Colloid Polym Sci 280:183–187 (2002)

SHORT COMMUNICATION

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

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

Received: 13 February 2001
Accepted: 20 June 2001

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

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

Part CCXIV of the series "Studies on suspension and emulsion"

Abstract Submicron-sized, comparatively monodisperse poly (methyl methacrylate) particles were produced by dispersion polymerization of methyl methacrylate with a poly(dimethylsiloxane)-based azoinitiator in supercritical carbon dioxide 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".

Keywords Supercritical carbon dioxide · Poly(dimethylsiloxane)-based azoinitiator · Dispersion polymerization · Submicron-size · Particle

Introduction

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

Recently, in addition to water, there has been increasing interest in supercritical carbon dioxide ($scCO_2$). The use of $scCO_2$ as a medium for polymerizations has several potential advantages: low cost, low toxicity, ease of medium removal and recycling, and marked variations in solubility power, viscosity and polarity by relatively small changes in temperature and pressure without altering the composition of the medium. Work describing the dispersion polymerization of vinyl monomers such as styrene and methyl methacrylate (MMA) in $scCO_2$ have been published in the past years [1–11].

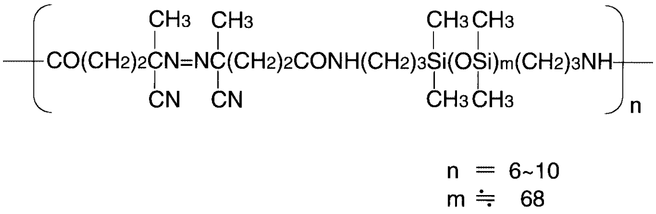
DeSimone and coworkers have pioneered the production of polystyrene (PS) particles by dispersion polymerizations of styrene in $scCO_2$ with 2,2′-azobis (isobutyronitrile) (AIBN) in the presence of PS-*b*-poly(1,1-dihydroperfluorooctyl acrylate) (PFOA) [1], PFOA [2], and poly(dimethylsiloxane) (PDMS)-based macromonomer [3] as colloidal stabilizers. Moreover, they reported that poly(MMA) (PMMA) particles were produced by dispersion polymerizations of MMA in $scCO_2$ with AIBN in the presences of PFOA [4–8] and PDMS-based macromonomer [3] as colloidal stabilizers. Lepilleur and Beckman [9] , Yates et al. [10], and Hems et al. [11] also produced PMMA particles in $scCO_2$ using poly(methyl methacrylate-*co*-hydroxyethyl methacrylate)-*g*-poly(perfluoropropylene oxide), PDMS-*b*-poly(methacrylic acid), and PMMA-*b*-poly(fluoroalkyl methacrylate), respectively. Some fluorinated polymers and PDMS-based polymers have been identified as being soluble in CO_2 or as CO_2-philic and have been used as colloidal stabilizers. In general, PDMS-based polymers may have advantages over fluorinated polymers from the viewpoint that PDMS-based polymers are much less expensive and their solubility in conventional organic solvents makes the characterization of the products obtained easy. In the reports previously described, PS and PMMA particles were not produced by the dispersion polymerizations without their colloidal stabilizers.

In this work, submicron-sized PMMA particles were produced by the dispersion polymerization of MMA in $scCO_2$ with a PDMS-based azoinitiator in the absence of colloidal stabilizer.

Experimental

Materials

MMA was purified by distillation under reduced pressure in a nitrogen atmosphere. Reagent grade AIBN was purified by recrystallization. The PDMS-based azoinitiator (VPS-0501), commercially supplied by Wako Pure Chemical Industries, was used as received. The chemical formula is given in Scheme 1.



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

$n = 6\sim10$

$m \fallingdotseq 68$

Scheme 1

The number-average molecular weight is in the range of about 3×10^4–5×10^4.

Industrial grade CO_2, with a purity of 99.5% or more, was used as received from Kobe Sanso Co. Guaranteed reagent hexane was used as received from Nacalai Tesque Co. PDMS homopolymer with a weight-average molecular weight of about 5,200 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.

Dispersion polymerization in $scCO_2$

The polymerizations were carried out in a 90-mL stainless steel reactor, equipped with sapphire windows for observation of the inside. The reactor was charged with MMA and VPS-0501 and purged with CO_2, and then pressurized with CO_2 to 10 MPa using a high-pressure pump (Nihon Seimitu Kagaku. Co., NP-D-321J) at room temperature with stirring at 750 rpm using a rotary impeller stirrer. It was confirmed with the naked eye through the sapphire windows that the CO_2 solution was homogeneous. The polymerization was started by heating the mixture to 65 °C, at which temperature 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 in 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 PDMS homopolymer (9.07 g) were conducted in a similar way. The particles produced were observed with a Hitachi S-2500 scanning electron microscope (SEM).

X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) data 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 the control of the spectrometer and data handling. The dried particles were stored under reduced pressure by continuous operation of a diffusion pump just before the XPS measurement. The dried particles were spread on an indium plate with a spatula.

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. The conversion of MMA was determined to be 87% with a gravimetrical method. The VPS-0501 concentration was determined on the basis of the idea described later. 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. ρ_i is expressed as $\rho_i = 2k_d[I]$, where k_d is the rate coefficient for initiator decomposition and [I] is the initiator concentration. In general, dispersion polymerizations were carried out in an R_i range of 10^{13}–10^{14} $mL^{-1}s^{-1}$ [12–14]. Guan et al. [15] reported that the 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 the low dielectric constant and the low viscosity of $scCO_2$. Assuming that the k_d value of VPS-0501 is equal to that of 4,4′-azobis(4-cyanopentanoic acid) [16], the f value of VPS-0501 is 0.24 [17], 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 earlier, the VPS-0501 concentration giving an R_i of 3.7×10^{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.

SEM photographs of PMMA particles produced before and after centrifugal washing with hexane, which is a nonsolvent for PMMA and a good solvent for VPS-

0501, are shown in Fig. 1. The boundary among the particles was not clear before washing, whereas it was clearly distinguished after washing. Free PDMS generated by complete decomposition of VPS-0501 and undecomposed and partially decomposed VPS-0501 should be removed by washing. The washed product was a free-flowing white powder, though the original product before washing was a tacky solid, which should be due to the existence of excessive free PDMS and undecomposed and partially decomposed VPS-0501. The number-average diameter and the coefficient of variation for the washed PMMA particles measured with image analysis software (MacScope, Mitani Co.) were 210 nm and 15.5%, respectively. The weight percentage of the PDMS component in the washed PMMA particles was determined to be 15% from ^{1}H NMR spectra measured with a Bruker DPX250 NMR spectrometer operating at 250 MHz for protons with 200 scans. When AIBN was used as the initiator in place of VPS-0501 with or without PDMS homopolymer, the PMMA prepared did not consist of particles but was a thick irregular film on the interior walls and the sapphire windows. These results indicate that VPS-0501 had two functions: initiator and colloidal stabilizer in the dispersion polymerization in scCO$_2$. Hereafter, it is called "inistab" (initiator plus stabilizer).

Gel permeation chromatograms with tetrahydrofuran as the eluant for the PMMA particles before and after the centrifugal washing with hexane are shown in Fig. 2 along with the chromatogram of the extracts . Each molecular weight was measured from the calibration obtained with PS standards. The molecular weights for the PMMA particles before and after the centrifugal washing and that of the extracts were 27×10^4, 33×10^4 and 5.4×10^4 g/mol, respectively. Because the molecular weight of VPS-0501 was 6.6×10^4, the extracts which were soluble in hexane should be free PDMS and undecomposed and partially decomposed VPS-0501. By washing, the M_w/M_n ratio decreased from 2.86 to 1.71, which was due to the removal of the extracts.

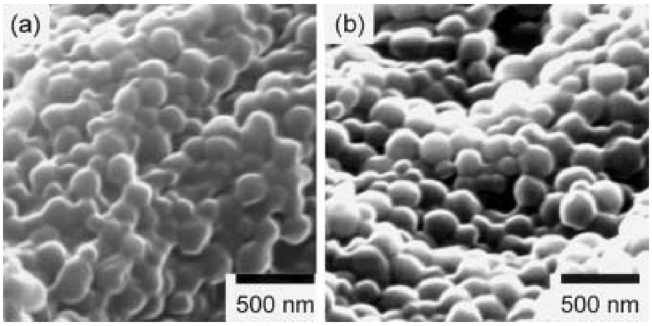


Fig. 1 Scanning electron microscopy photographs of poly(methyl methacrylate) (*PMMA*) particles produced by dispersion polymerization of methyl methacrylate (*MMA*) with the poly(dimethylsiloxane)-based azoinitiator VPS-0501 in supercritical carbon dioxide (*scCO$_2$*), **a** before and **b** after centrifugal washing with hexane

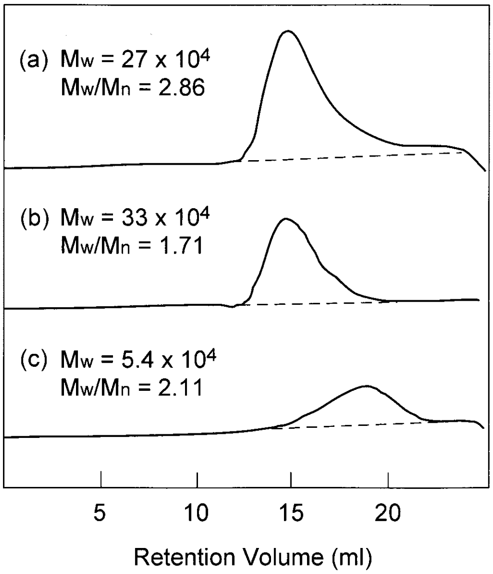


Fig. 2 Gel permeation chromatograms for PMMA produced by dispersion polymerization of MMA with VPS-0501 in scCO$_2$ **a** before and **b** after centrifugal washing with hexane, and **c** for soluble polymers in hexane washed away from PMMA particles

The results of C1*s* peak shape analyses of the XPS spectra for VPS-0501, purified PMMA prepared by solution polymerization with AIBN in toluene, and the washed PMMA particles are shown in Fig. 3. In Fig. 3a, a strong peak due to the PDMS component in VPS-0501 is observed at 284.3 eV in addition to some weak peaks due to the other components. In Fig. 3b, a peak due to carbonyl groups of PMMA is observed at 289.0 eV. In Fig. 3c, a strong peak due to the PDMS component at 284.3 eV and a small peak due to PMMA at 289.0 eV are observed. These indicate that the surfaces of the washed PMMA particles were occupied by the PDMS component.

Table 1 shows the number-average diameter (D_n) and hydrodynamic diameter (D_h) of the washed PMMA particles dispersed in hexane, which were, respectively, determined with a SEM and a dynamic light scattering (DLS) spectroscope (Otsuka Electronics DLS-7000DH, Kyoto, Japan) at a fixed 90° light scattering angle. D_h in hexane was larger than D_n in the dry state, and the difference was 191 nm. This suggests that the PDMS component covalently bonded at the particle surface extended into the hexane medium. Because the solubility parameter values of both PDMS and hexane are the same, 14.9 (MPa)$^{1/2}$ [18], and hexane is a good solvent of PDMS [18], the PDMS chains must expand in hexane. Since the PDMS component is soluble in scCO$_2$ as well as in hexane, it should effectively operate as a colloidal

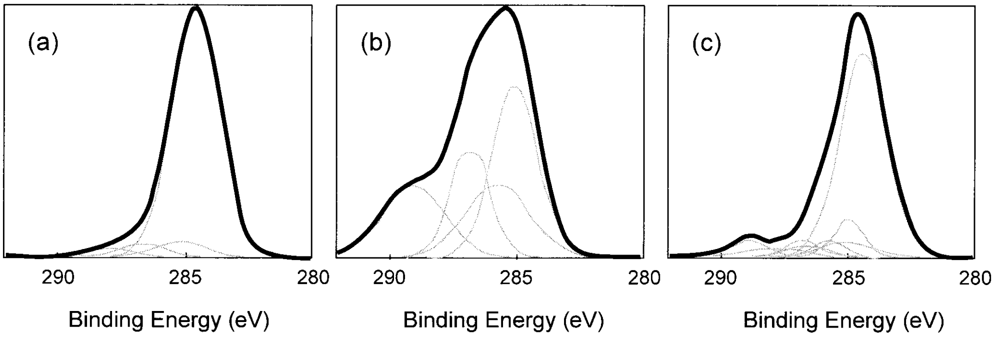


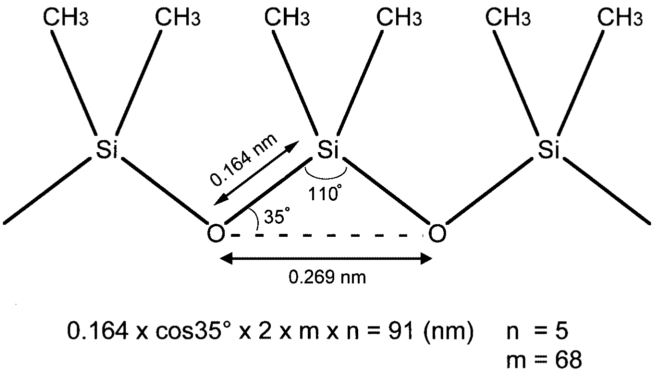
Fig. 3 C1*s* peak shape analyses of X-ray photoelectron spectroscopy spectra for **a** VPS-0501, **b** PMMA prepared by solution polymerization with 2,2′-azobis-(isobutyronitrile) in toluene, and **c** washed PMMA particles produced by dispersion polymerization with VPS-0501 in $scCO_2$

Table 1 Diameter of PMMA particles produced by dispersion polymerization of MMA with VPS-0501 in $scCO_2$. 65 °C; 24 h; 30 MPa; 200 rpm. D_n is the number-average diameter measured by scanning electron microscopy and D_h is the hydrodynamic diameter in hexane at 20 °C measured by dynamic light scattering

D_n (nm)	D_h (nm)
210	401

protective layer to disperse the PMMA particles stably in the $scCO_2$ medium of the dispersion polymerization system. The hydrodynamic thickness (95.5 nm) of the PDMS layer end-grafted to the particle surface in hexane accorded well with the length (91 nm) for five repeat units, $n = 5$, of VPS-0501. The length for the five repeat units was calculated as follows, assuming that the molecular weight for one repeat unit ($n = 1$) of VPS-0501 is 5,000, the Si–O bond length is 0.164 nm, and the Si–O chains form a planar zigzag conformation with a bond angle of 110° (Scheme 2).

Using the k_d value of VPS-0501 in $scCO_2$, it is calculated that 30% of the azo groups in VPS-0501 are 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 initiator radicals generated are recombined or disproportionated in their "cages" [19] without initiating the polymerization. The initiator radicals diffusing out of their "cages" initiate the polymerization, and they are covalently bonded as initiator fragments at the particle surface. Taking the amounts of the undecomposed azo groups and the recombined compounds into account, there should be a great possibility that five repeat units and more in the VPS-0501 molecule are covalently bonded at the particle surface. Assuming that all the PDMS chains consist of five repeat units ($n = 5$) for the sake of convenience and are covalently bonded at the particle surfaces, the molecular area of the PDMS chain occupied at the particle surface was calculated to be 7.4 nm^2 from the results obtained by the NMR and DLS measurements described earlier. The densities of PMMA and PDMS used in the calculation of the surface area of the PMMA particles are 1.19 and 0.97, respectively [18]. 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 repeat units of VPS-0501. This indicates that the grafting density at the particle surface is so high that the PDMS chains stretch out from their random-walk configurations as shown in Fig. 4.



Scheme 2

The hexane dispersion of the washed PMMA particles was kept at 65 °C for 3 days, and D_h was again measured by 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 hexane dispersions were treated at 60 °C both in the presence of Rheodol SP-O10 and Pronon 201 nonionic emulsifiers, hydrophilic–lipophilic balance values of which are 4.3 and 2.0, respectively. 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 into account that the PMMA particles dispersed in hexane before the heat treatment.

From the results, it was clarified that submicron-sized, comparatively monodisperse PMMA particles

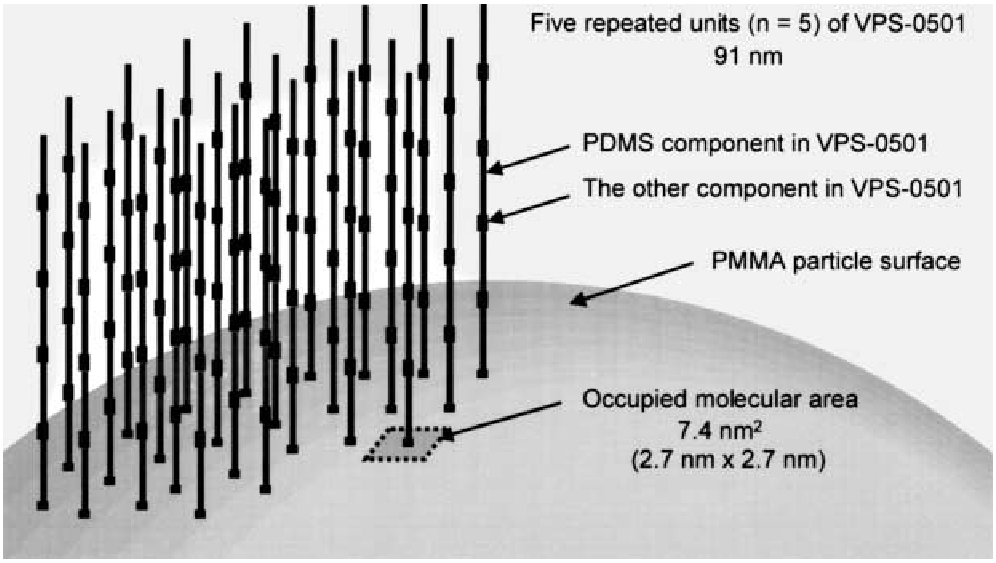


Fig. 4 A schematic diagram for five repeat units ($n = 5$) of VPS-0501 to be end-grafted to the particle surface

could be produced by the dispersion polymerization of MMA in $scCO_2$ with a PDMS-based azoinitiator as an inistab.

Acknowledgement This work was partially supported by Grant-in-Aid for Scientific Research (Grant 12450373) from the Japan Society for the Promotion of Science (JSPS).

References

1. Canelas DA, Betts DE, DeSimone JM (1996) Macromolecules 29:2818
2. Shiho H, DeSimone JM (1998) J Polym Sci Polym Chem 37:2429
3. Shaffer KA, Jones TA, Canelas DA, DeSimone JM (1996) Macromolecules 29:2704
4. DeSimone JM, Maury EE, Menceloglu YZ, McClain JB, Romack TJ, Combes JR (1994) Science 265:356
5. Hsiao YL, Maury EE, DeSimone JM, Mawson SM, Johnston KP (1995) Macromolecules 28:8159
6. Hsiao YL, Maury EE, DeSimone JM (1995) Polym Prepr Am Chem Soc Div Polym Chem 36:190
7. Hsiao YL, DeSimone JM (1997) J Polym Sci Polym Chem 35:2009
8. Hsiao YL, DeSimone JM (1996) Polym Prepr Am Chem Soc Div Polym Mater Sci Eng 74:260
9. Lepilleur C, Beckman EJ (1997) Macromolecules 30:745
10. Yates MZ, Shim GLJJ, Maniar S, Johnston KP, Lim KT, Webber S (1999) Macromolecules 32:1018
11. Hems WP, Yong TM, Nunen JLM, Cooper AI, Holmes AB, Griffin DA (1999) J Mater Chem 9:1403
12. Shen S, Sudol ED, El-Aasser MS (1993) J Polym Sci Part A Polym Chem 31:1393
13. Okubo M, Ikegami K, Yamamoto Y (1989) Colloid Polym Sci 267:193
14. Okubo M, Izumi J, Hosotani T, Yamashita T (1997) Colloid Polym Sci 275:797
15. Guan Z, Combes JR, Menceloglu YZ, DeSimone JM (1993) Macromolecules 26:2663
16. Anon. (1999) Technical bulletin – Macro azo initiator. Wako Pure Chemical Industries Ltd
17. Nakamura K, Fujimoto K, Kawaguchi H (1999) Colloids Surf 153:195
18. Brandrup J, Immergut EH, Grulke EA (1999) Polymer handbook, 4th edn. Wiley, New York
19. Ham GE (1967) Kinetics and mechanisms of polymerization, vol 1. Vinyl polymerization. Dekker, New York, chapter 1