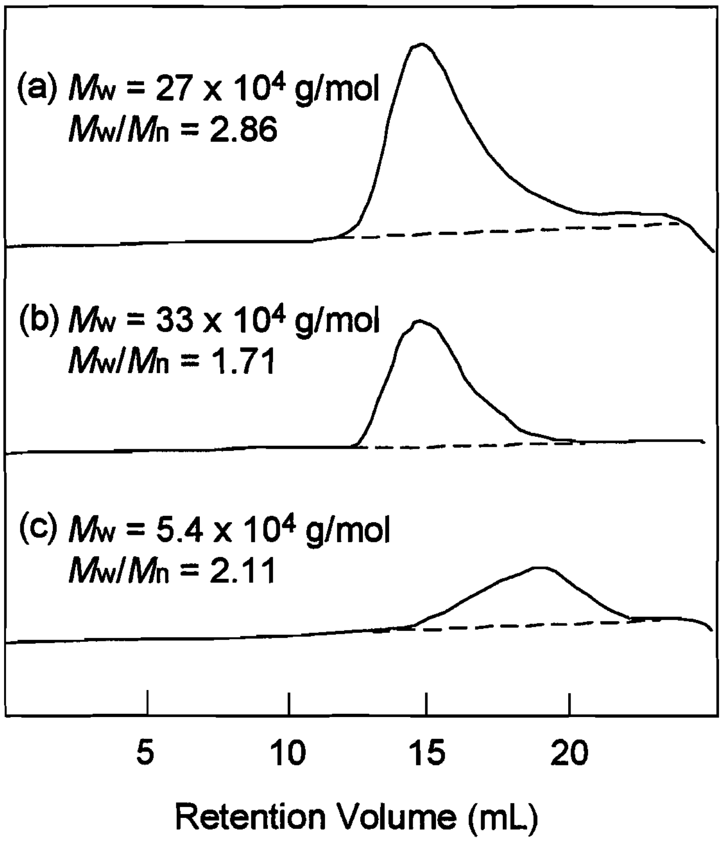


Figure 3 Gel permeation chromatograms for PMMA particles produced by the dispersion polymerization of MMA with VPS-0501 in $scCO_2$ before (a) and after (b) the centrifugal washing with *n*-hexane, and for soluble polymers in *n*-hexane (c) washed away from PMMA particles

dows. These results indicate that VPS-0501 had two functions of an initiator and a colloidal stabilizer in the dispersion polymerization in $scCO_2$. Hereafter, it will be called as "inistab"(initiator + stabilizer).

Figure 3 shows gel permeation chromatograms with THF as the eluent for the PMMA particles before (a) and after (b) the centrifugal washing with *n*-hexane, and their extracts (c). Each molecular weight was measured from calibration obtained with PS standards. The M_w for the PMMA particles before and after the centrifugal washing, and the extracts were, respectively, 27 x 10^4, 33 x 10^4 and 5.4 x 10^4 g/mol. Because the M_w of VPS-0501 was 6.6 x 10^4 g/mol (this molecular weight was determined from gel permeation chro-

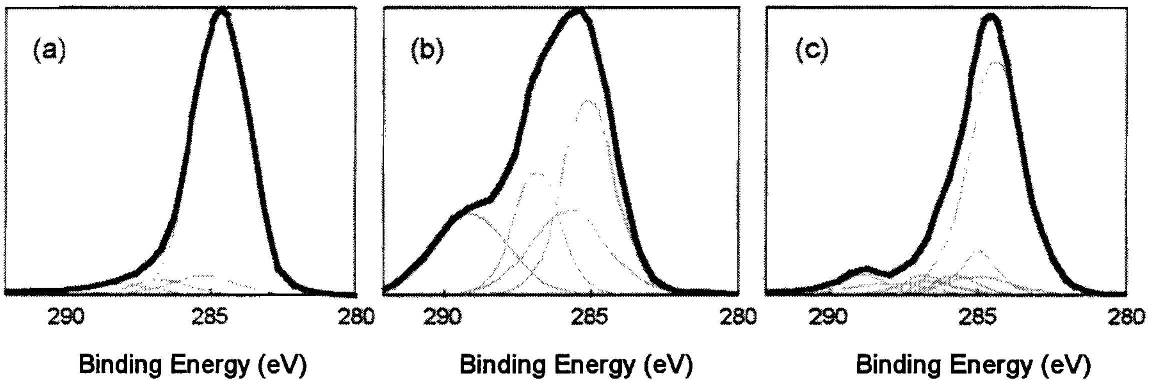


Figure 4 C$_{1s}$ peak shape analyses of X-ray photoelectron spectroscopy (XPS) spectra for VPS-0501 (a), PMMA (b) produced by solution polymerization with 2,2'-azobis(isobutyronitrile) (AIBN) in toluene, and the washed PMMA particles (c) produced by the dispersion polymerization of MMA with VPS-0501 in scCO$_2$

matogram), the extracts which were soluble in *n*-hexane should be free PDMS, and undecomposed and partially decomposed VPS-0501. By the washing,

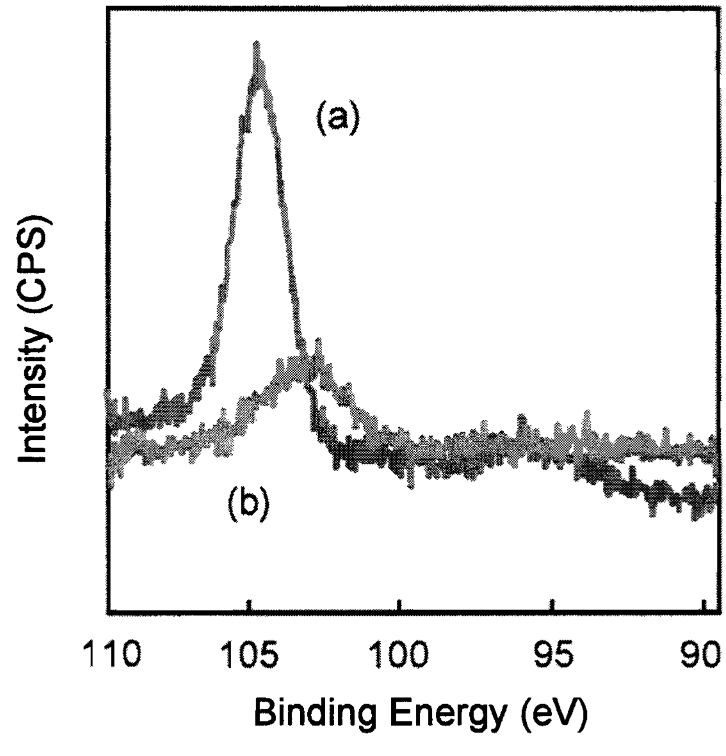


Figure 5 XPS Si$_{2p}$ spectra for PMMA particles produced by the dispersion polymerization of MMA in scCO$_2$ with VPS-0501 before (a) and after (b) argon ion sputtering for 200 sec at constant acceleration voltage of 1.5 kV and at ion beam current of 20 mA

Table 1 The number-average diameter and hydrodynamic diameter of the washed PMMA particles produced by the dispersion polymerization of MMA with VPS-0501 in $scCO_2$[a]

D_n[b] (nm)	D_h[c] (nm)
210	400

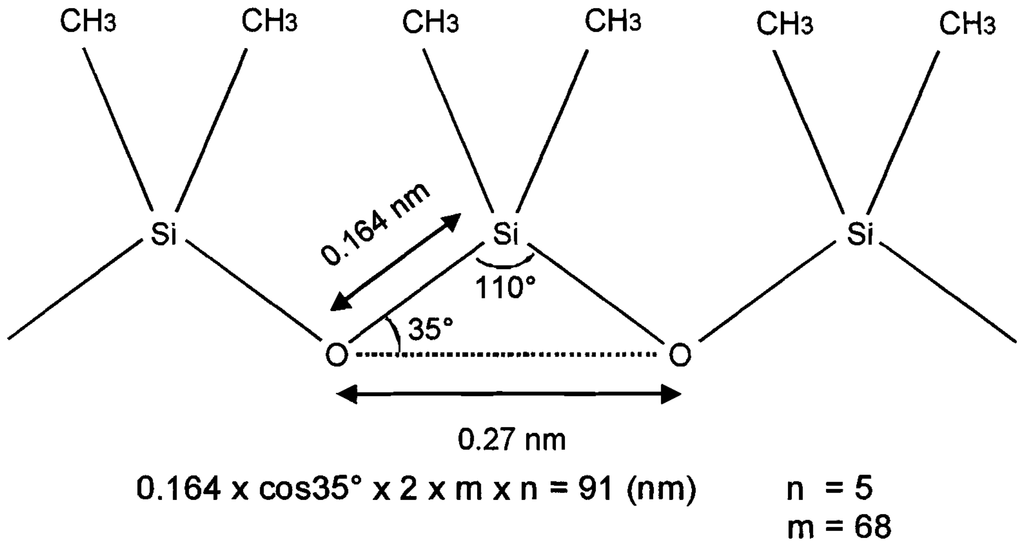
[a] 30 MPa; 65°C; 90-mL stainless steel reactor; 200 rpm; 24 h
[b] The number-average diameter determined with SEM
[c] The hydrodynamic diameter measured for the PMMA particles dispersed in *n*-hexane at 20°C by dynamic light scattering

Abbreviations: PMMA, poly(methyl methacrylate); MMA, methyl methacrylate

the M_w/M_n ratio was decreased from 2.86 to 1.71, which was due to the removal of the extracts.

Figure 4 shows the results of C_{1s} peak shape analyses of XPS spectra for VPS-0501 (a), purified PMMA (b) prepared by solution polymerization with AIBN in toluene, and the above washed PMMA particles (c). In Fig. 4a, a strong peak due to PDMS component in VPS-0501 was observed at 284.3 eV in addition to some weak peaks due to the other components. In Fig. 4b, a peak due to carbonyl groups of PMMA was observed at 289.0 eV. In Fig. 4c, a strong peak due to the PDMS component at 284.3 eV and small peaks due to PMMA at 289.0 eV were observed. These indicate that the surfaces of the washed PMMA particles were occupied by PDMS component.

Figure 5 shows XPS Si_{2p} spectra of the washed PMMA particles before (a) and after (b) argon ion sputtering. In Fig. 5a, a strong peak due to the PDMS component was observed at 103 eV, and in Fig. 5b, the peak was weakened after the argon ion sputtering. It has been confirmed that the intensity of Si_{2p}



Scheme 2

peak due to PDMS component was not weakened when pure VPS-0501 was sputtered under the same conditions. These results indicate that Si atom disappeared after argon ion sputtering, which means that the surfaces of the PMMA particles produced in $scCO_2$ were occupied by PDMS component.

Table 1 shows D_n and hydrodynamic diameter (D_h) of the washed PMMA particles dispersed in *n*-hexane, which were, respectively, determined with SEM and a dynamic light-scattering spectroscope (Otsuka Electronics DLS-7000DH, Kyoto, Japan) at a fixed 90° light-scattering angle. D_h in *n*-hexane was larger than D_n in dry state, and the difference was 191 nm. This suggests that PDMS component covalently bonded at the particle surface extended into the *n*-hexane medium. Because the solubility parameter values of both PDMS and *n*-hexane are the same value, 14.9 $(MPa)^{1/2}$ [13], and *n*-hexane is a good solvent of PDMS [13], PDMS chains must expand into the *n*-hexane medium. Since the PDMS component is soluble in $scCO_2$ as well as *n*-hexane, it should effectively operate as a colloidal protective layer to disperse the PMMA particles stably in $scCO_2$ medium of the dispersion polymerization system. The hydrodynamic thickness (95.5 nm) of the PDMS layer end-grafted to the particle surface in *n*-hexane accorded well with the length (91 nm) for five repeated units, n = 5, of VPS-0501. The length for the five repeated units was calculated as follows, assuming that the molecular weight for one repeated unit (n = 1) of VPS-0501 is 5000, the Si-O bond length is 0.164 nm, and the Si-O chains form the planar zigzag conformation with bond angle of 110° as shown in Scheme 2. Using the k_d value of VPS-0501 in $scCO_2$, it is calculated that 30% of azo-groups in VPS-0501 is randomly decomposed by the end of the dispersion polymerization. Using the f value of VPS-0501 in $scCO_2$, it is estimated that 64% of the generated initiator radicals is recombinated or disproportionated in their "cages" [14] without initiating the polymerization. The initiator radicals diffusing out of their

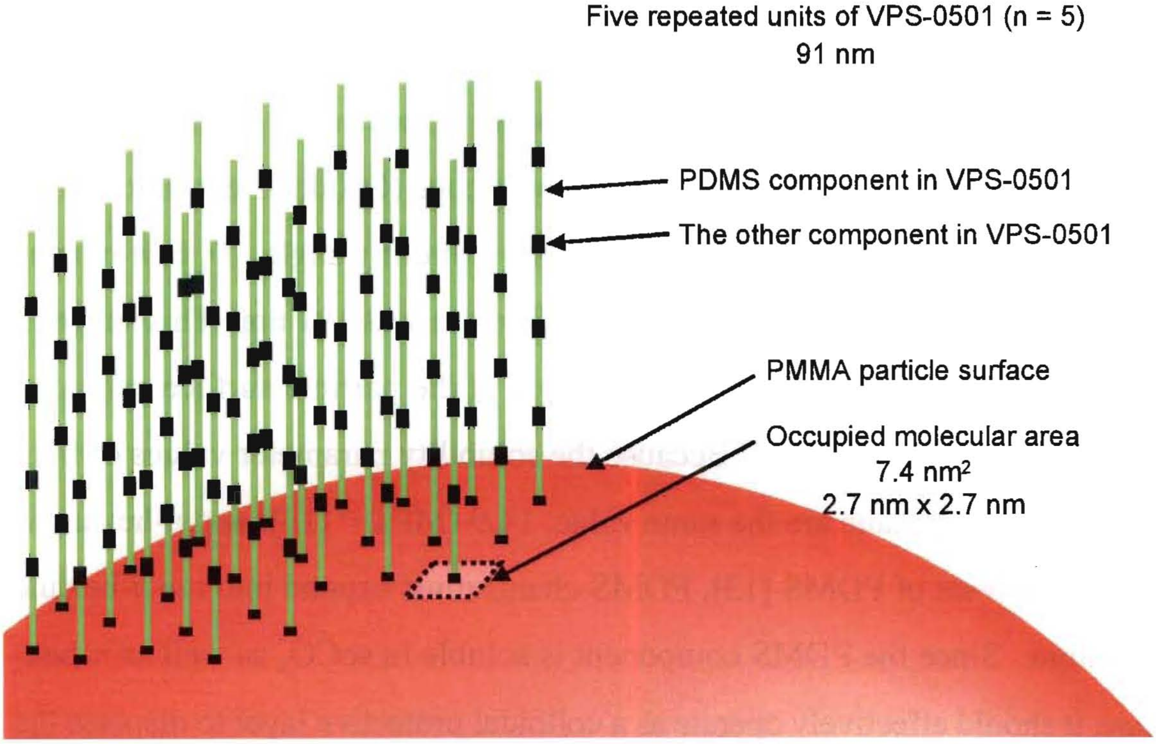


Figure 6 A schematic diagram for five repeated units (n = 5) of VPS-0501 to be end-grafted to the PMMA particle surface

Table 2 Recipes for the productions of PMMA particles by dispersion polymerizations of MMA with VPS-0501/AIBN in $scCO_2$[a]

Ingredients		VPS-0501/AIBN (molar ratio)								
		1/0	1/1	1/5	1/10	1/20	1/30	1/40	1/80	0/1
MMA[b]	(g)	18.0	18.0	18.0	18.0	18.0	18.0	18.0	18.0	18.0
VPS-0501[c]	(g)	9.1	4.5	1.5	0.75	0.42	0.29	0.22	0.11	—
AIBN[c]	(g)	—	0.15	0.25	0.27	0.28	0.29	0.29	0.29	0.30

[a] 30 MPa; 65°C; 90-mL stainless steel reactor, 200 rpm; 24 h

[b] 2.0 mol/L (20 w/v%)

[c] The concentration of azo-group in the mixture of VPS-0501 and AIBN, 20 mmol/L

Abbreviations: PMMA, poly(methyl methacrylate); MMA, methyl methacrylate; AIBN, 2,2'-azobis(isobutyronitrile)

"cages" initiate the polymerization, and they are covalently bonded as initiator fragment at the particle surface. Taking the amounts of the undecomposed azo-groups and the recombinated compounds into account, there should be much possibility that five repeated units and more in VPS-0501 molecule are covalently bonded at the particle surface. Assuming that all the PDMS chains consist of five repeated units ($n = 5$) for the sake of convenience and are covalently bonded at the particle surfaces, occupied molecular area of the PDMS chain at the particle surface was calculated to be 7.4 nm^2 from the results obtained by the NMR and DLS measurements described above. The densities of PMMA and PDMS used in the calculation of the surface area of the PMMA particles, respectively, are 1.19 and 0.97 [13]. The square root of the occupied molecular area (2.7 nm) is smaller than the mean square end-to-end distance (4.9 nm) for the five repeated units of VPS-0501. These indicate that the grafting density at the particle surface is so high that PDMS chains stretch out from their random walk configurations as shown in Fig. 6.

The *n*-hexane dispersion of the washed PMMA particles was kept at 65°C for 3 days, and D_h was again measured with DLS after centrifugal washing. The D_h value after the heat treatment was 934 nm, which was much larger than that (401 nm) before the heat treatment. This indicates that the PMMA particles coagulated during the heat treatment. To prevent the coagulation during the heat treatment, the *n*-hexane dispersions were treated at 60°C similarly in the presences of Rheodol SP-O10 and Pronon#201 nonionic emulsifiers of which hydrophilic-lipophilic balance values are, respectively, 4.3 and 2.0. The PMMA particles, however, still coagulated during the heat treatments. The coagulations seem to be caused by a decrease in the thickness of colloidal protective layer, which is due to the decomposition of the azo-groups in the PDMS molecules, taking it into that the PMMA particles dispersed in *n*-hexane before the heat treatment.

Figure 7 shows SEM photographs of PMMA particles produced with VPS-

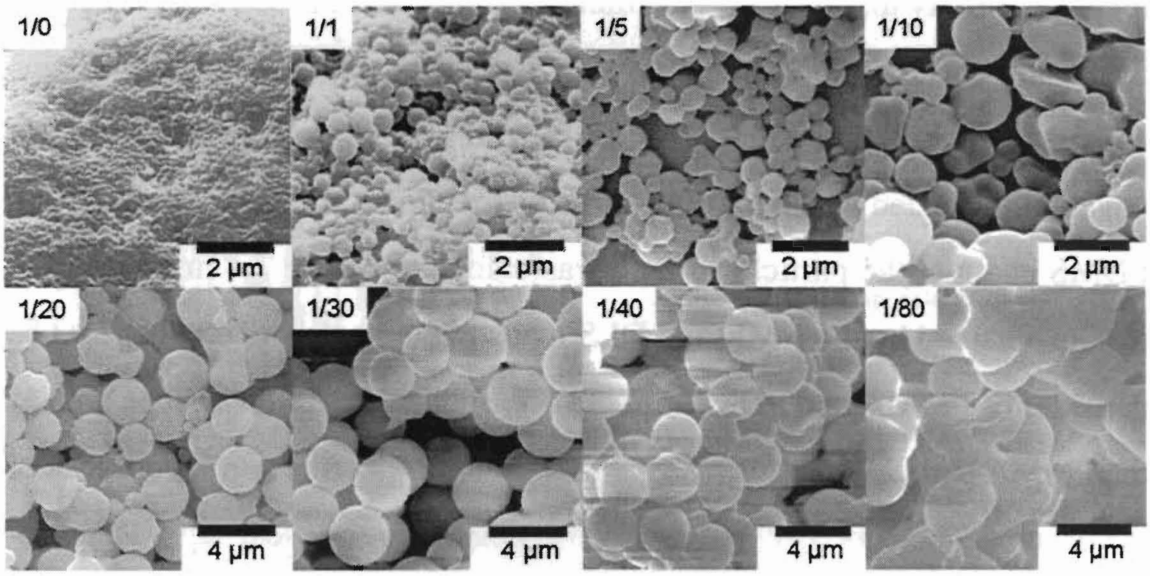


Figure 7 SEM photographs of PMMA particles produced by the dispersion polymerizations of MMA with VPS-0501/AIBN in $scCO_2$ after centrifugal washing with *n*-hexane. Ratios on the photographs indicate the molar ratios of VPS-0501/AIBN.

Table 3 Conversions, powder contents and solid states data for PMMA particles produced by the dispersion polymerization of MMA with VPS-0501/AIBN in $scCO_2$[a]

	VPS-0501/AIBN (molar ratio)								
	1/0	1/1	1/5	1/10	1/20	1/30	1/40	1/80	0/1
Conversion (%)	88	85	80	87	89	82	83	45	58
Powder contents (wt%)	0	23.8	31.3	36.3	84.2	60.9	58.9	44.0	0
Solid state	brittle[b] clammy[c]	brittle[b] clammy[c]	brittle[b] dried	brittle[b] dried	brittle[b] dried	brittle[b] dried	hard dried	hard dried	hard dried

[a] 30 MPa; 65°C; 90-mL stainless steel reactor, 200 rpm; 24 h
[b] Easily broken to powder with mortor and pestle
[c] Due to PDMS component contained in PMMA obtained

Abbreviations: PMMA, poly(methyl methacrylate); MMA, methyl methacrylate; AIBN, 2,2'-azobis(isobutyronitrile); PDMS, poly(dimethylsiloxane)

0501/AIBN mixtures under the conditions listed in Table 2. The amounts of azo-groups in the mixtures of VPS-0501 and AIBN were constant. The particle diameter increased from submicronsize to micronsize with a decrease in VPS-0501 amount in the mixture. This should be due to a decrease in the amount of PDMS component, which can work as a colloidal stabilizer. At the VPS-0501/AIBN molar ratio of 1/80, PMMA particles seemed to be coagulated.

Table 3 shows conversions, powder contents and solid states data for PMMA particles produced by the dispersion polymerizations with VPS-0501/AIBN mixtures under the conditions listed in Table 2. At the VPS-0501/AIBN molar ratios of 1/0 to 1/40, the conversions were relatively high up to 80%, however, at the ratios of 1/80 and 0/1, the conversions were lower. These results indicated that the conversions in the dispersion polymerization systems, in which PMMA particles could be stably produced, were higher than that obtained in the system, in which PMMA particles were coagulated or PMMA films were obtained.

Table 4 Number-average diameter (D_n), coefficient of variation (C_v), weight-average molecular weight (M_w), molecular weight distribution (M_w/M_n) and PDMS content data for PMMA particles produced by the dispersion polymerizations of MMA with VPS-0501/AIBN in $scCO_2$[a] after centrifugal washing with *n*-hexane

		VPS-0501/AIBN (molar ratio)								
		1/0	1/1	1/5	1/10	1/20	1/30	1/40	1/80	0/1
D_n	(μm)	0.21	0.41	0.53	1.03	2.49	2.64	3.16	—	—
C_v	(%)	15.5	21.6	35.5	61.3	13.3	13.0	5.96	—	—
M_w	(x 10^4)	32.8	29.6	25.0	21.1	21.9	15.7	19.4	14.1	29.0
M_w/M_n		1.71	1.76	1.42	2.09	1.53	1.71	1.76	1.53	1.33
PDMS content[b]	(wt%)	13.8	7.9	2.3	1.4	0.91	0.84	0.48	0.43	—

[a] 30 MPa; 65°C; 90-mL stainless steel reactor, 200 rpm; 24 h

[b] PDMS content in PMMA particles produced

Abbreviations: PMMA, poly(methyl methacrylate); MMA, methyl methacrylate; AIBN, 2,2'-azobisisobutyronitrile; PDMS, poly(dimethylsiloxane)

Table 4 shows D_n, C_v, M_w, M_w/M_n ratio and PDMS content data for the PMMA particles produced by the dispersion polymerizations with the mixture of VPS-0501 and AIBN under the conditions listed in Table 2. The D_n increased from submicronmeter to micrometer and the PDMS content in the particles produced decreased with an decrease in the ratio of VPS-0501/AIBN. At the VPS-0501/AIBN molar ratio of 1/30, relatively monodisperse PMMA particles with C_v of 13% were produced.

4.4 Conclusions

Submicron- to micron-sized, comparatively monodisperse PMMA particles were successfully produced by the dispersion polymerization of MM with PDMS-based azoinitiator in $scCO_2$ at 30 MPa for 24 h at 65°C. The initiator operated not only as a radical initiator but also as a colloidal stabilizer, and was named an "inistab".

4.5 References

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Chapter 5

Production of poly(methyl methacrylate) particles by dispersion polymerization in the presence of aminopropyl terminated poly(dimethylsiloxane) stabilizer in supercritical carbon dioxide

5.1 Introduction

There has been an increasing interest in conducting dispersion polymerizations in supercritical carbon dioxide ($scCO_2$), and great efforts were made to develop colloidal stabilizers which are effective in $scCO_2$ [1-11]. Poly(methyl methacrylate) (PMMA) particles were produced by the dispersion polymerization in $scCO_2$ in the presence of trimethylsiloxy terminated poly(dimethylsiloxane) (PDMS), mercaptopropyl terminated PDMS, and PDMS-based azoinitiator in Chapters 2, 3 and 4. In these polymerization systems, PDMS components were covalently bonded at the surface of PMMA particles and should effectively operate as colloidal protective layers to disperse the PMMA particles stably in the $scCO_2$ medium of the dispersion polymerization system.

Recently, Christian and coworkers produced PMMA particles by dispersion polymerization in $scCO_2$ using carboxylic terminated perfluoropolyether [12]. They showed that the perfluoropolyether, which was attached to the PMMA particles by hydrogen bonding interaction between the terminal acid group of the perfluoropolyether and the carbonyl group of PMMA particle surface, worked as an effective colloidal stabilizer in $scCO_2$. On the basis of these results, it is expected that aminopropyl terminated PDMS (AP-PDMS), whose chemical formula is given in Scheme 1, may work as an effective colloidal stabilizer in $scCO_2$, which should be attached to PMMA particles by hydrogen bonding interaction between the amino group and the carbonyl group of PMMA particle surface. AP-PDMS is commercially available and is much less expensive (ca. 60 euro/kg [13]) in comparison with general colloidal stabilizers used in $scCO_2$ (e.g., ca. 330 euro/450 g for the carboxylic terminated perfluoropolyether [14]; ca. 120 euro/50 g for the PDMS macromonomer [15]). Taking the industrialization into consideration, it will be advantageous to use AP-PDMS as a colloidal stabilizer in $scCO_2$.

In this chapter, PMMA particles will be produced by dispersion polymerization of MMA in $scCO_2$ with AP-PDMS as a colloidal stabilizer.

5.2 Experimental

5.2.1 Materials

MMA was purified by distillation under reduced pressure in a nitrogen atmosphere. Reagent grade 2,2'-azobis(isobutyronitrile) (AIBN) was purified by recrystallization. AP-PDMS (Silaplane FM-3321), supplied by Chisso Co., was used as received. The number-average molecular weight is about 5000 g/mol. Industrial grade CO_2, with a purity of 99.5% or more, was used. Guaranteed reagent *n*-hexane was used as received from Nacalai Tesque Co. Trimethylsiloxy terminated PDMS with a weight-average molecular weight (M_w) of about 5200 g/mol was used as received from Sigma-Aldrich Co.

5.2.2 Dispersion polymerization in $scCO_2$

Polymerizations were carried out in a 25-mL stainless steel reactor as described in Chapter 1. The reactor was charged with MMA (5.0 g), AIBN (0.025 g), AP-PDMS (0.25, 0.5 or 1.0 g) and a magnetic stir bar, and purged with N_2, and then pressurized with CO_2 to 10 MPa at 25°C using a high-pressure pump (Nihon Seimitsu Kagaku. Co., NP-D-321J) with shaking vigorously. The polymerization was started by heating the mixture to 65°C, at which temperature the pressure in the reactor reached about 30 MPa, with stirring at 420 rpm. After 24 h, the reactor was cooled in an ice water bath and the CO_2 was vented slowly. The polymerizations of MMA (5.0 g) with either AIBN (0.025 g) or the mixture of AIBN (0.025 g) and the trimethylsiloxy terminated PDMS (0.5 g) were conducted in a similar way. The particles produced were observed with a Hitachi S-2460N scanning electron microscope (SEM).

5.2.3 Characterizations of the PMMA particles

Specific surface area of PMMA particles was determined by BET measurement with Gemini-Micromeritics 2360 (Shimadzu Co.). Fourier transform (FT) IR measurement of AP-PDMS before and after the scCO$_2$ treatment at about 30 MPa for 1 h at 65°C was carried out with a FT-IR spectrometer (Perkin-Elmer Spectrum GX FT-IR spectrometer) at room temperature. The samples were placed between two sodium chloride plates. The polymer composition of the particle surface was estimated by X-ray photoelectron spectroscopy (XPS) with a Shimadzu ESCA-3400 electron spectrometer using magnesium K α radiation (1150 eV) at a potential of 8 kV and an X-ray current of 30 mA. Argon ion sputtering was conducted at 5.0×10^{-4} Pa for 100 sec at a constant acceleration voltage of 1.5 kV and at an ion beam current of 20 mA.

5.3 Results and discussion

Figure 1 shows photographs of states of AP-PDMS (1.8 g) in $scCO_2$ in the absence (a) and presence (b) of MMA, which were observed visually through sapphire windows of a 90-mL stainless steel reactor with a white light at the opposite side. In the absence of MMA, the system was turbid, which indicates that the AP-PDMS was insoluble in pure $scCO_2$ under the conditions of 30 MPa and 65°C. This result accords well with that obtained under the conditions of 30 MPa and 60°C [16]. On the other hand, in the presence of MMA, the system was transparent and the rotary impeller was clearly observed. This indicates that MMA acts as a cosolvent for the AP-PDMS.

The dispersion polymerizations of MMA were carried out with AIBN in

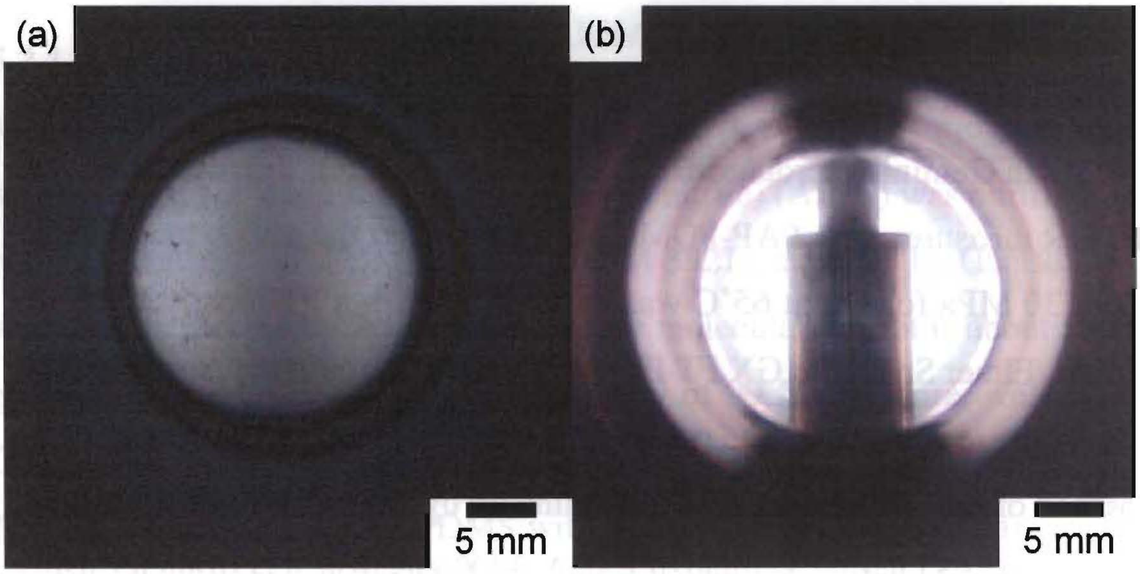


Figure 1 Optical photographs of states of the mixture of aminopropyl terminated poly(dimethylsiloxane) (AP-PDMS) and supercritical carbon dioxide ($scCO_2$) in the absence (a) and presence (b) of methyl methacrylate (MMA) observed through sapphire windows of the 90-mL stainless steel reactor with a white light at the opposite side

the absence and presence of the AP-PDMS in $scCO_2$ at about 30 MPa for 24 h at 65°C in the 25-mL stainless steel reactors. The AIBN concentration was determined on the basis of the idea described as follows. Initiation rate of radical polymerization, R_i, is given by $R_i = f\rho_i$, where f is the initiator efficiency and ρ_i is the generation rate of radicals. ρ_i is expressed as $2k_d[I]$, where k_d is the rate coefficient for initiator decomposition, and [I] is the initiator concentration. In general, dispersion polymerizations were carried out in R_i range of 10^{13}-10^{14} mL^{-1} s^{-1} [17-19]. Guan and coworkers [20] 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, the AIBN concentration giving R_i of 5.1 x 10^{13} $mL^{-1}s^{-1}$ was chosen. The k_d and f values used in the calculation were 7.7 x 10^{-6} s^{-1} and 0.9, 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 (THF) [21] and methanol [22] were higher than that in pure CO_2. In the absence of AP-PDMS, PMMA was obtained as a thick irregular film on the interior wall of the reactor. Whereas, in the presence of AP-PDMS, whose concentrations were 10 and 20 wt% based on MMA, the products were free-flowing white powders and the conversions of MMA were gravimetrically determined to be 96 and 98%, respectively. At AP-PDMS concentration of 5 wt%, PMMA was obtained as a free-flowing white powder and breakable white blocks. When the dispersion polymerization of MMA was conducted with AIBN in the presence of trimethylsiloxy terminated PDMS as a colloidal stabilizer in place of the AP-PDMS, no powder was obtained but a thick irregular film. These results indicate that aminopropyl group played an important role in anchoring of PDMS component at the surface of the PMMA particles during the dispersion polymerization of MMA.

Figure 2 shows SEM photographs of PMMA particles produced at different AP-PDMS concentrations (wt% based on MMA) of 5 (Figs. 2a and 2d), 10 (Figs. 2b and 2e) and 20 (Figs. 2c and 2f), before (Figs. 2a, 2b and 2c) and after (Figs. 2d, 2e and 2f) five times centrifugal washing with *n*-hexane which is a nonsolvent for PMMA and a good solvent for PDMS. The boundary among the particles was not clear before the washing, whereas it became

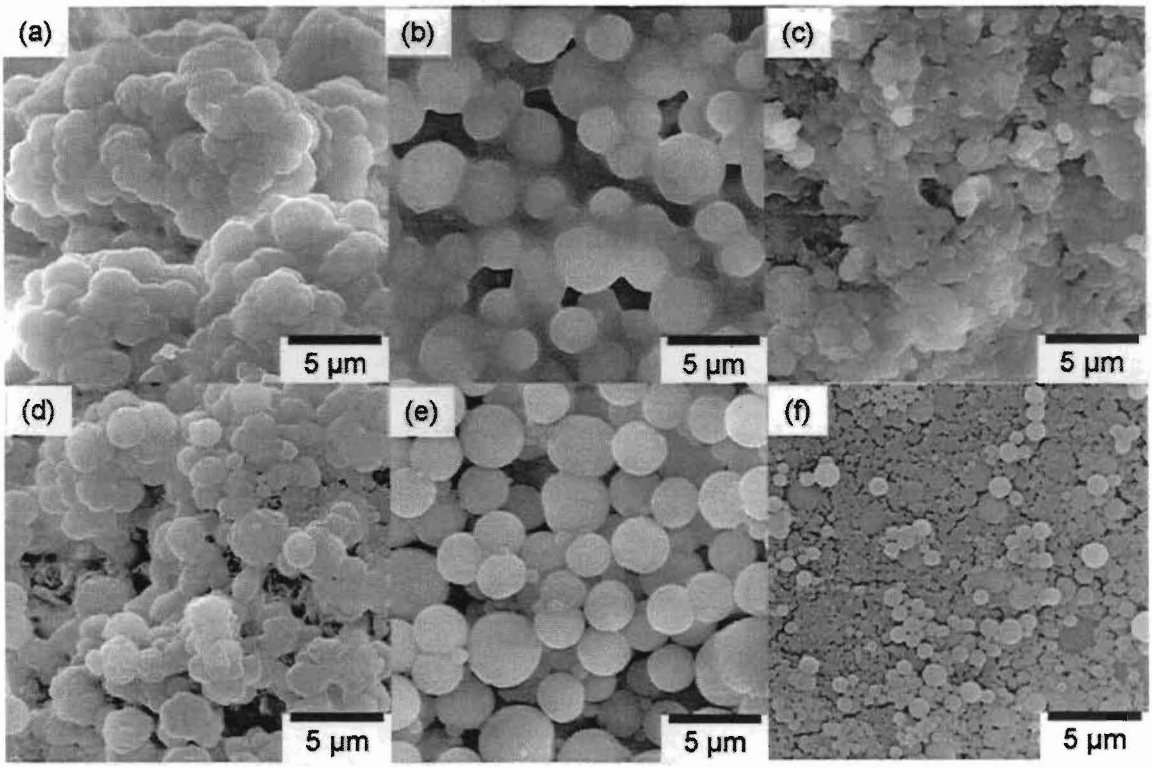


Figure 2 Scanning electron microscope (SEM) photographs of poly(methyl methacrylate) (PMMA) particles produced by the dispersion polymerization of MMA in $scCO_2$ with 2,2'-azobis(isobutyronitrile) (AIBN) at different AP-PDMS concentrations (wt% based on MMA): (a, d) 5; (b, e) 10; (c, f) 20, before (a, b, c) and after (d, e, f) centrifugal washing with *n*-hexane

clear after the washing. At 5 wt%, coagulated PMMA particles were observed, which should be due to the shortage of AP-PDMS stabilizer. At 10 wt%, micron-sized PMMA particles were observed, and the number-average diameter (D_n), the coefficient of variation (C_v) and particle size distribution (D_w/D_n) for the washed PMMA particles determined from the SEM photograph with image analysis software (MacScope, Mitani Co.) were 2.89 μm, 30% and 1.18, respectively. At 20 wt%, submicron-sized PMMA particles were observed, and D_n, C_v and D_w/D_n were 420 nm, 42% and 1.56, respectively. The particle diameter decreased with an increase in the AP-PDMS concentration. D_w/D_n obtained in this study were a little larger than those obtained using other kinds of stabilizers (1.01~1.52) [2, 3, 5, 23]. Even after the washing, the PMMA particles were stably dispersed in *n*-hexane. This suggests that PDMS component in the AP-PDMS bonded by hydrogen bonding interaction between the amino group and the carbonyl group at the par-

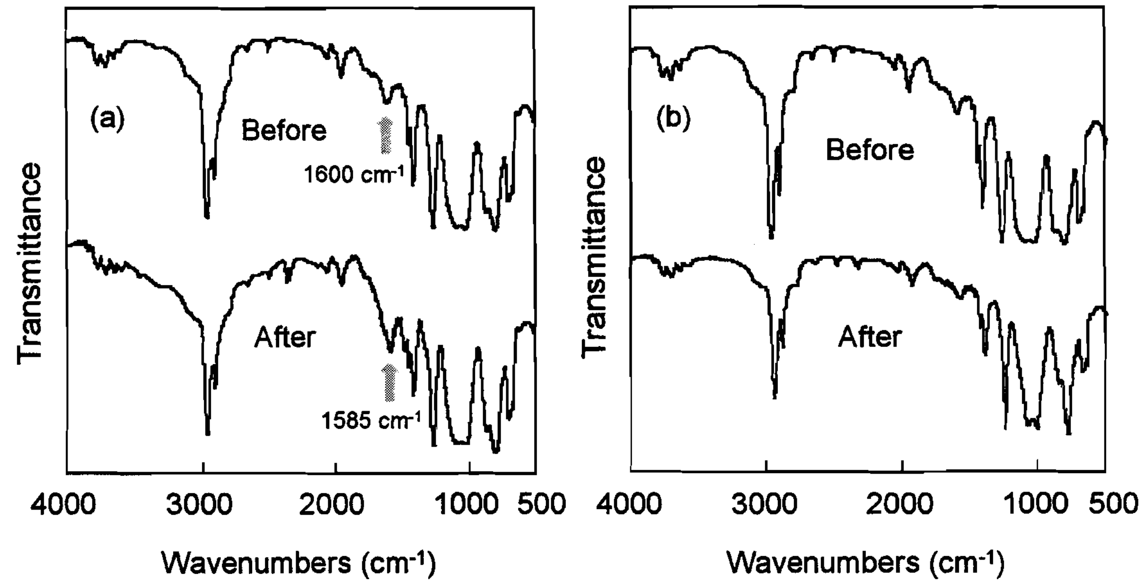
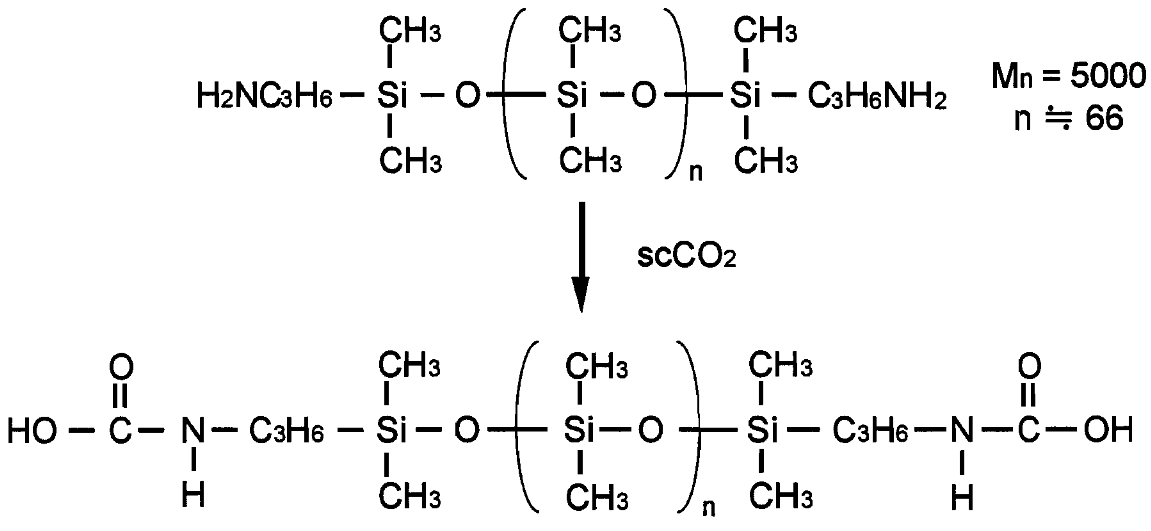


Figure 3 Fourier transform IR spectra of AP-PDMS (a) and trimethylsiloxy terminated poly(dimethylsiloxane) (b) before and after the scCO2 treatment at ca. 30 MPa for 1 h at 65°C

ticle surface extended into the *n*-hexane medium and worked as a colloidal stabilizer.

It is known that primary, aliphatic amines react with CO_2 to form carbamic acids [16]. Elsbernd indicated that AP-PDMS also reacted to form carbamic acid-terminated PDMS (CA-PDMS), which has carboxyl groups [24]. As described in the introduction of this chapter, it was reported that hydrogen bonding interaction between the carboxylic end group of perfluoropolyether and the carbonyl group of PMMA operated in $scCO_2$ [12].

Figure 3 shows FT-IR spectra of the AP-PDMS (a) and trimethylsiloxy terminated PDMS (b) before and after the $scCO_2$ treatment at about 30 MPa for 1 h at 65°C. In the spectra in Fig. 3a, before the $scCO_2$ treatment the absorption peak due to primary amine N-H bending vibration was observed at 1600 cm^{-1} [24], and after the treatment, the broad absorption from 3500 to 2300 cm^{-1} due to O-H stretching vibration of carbamic acid [24] and the absorption peak which should be due to C=O stretching vibration of carbamic acid at 1585 cm^{-1} were observed. The spectra of the AP-PDMS before and



Scheme 1 Chemical formulas of AP-PDMS and CA-PDMS

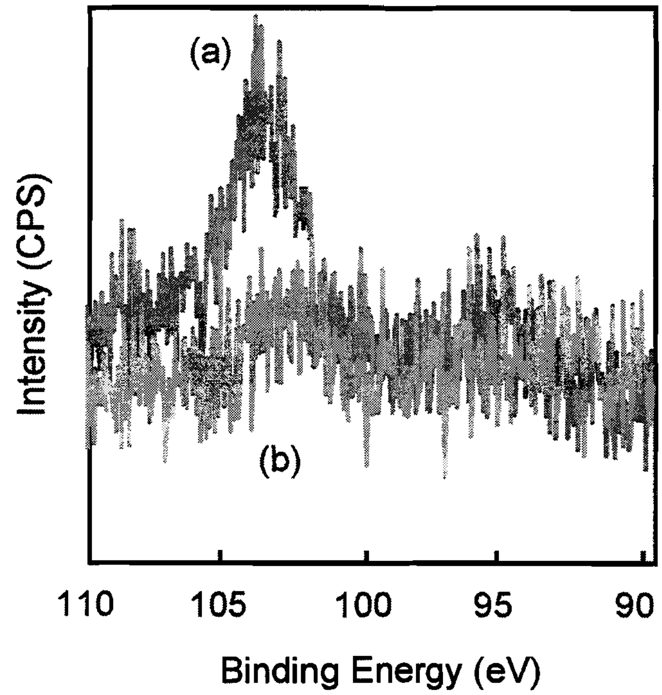


Figure 4 X-ray photoelectron spectroscopy Si_{2p} spectra for PMMA particles produced by the dispersion polymerization of MMA in scCO2 with AIBN at AP-PDMS concentration of 10 wt% before (a) and after (b) argon ion sputtering at 5.0 x 10^{-4} Pa for 100 sec at constant acceleration voltage of 1.5 kV and at an ion beam current of 20 mA

after the $scCO_2$ treatment indicate that the AP-PDMS reacted with CO_2 to form CA-PDMS as shown in Scheme 1. In Fig. 3b, for the trimethylsiloxy terminated PDMS, no difference in FT-IR spectra before and after the $scCO_2$ treatment was observed. In the dispersion polymerization system, there may be also a possibility that the CA-PDMS was formed and was attached to PMMA particles by hydrogen bonding interaction between the carbamic acid group and the carbonyl group, in addition to the interaction between the aminopropyl group and the carbonyl group. Moreover, there may be also the possibility that PMMA-*b*-PDMS, which may be generated by chain transfer reaction to terminal aminopropyl group in AP-PDMS, worked as a colloidal stabilizer.

Because the solubility parameter values of both PDMS and *n*-hexane are the same (14.9 $(\mathrm{MPa})^{1/2}$) [25], and *n*-hexane is a good solvent for PDMS [25], PDMS chains must extend into *n*-hexane medium. Since the PDMS component is soluble in $scCO_2$ as well as *n*-hexane, it should effectively operate as a colloidal protective layer to disperse the PMMA particles colloidally stable in $scCO_2$ medium of the dispersion polymerization.

In following, the PMMA particles produced at AP-PDMS concentration of 10 wt% was characterized. The weight percentages of the PDMS component in the PMMA particles before and after the washing were determined to be 8.0% and 1.4%, respectively, from ^{1}H NMR spectra measured with a Bruker DPX250 NMR spectrometer operating at 250 MHz with 200 scans. The specific surface area of the washed PMMA particles (1.73 m^2/g) was larger than that (0.86 m^2/g) before the washing, which were measured by BET method. These results indicate the removal of the free AP-PDMS. The number-average diameter for the washed PMMA particles was calculated to be 2.91 μm from the result obtained by the BET method. The densities of PMMA used for the calculation is 1.19 [25]. The diameter calculated from the specific surface area was in good agreement with that measured in the SEM photograph with image analysis software. This indicates that the PMMA particles have a smooth surface. The M_w and M_w/M_n ratio for the washed PMMA particles were, respectively, 5.6×10^5 g/mol and 2.4, which were determined from gel permeation chromatogram with THF as the eluent.

Figure 4 shows XPS Si_{2p} spectra of the washed PMMA particles before (a) and after (b) argon ion sputtering. In Fig. 4a, a strong peak due to the PDMS component was observed at 103 eV, and in Fig. 4b, the peak disappeared after the argon ion sputtering. It has been confirmed that 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 Si atom disappeared after argon ion sputtering, which means that the surfaces of the PMMA particles produced in $scCO_2$ were occupied by PDMS component.

5.4 Conclusions

Micron-sized PMMA particles were successfully produced by the dispersion polymerization of MMA with AIBN in the presence of AP-PDMS as a colloidal stabilizer in $scCO_2$ at about 30 MPa for 24 h at 65°C.

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Chapter 6

Production of polydivinylbiphenyl particles by precipitation polymerization in supercritical carbon dioxide

6.1 Introduction

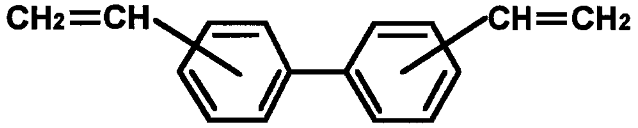
Precipitation polymerization is one of the methods to prepare stabilizer-free particles with clean surface [1-6]. This method requires only monomer, radical initiator and solvent. Stöver and coworkers produced highly crosslinked, monodisperse polydivinylbenzene (PDVB) particles by precipitation polymerization of divinylbenzene (DVB) in acetonitrile [1-3]. Recently, Cooper and coworkers reported that PDVB particles were also produced by precipitation polymerization of DVB in supercritical carbon dioxide ($scCO_2$) with 2,2'-azobis(isobutyronitrile) (AIBN) [4, 5]. There have been strong demands for crosslinked polymer particles with superior heat resistance, solvent resistance and clean surface. Such polymer particles can be used as carriers for chromatography, immobilizers of biomolecules and various spacers, because they are easy to separate from media and simple to maintain.

In this chapter, stabilizer-free polydivinylbiphenyl (PDVBP) particles with clean surface, having superior heat resistance and high refractive index in comparison with PDVB [7], will be produced by precipitation polymerization of divinylbiphenyl (DVBP) in $scCO_2$ with AIBN. The effects of initiation rate of polymerization on the conversion, the fluidity of powder, the degree of coagulation, the amounts of low-molecular-weight by-products, and the amounts of vinyl groups in the particles will be examined.

6.2 Experimental

6.2.1 Materials

DVBP, whose formula is given in Scheme 1, was supplied by Nippon Steel Chemical Co., and the purity was 51.7% [7]. DVBP was washed with 1 N NaOH aqueous solution and deionized water to remove polymerization inhibitors before use. Reagent grade AIBN was purified by recrystallization. Industrial grade CO_2, with a purity of 99.5% or more, was used as received.



Scheme 1 A chemical formula of DVBP

Table 1 Recipes for the production of PDVBP particles by precipitation polymerizations of DVBP in $scCO_2$[a]

Ingredients		AIBN concentration (mmol/L)							
		0.5[c]	1.0[c]	2.0[d]	4.9[d]	9.7[d]	19.4[e]	38.7[e]	58.1[e]
DVBP[b]	(g)	2	2	2	2	2	2	2	2
AIBN	(mg)	0.8	1.6	3.2	8.0	15.9	31.8	63.5	95.4

[a] ca. 30 MPa; 65°C; 10-mL stainless steel reactor; 60 cycles/min; 24 h

[b] Purity 53% (by catalog); 1.0 mol/L (20 w/v%)

[c] R_i (= $2k_d f$ [I]), $10^{12} \sim 10^{13}$ mL^{-1} s^{-1}; k_d, 7.7×10^{-6} s^{-1}; f, 0.9

[d] R_i (= $2k_d f$ [I]), $10^{13} \sim 10^{14}$ mL^{-1} s^{-1}; k_d, 7.7×10^{-6} s^{-1}; f, 0.9

[e] R_i (= $2k_d f$ [I]), $10^{14} \sim 10^{15}$ mL^{-1} s^{-1}; k_d, 7.7×10^{-6} s^{-1}; f, 0.9

Abbreviations: PDVBP, polydivinylbiphenyl; DVBP, divinylbiphenyl; AIBN, 2,2'-azobis(isobutyronitrile)

6.2.2 Precipitation polymerization in $scCO_2$

Polymerization was carried out in a 10-mL stainless steel reactor as described in Chapter 1 under the conditions listed in Table 1. The reactor was charged with DVBP, AIBN and three 3/16-inch-sized stainless steel balls to mix in the reactor, and purged with N_2, and then pressurized with CO_2 to 10 MPa at 25°C using high pressure pump (Nihon Seimitsu Kagaku Co., NP-D-321J) with shaking vigorously. The polymerization was started by heating the mixtures to 65°C, at which the pressure in the reactor reached about 30 MPa, 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 produced particles were observed with a Hitachi S-2500 scanning electron microscope (SEM). The particle size distributions were examined with a disc centrifuge photosedimentometer particle sizer (Union Giken Co., PA-101).

6.2.3 Angle of repose

The fluidity of PDVBP powder was estimated by measuring angle of repose as shown in Fig. 1. Obtained PDVBP powder was gently charged into a glass

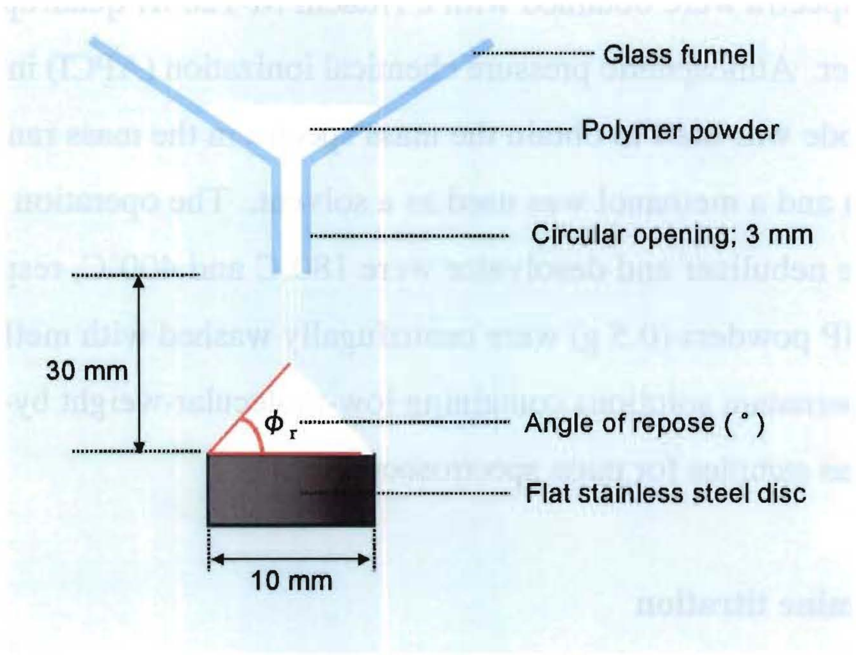


Figure 1 A schematic diagram for the measuremant of angle of repose

funnel, which had circular opening of about 3 mm, with its opening blocked by a finger. By removing the finger, the powder was allowed to flow directly onto a flat stainless steel disk (10 mm diameter) to form a powder heap. The circular opening was set 30 mm higher just above the flat stainless steel disk. Still photograph was then taken for the determination of the angle of repose which was defined as the angle of the free surface to the horizontal plane.

6.2.4 BET measurement

Specific surface area of PDVBP particles was determined from the amount of nitrogen gas adsorbed at the temperature of liquid nitrogen, which was measured with Gemini-Micromeritics 2360 (Shimadzu Co.). The PDVBP particles were dried under vacuum overnight and nitrogen atmosphere at 200°C for 4 h just prior to BET measurement.

6.2.5 Mass spectroscopy

The mass spectra were obtained with a Hitachi M-1200H quadrupole mass spectrometer. Atmospheric pressure chemical ionization (APCI) in the positive ion mode was used to obtain the mass spectra in the mass range of 70-2000 (m/z) and a methanol was used as a solvent. The operation temperatures of the nebulizer and desolvator were 180°C and 400°C, respectively. The PDVBP powders (0.5 g) were centrifugally washed with methanol (25 g), and supernatant solutions containing low-molecular-weight by-products were used as samples for mass spectroscopy.

6.2.6 Bromine titration

The amount of vinyl groups in PDVBP particles was measured by bromine titration method using an Aqua counter AQ-1 (Hiranuma Sangyo Co.). The residual monomers within the particles were removed by centrifugal washing with methanol prior to the measurement. After bromines (A moles) were generated by electrolysis in 70 mL of potassium bromide aqueous solution in a glass reactor, PDVBP particles (having X moles of vinyl groups) dispersed in methanol was injected with a syringe into the reactor. The vinyl groups were allowed to react with the bromine for a fixed reaction time. When the reaction time was up, sodium thiosulfate (B moles) aqueous solution, which quickly reacts completely with the residual bromines, was injected into the reactor. Afterwards, the unreacted sodium thiosulfate was titrated with bromine regenerated by electrolysis (C moles). The amount of vinyl groups (X moles) in the particles was calculated from the following equation.

$$\mathrm{X} = \mathrm{A} + \mathrm{C} - \mathrm{B}$$

6.3 Results and discussion

Precipitation polymerizations of DVBP were carried out with AIBN initiator in $scCO_2$ at about 30 MPa for 24 h at 65°C in the 10-mL stainless steel reactor under the conditions listed in Table 1. Where, the AIBN concentrations were determined on the basis of the idea described below. Initiation rate of radical polymerization, R_i is given by $R_i = f\rho_i$, where f is the initiator efficiency and ρ_i is the generation rate of radicals. The ρ_i is expressed as $2k_d[\mathrm{I}]$, where k_d is the rate coefficient for initiator decomposition, and [I] is the initiator concentration. In general, homogeneous radical polymerizations were carried out in R_i range of 10^{13}-10^{14} $\mathrm{mL^{-1}s^{-1}}$ [8-10]. DeSimone and coworkers 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 in benzene at the same temperature and at atmospheric pressure because of low dielectric constant and low viscosity of $scCO_2$ [11, 12]. On the other hand, precipitation polymerizations in $scCO_2$ were often carried out in relatively high R_i range of 10^{14}-10^{15} $mL^{-1}s^{-1}$ [4-6], which was calculated in consideration of k_d and f values of AIBN in $scCO_2$. In this article, in order to clarify the effects of R_i on the precipitation polymerization of DVBP in $scCO_2$, the AIBN concentration was changed in wide R_i range of 10^{12}-10^{15} $mL^{-1}s^{-1}$. The k_d and f values used in the calculation were 7.7×10^{-6} s^{-1} and 0.9, respectively. These values calculated for pure $scCO_2$ may be somewhat different from that for the mixture of $scCO_2$ and DVBP in the polymerization system. Actually, there are reports that the rates of AIBN decomposition in the mixture of CO_2 and cosolvent such as tetrahydrofuran [11, 12] and methanol [13].

Figure 2 shows the relationship between the AIBN concentration and the conversion of DVBP in the precipitation polymerizations in $scCO_2$ at different polymerization times of 3, 8 and 24 h. The conversion was determined by gravimetrical method described below. The purity of DVBP was 51.7% and other components in monomer mixture were ethylvinylbiphenyl (23.6%), methylvinylbiphenyl (6.2%), vinylbiphenyl (5.8%), diethylbiphenyl (4.7%), and solvents (8.0%) (Nippon Steel Chemical Co., personal communication). The total weight percentage of reactive components in the monomer mixture was 87.3%. After the polymerizations, the products were centrifugally washed with methanol for the removal of the residual monomers and solvents. The conversion of DVBP was defined as weight percentage of the products after centrifugal washing to total reactive components in monomer mixture. The conversions increased with an increase in the AIBN concentration at 3 and 8

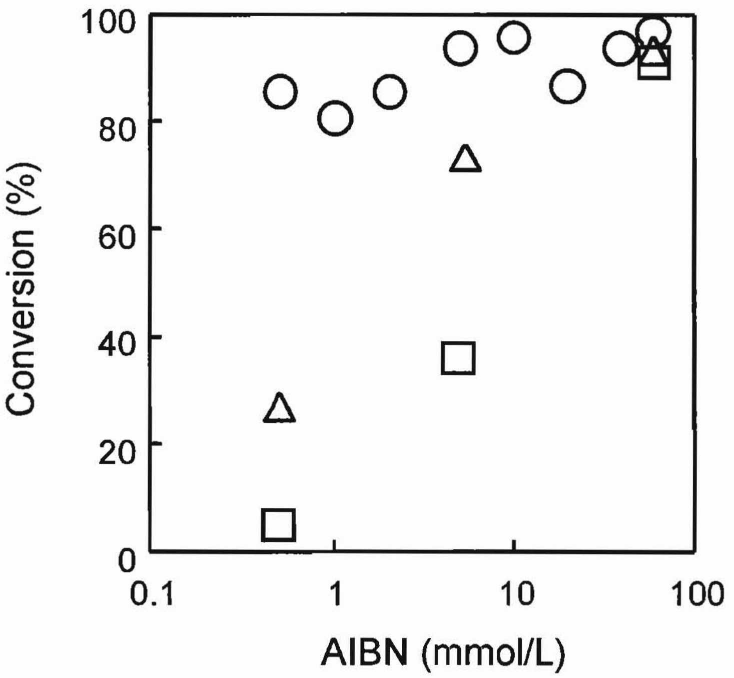


Figure 2 Relationship between the 2,2'-azobis(isobutyronitrile) (AIBN) concentration and the conversion of divinylbiphenyl (DVBP) in the precipitation polymerizations in supercritical carbon dioxide (scCO$_2$) at the different polymerization times (h): 3 (squares), 8 (triangles) and 24 (circles)

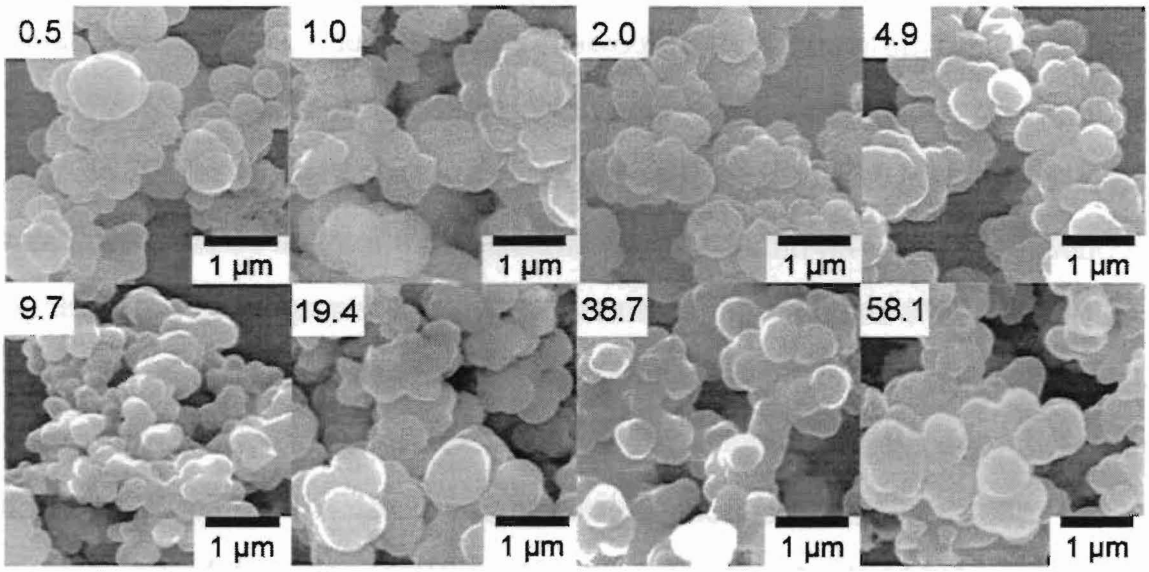


Figure 3 Scanning electron microscope (SEM) photographs of polydivinylbiphenyl (PDVBP) particles produced by the precipitation polymerizations of DVBP in scCO$_2$ for 24 h at different AIBN concentrations (mmol/L)

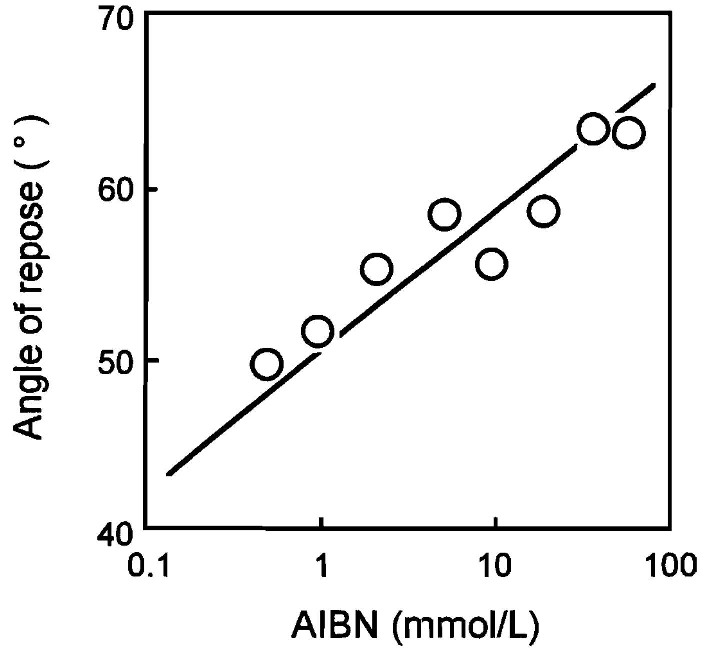


Figure 4 Relationship between the AIBN concentration and the angle of repose of PDVBP particles produced by the precipitation polymerizations of DVBP in $scCO_2$ for 24 h

h. The conversions at 24 h were relatively high (81%-96%) in all polymerization systems, even at the low AIBN concentrations of 0.5 and 1.0 mmol/L, and free-flowing white PDVBP powder was obtained. This is a remarkable point in this polymerization system as compared with the case of DVB. The conversion of DVB in the precipitation polymerization in $scCO_2$ at AIBN concentration of 24.4 mmol/L under similar conditions (at 31 MPa for 24 h at 65°C) was 71% and that of 97.4 mmol/L managed to reach 89%. Cooper and coworkers showed that rather high AIBN concentrations seemed necessary to achieve good monomer conversions. The higher conversion of DVBP, even at the low AIBN concentrations in comparison with DVB, might be accounted for by the fact that the rate of crosslinking reaction of the second vinyl groups of PDVBP is faster than that of PDVB [7].

Figure 3 shows SEM photographs of PDVBP particles produced by the

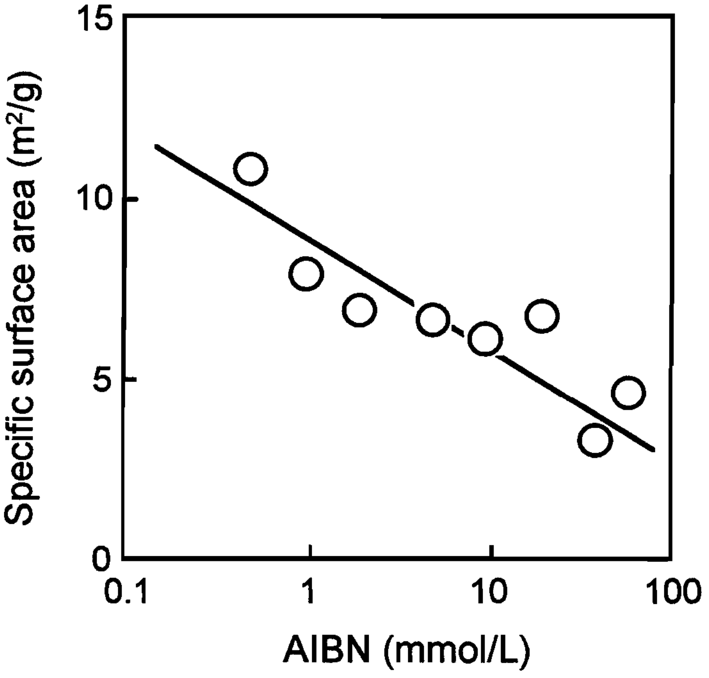


Figure 5 Relationship between the AIBN concentration and the specific surface area of PDVBP particles produced by the precipitation polymerizations of DVBP in $scCO_2$ for 24 h

precipitation polymerizations of DVBP in $scCO_2$ at the different AIBN concentrations. In all AIBN concentration systems, the produced PDVBP particles partially coagulated, and there was little difference in the particle size in all the systems. As far as the author is aware, there has been no study on the relationship between the initiator concentration and the degree of coagulation, though the degree of coagulation will play an important role when the applications of the particles produced are taken into consideration. The degree of coagulation could not be estimated directly from SEM photographs, because it was difficult to separate exactly individual PDVBP particles from the aggregate. To examine the effect of the AIBN concentration on the degree of coagulation, for convenience, an angle of repose was measured, as it shows a general index to fluidity of powder [14-16]. It is known that the angle of repose increases with a decrease in the fluidity of powder, which

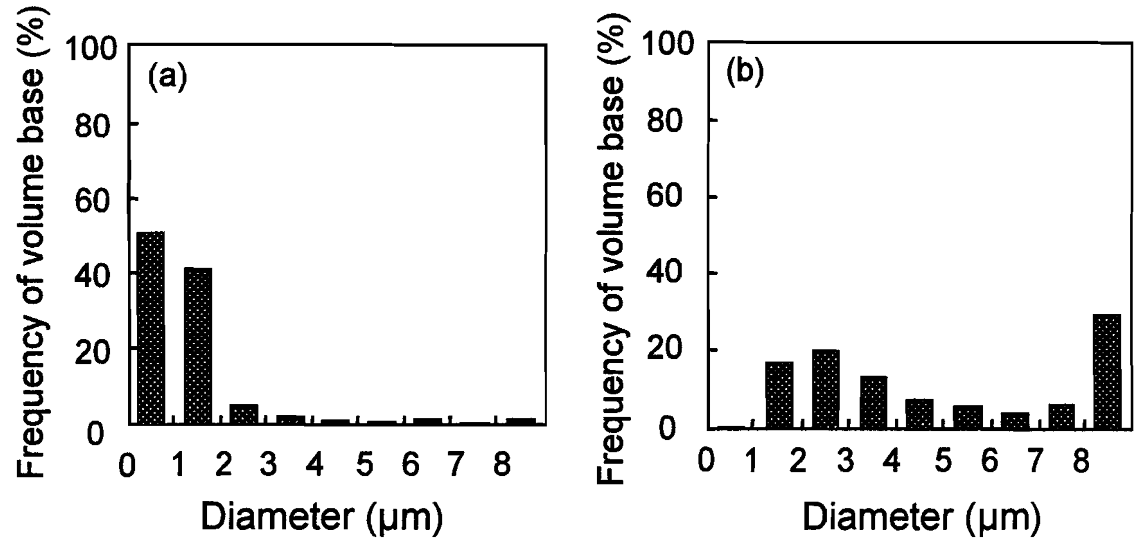


Figure 6 Particle-size distributions of PDVBP particles produced at different AIBN concentrations (mmol/L): (a) 0.5, (b) 58.1, measured with disc centrifuge photosedimentometer particle sizer

seems to be caused by the increase of the degree of coagulation.

Figure 4 shows the relationship between the AIBN concentration and the angle of repose of the PDVBP powders. The angle of repose decreased (the fluidity of PDVBP powder increased) with a decrease in the AIBN concentration. This result indicates that the degree of coagulation decreased with the decrease in the AIBN concentration.

Figure 5 shows the relationship between the AIBN concentration and the specific surface area of the PDVBP particles. The specific surface area increased with the decrease in the AIBN concentration. Considering that the particle sizes observed in the SEM photographs were not so different in all the systems, this result indicates that the degree of coagulation decreased with the decrease in the AIBN concentration. This tendency agreed with that of the angle of repose.

Figure 6 shows the particle size distributions of PDVBP particles produced at AIBN concentrations (mmol/L) of 0.5 and 58.1, measured with disc centri-

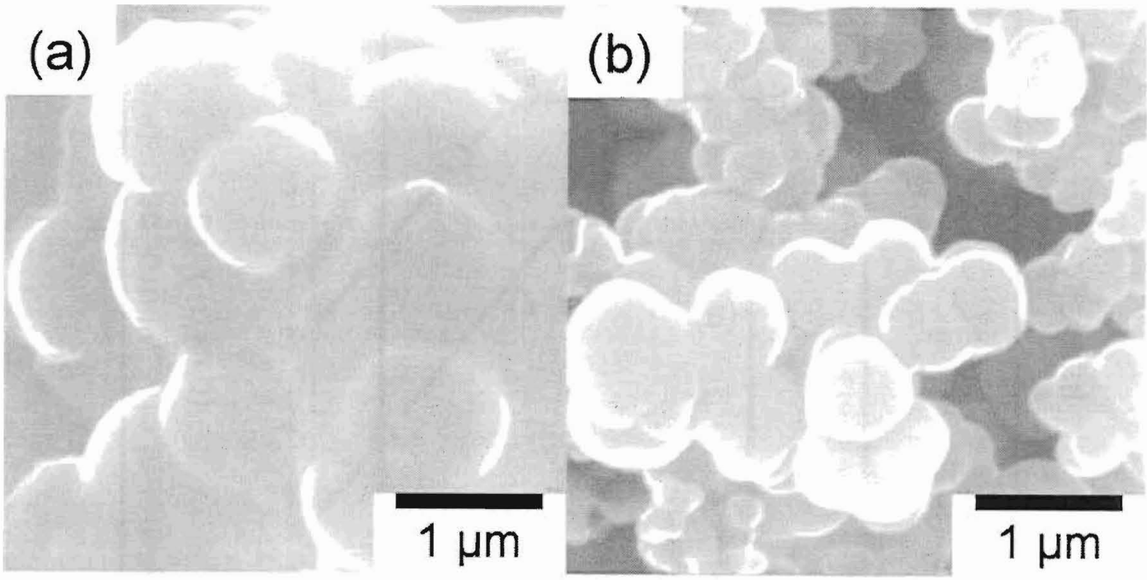


Figure 7 SEM photographs of PDVBP particles produced by the precipitation polymerization of DVBP in $scCO_2$ for 24 h before (a) and after (b) centrifugal washing with methanol: AIBN concentration, 58.1 mmol/L

fuge photosedimentometer particle sizer. In the low AIBN concentration system, the particle size distribution was relatively sharp and the particle size was mostly less than 2 μm, which shows relatively good agreement with the results of the SEM observation. On the other hand, in the high AIBN concentration system, the particles size and the particle size distribution were larger and broader (1-8 μm and over) in comparison with the results of the SEM observation. In these ways, the high AIBN concentration, which seemed to be generally used in the reported experiments [4-6], caused high degree of particle coagulation in the precipitation polymerization of DVBP.

Figure 7 shows SEM photographs of the PDVBP particles produced at the high AIBN concentration (58.1 mmol/L) before (a) and after (b) centrifugal washing with methanol. After washing, the boundary among the particles became clearer, which seems to be due to the removal of sticky low-molecular-weight by-product on PDVBP particles, and a decrease in weight of PDVBP particles (0.6 wt%) was observed. Such sticky low-molecular-weight by-

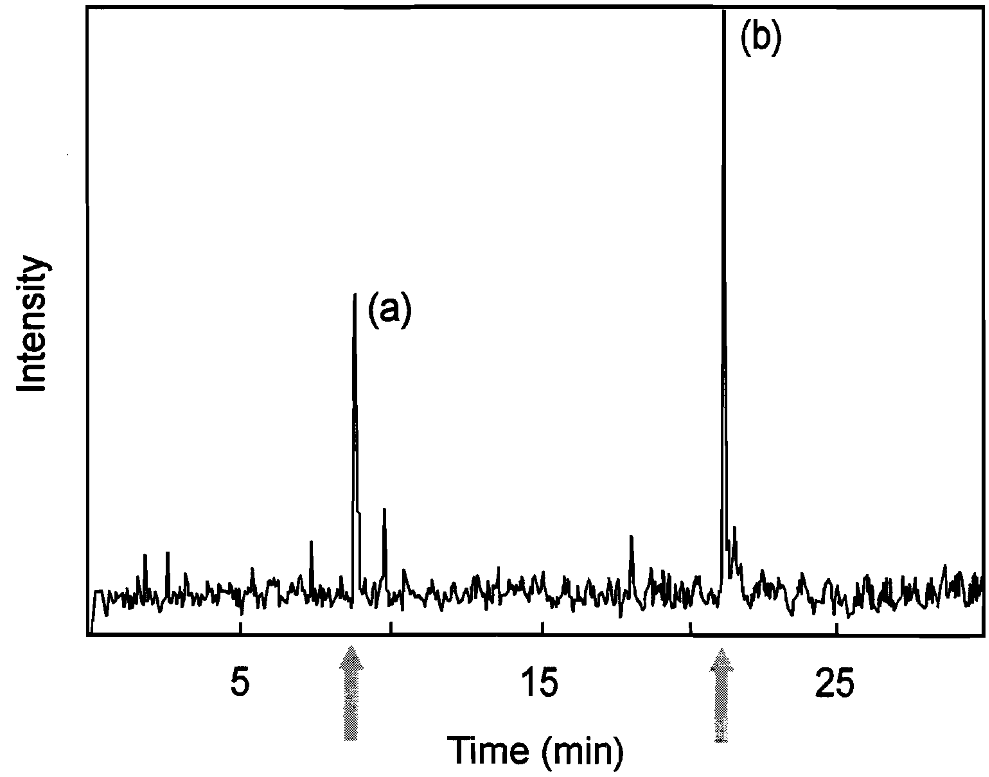


Figure 8 Total ion charge chromatogram of low-molecular-weight by-products generated in the process of the precipitation polymerizations of DVBP in $scCO_2$ for 24 h at different AIBN concentrations (mmol/L): (a) 0.5, (b) 58.1. The arrows show sample injection times.

products may be PDVBP oligomers and thermal decomposition products of AIBN such as tetramethylsuccinodinitrile and isobutyronitrile that are generated, respectively, from the recombination and the disproportionation of primary radicals. Methacrylonitrile, which is also generated from the disproportionation of the primary radicals, should copolymerize with DVBP to be incorporated in PDVBP particles [17] under the consideration that both methacrylonitrile and DVBP are conjugated monomer. At the high AIBN concentration (58.1 mmol/L), a number of primary radicals are generated and collision frequency between the radicals is high, which should result in the generation of the by-products. At the low AIBN concentration (0.5 mmol/L), the boundary among the particles was comparatively clear even before wash-

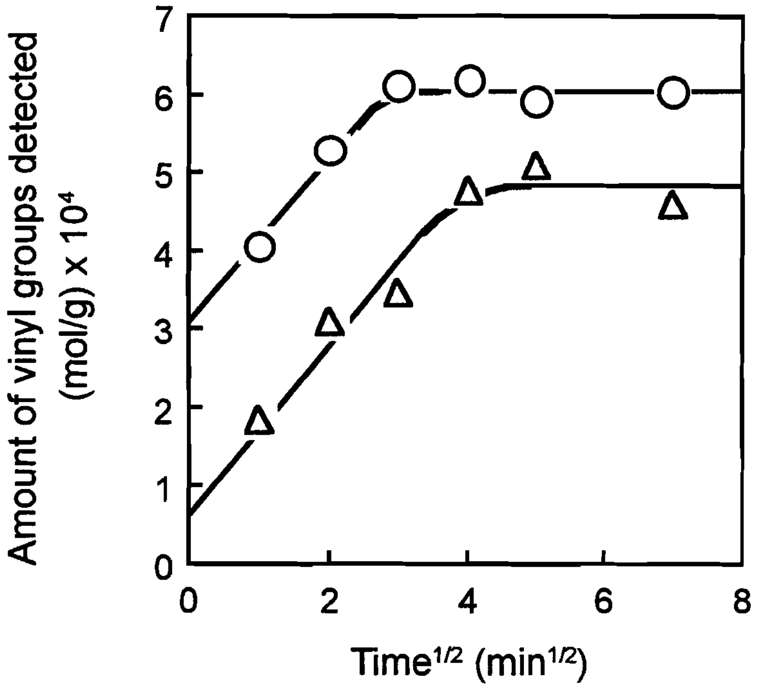


Figure 9 Relationship between the square root of brominates reaction time and the amount of vinyl groups detected for two kinds of PDVBP particles produced by the precipitation polymerizations of DVBP in scCO$_2$ for 24 h at different AIBN concentrations (mmol/L): (circles) 0.5, (triangles) 58.1

ing (data were omitted), and the decrease in weight of PDVBP particles after washing was negligible.

Figure 8 shows total ion charge (TIC) chromatogram of the low-molecular-weight by-products generated in the processes of the precipitation polymerizations of DVBP in scCO$_2$ at the two AIBN concentrations (mmol/L) of 0.5 and 58.1. The arrows show sample injection times. The TIC peak strength of the high AIBN system was stronger than that of the low AIBN system. This result indicates that the low-molecular-weight by-products were prepared less in the low AIBN system than in the high AIBN system. Such a low-molecular-weight by-product should cause the increase of coagulation of the particles and is not desirable because of a decline of the products quality.

Figure 9 shows the relationship between the square root of brominate reaction time and the amount of vinyl groups detected for the PDVBP particles produced at the two AIBN concentrations. The total amount of detected vinyl groups in the particles was 6.1 x 10^{-4} mol/g in the low AIBN system, which was larger than that (4.9 x 10^{-4} mol/g) in the high AIBN system. The amount of vinyl groups detected at 0 min, which is determined by extrapolation, means the amount of vinyl groups at the particles surfaces [18]. The amounts of vinyl groups at the particles surfaces in the low and high AIBN systems were 3.1 x 10^{-4} and 0.6 x 10^{-4} mol/g, respectively. The occupied area of each vinyl group was 5.8 $Å^2$ in the low AIBN system, which was calculated from the amount of vinyl groups at the particles surfaces and the specific surface area. This value was smaller than that (12.7 $Å^2$) in the high AIBN system. These results suggest that a number of primary radicals generated in the high AIBN system decrease the amount of the second vinyl groups of PDVBP.

6.4 Conclusions

PDVBP particles were produced by precipitation polymerization of DVBP without any stabilizer in $scCO_2$ as polymerization medium at ca. 30 MPa for 24 h at 65°C at different initiator concentrations (0.5-58.1 mmol/L). The conversions in all polymerization systems were relatively high, and the increase in the initiator concentration led to the increases in the degree of coagulation and the amount of low-molecular-weight by-products and to the decrease in the amount of vinyl groups in the particle.

6.5 References

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Chapter 7

Production of polyacrylonitrile particles by precipitation polymerization in supercritical carbon dioxide

7.1 Introduction

Precipitation polymerization is one of the methods to prepare stabilizer-free particles [1-6]. This method requires only monomer, radical initiator and solvent. Cooper and coworkers reported that polydivinylbenzene particles were produced by precipitation polymerization of divinylbenzene in supercritical carbon dioxide ($scCO_2$) with 2,2'-azobis(isobutyronitrile) (AIBN) [4, 5]. In Chapter 6, we succeeded in producing stabilizer-free polydivinylbiphenyl particles by precipitation polymerization of divinylbiphenyl in $scCO_2$ with AIBN and examined the effect of initiation rate of polymerization on the conversion, the fluidity of powder, the degree of coagulation, the amount of low-molecular-weight by-products, and the amount of vinyl groups in the particles. Romack and coworkers reported that poly(acrylic acid) (PAA) were produced by precipitation polymerization of acrylic acid in $scCO_2$ with AIBN and pointed that PAA produced were large aggregates of primary particles (~100 nm diameter) from scanning electron microscope (SEM) observation [6].

Polyacrylonitrile (PAN) is an interesting polymer for a wide range of engineering applications such as fibers, films, engineering plastics and precursors for carbon fibers [7-11]. Moreover, PAN is known to form crystallites by virtue of the mutual segregation of crystallizable sequences [10, 11]. The strong mutual interaction between the polymer chains and the crystalline nature is the base for the use of PAN in fibers and as a component in engineering plastics. Shiho and DeSimone carried out precipitation polymerization of acrylonitrile (AN) in scCO$_2$ and pointed out from SEM observation that coagulation occurred, but there were no detailed data besides the conversion [12]. In their study, they also indicated that colloidal stabilizer was indispensable in order to prevent coagulation of PAN particles and to produce stable dispersion of PAN particles.

In this chapter, stabilizer-free, “micron-sized”, relatively “monodisperse” PAN particles with clean surfaces will be produced by precipitation polymerization in scCO$_2$. And the effects of initiation rate of polymerization and AN concentration on the conversion, the fluidity of powder, the degree of coagulation, the viscosity-average molecular weight (M_v) and the crystallinity were investigated.

Table 1 Recipes for the production of PAN particles by precipitation polymerizations[a] of AN in scCO$_2$ at different AIBN concentrations and at a constant AN concentration[b]

Ingredients		AIBN concentration (mmol/L)							
		0.8[c]	1.5[d]	3.0[d]	7.5[d]	15.1[e]	30.2[e]	37.7[e]	45.2[e]
AN[b]	(g)	2	2	2	2	2	2	2	2
AIBN	(mg)	1.2	2.5	5.0	12.4	24.8	49.5	61.9	74.3

[a] ca. 30 MPa; 65°C; 10-mL stainless steel reactor; 60 cycles/min; 24 h

[b] 3.8 mol/L (20 w/v%)

[c] R_i (= $2k_d f[I]$), $10^{12} \sim 10^{13}$ mL^{-1} s^{-1}; k_d, 7.7×10^{-6} s^{-1}; f, 0.9

[d] R_i (= $2k_d f[I]$), $10^{13} \sim 10^{14}$ mL^{-1} s^{-1}; k_d, 7.7×10^{-6} s^{-1}; f, 0.9

[e] R_i (= $2k_d f[I]$), $10^{14} \sim 10^{15}$ mL^{-1} s^{-1}; k_d, 7.7×10^{-6} s^{-1}; f, 0.9

Abbreviations: PAN, polyacrylonitrile; AN, acrylonitrile; AIBN, 2,2'-azobis(isobutyronitrile)

Table 2 Recipes for the production of PAN particles by precipitation polymerizations[a] in $scCO_2$ at different AN concentrations and at a constant AIBN concentration[b]

Ingredients		AN concentration (w/v%)		
		10[c]	20[d]	40[e]
AN	(g)	1	2	4
AIBN[b]	(mg)	5.0	5.0	5.0

[a] 65°C; 10-mL stainless steel reactor; 60 cycles/min; 24 h

[b] 3.0 mmol/L; R_i (= $2k_d f$[I]), 2.5 x 10^{13} mL^{-1} s^{-1}; k_d, 7.7 x 10^{-6} s^{-1}; f, 0.9

[c] 1.9 mmol/L (10 w/v%)

[d] 3.8 mmol/L (20 w/v%)

[e] 7.5 mmol/L (40 w/v%)

Abbreviations: PAN, polyacrylonitrile; AN, acrylonitrile; AIBN, 2,2'-azobis(isobutyronitrile)

7.2 Experimental

7.2.1 Materials

AN was purified by inhibitor remover (Aldrich Co., AL-154) before use. Reagent grade AIBN was purified by recrystallization. Industrial grade CO_2, with a purity of 99.5% or more, was used as received from Kobe Sanso Co. Guaranteed grade tetrahydrofuran (THF), *n*-hexane, and *N*,*N*-dimethylformamide (DMF) were used as received from Nacalai Tesque Co.

7.2.2 Precipitation polymerization in $scCO_2$

Precipitation polymerization was carried out in a 10-mL stainless steel reactor as described in Chapter 1 under the conditions listed in Tables 1 and 2. The reactor was charged with AN, AIBN and three 3/16-inch-sized stainless steel balls 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 Seimitsu Kagaku Co., NP-D-321J) with shaking vigorously. The polymerization was started by heating the mixture to 65°C with shaking at 60 cycles/minute. After 24 h, the reactor was cooled by dipping in an ice water bath and the CO$_2$ was vented slowly. The particles produced were observed with a Hitachi S-2500 SEM, a Jeol JEM-2010 transmission electron microscope (TEM), and a Nikon Microphot-FXA optical microscope. The number-average diameter (D_n) and the coefficient of variation (C_v) for the PAN particles were measured on the SEM photograph with image analysis software (MacScope, Mitani Co.). The M_v were determined with an Ostwald capillary viscometer at 30°C using DMF as solvent.

7.2.3 Observation of the ultrathin cross sections of particles

PAN particles were dipped in an epoxy matrix, and cured at room temperature for 24 h before being microtomed. The ultrathin cross sections were observed with the TEM.

7.2.3 Angle of repose

The fluidity of PAN powder was estimated by measuring angle of repose as follows. Obtained PAN powder was gently charged into a glass funnel that had a circular opening of about 3 mm, with its opening blocked by a finger. By removing the finger, the powder was allowed to flow directly onto a flat stainless steel disk (10 mm diameter) to form a powder heap. The circular opening was set 30 mm higher just above the flat stainless steel disk. A optical photograph was then taken for the determination of the angle of repose, defined as the angle of free surface to the horizontal plane.

7.2.4 Wide-angle X-ray patterns from the PAN particles

The crystallinity of PAN particles was estimated by a wide-angle X-ray diffractogram. The X-ray diffractgrams were obtained with an X-ray diffractometer (Rigaku Co., RINT2000). Nickel-filtered Cu Kα ($\lambda = 1.542$ Å) radiation was used for analysis and the operating voltage and current were 40 kV and 40 mA, respectively. The radial scans on the samples were carried out in the region $2\theta = 4°$ to 180°. The obtained data were analyzed using the software (Microcal Co., Origin ver. 5.0), and crystallinity was determined by integration of wide angle X-ray scattering peaks.

7.3 Results and discussion

Precipitation polymerizations of AN were carried out with AIBN initiator in $scCO_2$ at about 30 MPa for 24 h at 65°C in the 10-mL stainless steel reactors under the conditions listed in Table 1. The AIBN concentration was selected on the basis of the idea described as follows. In radical polymerization, the initiation rate of polymerization, R_i is given by $R_i = f\rho_i$, where f is the initiator efficiency and ρ_i is the generation rate of radicals. The ρ_i is expressed as $2k_d[I]$, where k_d is the rate coefficient for initiator decomposition, and [I] is the initiator concentration. DeSimone and coworkers 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 in benzene at the same temperature and at atmospheric pressure because of the low dielectric constant and the low viscosity of $scCO_2$ [13, 14]. In general, homogeneous radical polymerizations in organic solvent were carried out in the R_i range of 10^{13}-10^{14} $mL^{-1}s^{-1}$ [15-17]. On

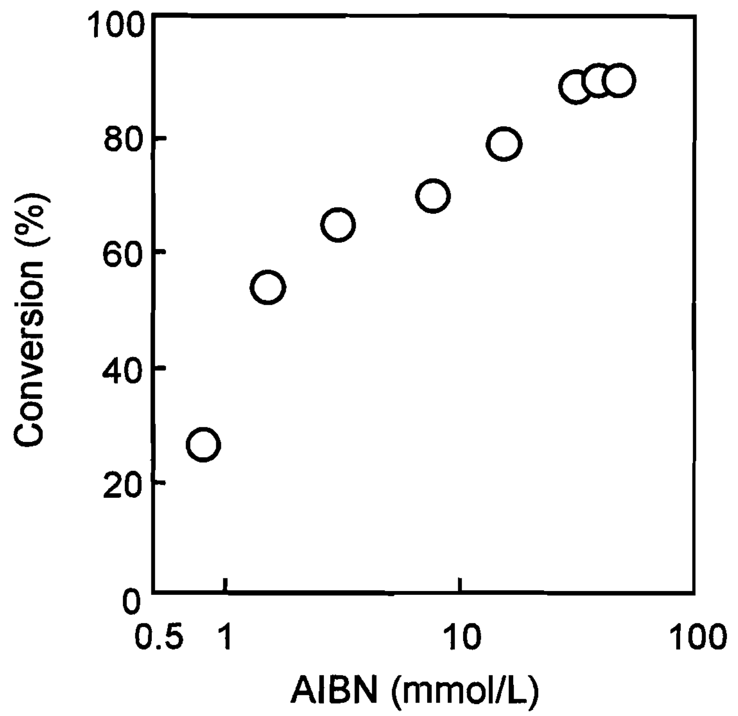

Figure 1 Relationship between the 2,2'-azobis(isobutyronitrile) (AIBN) concentration and the conversion of acrylonitrile (AN) in the precipitation polymerizations in supercritical carbon dioxide (scCO$_2$) for 24 h

the other hand, precipitation polymerizations in scCO$_2$ were often carried out in relatively high R_i range of 10^{14}-10^{15} mL^{-1}s^{-1} [4-6], which was calculated in consideration of k_d and f values of AIBN in scCO$_2$. In this article in order to clarify the effects of R_i on the precipitation polymerization of AN in scCO$_2$, the AIBN concentration was changed in the wide R_i range of 10^{12}-10^{15} mL^{-1}s^{-1}. The k_d and f values used in the calculation were 7.7 x 10^{-6} s^{-1} and 0.9, respectively. These values calculated for pure scCO$_2$ may be somewhat different from those for the mixture of scCO$_2$ and AN in the polymerization system. Actually, there are reports that the rates of AIBN decomposition in a mixture of CO$_2$ and cosolvent such as THF [13, 14] and methanol [18] were higher than that in pure CO$_2$.

Figure 1 shows the relationship between the AIBN concentration and the

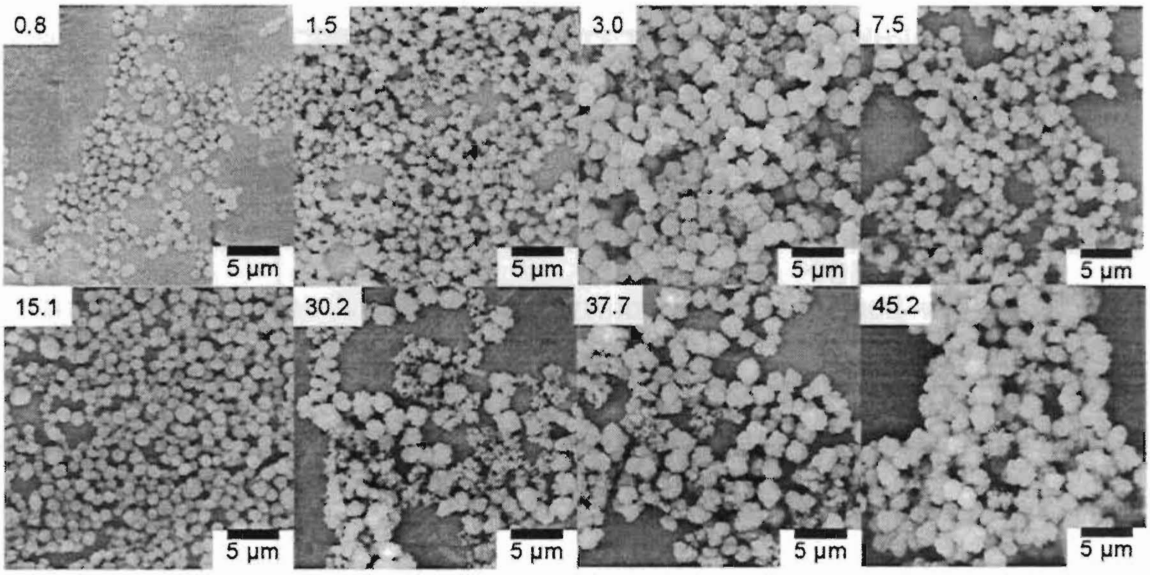

Figure 2 Scanning electron microscope (SEM) photographs of polyacrylonitrile (PAN) particles, which were produced by the precipitation polymerizations of AN in $scCO_2$ for 24 h at different AIBN concentrations (mmol/L)

conversion of AN in the precipitation polymerizations in $scCO_2$ for 24 h. The conversion was determined by gravimetrical method. The conversion increased with an increase in the AIBN concentration. At a low AIBN concentration of 0.8 mmol/L, the conversion was 26%. On the other hand, at a high AIBN concentration of 45.2 mmol/L, the conversion increased up to 90%. In the R_i range of 10^{12}-10^{14} $mL^{-1}s^{-1}$, free-flowing white PAN powders were obtained.

As shown in Fig. 2, the PAN powders consisting of micron-sized, relatively monodisperse PAN particles having uneven surface. The particle size increased from 1.1 to 1.9 μm with the increase in the AIBN concentration from 0.8 to 3.0 mmol/L. At the AIBN concentration of 3.0 mmol/L, C_v value was measured to be 15%.

The degree of coagulation could not be estimated by the SEM observation, because it was difficult to separate individual PAN particles from the aggregate exactly due to their uneven appearances. The degree of coagula-

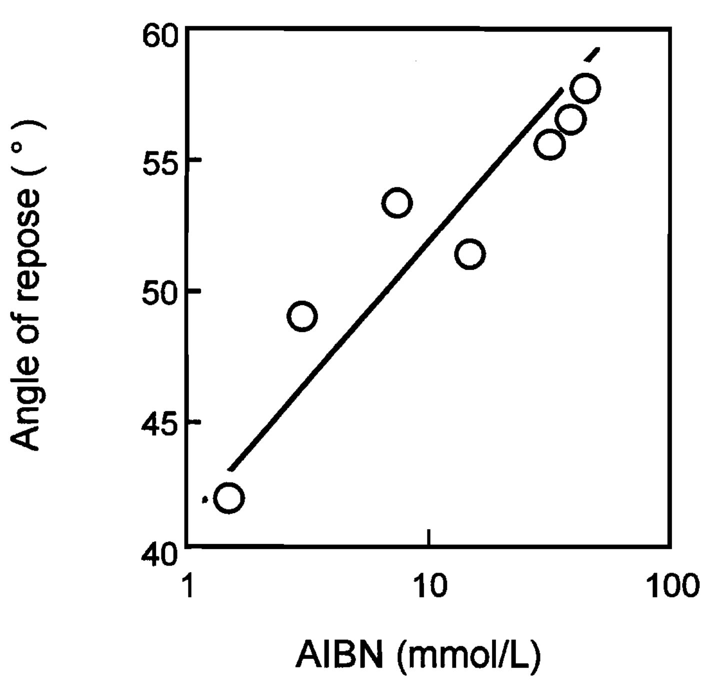

Figure 3 Relationship between the AIBN concentration and the angle of repose of PAN particles produced by the precipitation polymerizations of AN in scCO$_2$ for 24 h

tion may be important in their applications of the particles. In order to examine the effect of the AIBN concentration on the degree of coagulation, for convenience, an angle of repose was measured. Because the angle of repose increases with a decrease in the fluidity of powder [19-21], the increase in the angle of repose must show the increase of the degree of coagulation.

Figure 3 shows the relationship between the AIBN concentration and the angle of repose of the PAN powders. The angle of repose decreased (the fluidity of PAN powder increased) with a decrease in the AIBN concentration. Assuming that the particle size was almost the same in all AIBN concentration systems, this result should indicate that the degree of coagulation decreased with the decrease in the AIBN concentration.

Figure 4 shows optical micrographs of PAN particles, which were pro-

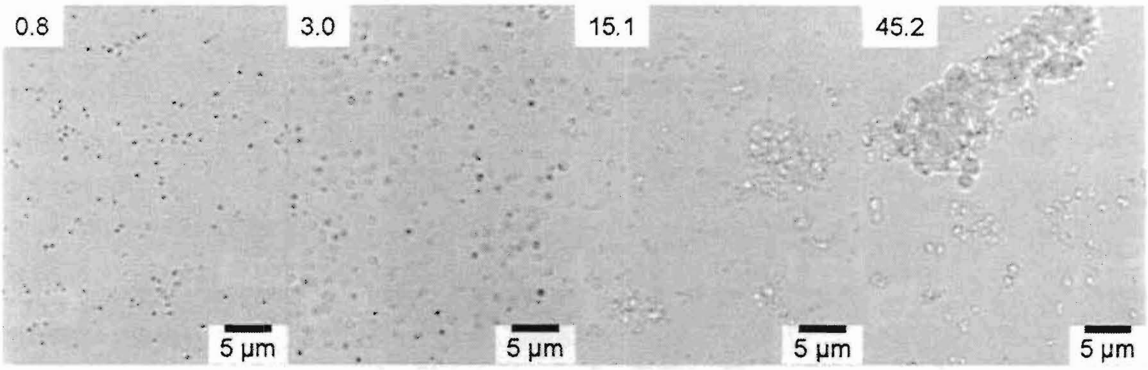

Figure 4 Optical micrographs of PAN particles, which were produced by the precipitation polymerizations of AN in $scCO_2$ for 24 h at different AIBN concentrations (mmol/L). PAN particles were redispersed in tetrahydrofuran (THF).

duced by the precipitation polymerization of AN in $scCO_2$ for 24 h at different AIBN concentrations of 0.8, 3.0, 15.1 and 45.2 mmol/L. PAN particles were redispersed in THF with ultrasonication. At low AIBN concentrations of 0.8 and 3.0 mmol/L, PAN particles were almost finely redispersed as single particles and the particle diameters accorded well with those measured with SEM. On the other hand, at high AIBN concentrations of 15.1 and 45.2 mmol/L, the number of single particles decreased and coagulants with irregular forms were observed. This optical microscope study seems to provide good information on the degree of coagulation during the precipitation polymerization.

Figure 5 shows the relationship between the AIBN concentration and M_v of the PAN particles after centrifugal washing with methanol. The M_v was calculated using Mark-Houwink-Sakurada equation given by $[\eta] = KM_v^{\alpha}$, where the K and α values used in the calculation are 20.9×10^{-3} mL/g and 0.75, respectively [22]. The M_v increased linearly from 3.8×10^4 to 18.9×10^4 g/mol with the decrease in the AIBN concentration.

Figure 6 shows SEM photographs of PAN particles produced at different AN concentrations under the conditions listed in Table 2. The particle size

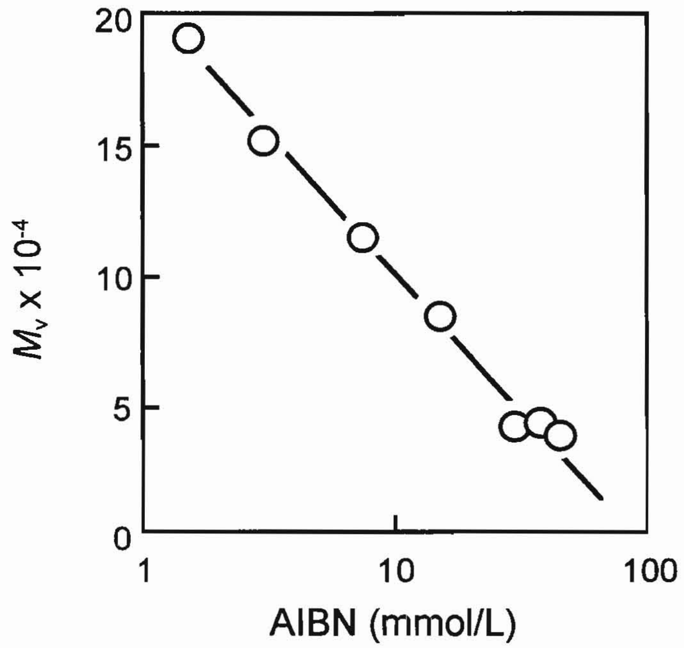

Figure 5 Relationship between the AIBN concentration and the M_v of PAN particles produced by the precipitation polymerizations of AN in $scCO_2$ for 24 h

increased with an increase in the AN concentration. At the AN concentration of 10 w/v%, the irregularly coagulated particles were observed and this result was good agreement with that obtained by Shiho and DeSimone who conducted the precipitation polymerization of AN at the monomer concentration of 8 w/v% [12]. At 20 w/v%, micron-sized, relatively monodisperse particles

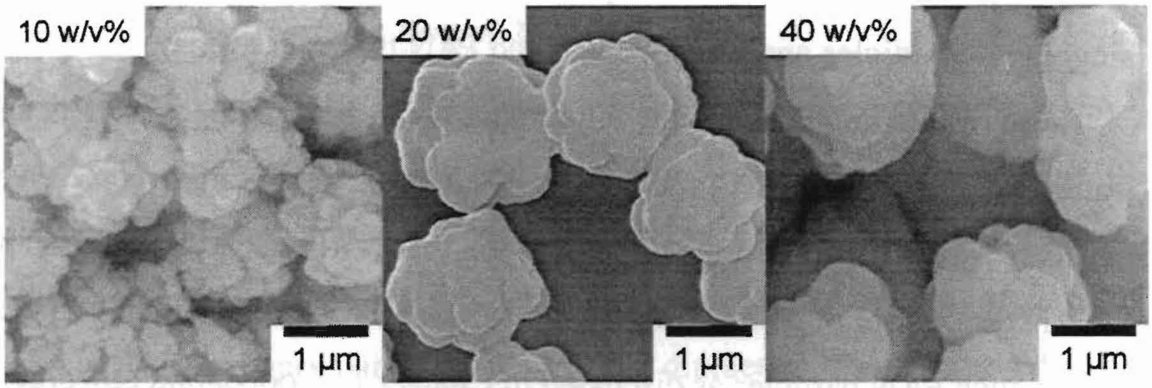

Figure 6 SEM photographs of PAN particles, which were produced by the precipitation polymerizations of AN in $scCO_2$ for 24 h at different AN concentrations (w/v% based on the reactor volume)

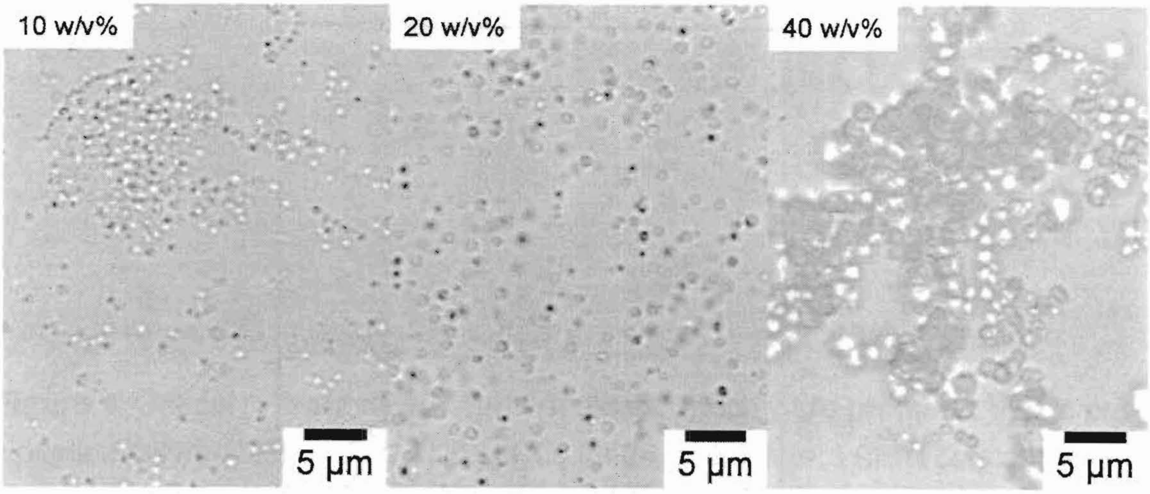

Figure 7 Optical micrographs of PAN particles, which were produced by the precipitation polymerizations of AN in $scCO_2$ for 24 h at different AN concentrations (w/v% based on the reactor volume). PAN particles were redispersed in THF.

having uneven surfaces were observed. At 40 w/v%, the particles seemed to be little coagulated. Cooper and coworkers reported a similar tendency in the precipitation polymerization of DVB in $scCO_2$ [4, 5].

Figure 7 shows optical micrographs of the PAN particles, which were produced at the AN concentrations of 10, 20, and 40 w/v%, redispersed in THF. At the AN concentration of 20 w/v%, PAN particles were almost finely redispersed as single particles as described before. However, at 10 w/v%, some single and coagulated PAN particles were observed. At 40 w/v%, no single PAN particles and larger coagulated PAN particles were observed.

These results indicate that it is important to select the suitable AN concentration for the production of the micron-sized, relatively monodisperse PAN particles by the precipitation polymerization of AN in $scCO_2$. In addition to the AN concentration, the stirring method should have effects on the production of such PAN particles as discussed in Chapter 1. Cooper and coworkers also showed that particle size in precipitation polymerization in $scCO_2$ was influenced strongly by the type of stirring [5].

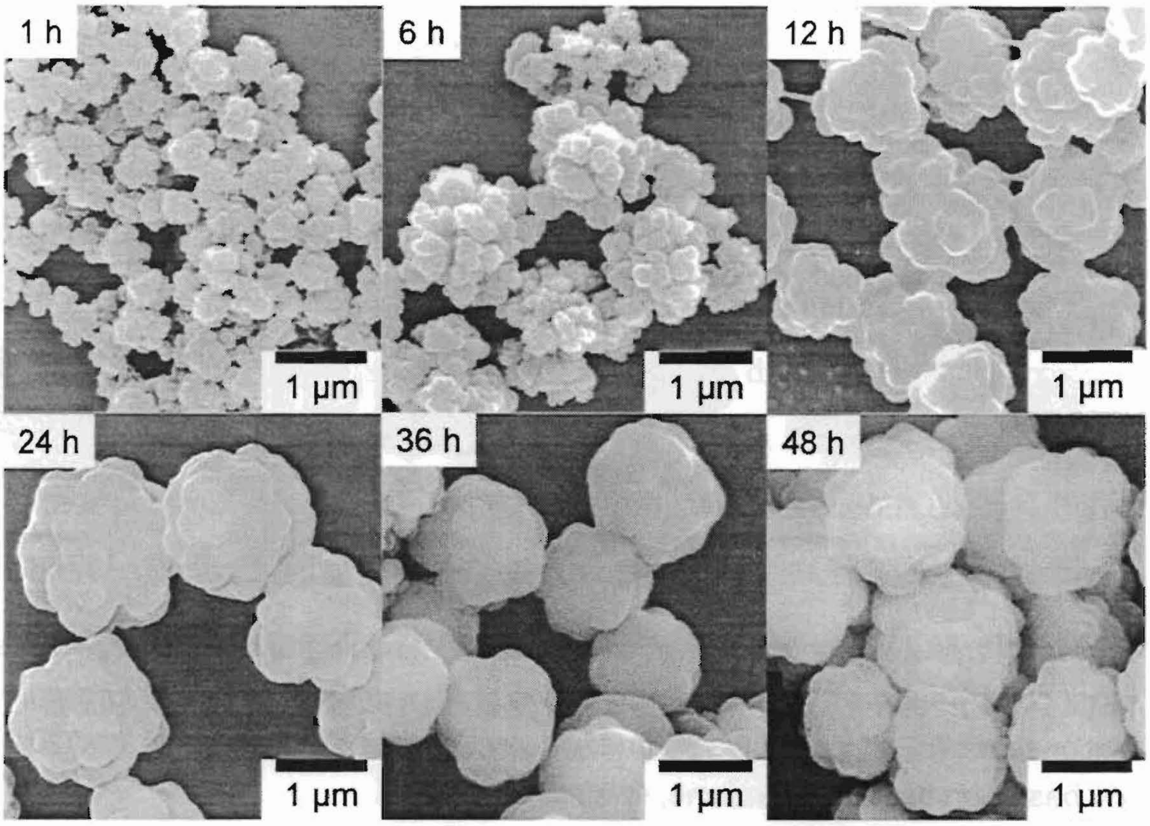

Figure 8 SEM photographs of PAN particles produced by the precipitation polymerization of AN in scCO$_2$ for different polymerization times (h) at constant AIBN and AN concentrations of 3.0 mmol/L and 20 w/v% based on the reactor volume, respectively

On the basis of above results, in following, the precipitation polymerization of AN in scCO$_2$ was carried out at the AIBN concentration of 3.0 mmol/L and at the AN concentration of 20 w/v%.

Figures 8 and 9, respectively, show typical SEM and TEM photographs of PAN particles at different polymerization times. A time-conversion curve of the precipitation polymerization is shown in Fig. 10. As shown in Figs. 8 and 9, submicron-sized PAN particles, which were likely to be aggregates of smaller PAN primary particles (80-150 nm diameter), were observed at 1 h. As the polymerization proceeded, micron-sized PAN particles, which seemed to be aggregates of the submicron-sized PAN particles formed at 1 h, were

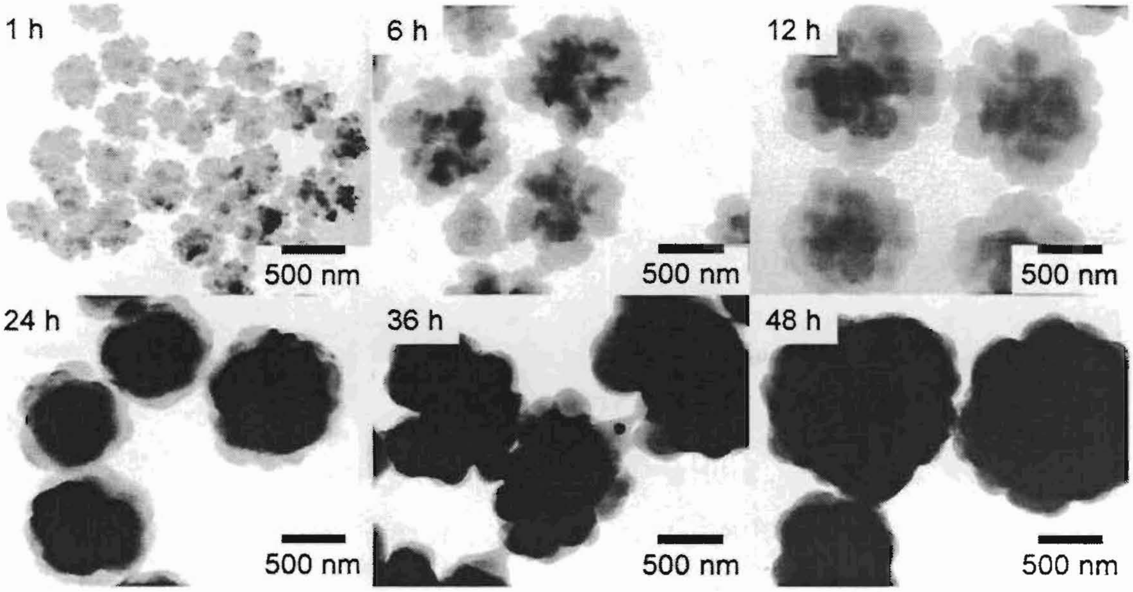

Figure 9 Transmission electron microscope (TEM) photographs of PAN particles produced by the precipitation polymerization of AN in $scCO_2$ for different polymerization times (h) at constant AIBN and AN concentrations of 3.0 mmol/L and 20 w/v% based on the reactor volume, respectively

observed at 6 h. After 6 h, the aggregation ended and the uneven surfaces gradually became smoother, and the distinct change was not observed after 24 h. At 6 and 12 h in Fig. 9, some light points were observed in the PAN particles, which seem to be due to some voids. However, such a contrast was not observed after 24 h. As shown in Fig. 10, the conversion of AN gradually increased until 24 h and after that it increased slowly. These results indicate that the micron-sized PAN particles were formed as aggregates of smaller PAN particles at the early stage of the polymerization and then the polymerization of AN adsorbed by the micron-sized PAN particles [23] occurred mainly at their surfaces and in the voids, which should lead to the degree of depression at the surface and the size of the voids, respectively, being smoother and smaller.

Figure 11 shows TEM photographs of ultrathin cross sections of PAN particles produced at different polymerization times of 1 and 24 h, at which the conversions were, respectively, about 1 and 66%. At 1 h, some darker points, which had 50-200 nm diameter, were observed, and their size accorded with that of the primary particles observed at 1 h in Fig. 9. At 24 h, the contrast in the ultrathin cross section of the PAN particle was heterogeneous. There were some darker points, which had 50-270 nm diameter, in each particle, and their size was almost in accord with or was a little larger than that of darker points observed at 1 h in Fig. 11. This heterogeneous contrast might be due to the heterogeneity of the electron density. That is, electron density at the darker points is higher than that of other area. Judging from little difference in contrast between lighter area in the particles and epoxy matrix at 24 h

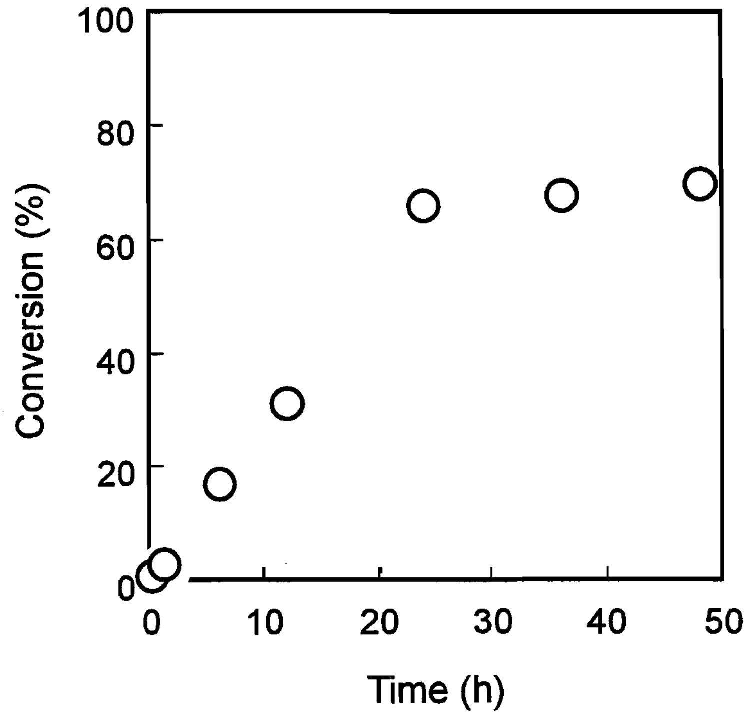

Figure 10 A time-conversion curve for the precipitation polymerization of AN in scCO$_2$ at constant AIBN and AN concentrations of 3.0 mmol/L and 20 w/v% based on the reactor volume, respectively

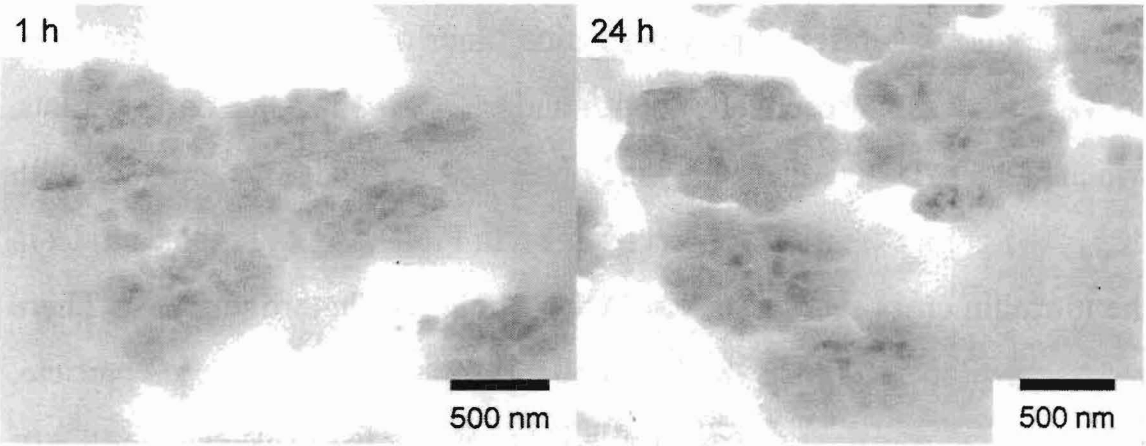

Figure 11 TEM photographs of ultrathin cross sections of PAN particles produced by the precipitation polymerization of AN in $scCO_2$ for 1 and 24 h at constant AIBN and AN concentrations of 3.0 mmol/L and 20 w/v% based on the reactor volume, respectively

in Fig. 11, there might be a possibility that the lighter contrast area was made of epoxy resin. This meant that the voids observed at 6 and 12 h in Fig. 9 could not be buried completely with PAN by the following polymerization and be buried with epoxy resin during the process of dipping in the epoxy matrix for the preparation of ultrathin cross section.

Figure 12 shows wide–angle X-ray diffractograms of PAN particles produced by the precipitation polymerization in $scCO_2$ at the AIBN concentration of 3.0 mmol/L at different polymerization times of 6 and 24 h. There was little difference in the diffractograms at 6 and 12 h beside some small peaks observed between 20° and 28° at 6 h. In both PAN particles, a strong peak and a weak one were, respectively, observed at $2\theta = 16.7°$ and at $2\theta = 29.3°$. These correspond to *d*-spacings of 5.30 and 3.04 Å, which attribute to diffractions of (0 1 0) and (3 0 0) planes, respectively [10]. The crystallinities of the PAN particles produced in $scCO_2$ at 6 and 24 h were 17 and 19%, respectively. The crystallite sizes of both PAN particles were nearly equal to be about 60 Å, and were similar to that of PAN powder produced by slurry

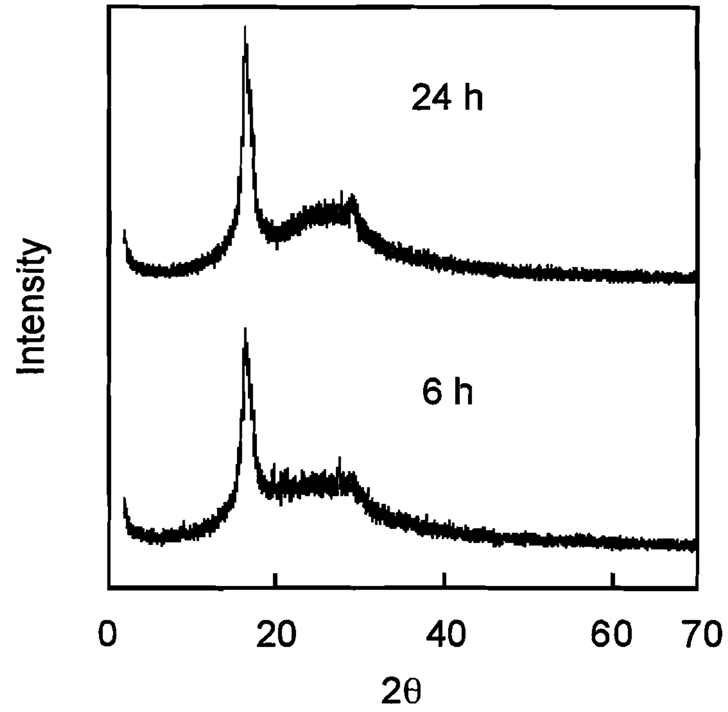

Figure 12 Wide-angle X-ray diffractograms of PAN particles produced by the precipitation polymerization of AN in $scCO_2$ for 6 and 24 h at constant AIBN and AN concentrations of 3.0 mmol/L and 20 w/v% based on the reactor volume, respectively

polymerization (70 Å) [10], and was smaller than that of PAN particles produced by miniemulsion polymerization (120 Å) [11]. The crystallite sizes were calculated from the widths at half height of the peaks at $2\theta = 16.7°$ using Scherrer equation given by $D = K\lambda/\beta\cos\theta$, where D is the average crystallite size, K is the constant ($K = 0.9$), λ is the wave length of Cu Kα radiation ($\lambda = 1.542$ Å), β is the half width of the diffraction peak which is measured in radian and θ is Bragg angle for crystal diffraction. These results indicate that there was little difference in crystallinity and crystallite size between the PAN particles produced in $scCO_2$ at different polymerization times of 6 and 24 h, at which the conversions were, respectively, 17 and 66%, though there was a remarkable difference in particle morphology.

7.4 Conclusions

PAN particles were produced by the precipitation polymerization of AN without any colloidal stabilizer in $scCO_2$ as a polymerization medium at about 30 MPa for 24 h at 65°C at different initiator concentrations (0.8-45.2 mmol/L) and at different AN concentrations (10-40 w/v%). The increase in the initiator concentration led to the increases in the conversion and in the degree of coagulation and to the decrease in the molecular weight. At AN concentration of 20 w/v%, micron-sized, relatively monodisperse PAN particles with clean and uneven surfaces were produced.

7.5 References

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Conclusions

In the present work, productions of polymer particles in supercritical carbon dioxide ($scCO_2$) were studied from the viewpoint of polymer colloid chemistry. The results have been summarized here.

PART I concerns the construction and development of high-pressure reactors for the production of polymer particles in $scCO_2$.

In **Chapter 1**, small-scale high-pressure reactors for the production of polymer particles in $scCO_2$ were designed, constructed and developed. The effects of the small-scale high-pressure reactors, including 90-mL reactor, on the productions of polymer particles in $scCO_2$ were discussed. The constructed small-scale reactors in these experiments were convenient for the preparations.

PART II concerns the productions of polymer particles by dispersion and precipitation polymerizations in $scCO_2$.

In **Chapter 2**, the dispersion polymerizations of methyl methacrylate (MMA) with different types of organic peroxides in the presence of trimethylsiloxy terminated poly(dimethylsiloxane) (PDMS) stabilizer were conducted in $scCO_2$. When benzoyl peroxide, which has high cross-linking efficiency, was used as an organic peroxide, micron-sized, relatively monodisperse poly(MMA) (PMMA) particles were obtained.

In **Chapter 3**, PMMA particles were produced by the dispersion polymerization of MMA with 2,2'-azobis(isobutyronitrile) (AIBN) in the presence of mercaptopropyl terminated PDMS stabilizer in $scCO_2$ at about 30 MPa for 24 h at 65°C. The particle diameter could be controlled from submicronsize to micronsize by varying mercaptopropyl terminated PDMS concentration. It was clarified that the mercaptopropyl terminated PDMS operated as not only a chain transfer agent but also a colloidal stabilizer, which was named "tran stab".

In **Chapter 4**, submicron-sized, comparatively monodisperse PMMA particles were produced by the dispersion polymerization of MMA with PDMS-based azoinitiator, VPS-0501, in $scCO_2$ at 30 MPa for 24 h at 65°C. The initiator operated as not only a radical initiator but also a colloidal stabilizer, which was named "ini stab".

In **Chapter 5**, the production of the PMMA particles by the dispersion polymerization with AIBN in the presence of aminopropyl terminated PDMS stabilizer at about 30 MPa for 24 h at 65°C was presented, and aminopropyl terminated PDMS should be attached to PMMA particles by hydrogen bonding interaction between aminopropyl group and carbonyl group at PMMA particle surface. It was clarified that aminopropyl terminated PDMS worked as an effective colloidal stabilizer in $scCO_2$.

In **Chapter 6**, polydivinylbiphenyl particles were produced by the precipitation polymerization of divinylbiphenyl without any stabilizer in $scCO_2$ at ca. 30 MPa for 24 h at 65°C at different AIBN concentrations (0.5-58.1 mmol/L). The conversions in all polymerization systems were relatively high, and the increase in the AIBN concentration led to the increases in the degree of coagulation and the amount of low-molecular-weight by-products and to the decrease in the amount of vinyl groups in the particle.

In **Chapter 7**, polyacrylonitrile (PAN) particles were produced by the precipitation polymerization of acrylonitrile (AN) without any colloidal stabilizer in supercritical carbon dioxide at about 30 MPa for 24 h at 65°C at different AIBN concentrations (0.8-45.2 mmol/L) and at different AN concentrations (10-40 w/v%). An increase in the AIBN concentration led to increases in the conversion and in the degree of coagulation and to a decrease in the molecular weight. At AN concentration of 20 w/v%, micron-sized, relatively monodisperse PAN particles with clean and uneven surfaces were produced.

Small-scale high-pressure reactors for the production of polymer particles in $scCO_2$ were designed, constructed and developed, and polymer particles were successfully produced by dispersion and precipitation polymerizations in $scCO_2$ utilizing these reactors. And then, characterizations of the particles produced by a wide range of methods were conducted in detail from the viewpoint of polymer colloid chemistry.

Publication List

Chapter 1

Preparation of polymer particles by dispersion and precipitation polymerizations in supercritical carbon dioxide using small-scale high-pressure reactors

S. Fujii, M. Okubo, H. Minami, H. Maenaka

Memoirs of the Graduate School of Science and Technology, Kobe University, in press

Chapter 2

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

M. Okubo, S. Fujii, H. Minami

Colloid and Polymer Science, in preparation

Chapter 3

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

M. Okubo, S. Fujii, H. Minami

Colloid and Polymer Science, in preparation

Chapter 4

Production of submicron-sized poly(methyl methacrylate) particles by dispersion polymerization in supercritical carbon dioxide with poly(dimethylsiloxane)-based azoinitiator

M. Okubo, S. Fujii, H. Minami, H. Maenaka

Colloid and Polymer Science, **280**, 183 (2002)

Chapter 5

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

M. Okubo, S. Fujii, H. Minami

Progress in Colloid and Polymer Science, submitted

Chapter 6

Production of polydivinylbiphenyl particles by precipitation polymerization in supercritical carbon dioxide

M. Okubo, S. Fujii, H. Maenaka, H. Minami

Colloid and Polymer Science, **280**, 1084 (2002)

Chapter 7

Production of polyacrylonitrile particles by precipitation polymerization in supercritical carbon dioxide

M. Okubo, S. Fujii, H. Maenaka, H. Minami

Colloid and Polymer Science, submitted

Related Publications

Production of core/shell polystyrene/poly(3,5-xylidine) composite particles by chemical oxidative seeded dispersion polymerization

M. Okubo, H. Minami, S. Fujii, T. Mukai

Colloid and Polymer Science, **277**, 895 (1999)

Production of micron-sized, monodispersed, multihollow polystyrene/poly(3,5-xylidine) composite particles by chemical oxidative seeded polymerization

M. Okubo, T. Mukai, H. Minami, S. Fujii

Colloid and Polymer Science, **278**, 275 (2000)

Production of electrically conductive, core/shell, polystyrene/polyaniline composite particles by chemical oxidative seeded dispersion polymerization

M. Okubo, S. Fujii, H. Minami

Colloid and Polymer Science, **279**, 139 (2001)

Production of electrically conductive, hollow pyropolymer particles by heat treatment of core/shell polystyrene/poly(3,5-xylidine) composite particles

M. Okubo, S. Fujii, H. Minami

Colloid and Polymer Science, in preparation