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Dispersion polymerization of *N*-vinyl caprolactam in supercritical carbon dioxide

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Abstract−Dispersion polymerization of *N*-vinyl caprolactam (NVCL) was carried out in supercritical carbon dioxide ($scCO_2$) using three surfactants. The polymerization was performed in the presence of fluorine-based poly(heptadecafluorodecyl acrylate) (PHDFDA), poly(heptadecafluorodecyl methacrylate) (PHDFDMA) or siloxane-based PDMS-*g*-pyrrolidonecarboxylic acid (Monasil PCA) as a surfactant. FE-SEM and image analyzer were used to characterize particle morphology, size, and size distribution. When fluorine-based surfactants were used, spherical PVCL particles were obtained. Using Monasil PCA resulted in agglomerated and irregular polymer particles. The effect of concentration of surfactants, initiators, and monomer, and reaction pressure on the particle morphology, average particle size and particle size distribution (PSD) was also investigated with fluorine-based surfactant, PHDFDA or PHDFDMA.

Key words: Supercritical Carbon Dioxide, *N*-vinyl Caprolactam, Dispersion Polymerization, Fluorine-based Surfactant

INTRODUCTION

Micron-size monodisperse polymer particles are used in various applications such as printer toners, packing materials for chromatography and biochemical analysis [1,2]. The preparation of microspheres has been an active research topic, because of the commercial and scientific interest in these particles. Dispersion polymerization has many advantages for preparation of spherical, monodisperse polymer particles from 0.1 μm to 10 μm in diameter. In particular, dispersion polymerization is a more attractive method compared to other heterogeneous polymerization methods such as emulsion and suspension polymerization to prepare micron-size polymer particles in a single step [3].

Dispersion polymerization in supercritical carbon dioxide ($scCO_2$) has been extensively studied over the past decade [4-7], since the environmental friendly properties of the supercritical carbon dioxide ($scCO_2$) have been widely recognized [8-10]. $ScCO_2$ is considered a useful alternative to organic solvents for polymer synthesis and processing because it has relatively mild critical conditions (T_c= 31.1 °C, P_c=73.8 bar) and tunable physical properties, is non-flammable, non-toxic, and relatively inert properties. In general, low molecular weight alcohols or alkanes were used as continuous phase in dispersion polymerization. However, when CO_2 was alternatively used as a solvent, drying or devolatilization was easy to separate polymer powder from the continuous phase [10].

Poly (*N*-vinyl caprolactam) (PVCL) is one of the synthetic tem-

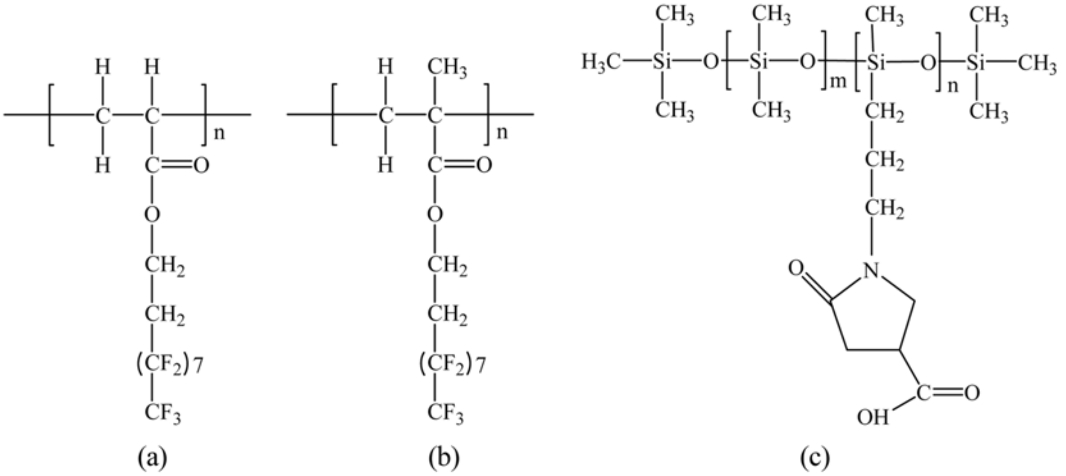

Fig. 1. Chemical structures of surfactants: (a) PHDFDA, (b) PHDFDMA, and (c) Monasil PCA.

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perature-sensitive polymer which can easily form thermally reversible hydrogels under mild conditions, in particular by raising the temperature from 20 to 37-40 °C [11]. In addition, PVCL has characteristics such as water-solubility, non-adhesiveness, thermal sensitivity, and biocompatibility. These properties are utilized in the field of the UV-curable adhesive, synthetic resin in stereotypes, and intermediate for preparing some organic compounds [12-16].

In this work, dispersion polymerization was carried out using $scCO_2$ to prepare the PVCL particles. The polymerization was performed in the presence of fluorine-based poly(heptadecafluorodecyl acrylate) (PHDFDA), poly(heptadecafluorodecyl methacrylate) (PHDFDMA) or siloxane-based PDMS-*g*-pyrrolidonecarboxylic acid (Monasil PCA) as a surfactant. The effects of concentration of surfactant, initiator, monomer, and reaction pressure on the particle morphology, average particle size, and particle size distribution (PSD) were investigated.

EXPERIMENTS

1. Materials

N-vinyl caprolactam (NVCL, min. 98%), 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 dissolved oxygen was removed by nitrogen purging. Poly (heptadecafluorodecyl acrylate) (PHDFDA) and poly(heptadecafluorodecyl methacrylate) (PHDFDMA) were prepared by solution polymerization in $scCO_2$ at 70.0 °C and 300 bar. PDMS-*g*-pyrrolidonecarboxylic acid (Monasil PCA, Uniqema) was used without further purification. The chemical structures of the surfactants are illustrated in Fig. 1. 2,2′-azobisisobutyronitrile

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

Entry	Surfactant	Particles size (μm)[b]	PSD[c]	Morphology
S1	PHDFDA	0.47	1.06	Spherical
S2	PHDFDMA	0.45	1.07	Spherical
S3	Monasil PCA	NA	NA	Agglomerated

[a] Reaction conditions: 2.0 g of NVCL, 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

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

Entry	Surfactant (wt%)		Particles size (μm)[b]	PSD[c]	Morphology
P1	-	0.0	NA	NA	-
A1	PHDFDA	3.0	NA	NA	Agglomerated
A2		5.0	1.44	1.03	Spherical
A3		10.0	0.67	1.05	Spherical
A4		15.0	0.47	1.06	Spherical
M1	PHDFDMA	5.0	NA	NA	Agglomerated
M2		10.0	0.56	1.05	Spherical
M3		15.0	0.45	1.07	Spherical

[a] Reaction conditions: 2.0 g of NVCL, 1.0 wt% of AIBN, 70 °C, 315±5 bar, 24 h, with stirring

[b] Determined by FE-SEM

[c] Particle size distribution

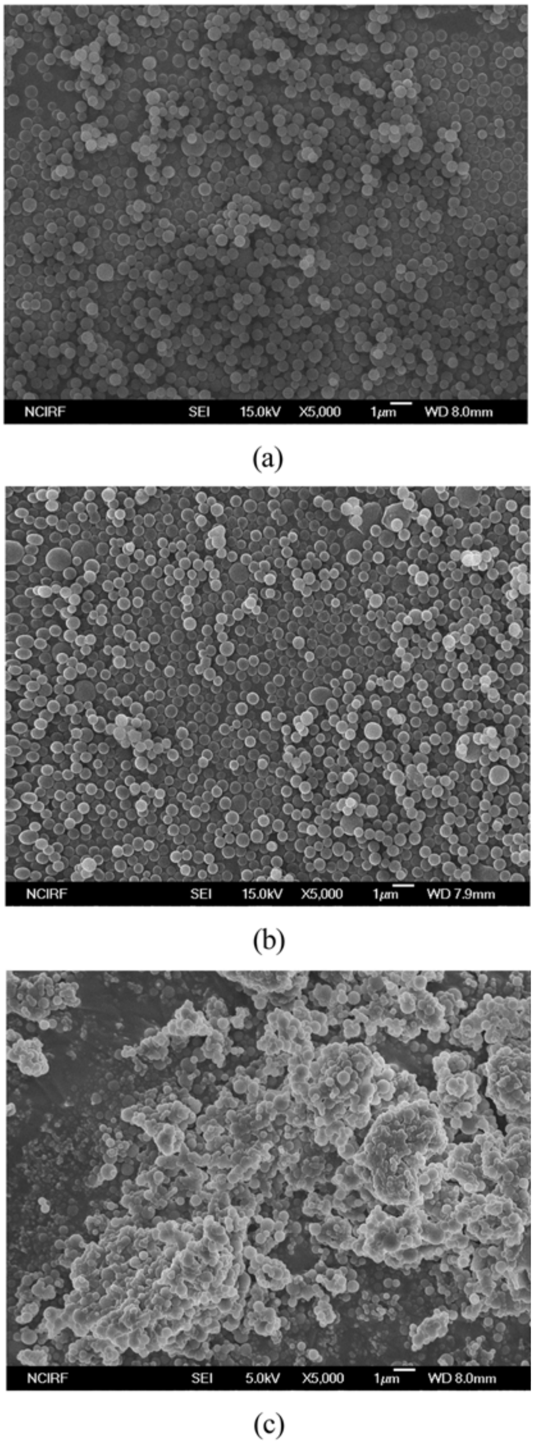
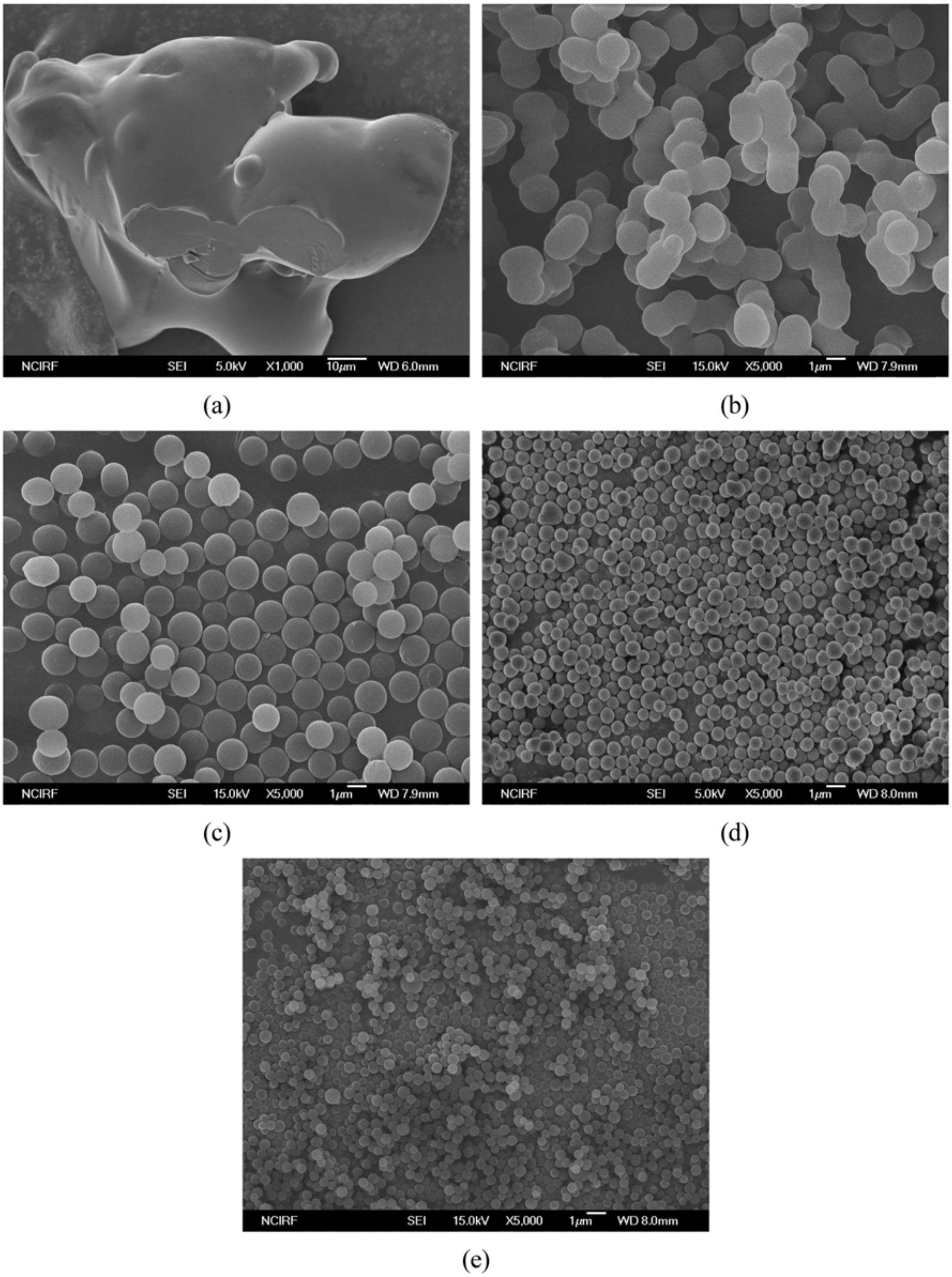


Fig. 2. SEM images of the PVCL particles obtained with 15.0 wt% (a) PHDFDA, (b) PHDFDMA, and (c) Monasil PCA as the surfactant in $scCO_2$ at 70 °C and 315±5 bar.

(AIBN, min. 98%), obtained from Junsei Chemical, was recrystallized from methanol. Carbon dioxide (min. 99.99%) was purchased from Korea industrial gases.

2. Apparatus and Procedures

Dispersion polymerization of NVCL was carried out in a 30-mL SUS 316 reactor [17]. 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 300-mL reservoir between pump and reactor. Pressure inside the reactor was measured by a pressure transducer (Data Instruments



(a) (b) (c) (d) (e)

Fig. 3. SEM images of the PVCL particles obtained with (a) 0.0 wt%, (b) 3.0 wt%, (c) 5.0 wt%, (d) 10.0 wt%, and (e) 15.0 wt% PHDFDA as the surfactant in scCO$_2$ at 70 °C and 315±5 bar.

Inc. Model AB/HP, accuracy 0.25%) and 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).

The reactor was charged with 1.0-6.0 g of NVCL, AIBN (1.0-4.0 wt% relative to the total monomer) and surfactant (3.0-15.0 wt% relative to the total monomer). Then, the reactor was purged using 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 to agitate the reaction mixture. After polymerization was completed, the reactor was cooled below 20 °C. When the reactor pressure had decreased to approximately 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 under 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, determined by measuring the diameter of 150-200 particles. Number-average (D_n) and weight-average (D_w) particle diameters were calculated from the following equations [2].

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

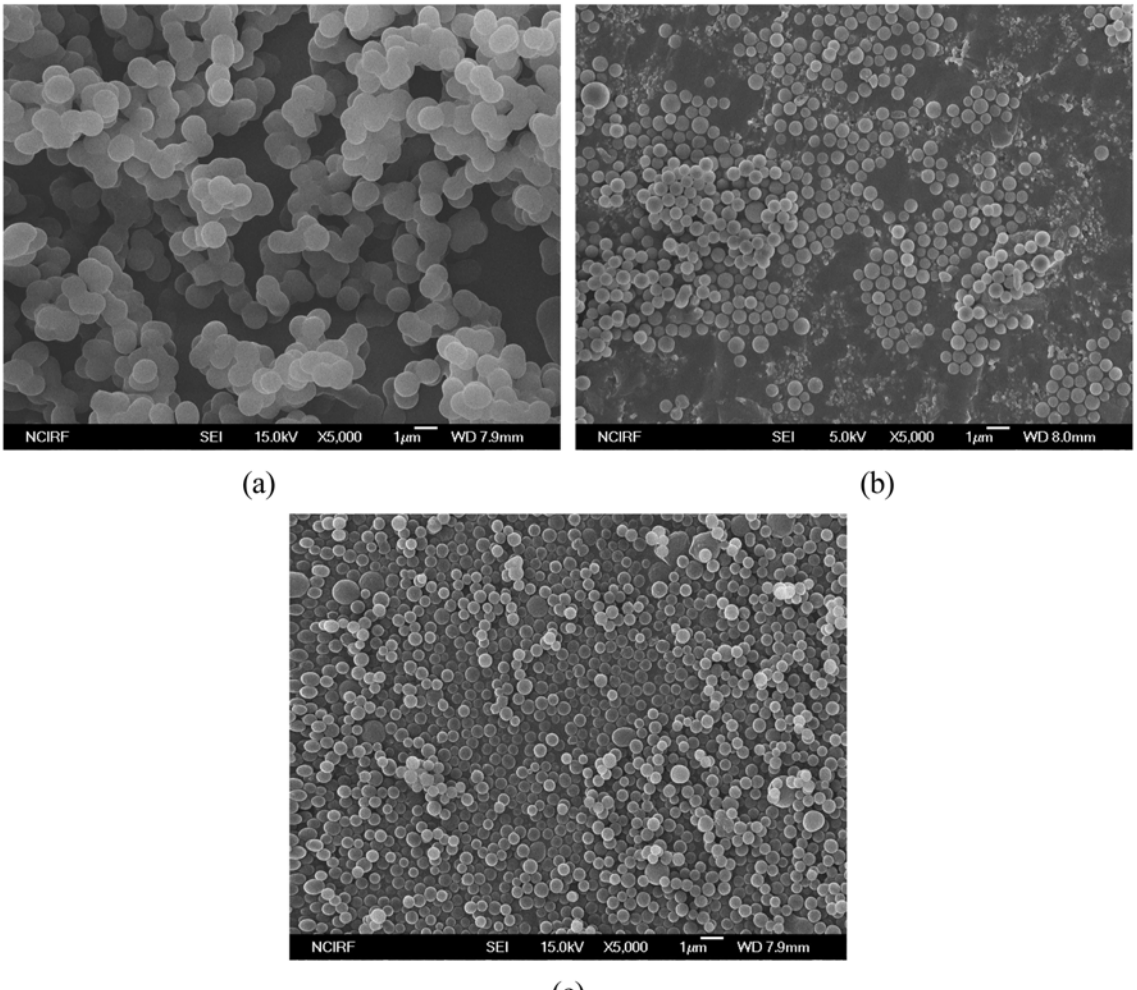
$$D_w = \frac{\Sigma_{i=1}^{N} d_i^4}{\Sigma_{i=1}^{N} d_i^3} \tag{2}$$

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) that indicates the particle size distribution (PSD) is defined as D_w/D_n.

RESULTS AND DISCUSSIONS

1. Effect of the Surfactant Structure

The choice of surfactant is very important in dispersion poly-



(a) (b) (c)

Fig. 4. SEM images of the PVCL particles obtained with (a) 5.0 wt%, (b) 10.0 wt%, and (c) 15.0 wt% PHDFDMA as the surfactant in $scCO_2$ at 70 °C and 315±5 bar.

merization in $scCO_2$. To investigate the effect of the surfactant structure, NVCL was polymerized with two fluorine-based polymer surfactants, PHDFDA and PHDFDMA, and siloxane-based polymer surfactant, namely Monasil PCA under the same reaction conditions, 70 °C and 315±5 bar for 24 h. For dispersion polymerization, surfactant and monomer have to be dissolved in CO_2 at the previously given conditions. The solubility of the three surfactants and monomer in CO_2 was measured in a previous study [18-21]. From the solubility data, we confirmed that all surfactants and the monomer are soluble in CO_2 under the NVCL polymerization conditions. Table 1 and Fig. 2 show the results obtained with different surfactants. Spherical and uniform PVCL particles of average particle size 0.45-0.47 μm were obtained with fluorine-based surfactants. The results using Monasil PCA were agglomerated and irregular particles. To obtain spherical PVCL particles in $scCO_2$, the fluo- they are more suitable surfactants than Monasil PCA.

2. Effect of the Surfactants Concentration

The results for the dispersion polymerization of NVCL in $scCO_2$ with different concentration of fluorine-based surfactants, PHDFDA and 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 PVCL particles obtained with different concentrations of PHDFDA and PHDFDMA, respectively. The result obtained from precipitation polymerization in the absence of surfactant has not formed particles as shown in Fig. 3(a). And the particles obtained with 3.0 wt% PHDFDA and 5.0 wt% PHDFDMA were a formation of coalesced particles (Fig. 3(b) and Fig. 4(a)). The average particle size decreased and particle size distri-

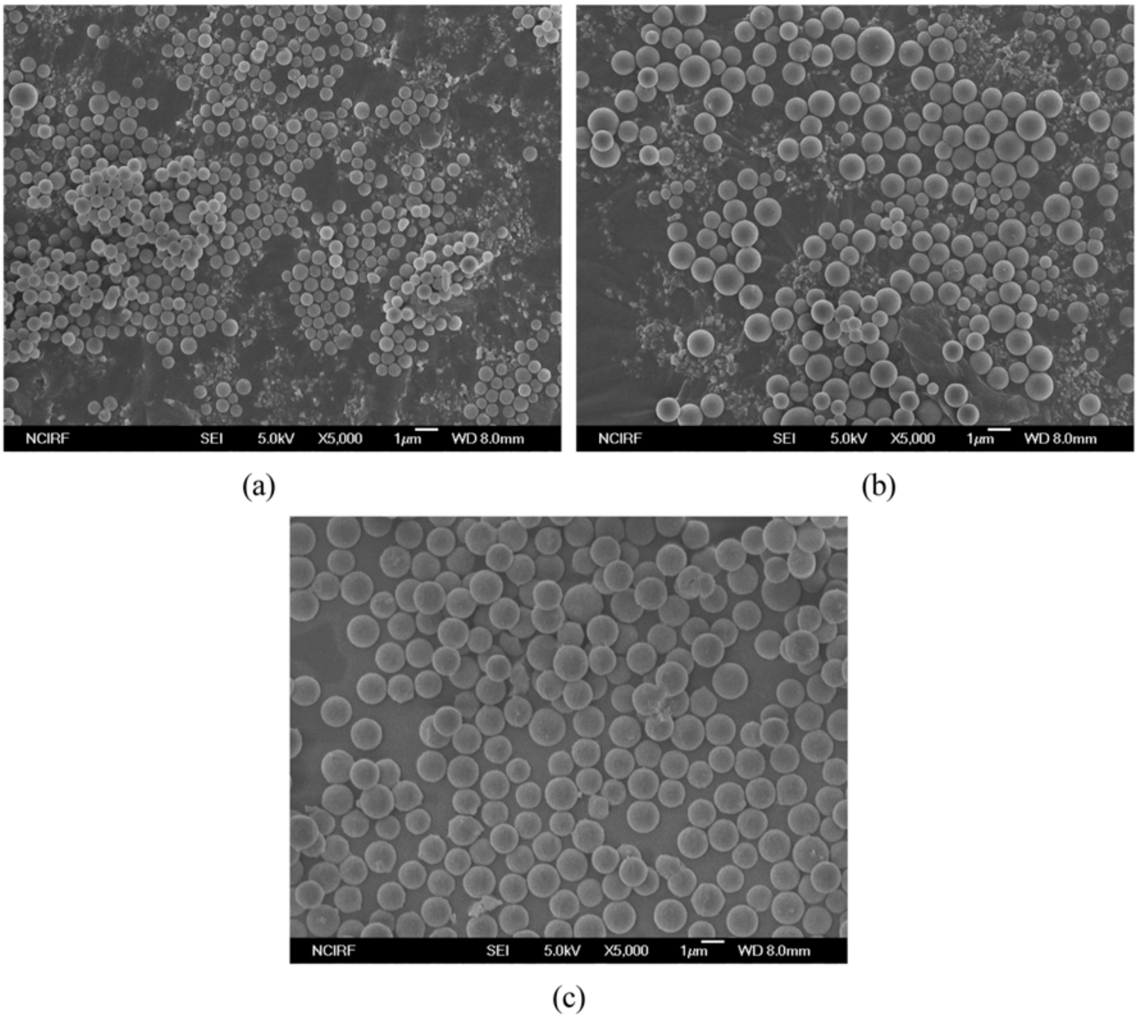
Table 3. Effect of the AIBN concentration on the dispersion polymerization of NVCL in $scCO_2$[a]

Entry	AIBN (wt%)	Particles size (μm)[b]	PSD[c]	Morphology
M4	1.0	0.56	1.05	Spherical
M5	2.0	0.83	1.20	Spherical
M6	4.0	1.20	1.03	Spherical

[a] Reaction conditions: 2.0 g of NVCL, 10.0 wt% of PHDFDMA, 70 °C, 315±5 bar, 24 h, with stirring

[b] Determined by FE-SEM

[c] Particle size distribution



(a) (b)

(c)

Fig. 5. SEM images of the PVCL particles obtained with (a) 1.0 wt%, (b) 2.0 wt%, and (c) 4.0 wt% AIBN as the initiator and 10.0 wt% PHDFDMA as the surfactant in $scCO_2$ at 70 °C and 315±5 bar.

bution (PSD) slightly increased as surfactant concentration increased, as shown in Table 2, Figs. 3, and 4.

3. Effect of the Initiator Concentration

The dispersion polymerizations 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 0.2 g (10.0 wt% on the monomer) and 2.0 g, respectively. The average particle size increased as initiator increased from 1.0 wt% to 4.0 wt% as shown in Table 3 and Fig. 5. This trend has been reported in the literature for the dispersion polymerization of styrene [22,23], methyl methacrylate [24] and 1-vinyl-2-pyrrolidone [25] in organic solvent.

4. Effect of the Monomer Concentration

In addition, the effect of monomer concentration was studied,

Table 4. Effect of the NVCL concentration on the dispersion polymerization of NVCL in $scCO_2$[a]

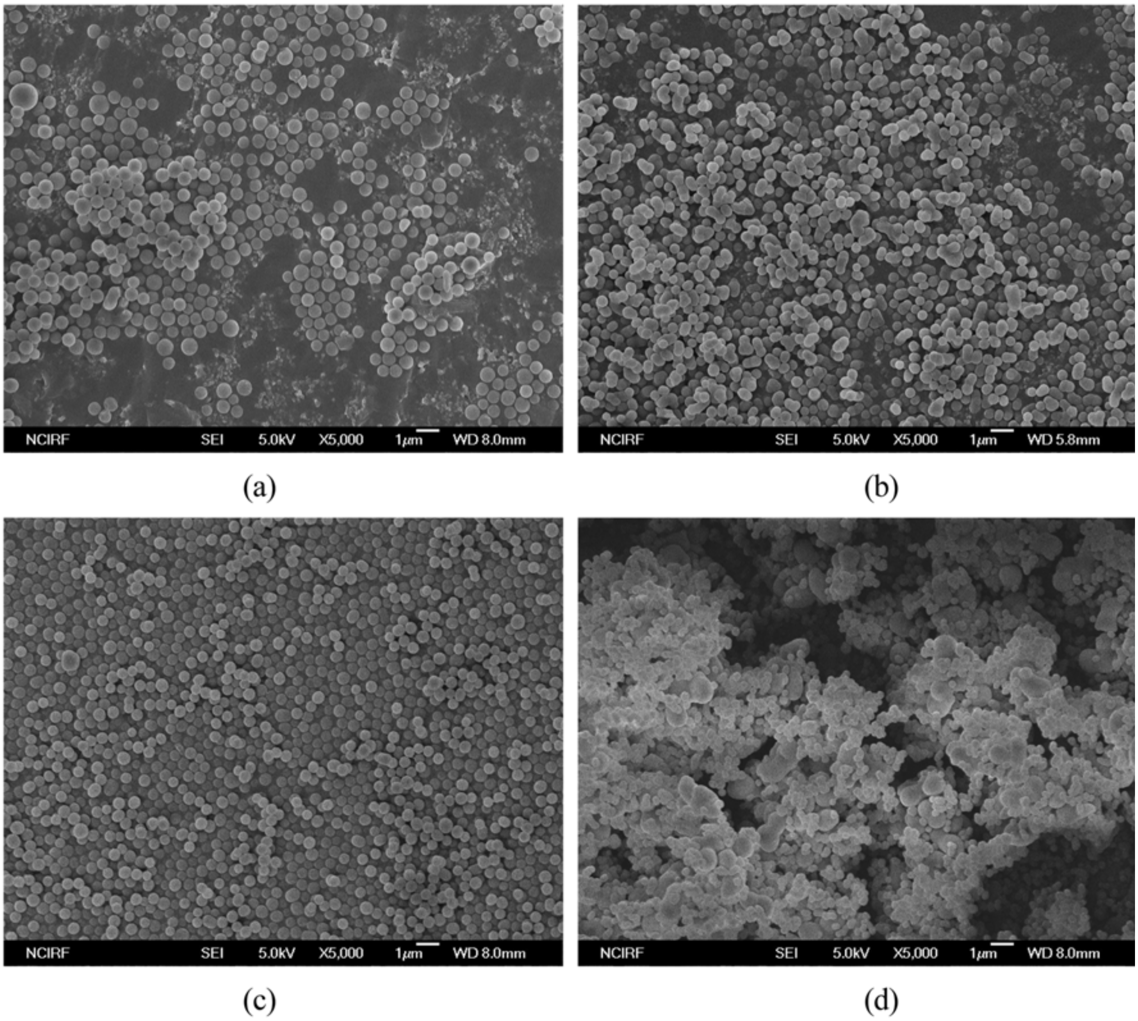
Entry	NVCL (g)	Particles size (μm)[b]	PSD[c]	Morphology
M7	1.0	NA	NA	-
M8	2.0	0.56	1.05	Spherical
M9	3.0	0.41	1.08	Spherical
M10	4.0	0.45	1.02	Spherical
M11	6.0	NA	NA	Agglomerated

[a]Reaction conditions: 1.0 wt% of AIBN, 10.0 wt% of PHDFDMA, 70 °C, 315±5 bar, 24 h, with stirring
[b]Determined by FE-SEM
[c]Particle size distribution

Table 5. Effect of the polymerization pressure on the dispersion polymerization of NVCL in $scCO_2$[a]

Entry	Pressure (bar)	Particles size (μm)[b]	PSD[c]	Morphology
M12	210	NA	NA	Irregular spherical
M13	250	0.83	1.32	Spherical
M14	280	1.02	1.07	Spherical
M15	320	0.56	1.05	Spherical
M16	345	0.70	1.02	Spherical

[a]Reaction conditions: 2.0 g of NVCL, 1.0 wt% of AIBN, 10.0 wt% of surfactant, 70 °C, 315±5 bar, 24 h, with stirring
[b]Determined by FE-SEM
[c]Particle size distribution

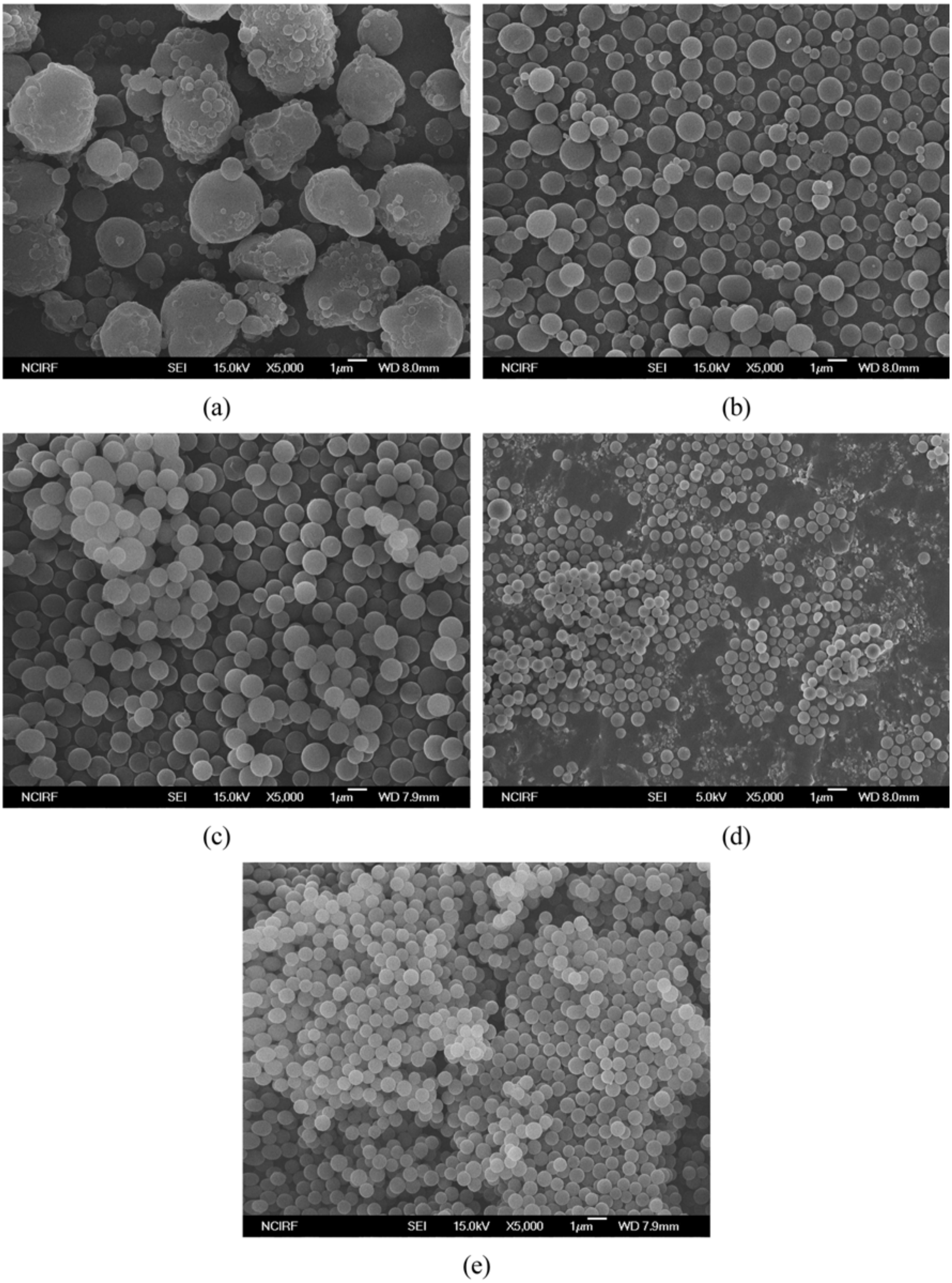


(a) (b) (c) (d)

Fig. 6. SEM images of the PVCL particles obtained with (a) 2.0 g, (b) 3.0 g, (c) 4.0 g, and 6.0 g NVCL and 10.0 wt% PHDFDMA as the surfactant in $scCO_2$ at 70 °C and 315±5 bar.

and the polymerization results of PVCL from these reactions are given in Table 4 and Fig. 6. The PHDFDMA surfactant 10.0 wt% and initiator 1.0 wt% on the monomer were added to the reactor.

The polymerization reaction could not be performed when amount of NVCL monomer was 1.0 g. When monomer 6.0 g was also used, the resulting polymers were nearly spherical and highly aggregated. In general, results published in literature [26,27] have mentioned that the polymer particle size increased as the amount of monomer increased. However, PVCL particles showed similar size when amount of monomer was 2, 3, and 4 g.



(a) (b) (c) (d) (e)

Fig. 7. SEM images of the PVCL particles obtained with 10.0 wt% PHDFDMA at 70 °C, (a) 210 bar, (b) 250 bar, (c) 280 bar, (d) 320 bar, and (e) 345 bar.

5. Effect of the Reaction Pressure

Table 5 and Fig. 7 show the effect of the polymerization pressure on the dispersion polymerization. The amount of monomer, PHDFDMA surfactant, and initiator was kept constant at 2.0 g, 0.2 g (10.0 wt% on the monomer), and 0.02 g (1.0 wt% on the monomer), respectively. In all cases, polymerization temperature was 70.0± 0.5 °C at varying pressure from 210 to 345 bar.

More spherical and more monodisperse PVCL particles were obtained as pressure increased. When pressure was 210 bar where PHDFDMA and NVCL are insoluble in CO_2, PVCL particle size distribution (PSD) was very broad and size was larger than those obtained at higher pressure. However, when pressure was 250 bar where PHDFDMA and NVCL are totally soluble CO_2, resulting particles were much smaller and PSD was more narrow even though pressure slightly changed. From pressure 280 bar to 320 bar, the resulting particles had smaller particle size and narrower PSD.

CONCLUSION

Dispersion polymerization of NVCL was performed using fluorine-based surfactant, PHDFDA or PHDFDMA, or siloxane-based surfactant, Monasil PCA in $scCO_2$. Particle morphology, size, and size distribution were characterized by FE-SEM and image analyzer.

Spherical and micron-size PVCL particles were successfully obtained with relatively narrow particle size distribution via dispersion polymerization in $scCO_2$ using fluorine-based surfactants, PHDFDA, or PHDFDMA. Using Monasil PCA resulted in a polymer agglomerated and irregular particles. There are various factors that have an effect on the particle morphology, average particle size, and particle size distribution. Therefore, to obtain spherical and monodisperse polymer particles dispersion polymerization condition, such as the concentration of the surfactant, initiator and monomer, and reaction pressure have to be controlled. More spherical, smaller size, narrower PSD PVCL particles were obtained when using fluorine-based surfactants, and as surfactant increased, initiator decreased and pressure increased.

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