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SHORT COMMUNICATION

Synthesis of polystyrene microspheres by dispersion polymerization in supercritical carbon dioxide using a poly (dimethylsiloxane)-based macroazoinitiator

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Abstract The synthesis of polystyrene microspheres was achieved by the dispersion polymerization of styrene in supercritical carbon dioxide using azobisisobutylonitrile (AIBN) and a poly(dimethylsiloxane) (PDMS)-based macroazoinitiator, VPS-1001. VPS-1001 contained seven to nine molecules of the azo groups and the PDMS blocks with a molecular weight of 10,000 per molecule. The polymerization in the presence of both VPS-1001 and AIBN produced polystyrene microspheres with a diameter below 4 μm in over 85% yields, whereas the polymerization with VPS-1001 in the absence of AIBN provided a nonspecific polystyrene in only 20% yield. The particle size decreased as a result of increasing the concentration of VPS-1001. It was confirmed that the polystyrene particles were stabilized by the PDMS-*block*-polystyrene formed through the polymerization initiated by VPS-1001 because the polymerization using a PDMS homopolymer provided nonspecific polystyrene as a precipitate during the polymerization.

Keywords Dispersion polymerization · Supercritical carbon dioxide · Microspheres · Polystyrene · Poly (dimethylsiloxane)-based macroazoinitiators · Azobisisobutylonitrile

Introduction

Heterogeneous polymerization in supercritical carbon dioxide ($scCO_2$) is superior in preparing microspheres based on the characteristics of CO_2, such as being nontoxic, odorless, spontaneous, and volatile, and also based on the industrial utilities of having mild critical conditions (31.1 °C, 73.8 bar) [1] and recyclable properties. The industrial advantages of the polymerization in $scCO_2$ over the conventional polymerization in water or organic solvents include the simplification of drying process and the reduction of huge amounts of the waste water and organic solvents. The heterogeneous polymerization in $scCO_2$ involves the dispersion polymerization, the suspension polymerization, and the emulsion polymerization. To efficiently obtain spherical particles, surfactants are often added to these polymerization systems and a great variety have been developed. Examples include a poly(1,1-dihydroperfluorooctyl acrylate) homopolymer [2, 3] and its block copolymers [4], end-functional poly (hexafluoropropylene oxide) [5], and poly(ethylene glycol) methyl ether perfluorooctanoate [6]. Poly(dimethylsiloxane) (PDMS) has also been used as a component of surfactants for $scCO_2$ based on the fact that PDMS is as much CO_2-philic as fluoropolymers [7]. PDMS has advantages over the fluoropolymers in being less expensive and easier to handle because PDMS can be dissolved by many organic solvents. Some PDMS-containing surfactants were prepared for the dispersion polymerization in $scCO_2$: PDMS-combined with a fluoropolymer [8], PDMS block copolymers [9–11] and graft copolymers [12], vinyl-terminated PDMS [13–15], and poly (propyl methacrylate) supporting oligo(dimethylsiloxane) [16].

I found a convenient method to prepare polystyrene microspheres by the dispersion polymerization in $scCO_2$ using a PDMS-based macroazoinitiator. The dispersion polymerizations using the PDMS-based macroazoinitiators have already been separately reported by Dinçer and Okubo. Dinçer et al. performed the dispersion polymerization of styrene using PDMS having only one azo group per

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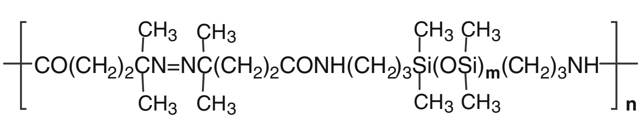
molecule [17]. However, they could not obtain spherical particles and concluded that the PDMS macroinitiator did not serve as a surfactant during the polymerization. Okubo et al. [18] used PDMS containing six to ten azo groups per molecule as both the initiator and surfactant for the dispersion polymerization of methyl methacrylate. While they obtained hundreds of nanometer-sized particles, the particles were coagulated. I attained the synthesis of polystyrene microspheres by the dispersion polymerization using azobisisobutylonitrile (AIBN) as the initiator and a PDMS-based macroazoinitiator as the precursor of the surfactant. This short communication describes the convenient synthesis of polystyrene microspheres using an easily available PDMS-based macroazoinitiator.

Experimental

Instrumentation The size exclusion chromatography was performed using a Tosoh GPC-8020 instrument equipped with a DP-8020 dual pump, a CO-8020 column oven, and a RI-8020 refractometer. Two polystyrene gel columns, Tosoh TSK G2000$\mathrm{H_{XL}}$ and G4000$\mathrm{H_{XL}}$, were used with THF as the eluent at 40 °C. The scanning electron microscopy (SEM) measurements were made using a JEOL JSM-6300 electron microscope.

Materials PDMS-based macroazoinitiators, VPS-1001 (M_n=70,000–90,000, M_n of a PDMS block=10,000, azo content=0.09 mmol/g) and VPS-0501 (M_n=30,000–50,000, M_n of a PDMS block=5,000, azo content=0.2 mmol/g) were obtained from Wako Pure Chemical Industries. The structure of the PDMS-based macroazoinitiators is shown in Fig. 1. A PDMS homopolymer (M_n=46,000 and M_w/M_n=1.96) was purchased from Sigma-Aldrich. Styrene was washed with aqueous alkaline solution and water and distilled under reduced pressure over calcium hydride. The styrene was deoxygenated by bubbling nitrogen at room temperature for 15 min. AIBN was recrystallized in methanol. Industrial grade CO_2 with a purity of 99.5% or higher was purchased from Sanyo Shoji.



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

PDMS-base macroazoinitiator

	m	n
VPS-1001	135	7-9
VPS-0501	68	6-10

Fig. 1 PDMS-based macroazoinitiators

Dispersion polymerization of styrene in scCO$_2$ The polymerization was conducted in CO_2 in a 10 ml high-pressure view cell equipped with tempered glass windows, which permit visual observation of the reaction mixture. The reactor was purged with a flow of nitrogen before the addition of the following reaction mixture. VPS-1001 (100 mg, 5 wt%) dissolved in deoxygenated styrene (2.00 g, 19.2 mmol) and AIBN (95 mg, 3 mol%) were placed in the reactor and were purged with a flow of nitrogen again. A Nihon Seimitsu Kagaku NP-D-321 personal pump equipped with an Eyela CCA-1110 cooler was used to pressurize the reactor with CO_2 to ~180 bars at 35 °C, and the reaction mixture was heated to 65 °C. The pressure was reached to ~350 bars at 65 °C. The remaining CO_2 was added to the system until the pressure was reached to 400 bars. Once the final conditions were obtained, the reaction was allowed to proceed with stirring for 24 h. At the end of the reaction, the vessel was cooled to room temperature. The CO_2 was slowly vented from the cell through a pressure let down valve to a 500-ml Erlenmeyer flask to collect any polymer that sprayed out during the venting process. The polymer product was removed from the reaction vessel. The remaining polymer in the vessel was dissolved in dichloromethane and was evaporated, then dried in vacuo for several hours. The yield of the polymer was determined gravimetrically.

SEM measurement

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

Results and discussion

The polymerization of styrene in $scCO_2$ was performed by AIBN at 65 °C for 24 h at 400 bars as the initial pressure to produce a styrene oligomer in a moderate yield. On the other hand, the polymerization by VPS-1001 instead of AIBN provided a polymer with the high molecular weight of M_n=53,000; however, the yield was only 20%. Most of the monomers remained unreacted in the cell, so that the resulting polymer dissolved in the monomer. It was considered that the low conversion of styrene was due to the slow polymerization when it is taken into account that only 0.05 mol% of the azo groups to styrene was present in the macroazoinitiator.

Accordingly, I added AIBN to the polymerization system to compensate for the low concentration of the initiator species for VPS-1001 and to accelerate the polymerization. During the initial stage of the polymerization, it was totally dark because VPS-1001 did not

Table 1 Dispersion polymerization of styrene by the PDMS macroazoinitiators and AIBN in $scCO_2$

Surfactant	wt%	AIBN (mol%)	Yield (%)	M_n	M_w/M_n	D_n (μm)	D_w/D_n[b]	State
–	0	3	54	3,210	1.46	–[a]	–[a]	Nonspecific
VPS-1001	5.00	0	20	53,000	3.24	–[a]	–[a]	Nonspecific
VPS-1001	0.625	3	89	5,900	2.48	3.96	2.84	Spherical
VPS-1001	1.25	3	92	6,580	2.45	2.06	2.37	Spherical
VPS-1001	2.50	3	90	7,060	2.25	1.06	2.60	Spherical
VPS-1001	5.00	3	86	7,140	2.17	1.02	1.20	Spherical
VPS-0501	5.00	3	97	7,020	2.31	0.805	1.20	Coagulated
PDMS[c]	5.00	3	53	2,740	1.42	–[a]	–[a]	Nonspecific

Temperature, 65 °C; initial pressure, 400 bars; polymerization time, 24 h

[a] Could not estimated

[b] Ref. [19]

[c] A PDMS homopolymer

completely dissolve in $scCO_2$ even over 400 bars at 65 °C. As the polymerization proceeded, the system turned from dark to white. After the polymerization for 24 h, the pressure was approximately 20 bars lower than the initial pressure. It was confirmed that white powders rapidly precipitated when the rotation of the stirrer was stopped at the end of the polymerization. These results are summarized in Table 1. The polystyrene was obtained in the high yields over 85%. The molecular weight of the polystyrene increased as a result of increasing the concentration of

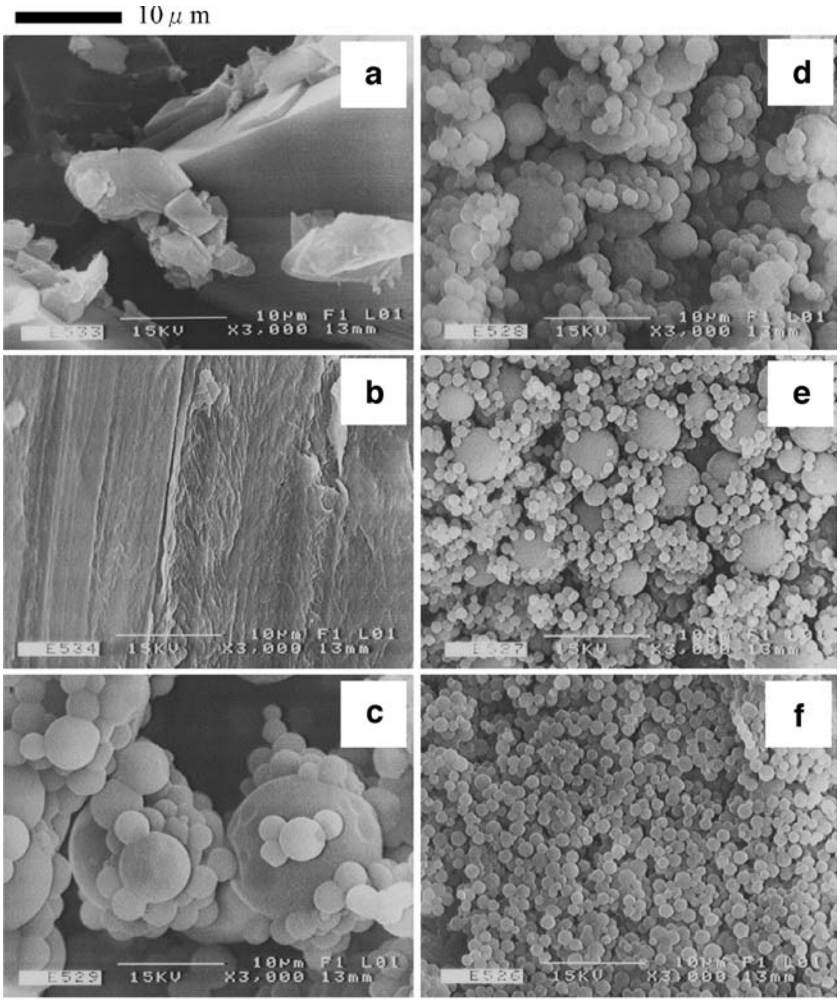


Fig. 2 SEM images of the polystyrene obtained by the polymerization with VPS-1001 at **a** 0, **b** 5 without AIBN, **c** 0.625, **d** 1.25, **e** 2.50, and **f** 5.00 wt% in the presence of AIBN

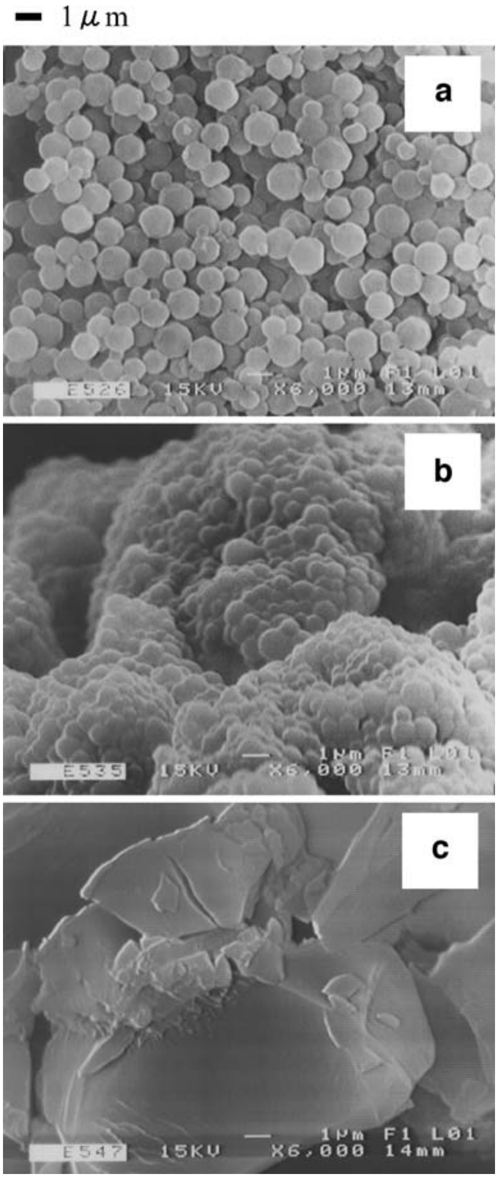


Fig. 3 SEM images of the polystyrene obtained by the polymerization with **a** VPS-1001, **b** VPS-0501, and **c** the PDMS homopolymer

VPS-1001, although the molecular weights were not very high. The molecular weight distribution decreased with an increase in the VPS-1001 concentration.

The SEM observations demonstrated that the spherical polystyrene particles were obtained by the dispersion polymerization with AIBN and VPS-1001, whereas the polymerization without AIBN or the macroazoinitiator produced nonspecific forms of the polymers. The result that the polymer prepared by the polymerization with VPS-1001 without AIBN took nonspecific forms should be based on the fact that the polymer was produced in a state of dissolving in the unreacted monomers. Figure 2 shows the SEM images of the microspheres produced by the polymerization at the different VPS-1001 concentrations. The particle size decreased as a result of increasing the concentration of VPS-1001. The size distribution of the particles also decreased with the increase in the VPS-1001 concentration. At a 5-wt% VPS-1001 concentration, microspheres with a 1 μm diameter and a distribution of 1.20 were obtained.

I also performed the dispersion polymerization of styrene using VPS-0501 having shorter PDMS blocks instead of VPS-1001 in the presence of AIBN. The resulting polystyrene had a molecular weight and molecular weight distribution similar to those of the polystyrene prepared from VPS-1001. The particle size was smaller than that obtained from VPS-1001, although the size distribution was the same. SEM revealed that the particles prepared from VPS-0501 had coagulated, although each of the particles took spherical forms (Fig. 3). Okubo et al. [18] also obtained particles coagulated by the polymerization of methyl methacrylate using VPS-0501, although they did not add AIBN to the polymerization system. It was suggested that over a certain length of PDMS blocks was needed to stabilize the polystyrene particles.

Furthermore, it was suggested that the polystyrene particles were stabilized by the PDMS-*block*-polystyrene produced through the polymerization initiated by the PDMS macroazoinitiator (Fig. 4). This is based on the fact that the polymerization with AIBN and a PDMS homopolymer as a surfactant precipitated polystyrene with a low molecular weight during the polymerization. The molecular weight, coupled with the molecular weight distribution and yield of the polystyrene, were similar to those for the polystyrene produced by the polymerization with AIBN without VPS-1001. The polystyrene produced from the PDMS homopolymer also took nonspecific forms similar to those of the polystyrene by the polymerization without VPS-1001. These results indicate that the PDMS homopolymer did not serve as a surfactant for the dispersion polymerization of styrene in $scCO_2$.

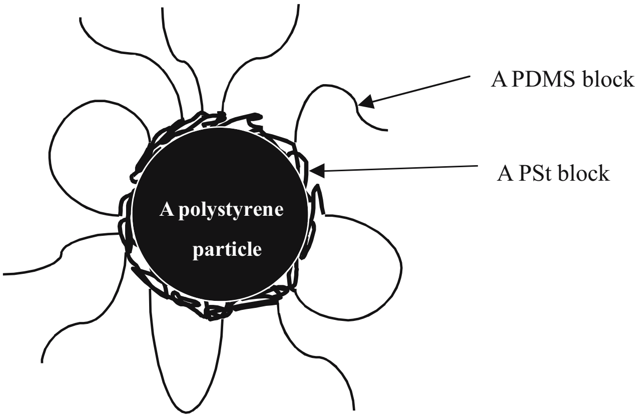


Fig. 4 The polystyrene particles stabilized by the PDMS-*block*-polystyrene block copolymers

Conclusion

Polystyrene microspheres were prepared by the dispersion polymerization in $scCO_2$ using the PDMS-based macroazoinitiator as the precursor of the surfactant and AIBN as the initiator. The particle size decreased as a result of increasing the concentration of VPS-1001. Microspheres with a 1 μm diameter and a size distribution of 1.20 were obtained by the polymerization with 5 wt% VPS-1001 and 3 mol% AIBN. It was found that the polystyrene particles were stabilized by the PDMS-*block*-polystyrene block copolymers formed by the polymerization initiated by VPS-1001, based on the fact that the PDMS homopolymer did not serve as a surfactant for the dispersion polymerization of styrene in $scCO_2$.

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