Korean J. Chem. Eng., **27**(3), 1021-1027 (2010)
DOI: 10.1007/s11814-010-0137-3

Dispersion polymerization of *N*-vinyl-2-pyrrolydone using fluorine-based surfactants in supercritical carbon dioxide

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(*Received 1 September 2009 • accepted 5 October 2009*)

Abstract−We carried out a dispersion polymerization of *N*-vinyl-2-pyrrolydone using fluorine-based surfactants, which included poly(heptadecafluorodecyl acrylate) (PHDFDA) or poly(heptadecafluorodecyl methacrylate) (PHDFDMA) in supercritical carbon dioxide (scCO$_2$). An FE-SEM and an image analyzer were used to characterize particle morphology, size, and size distribution of the resulting polymer taking into account effect of the surfactant, initiator, and monomer concentrations.

Key words: *N*-vinyl-2-pyrrolydone, Supercritical Carbon Dioxide, Dispersion Polymerization

INTRODUCTION

There are numerous advantages to using carbon dioxide (CO$_2$) in the polymer process and in synthesis, ranging from being environmentally responsible to improved material properties [1]. CO$_2$ has mild and easily accessible critical temperature and pressure (T_c= 31.1 °C and P_c=73.8 bar), is relatively inert, non-flammable, non-toxic, and has tunable physical properties [2-4]. In addition, CO$_2$ has benefits to its use in separation technology, because it can be removed by simple depressurization [4]. For these reasons, carbon dioxide has been a replacement for many typical organic solvents in various reaction systems either as an expanded liquid or as a supercritical fluid. In particular, scCO$_2$ has been used as a solvent medium for dispersion polymerization over the past decade [1,4-7].

Micron-size spherical polymer particles with narrow particle size distribution have been synthesized using various heterogeneous polymerization methods, such as precipitation, dispersion, emulsion and suspension. Dispersion polymerization is a unique method to prepare spherical and monodisperse polymer particles with diameter 0.1 μm to 10 μm in single step [8]. Micron-size spherical particles obtained from dispersion polymerization are used in various applications, such as drug delivery, printer toner, packing materials for chromatography and cosmetics [9,10].

Poly(*N*-vinyl-2-pyrrolydone) (PVP) is a water-soluble polymer made from the monomer *N*-vinylpyrrolidone. When dry it is a light flaky powder that readily absorbs up to 40% of its weight in atmospheric water. In solution, it has excellent wetting properties and readily forms films. Thus, it is good for use as a coating or as an additive to coatings. PVP has been widely used as an adhesive, emulsifier, photoresist, binder, and aid for increasing the solubility of drugs in liquid and in semi-liquid dosage forms.

Few studies on dispersion polymerization of NVP in scCO$_2$ have been reported: the dispersion polymerization of NVP in scCO$_2$ using poly(1,1-dihydroperfluorooctyl acrylate) (poly(FOA)) [11], poly(dimethylsiloxane) monomethacrylate (PDMS-mMA) [12], diblock copolymer, poly(styrene-*b*-dimethylsiloxane) [13], and PDMS-*g*-pyrrolidone carboxylic acid (Monasil PCA) and KF-6017 as a surfactant [14].

In this study, dispersion polymerization of NVP was carried out in scCO$_2$ using fluorine-based surfactant, poly(heptadecafluorodecyl acrylate) (PHDFDA) or poly(heptadecafluorodecyl methacrylate) (PHDFDMA). The effect of surfactants, initiator, and monomer concentrations on the particle morphology, average particle size, and particle size distribution (PSD) was investigated.

EXPERIMENTS

1. Materials

N-vinyl-2-pyrrolydone (NVP, min. 99%), 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl acrylate (HDFDA, min. 97%), and 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl methacrylate (HDFDMA, min. 97%) were obtained from Aldrich. These monomers were pretreated on an alumina column to remove methyl ether of hydroquinone (MEHQ), then the dissolved oxygen was removed through nitrogen purging. Poly(heptadecafluorodecyl acrylate) (PHDFDA) and poly(heptadecafluorodecyl methacrylate) (PHDFDMA) were prepared for the use as a surfactant via solution polymerization in scCO$_2$ at 70.0 °C and 300 bar [15]. The chemical structures of the surfactants are illustrated in Fig. 1. 2,2-azobisisobutyronitrile (AIBN, min. 98%) obtained from Junsei Chemical was recrystallized using methanol. Carbon dioxide (min. 99.99%) was purchased from Korea industrial gases.

2. Apparatus and Procedures

Dispersion polymerization of NVP was performed in a 30-ml SUS 316 reactor [16]. CO$_2$ was supplied with gas booster pump (Maxpro Technologies Inc. Model DLE 75-1). To minimize the fluctuation from the pump and to maintain stable feeding, we used a

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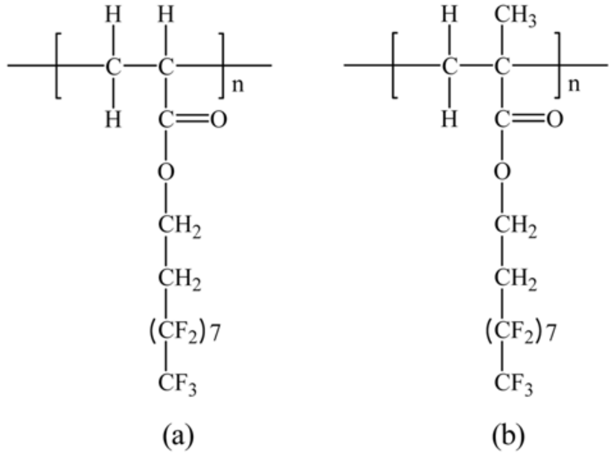


Fig. 1. Chemical structure of surfactants (a) PHDFDA and (b) PHDFDMA.

300-ml reservoir between pump and reactor. Pressure inside the reactor was measured by a pressure transducer (Data Instruments Inc. Model AB/HP, accuracy 0.25%) and by an indicator (Laurel Electronics Inc. L20010WM1). Temperature was measured by K(CA) type thermocouple (accuracy 0.05 K) and indicator (Hanyoung Electronics Inc. Model DX-7).

Between 1.0-4.0 g of the monomer, AIBN (0.5-4.0 wt% relative to the total monomer) and surfactant (1.0-15.0 wt% relative to the total monomer) was placed into a 30-ml reactor. Then the reactor was purged by CO_2 several times to remove residual air and then charged with a known amount of CO_2 at room temperature. A PTFE-coated magnetic stirring bar was used for agitation of reacting mixture. After polymerization was completed, the reactor was cooled down below 20 °C. When the pressure of the reactor decreased to about 60 bar, where vapor/liquid phase separation occurred, CO_2 was vented from vapor phase through two glass traps. To prevent discharge of unreacted monomer to atmosphere during CO_2 separation, glass traps were filled with methanol and kept cold in an ice water bath. The polymer particles were washed with methanol to remove unreacted monomer. The resulting polymer was dried in vacuum at room temperature.

3. Polymer Characterization

Particle morphology and size were characterized by FE-SEM (Joel5410LV). The number-average particle size and the particle size distribution (PSD) were measured with an image analyzer (TDI Scope Eye™ ver 3.1) with SEM images and determined by measuring the diameter of 200 particles. Number-average (D_n) and weight-

Table 1. Effect of the surfactants structure on the dispersion polymerization of NVP in $scCO_2$[a]

Entry	Surfactant	Particles size (μm)[b]	PSD[c]	Morphology
S1	PHDFDA	NA	NA	Agglomerated
S2	PHDFDMA	0.36	1.05	Spherical

[a]Reaction conditions: 2.0 g of NVP, 1.0 wt% of AIBN, 15.0 wt% of surfactant, 70 °C, 315±5 bar, 24 h, with stirring
[b]Determined by FE-SEM
[c]Particle size distribution

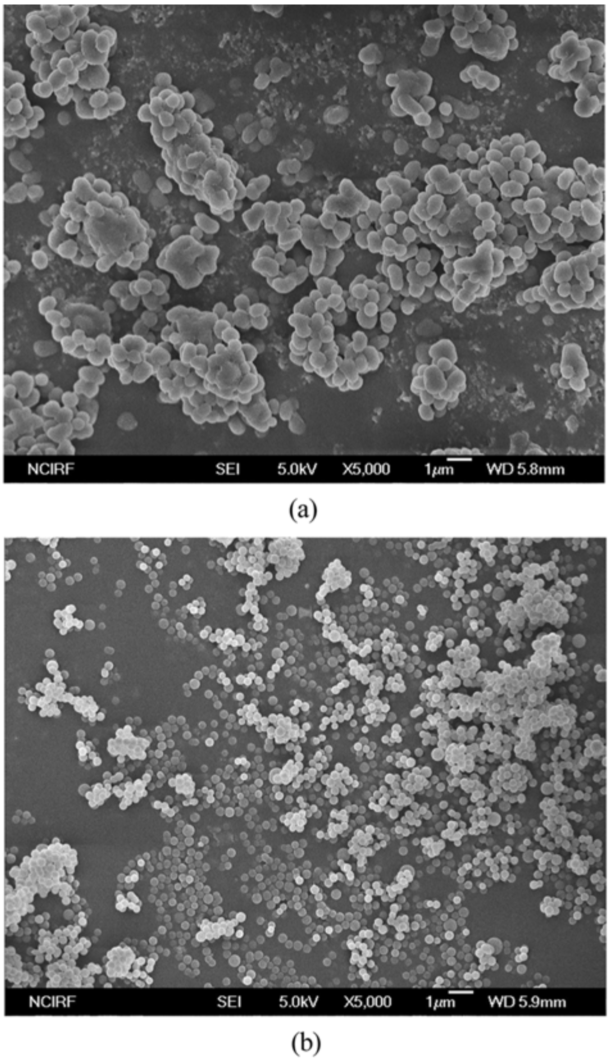

(a)
(b)

Fig. 2. SEM images of the PVP particles obtained with 15.0 wt% (a) PHDFDA and (b) PHDFDMA as the surfactant in $scCO_2$ at 70 °C and 315±5 bar.

Table 2. Effect of the surfactants concentration on the dispersion polymerization of NVP in $scCO_2$[a]

Entry	Surfactant (wt%)		Particles size (μm)[b]	PSD[c]	Morphology
P1	-	0.0	NA	NA	-
A1	PHDFDA	1.0	NA	NA	Agglomerated
A2		5.0	NA	NA	Agglomerated
A3		10.0	NA	NA	Agglomerated
A4		15.0	NA	NA	Agglomerated
M1	PHDFDMA	1.0	NA	NA	Irregular spherical
M2		5.0	NA	NA	Agglomerated
M3		10.0	NA	NA	Agglomerated
M4		12.0	0.65	1.14	Spherical
M5		15.0	0.36	1.05	Spherical

[a]Reaction conditions: 2.0 g of NVP, 1.0 wt% of AIBN, 70 °C, 315±5 bar, 24 h, with stirring
[b]Determined by FE-SEM
[c]Particle size distribution

average (D$_w$) particle diameters were calculated from the following equations [17].

$$D_n = \frac{\Sigma_{i=1}^{n} d_i}{N} \tag{1}$$

$$D_w = \frac{\Sigma_{i=1}^{N} d_i^4}{\Sigma_{i=1}^{N} d_i^3} \tag{2}$$

Where d$_i$ is the diameter of particle i, and N is the total number of particles measured in the SEM images. The polydispersity index (PDI), which indicates the particle size distribution (PSD), is defined as D$_w$/D$_n$.

RESULTS AND DISCUSSIONS

1. Effect of the Surfactants Structure

Table 1 and Fig. 2 show the effect of the surfactant structure on dispersion polymerization of NVP in scCO$_2$. NVP was polymer-

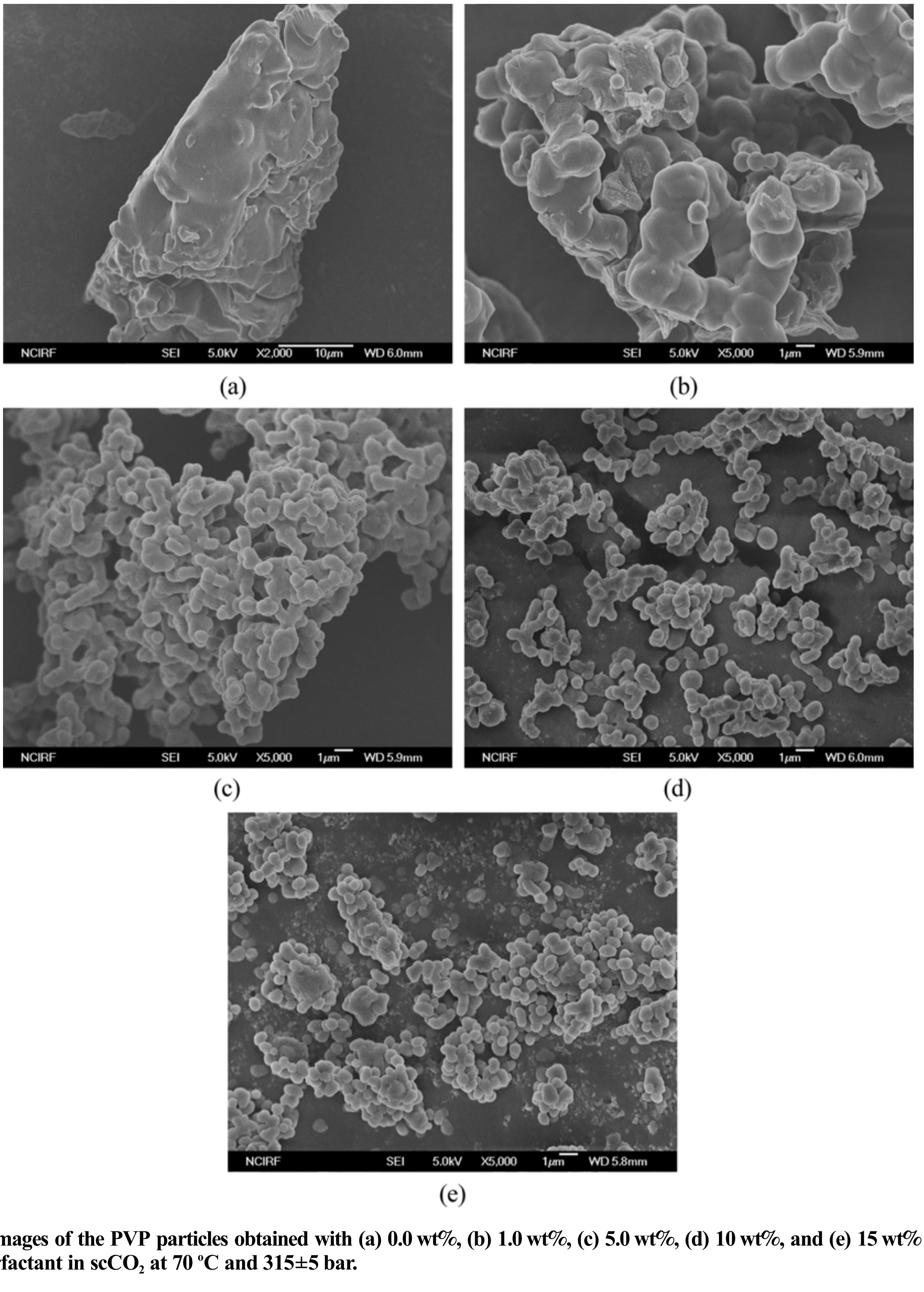


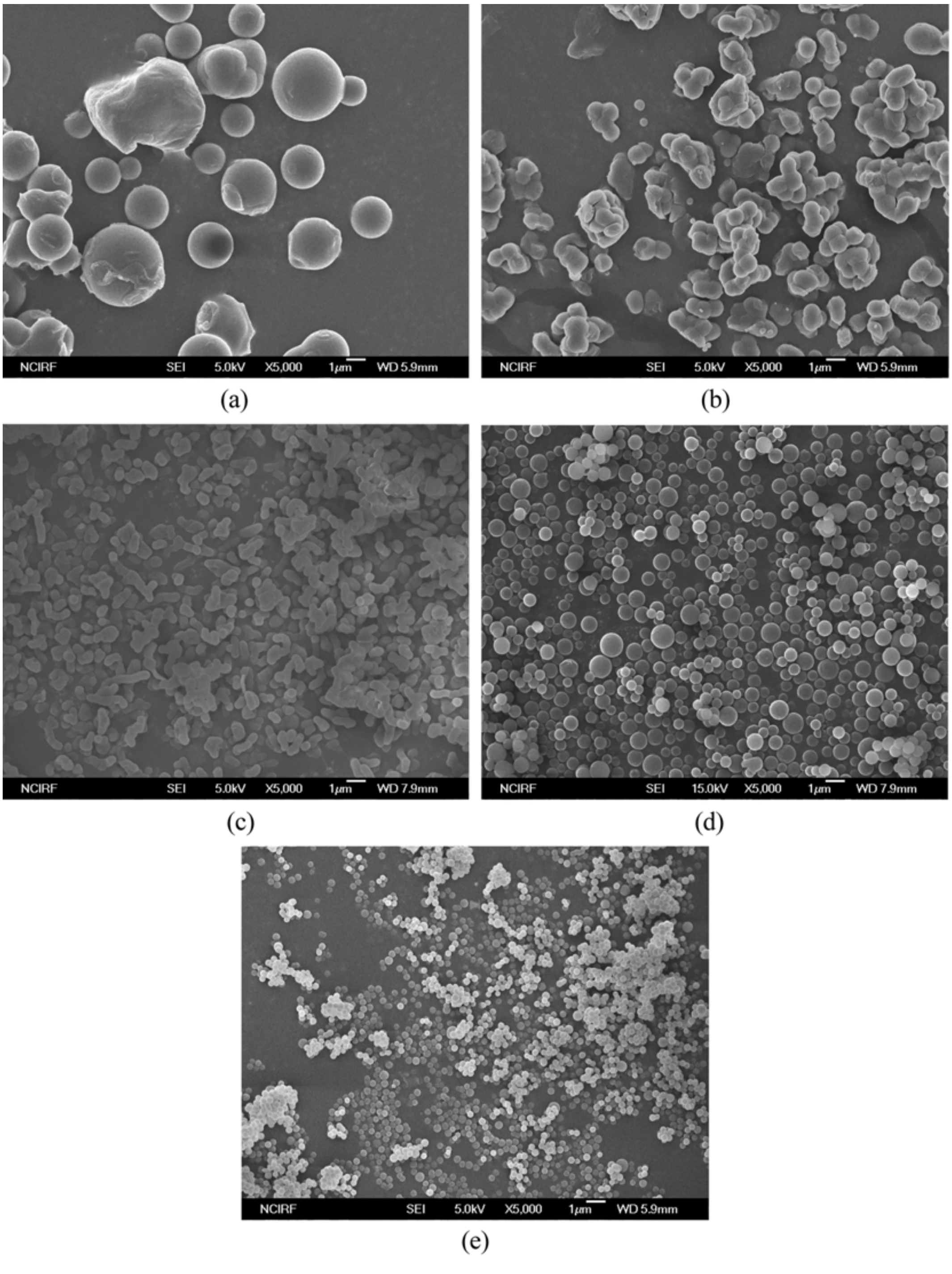
Fig. 3. SEM images of the PVP particles obtained with (a) 0.0 wt%, (b) 1.0 wt%, (c) 5.0 wt%, (d) 10 wt%, and (e) 15 wt% PHDFDA as the surfactant in scCO$_2$ at 70 °C and 315±5 bar.

ized with two fluorine-based polymer surfactants 15.0 wt% of monomer, namely, PHDFDA or PHDFDMA under the same reaction conditions, 70 ºC and 315±5 bar for 24 h. For dispersion polymerization, surfactant and monomer have to be dissolved in CO_2 at the specified conditions. The solubility of the two surfactants and monomer in CO_2 had been determined in a previous study [18-20]. From the solubility data, we confirmed that all surfactants and monomer were soluble in CO_2 under the NVP polymerization conditions.

As shown in Fig. 2, resulting polymer particles obtained using PHDFDA and PHDFDMA, they are very different respectively, even though the chemical structure of surfactants is very similar. Very spherical and uniform PVP particles of average particle size 0.36 μm with PHDFDMA were successfully obtained. The results using PHDFDA were agglomerated and irregular particles. PHDFDMA is more suitable surfactant than PHDFDA for obtaining spherical PVP particles in $scCO_2$.

2. Effect of the Surfactants Concentration

The results for the dispersion polymerization of NVP in $scCO_2$



(a) (b)

(c) (d)

(e)

Fig. 4. SEM images of the PVP particles obtained with (a) 1.0 wt%, (b) 5.0 wt%, (c) 10.0 wt% , (d) 12.0 wt%, and (e) 15.0 wt% PHDFDMA as the surfactant in $scCO_2$ at 70 ºC and 315±5 bar.

with different concentrations of PHDFDA or PHDFDMA are summarized in Table 2. The amounts of the monomer and initiator were kept constant at 2.0 g and 0.02 g (1.0 wt% on the monomer), respectively. The polymerization was carried out at 70 °C and 315±5 bar for 24 h.

Figs. 3 and 4 show the SEM images of PVP particles obtained with different concentrations of PHDFDA and PHDFDMA. The result obtained from precipitation polymerization in the absence of surfactant has no particle and shape as shown in Fig. 3(a). The particles obtained with 1.0, 5.0, 10.0 and 15.0 wt% PHDFDA were agglomerated particles (Fig. 3(b), (c), (d), and (e)). More discrete and smaller particles were obtained as PHDFDA concentration increased.

On the other hand, in the case of using PHDFDMA as a surfactant, more spherical, more discrete, and smaller PSD-PVP particles were obtained as PHDFDMA concentration increased.

From these results, PHDFDMA is the more proper surfactant than PHDFDA to obtain more spherical and better dispersed PVP particles. Therefore, the effect of monomer and initiator concentration was investigated using PHDFDMA as the surfactant.

3. Effect of the Initiator Concentration

The dispersion polymerizations of NVP were performed with different concentrations of initiator as shown in Table 3. In all cases, the amount of PHDFDMA surfactant and monomer was kept constant at 0.3 g (15.0 wt% on the monomer) and 2.0 g, respectively.

Table 3. Effect of the AIBN concentration on the dispersion polymerization of NVP in $scCO_2$[a]

Entry	AIBN (wt%)	Particles size (μm)[b]	PSD[c]	Morphology
M6	0.5	0.52	1.09	Spherical
M7	1.0	0.36	1.06	Spherical
M8	2.0	0.70	1.05	Spherical
M9	4.0	NA	NA	Agglomerated

[a] Reaction conditions: 2.0 g of NVP, 15.0 wt% of PHDFDMA, 70 °C, 315±5 bar, 24 h, with stirring

[b] Determined by FE-SEM

[c] Particle size distribution

The average particle size decreased as initiator concentration increased from 0.5 wt% to 1.0 wt% and increased as initiator concentration increased from 1.0 wt% to 4.0 wt% as shown in Table 3 and Fig. 5. PSD decreased slightly as the initiator concentration increased. When initiator 4.0 wt% was used, the resulting polymer was agglomerated.

4. Effect of the Monomer Concentration

The effect of monomer concentration was also studied, and the polymerization results of PVP from these reactions are given in Table 4 and in Fig. 6. The PHDFDMA surfactant 15.0 wt% and initiator 1.0 wt% as part of the monomer were added to the reactor. The par-

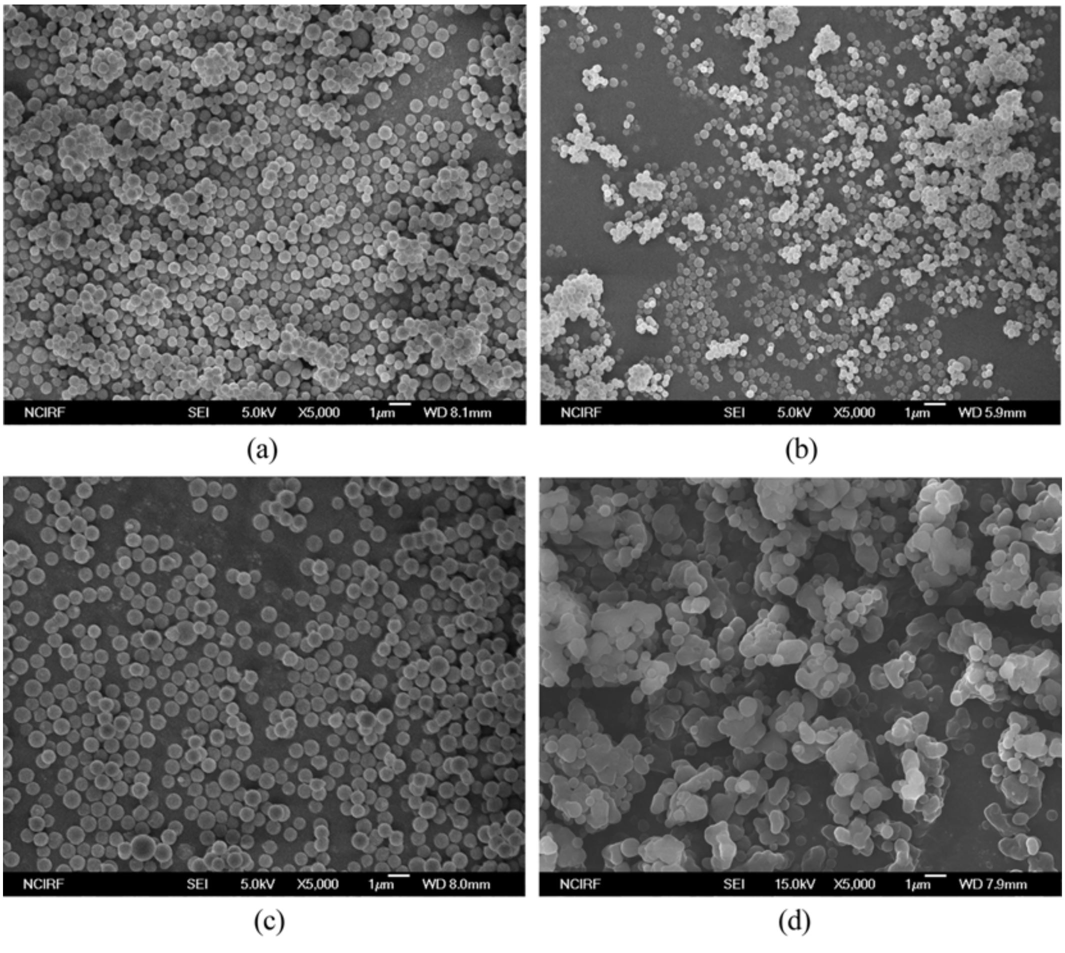


Fig. 5. SEM images of the PVP particles obtained with (a) 0.5 wt%, (b) 1.0 wt%, (c) 2.0 wt%, and (d) 4.0 wt% AIBN as the initiator and 15.0 wt% PHDFDMA as the surfactant in $scCO_2$ at 70 °C and 315±5 bar.

Table 4. Effect of the NVP concentration on the dispersion polymerization of NVP in scCO$_2$[a]

Entry	NVP (g)	Particles size (μm)[b]	PSD[c]	Morphology
M10	1.0	NA	NA	Irregular spherical
M11	2.0	0.36	1.05	Spherical
M12	3.0	0.31	1.02	Spherical
M13	4.0	0.30	1.02	Spherical

[a] Reaction conditions: 1.0 wt% of AIBN, 15.0 wt% of PHDFDMA, 70 °C, 315±5 bar, 24 h, with stirring

[b] Determined by FE-SEM

[c] Particle size distribution

ticles obtained with lower monomer were irregular in shape, but the resulting polymer obtained with higher monomer was agglomerated.

The particles had large particle sizes and some sticklike and elongated shapes when using 1.0 g NVP. When 2.0 g of NVP was used, PVP particles were very small, homogeneous, and discrete. The resulting polymer particles obtained with 3.0 g and 4.0 g of NVP were similar to those obtained with 2.0 g NVP, but some particles were not spherical.

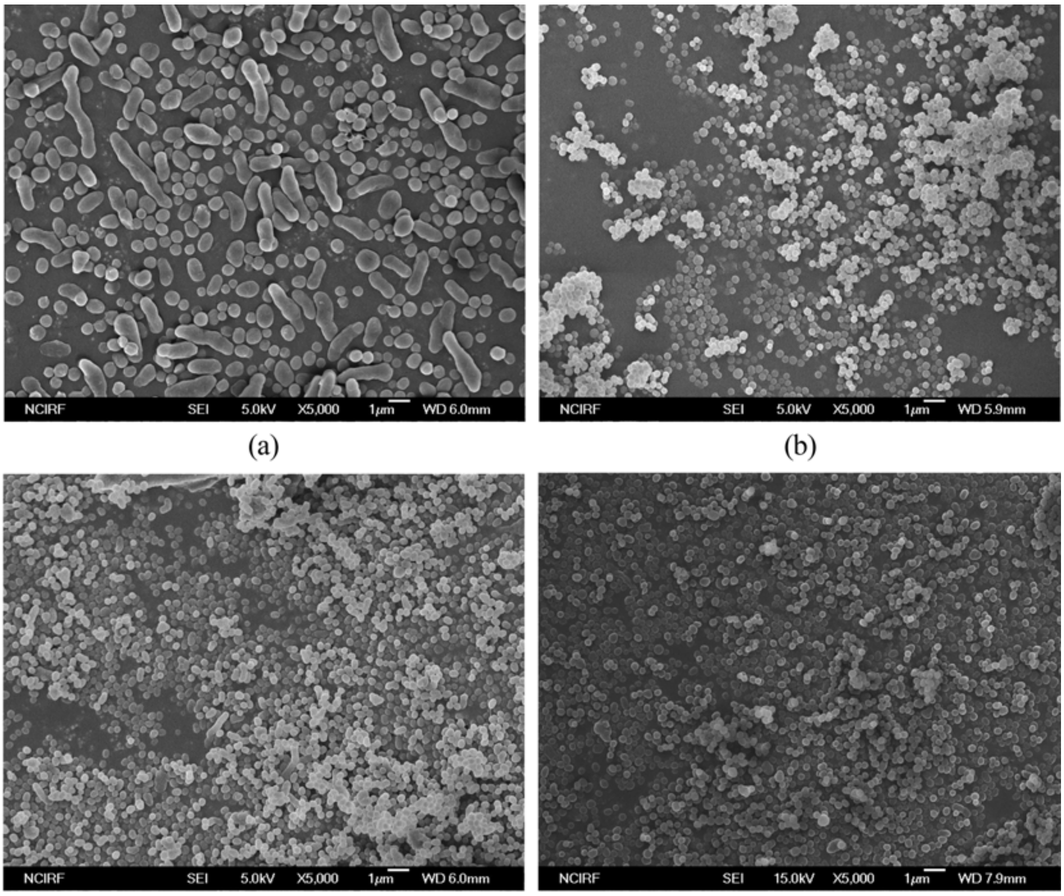
In general, results in the literature [21,22] have mentioned that the polymer particle size increased as the amount of monomer increased. However, size of PVP particles slightly decreased as amount of monomer increased from 2.0 g to 4.0 g.

CONCLUSION

The dispersion polymerization of NVP was performed in scCO$_2$ using the fluorine-based surfactant, PHDFDA or PHDFDMA. Particle morphology, size, and size distribution were characterized using FE-SEM and image analyzer. Spherical and micron-size PVP particles were successfully obtained with relatively narrow particle size distribution via dispersion polymerization in scCO$_2$ using PHDFDMA as a surfactant. Dispersion polymerization conditions, such as the concentration of the surfactant, initiator and monomer have to be controlled to obtain spherical and monodisperse polymer particles. In the case of PVP, more spherical, smaller size and narrower PSD particles were obtained when initiator 1.0 wt% on the monomer was used, as surfactant and monomer increased.

ACKNOWLEDGMENT

This work was supported by the BK21 project of the Ministry of Education and the Korea Science and Engineering Foundation (KOSEF) grant funded by Korea government (MEST) (No. 2009-



(a) (b)

(c) (d)

Fig. 6. SEM images of the PVP particles obtained with (a) 1.0 g, (b) 2.0 g, (c) 3.0 g, and 4.0 g NVP and 15.0 wt% PHDFDMA as the surfactant in scCO$_2$ at 70 °C and 315±5 bar.

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REFERENCES

1. J. M. DeSimone and W. Tumas, *Green chemistry using liquid and supercritical carbon dioxide*, Oxford University Press, Inc. (2003).
2. M. A. McHugh and V. J. Krukonis, *Supercritical fluid extraction: principle and practice*, 2nd Ed. Butterworth-Heinemann, Boston (1994).
3. A. I.Cooper, *J. Mater. Chem.*, **10**, 207 (2000).
4. E. J. Beckman, *J. Supercrit. Fluids*, **28**, 121 (2004).
5. J. L. Kendall, D. A. Canelas, J. L. Young and J. M. DeSimone, *Chem. Rev.*, **99**, 543 (1999).
6. D. A. Canelas, D. E. Betts and J. M. DeSimone, *Macromolecules*, **28**, 2818 (1996).
7. H. Shiho and J. M. DeSimone, *J. Polym. Sci., Part A: Polym. Chem.*, **37**, 2429 (1999).
8. C. M. Tseng, Y. Y. Lu, M. S. El-Aasser and J. W. Vanderhoff, *J. Polym. Sci., Part A: Polym. Chem. Ed.*, **24**, 2995 (1986).
9. S. Kawaguchi and K. J. Ito, *Adv. Poym. Sci.*, **175**, 299 (2005).
10. J. M. Saenx and J. M. Asua, *J. Polym. Sci., Part A: Polym. Chem.*, **33**, 1511 (2000).
11. T. Carson, J. Lizotte and J. M. DeSimone, *Macromolecules*, **33**, 1917 (2000).
12. A. Galia, A. Giaconia, V. Iaia and G. Filardo, *J. Polym. Sci., Part A: Polym. Chem.*, **42**, 173 (2004).
13. T. Beger, B. McGhee, U. Scherf and W. Steffen, *Macromolecules*, **33**, 3505 (2000).
14. S. Kwon, K. Lee, W. Bae and H. Kim, *J. Supercrit. Fluids*, **45**, 391 (2008).
15. J. Shin, W. Bae, Y.-W. Lee and H. Kim, *Korean J. Chem. Eng.*, **24**, 664 (2007).
16. J. Shin, K. S. Oh, W. Bae, Y.-W. Lee and H. Kim, *Ind. Eng. Chem. Res.*, **47**, 5680 (2008).
17. J. M. Saenx and J. M. Asua, *J. Polym. Sci., Part A: Polym. Chem.*, **33**, 1511 (2000).
18. J. Shin, W. Bae, Y.-W. Lee and H. Kim, *J. Chem. Eng. Data*, **51**, 1571 (2006).
19. J. Shin, W. Bae, H. Kim and Y.-W. Lee, *J. Chem. Eng. Data*, **53**, 1523 (2008).
20. W. Bae, S. Kwon, H. Byun and H. Kim, *J. Supercrit. Fluids*, **30**, 127 (2004).
21. Y. L. Hsiao, E. E. Maury, J. M. DeSimone, S. Mawson and K. P. Johnston, *Macromolecules*, **28**, 8159 (1995).
22. T. Carson, J. Lizotte and J. M. DeSimone, *Macromolecules*, **33**, 1917 (2000).