Colloid Polym Sci (2009) 287:179–188
DOI 10.1007/s00396-008-1961-4

ORIGINAL CONTRIBUTION

Synthesis of monodispersed poly(acrylonitrile) microspheres by dispersion polymerization in compressed liquid dimethyl ether

Dong Woo Cho · Kyoung Shil Oh · Won Bae · Hwayong Kim · Youn-Woo Lee

Received: 5 September 2008 / Revised: 17 October 2008 / Accepted: 25 October 2008 / Published online: 21 November 2008

Abstract In this study, monodispersed spherical particles of poly(acrylonitrile) were synthesized via dispersion polymerization in compressed liquid dimethyl ether using 2,2′-azobisisobutyronitrile (AIBN) as an initiator and five kinds of surfactants: PDMS-*g*-pyrrolidonecarboxylic acid (Monasil PCA™), PDMS modified surfactants, SS-5050K™, KF-6017™, poly(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10- heptadecafluorodecyl acrylate), and poly(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl methacrylate). Using Monasil PCA as a surfactant, uniform and spherical polymer particles were generated. The size of the microsphere particles was reduced via an increase in the concentration of Monasil PCA and a reduction in the monomer concentration. Increases in the concentration of AIBN resulted in a broad distribution of microspheres. Reaction temperature and pressure did not exert significant effects on the size and size distribution of the polymer particles.

Keywords Dispersion polymerization · DME · Acrylonitrile · Dimethyl ether · Polymer particle

D. W. Cho · K. S. Oh · H. Kim · Y.-W. Lee (✉)
School of Chemical and Biological Engineering,
Seoul National University,
599 Gwanangno, Gwanak-gu,
Seoul 151-744, South Korea
e-mail: ywlee@snu.ac.kr

W. Bae
R&D Institute, Miwon Commercial Co.,
Ltd 405-3, Mokane-dong, Ansan-si,
Gyounggi 425-100, South Korea

Introduction

Poly (acrylonitrile) (PAN) microspheres are an interesting polymer for engineering applications, including enzyme immobilization, carbon sources, separation processes, and pigments [1–6]. In order to generate the spherical PAN particles, many research groups have developed dispersion polymerization techniques, largely due to the simplicity of such methods [7–9].

Some groups have developed methods in which organic solvents employed traditionally by the polymer industry can be utilized. The use of such common organic solvents, though, has been associated with several problems, including waste treatment and product separation disadvantages.

In the past decade, DeSimone and others have developed a dispersion polymerization technique involving the use of supercritical carbon dioxide, which has been recognized as an attractive replacement for general solvents [10–13]. This is also an appealing approach because carbon dioxide is an inexpensive, non-toxic, non-flammable, and environmentally benign substance. However, supercritical carbon dioxide evidences low solubility for high molecular weight or polar monomeric materials because of its low dielectric constant and lack of dipole moment when used as a medium. In addition, the use of supercritical carbon dioxide requires high pressure for dispersion polymerization. This causes the necessary apparatus to be quite costly. In an effort to circumvent these issues, we have attempted to apply dimethyl ether (DME) to the polymerization medium [14, 15].

DME is a volatile organic compound (VOC), which is flammable, non-toxic, and eco-friendly [16, 17]. A variety of monomers can be dissolved in the compressed liquid phase of DME due to its chemically polar property (μ=1.3 Debye) [18]. Therefore, it is possible to conduct polymer-

ization in compressed liquid DME under milder conditions than can be utilized in the supercritical carbon dioxide approach. Our research group has successfully developed a dispersion polymerization method using *N*-vinylcarbazole [14] and 2-hydroxyethyl methacrylate [15] in compressed liquid DME as a solvent.

In this study, the dispersion polymerization of acrylonitrile was conducted in compressed liquid DME in order to manufacture spherical polymer particles with changing surfactant types, surfactant concentrations, initiators, monomers, and polymerization pressures.

Experiment

Materials

DME (purity of 99.99%) was acquired from LG Chem. Acrylonitrile (min 99%) was purchased from Aldrich. 2,2′-Azobisisobutyronitrile (AIBN; min 98%) was purchased from Junsei Chemical and purified via recrystallization from methanol. PDMS-*g*-pyrrolidone carboxylic acid (Monasil PCA), SS-5050K, and KF-6017 were all obtained from Uniquema, Nihon Emulsion, and Shin-Etsu Silicone, respectively. 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Heptadecafluorodecyl acrylate (HDFDA) and 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl methacrylate (HDFDMA) were purchased from Aldrich. Poly(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl acrylate) (poly(HDFDA)) and poly(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl methacrylate)(poly(HDFDMA)) were prepared via solution polymerization in supercritical carbon dioxide at 70 °C and a pressure of 300 bar [19]. Figure 1 shows the chemical structure of Monasil PCA, SS-5050K, KF-6017, poly(HDFDA), and poly(HDFDMA).

Polymerization apparatus and procedure

A schematic diagram of the polymerization apparatus is provided in previous work [14, 15]. Dispersion polymerization of acrylonitrile was conducted in a 30-ml SUS 316 reactor. The reaction pressure was measured using a Bourdon tube pressure gauge (WIKA, type 213.53.063,

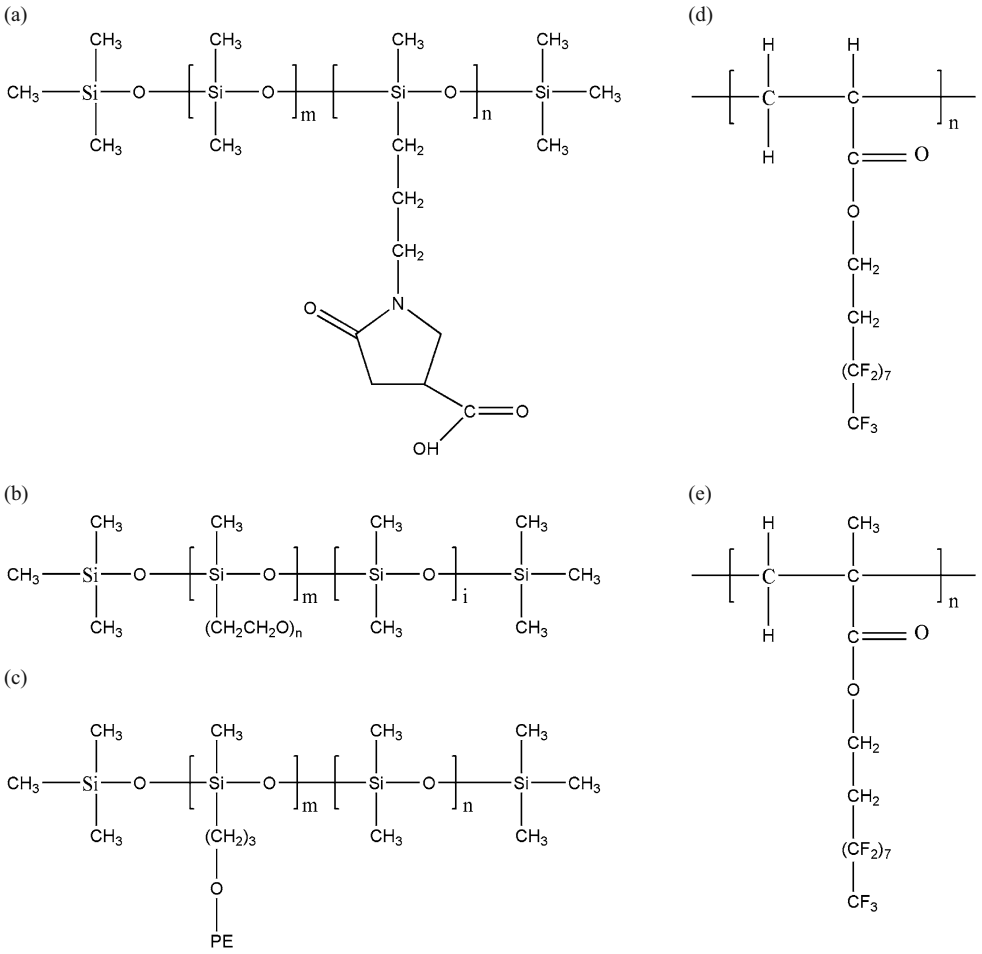

Fig. 1 Chemical structure of **a** Monasil PCA, **b** SS-5050K, **c** KF-6017, **d** poly(HDFDA), and **e** poly (HDFDMA)

accuracy class 1.0). The reaction temperature was measured using a K(CA) type thermocouple and indicator (Hanyoung Electronics Inc. Model DX-7; accuracy 0.05 °C).

The reactant consists of the desired quantity of acrylonitrile as a monomer, AIBN as an initiator, and a surfactant such as poly(HDFDMA), poly(HDFDA), Monasil PCA, SS-5050K, and KF-6017, all of which were introduced to the reactor. After assembling the reactor, the reactor was purged with DME. The reactor was placed in an ice water bath and cooled to below 10 °C, then filled with DME using a small high-pressure bomb. The reactor was heated to the desired temperature, followed by the final pressurization or desired pressure. As the monomer, initiator, and surfactant were dissolved in compressed liquid DME, the mixture constituted a homogenous phase at the beginning state of polymerization. As time elapsed, the mixture within the reactor became hazy and eventually turned into a polymer.

Polymerization was conducted at the desired temperature and desired pressure for 24 h with stirring. After completion of the polymerization, the reactor was cooled to below 10 °C. The solution phase was separated into two phases—vapor and liquid. DME was vented from the vapor phase through two glass traps. In order to prevent the exhaust of unreacted monomer to the atmosphere during DME venting, the glass traps were filled with methanol. The polymer particles were washed with methanol or hexane in order to remove the unreacted monomer and remaining surfactant. The final polymer particle was then dried in vacuo at room temperature.

Polymer characterization

Particle morphology was characterized using a field emission scanning electron microscope (FE-SEM; Jeol 5410LV). The number-average particle size and the particle size distribution (PSD) were assessed with an image analyzer (TDI Scope Eye™ ver 3.1) with FE-SEM images. The number-average particle diameter (D_n) and the weight-average particle diameter (D_w) were calculated via the following equation:

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

$$D_w = \frac{\sum_{i=1}^{N} d_i^4}{\sum_{i=1}^{N} d_i^3}$$

where d_i is the diameter of particle i, and n is the total number of particles measured in the SEM images. The PSD indicating the polydispersity index is defined as D_w/D_n.

Results and discussion

Effect of the surfactant type

The surfactant plays a significant role in successful dispersion polymerization. The surfactant should be dissolved in the solvent to perform its functions properly. Prior to performing the dispersion polymerization, the phase behavior of the surfactant and DME binary mixture systems were assessed to determine whether the mixture systems were in homogenous phase. The experiments were conducted with typical variable volume cells at surfactant concentrations of 5.0±0.5 wt.% and at temperatures from 40 °C to 80 °C [20]. In accordance with the phase behavior data, the surfactants and DME binary mixture systems were found to be in homogeneous phase at 70 °C and 20 bar [15]. In addition, acrylonitrile was dissolved in DME under identical conditions (70 °C and 20 bar).

In an effort to assess the effects on the chemical structure of the surfactant, acrylonitrile was polymerized in compressed liquid DME with fluorine-based polymer surfactants, poly(HDFDA) and poly(HDFDMA), and siloxane-based polymer surfactants, Monasil PCA, SS-5050K, and KF-6017 under identical reaction conditions at 70 °C and 20 bar. Table 1 shows the data for the polymerization of

Table 1 Effect of the chemical structure of surfactant on the dispersion polymerization of acrylonitrile in compressed liquid DME[)]

Entry	Surfactant	Particle size (μm)[a]	PSD[b]	Particle morphology
DPAN1	Monasil PCA	0.40	1.04	Spherical
DPAN2	SS-5050K	–	–	Irregular
DPAN3	KF-6017	–	–	Irregular
DPAN4	Poly(HDFDA)	–	–	Irregular
DPAN5	Poly(HDFDMA)	–	–	Irregular

Reaction condition: 2.0 g of acrylonitrile, 1.0 wt.% of AIBN, 15.0 wt.% of surfactant, 20±5 bar, 70 °C, 24 h, with stirring
[a] Determined by FE-SEM
[b] Particle size distribution

acrylonitrile in compressed liquid DME using various surfactants with 15.0 wt.% (based on the monomer). Figure 2 shows the SEM images of the resultant polymer particles. In the case of the fluorine-based surfactants, spherical polymer particles did not accumulate. We assumed that the poor results were attributable to the inefficient anchoring of poly(HDFDMA) and poly(HDFDA) to the surfaces of the PAN particles because the head and tail groups of poly (HDFDMA) and (HDFDA) are DME-philic. As compared to the siloxane-based surfactants, monodispersed polymer particles were manufactured. In the case of KF-6017, spherical PAN particles were manufactured, but the size distribution was wider than that observed with Monasil PCA. When SS-5050K and KF-6017 were used as the surfactants, uniform microspheres were not generated due to the weak interaction occurring between the surfactant and the polymer surface. When Monasil PCA is used, the uniform microspheres were formed. Monasil PCA has two directly opposed functional groups, DME-philic and DME-phobic group. The micelles have the two kinds of strong interactions, between the surfactant and polymer and between the surfactant and solvent. Such strong interactions have a positive effect on the formation of micelle.

Effect of surfactant concentration

As shown in "Effect of the surfactant type", Monasil PCA is one of the most suitable surfactants for the production of the monodispersed PAN microspheres in compressed liquid DME. The surfactant concentration is the most crucial

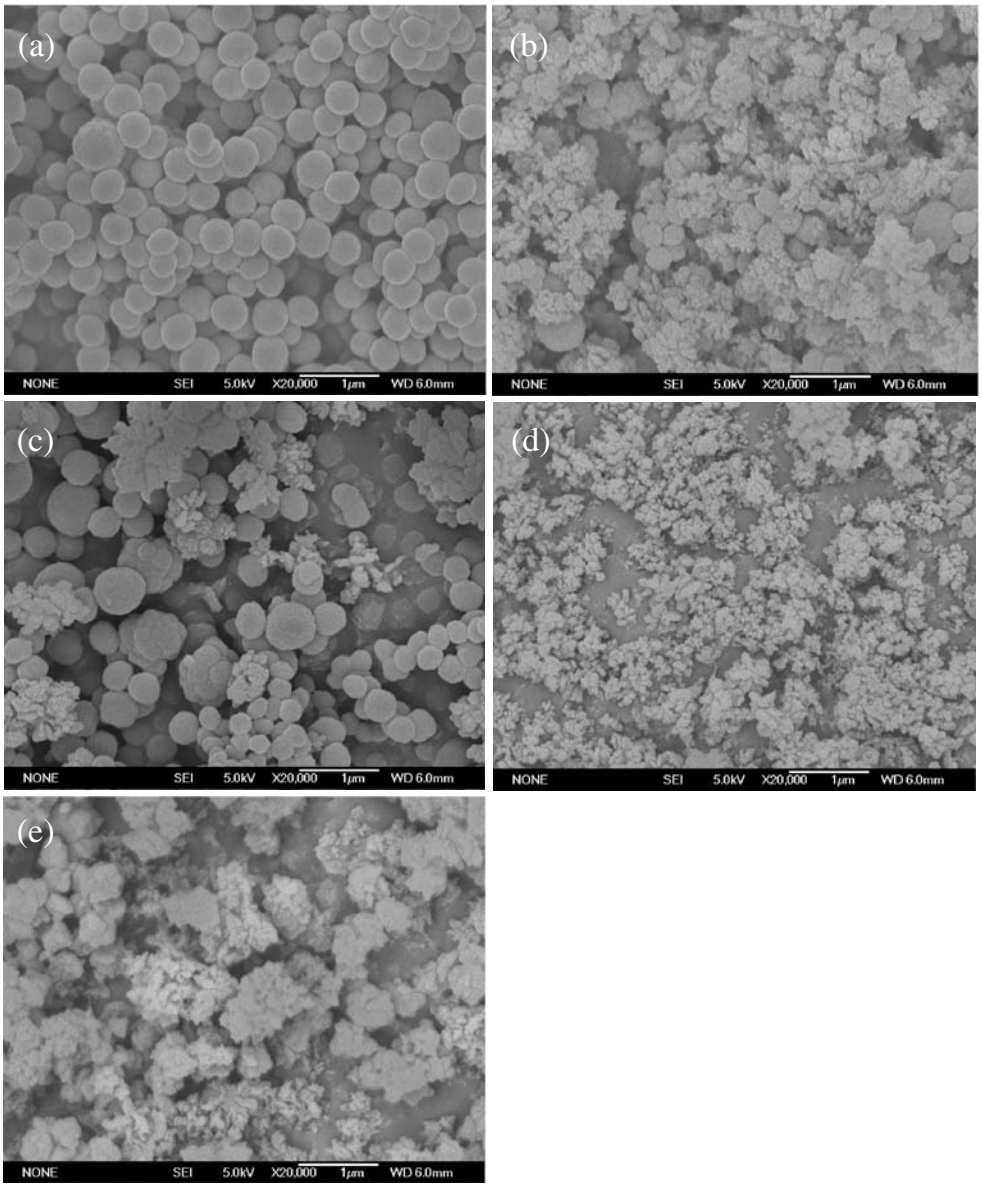

Fig. 2 The SEM images for the polymer particle synthesized with changing the surfactant type, **a** Monasil PCA, **b** SS-5050K, **c** KF-6017, **d** poly (HDFDA), and **e** poly (HDFDMA)

Table 2 Effect of the Monasil PCA concentration on the dispersion polymerization of acrylonitrile in compressed liquid dimethyl ether

Entry	Surfactant concentration (wt.%)	Particle size (μm)[a]	PSD[b]	Particle morphology
PAN6	5	–	–	Irregular
PAN7	10	–	–	Irregular
PAN8	15	0.40	1.04	Spherical
PAN9	20	0.35	1.01	Spherical
PAN10	25	0.34	1.01	Spherical

Reaction condition: 2.0 g of acrylonitrile, 1.0 wt.% of AIBN, 20±5 bar, 70 °C, 24 h, with stirring
[a] Determined by FE-SEM
[b] Particle size distribution

factor in controlling the particle size and PSD. Dispersion polymerization was conducted at five different concentrations of Monasil PCA. Table 2 and Fig. 3 show the data for the polymer particles obtained in this work, as well as the SEM images. Under the experimental conditions using 5 and 10 wt.% surfactant, the particles formed were neither uniform nor spherical. The amount of surfactant was insufficient for the micelles to generate the polymer

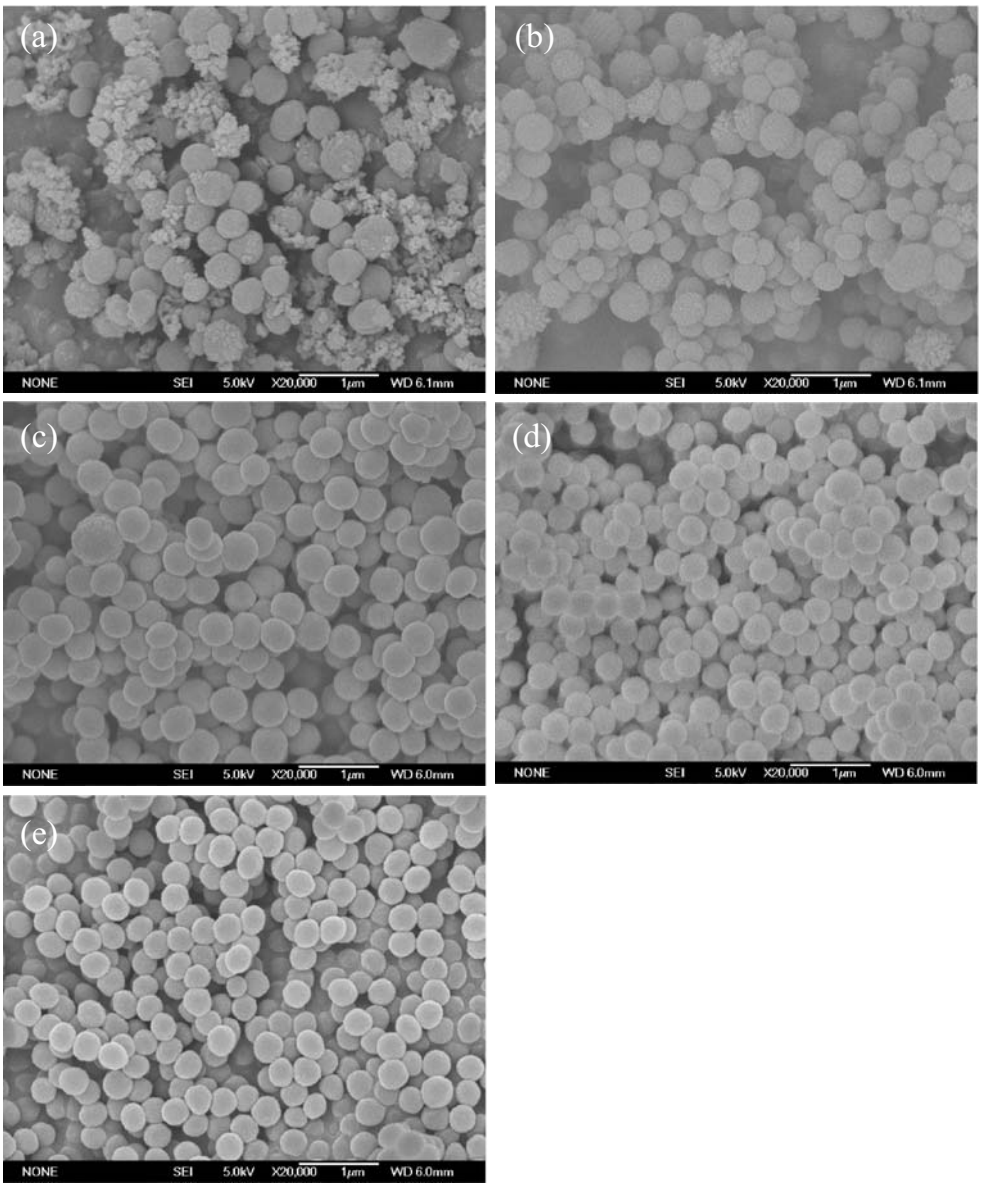

Fig. 3 The SEM images for the polymer particle synthesized with changing the Monasil PCA concentration, **a** 5, **b** 10, **c** 15, **d** 20, and **e** 25 wt.%

Table 3 Effect of the AIBN concentration on the dispersion polymerization of acrylonitrile in compressed liquid dimethyl ether

Entry	AIBN concentration (wt.%)	Particle size (μm)[a]	PSD[b]	Particle morphology
PAN11	0.5	0.35	1.01	Spherical
PAN12	1	0.40	1.04	Spherical
PAN13	2	0.40	1.13	Spherical
PAN14	4	–	–	Irregular

Reaction condition: 2.0 g of acrylonitrile, 0.3 g of Monasil PCA, 20±5 bar, 70 °C, 24 h, with stirring
[a] Determined by FE-SEM
[b] Particle size distribution

particles. At above 15 wt.%, uniform and spherical particles were formed. With increases in the surfactant concentration, the particle size decreased at moderate concentrations, from 15 to 25 wt.%. This result may be explained by the increase in the amount of surfactant adsorbed on the surface of the shaped particles. During polymerization, the monomer was polymerized in the solvent. The polymer chain was adsorbed in the micelles. Higher surfactant concentrations yield more micelles in the constant reactor volume during the dispersion polymerization procedure. More micelles contain the less weight of monomer in the unit of micelle due to the limited weight of monomer. In general, the particle size decreased with increasing surfactant concentrations, and more uniform polymer particles are generated. This general tendency was exploited in this study [7, 11, 21].

Effect of the initiator concentration

The effects of the concentration of initiator on the dispersion polymerization of acrylonitrile were investigated using four different concentrations of AIBN. Table 3 and Fig. 4 show the results of polymerization with 0.5, 1.0, 2.0, and 4.0 wt.% of AIBN of the monomer. Throughout these experiments, the bigger and more broadly distributed polymer particles were formed as the result of an increase in the initiator concentration. The number of free radicals and the concentration of the polymer chains increase. As the aggregation process progresses, larger particles are formed. However, these larger particles capture less nuclei or oligo-radicals from the continuous phase due to the lower total surface area. Thus, the particle size distribution will be broadened [9].

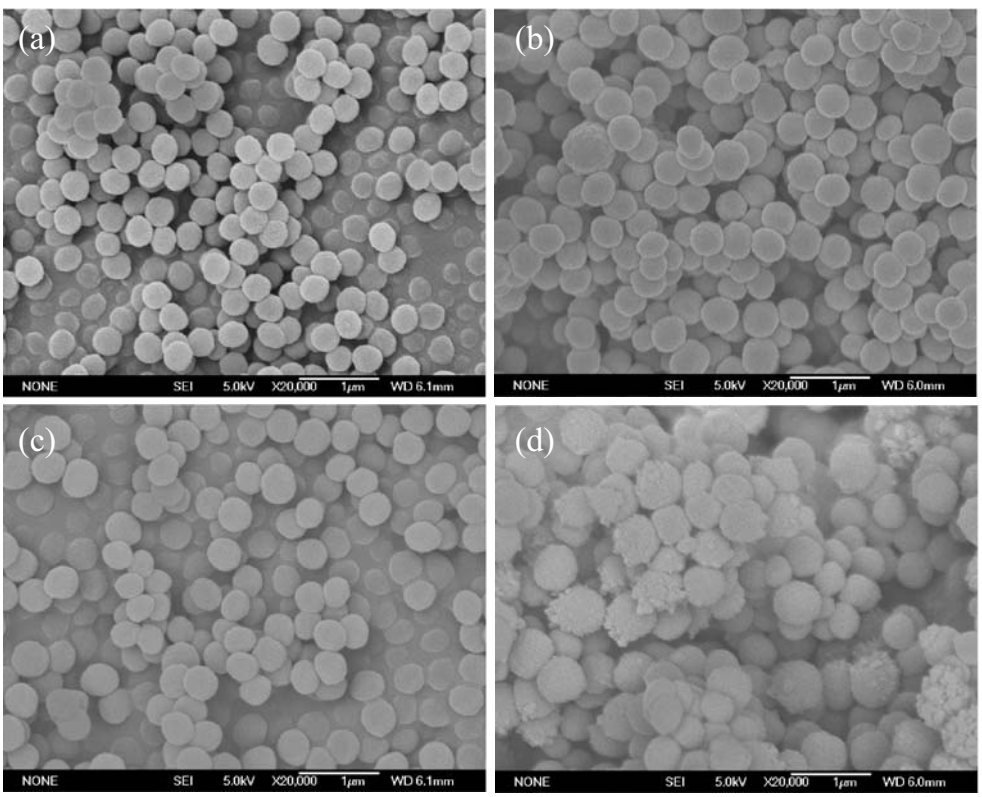

Fig. 4 The SEM images for the polymer particle synthesized with changing the AIBN concentration, **a** 0.5, **b** 1.0, **c** 2.0, and **d** 4.0 wt.%

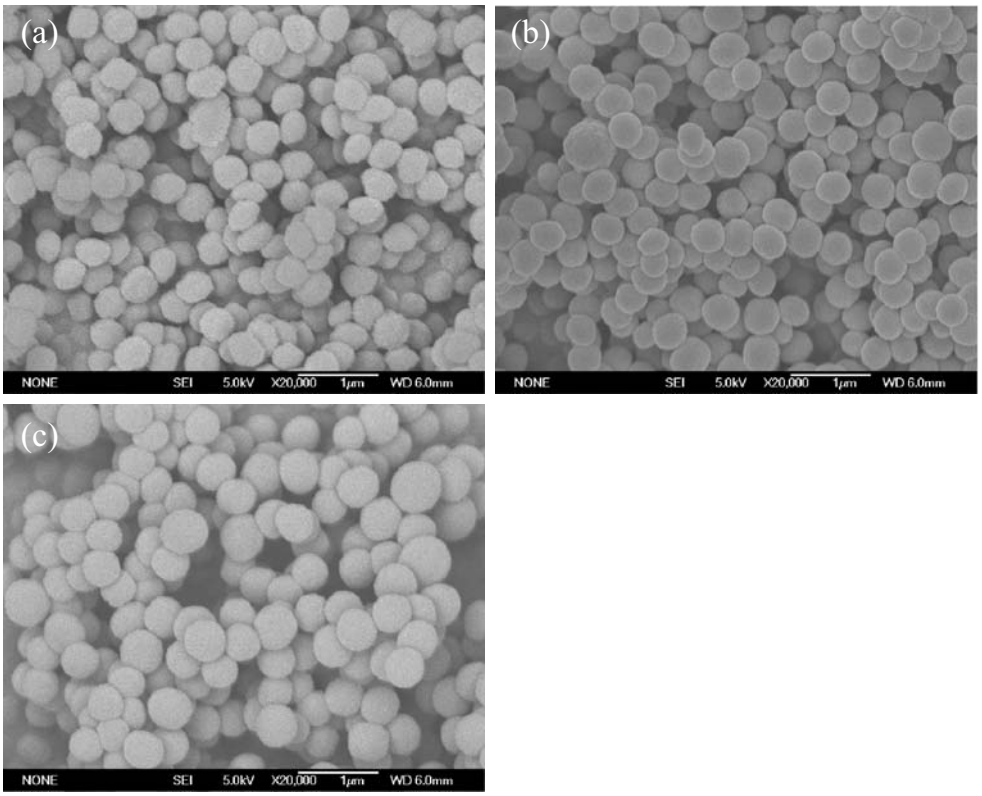

Fig. 5 The SEM images for the polymer particle synthesized with changing the monomer concentration, **a** 1, **b** 2, and **c** 4 g

In the SEM images of 4 wt.% AIBN concentration (Fig. 5d), very small polymer particles can be observed near the larger ones. During polymerization at a high initiator concentration, the nucleases produced in the late phases of polymerization were relatively small polymer particle seeds, which did not grow [22].

Effect of the monomer concentration

The dispersion polymerization was conducted at three different monomer concentrations. Table 4 and Fig. 5 demonstrate the experimental conditions and the results of polymerization with 1.0, 2.0, and 4.0 g of acrylonitrile. With increases in the monomer concentration, the polymer particle size increases. Due to the higher monomer concentration, longer and more abundant polymer chains are generated. The monomer concentration affects the initial solvency of the solvent. Monomer in the solvent functions as the co-solvent. Increases in the monomer concentration were shown to result in increases in the solubility of the oligomers formed. They also formed longer chains prior to precipitation. In addition, the monomer concentration affects the solubility of the surfactant. An increase in the concentration of the monomer increases the surfactant solubility, thus reducing its adsorption to the growing particles. Both effects contribute to the observed increase in particle size [7, 23–25]. The PAN particles shown in Fig. 5a did not form a spherical shape due to an insufficient quantity of monomer—after the initiator became the nucleus, the growth of the polymer chain proved too difficult.

Table 4 Effect of the monomer concentration on the dispersion polymerization of acrylonitrile in compressed liquid dimethyl ether

Entry	Monomer concentration (g)	Particle size (μm)[a]	PSD[b]	Particle morphology
PAN15	1	–	–	Irregular
PAN16	2	0.40	1.04	Spherical
PAN17	4	0.48	1.03	Spherical

Reaction condition: 1 wt.% AIBN, 15 wt.% Monasil PCA, 20±5 bar, 70 °C, 24 h, with stirring
[a] Determined by FE-SEM
[b] Particle size distribution

Table 5 Effect of the polymerization temperature on the dispersion polymerization of acrylonitrile in compressed liquid dimethyl ether[)]

Entry	Polymerization temperature (°C)	Particle size (μm)[a]	PSD[b]	Particle morphology
PAN24	60	0.37	1.01	Spherical
PAN25	70	0.40	1.04	Spherical
PAN26	80	0.39	1.01	Spherical

Reaction condition: 2 g acrylonitrile, 1 wt.% AIBN, 15 wt.% Monasil PCA, 20±5 bar, 24 h, with stirring
[a] Determined by FE-SEM
[b] Particle size distribution

Effect of the polymerization temperature

Dispersion polymerization was conducted at three different polymerization temperatures, 60 °C, 70 °C, and 80 °C. Table 5 and Fig. 6 show the experimental conditions and results regarding the polymer particles generated. With the general organic solvent, increased reaction temperatures led to increased particle sizes. An increase in temperature during the dispersion polymerization procedure contributed to an increase in the critical chain length of the oligo-radical due to the increase in the solvency of the continuous phase, the concentration of precipitated oligomer chains, and the solubility of the surfactant molecules in the continuous phase [25, 26]. However, when DME was employed as the reaction medium, the temperature proved not to be a crucial factor because an increase in temperature under constant pressure resulted in a reduction in the solvent density and a reduction in solvency.

Effect of the polymerization pressure

Dispersion polymerization was conducted at five different pressures. Table 6 and Fig. 7 show the experimental condition and results of polymerization at 20, 50, 90, 130, and 340 bar.

In the case of supercritical carbon dioxide, the solvent density and dielectric constant could be readily altered simply by changing the pressure. This property allows for explorations of the effects of the solvent on acrylonitrile polymerization, without the requirement for an added co-solvent. The solvency of the solvent for the growing polymer chains increases with increasing pressure. Although increasing pressure induces a reduction in the

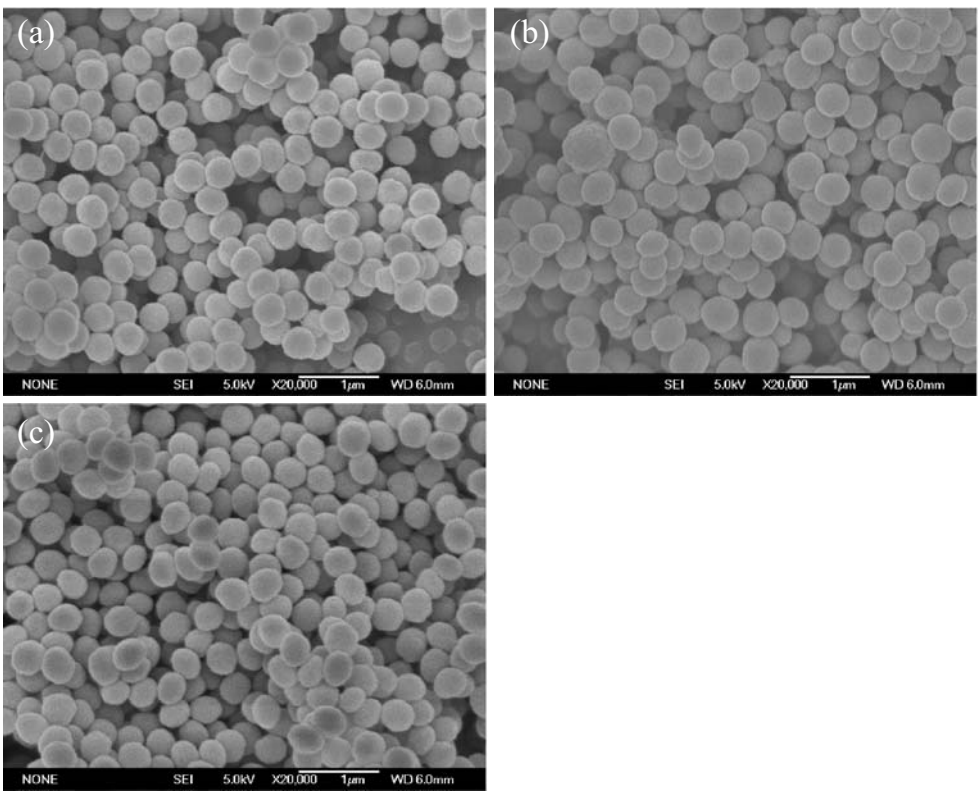

Fig. 6 The SEM images for the polymer particle synthesized with changing the polymerization temperature, **a** 60 °C, **b** 70 °C, and **c** 80 °C

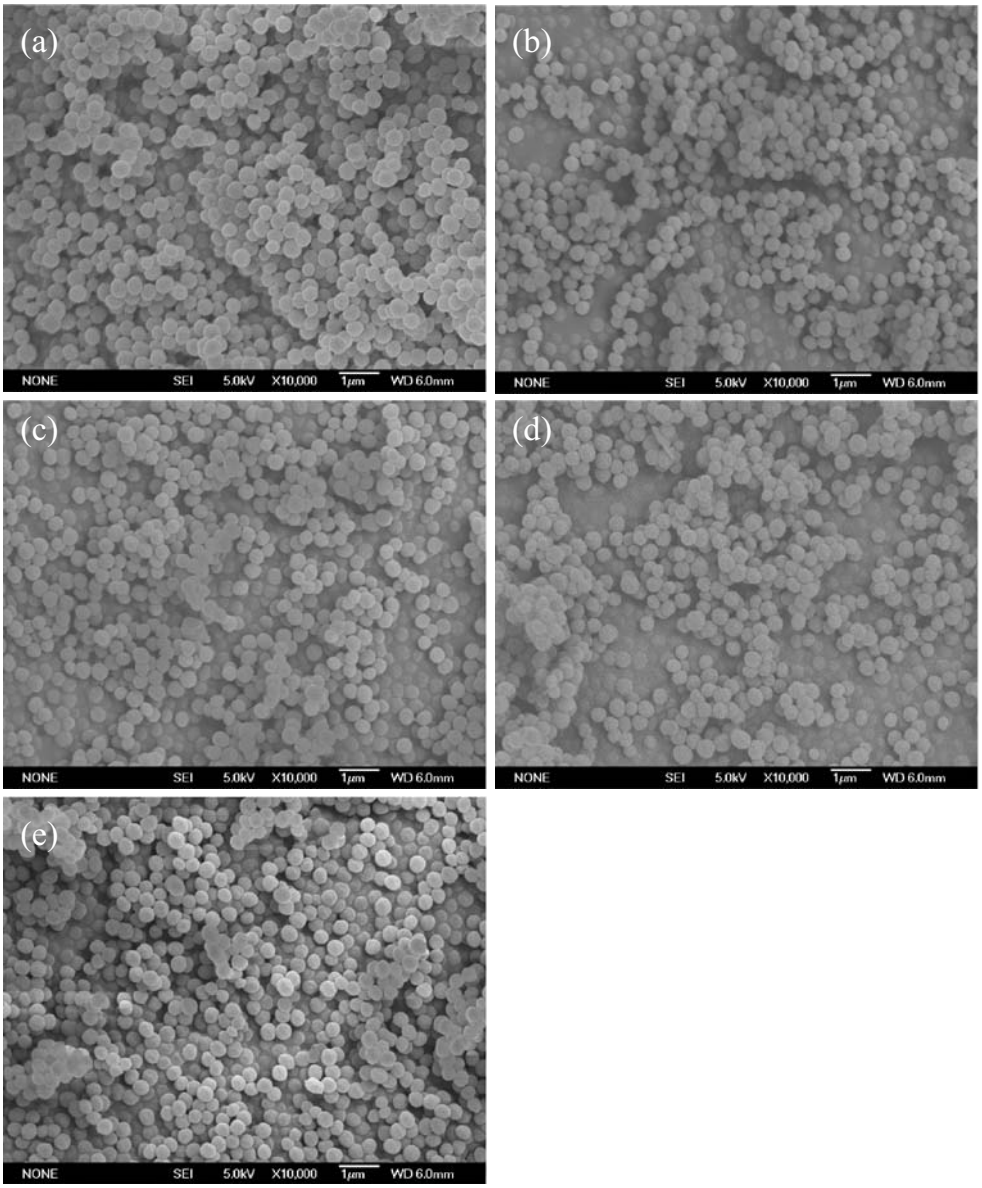

Fig. 7 The SEM images for the polymer particle synthesized with changing the polymerization pressure, **a** 20, **b** 50, **c** 90, **d** 130, and **e** 340 bar

monomer ratio, the particle size increases with increases in pressure [11]. DME also increases the density with increasing pressure. However, the change in the density of compressed liquid DME with changes in pressure is smaller than that observed when supercritical carbon dioxide is utilized [27]. Thus, there is no tendency regarding the results of dispersion polymerization because the monomer ratio was reduced slightly with increases in the pressure.

Table 6 Effect of the polymerization pressure on the dispersion polymerization of acrylonitrile in compressed liquid dimethyl ether[a]

Entry	Polymerization pressure (bar)	Particle size (μm)[a]	PSD[b]	Particle morphology
PAN18	20	0.40	1.04	Spherical
PAN19	50	0.38	1.01	Spherical
PAN20	90	0.39	1.02	Spherical
PAN22	130	0.39	1.04	Spherical
PAN23	340	0.38	1.02	Spherical

Reaction condition: 2 g acrylonitrile, 1 wt.% AIBN, 15 wt.% Monasil PCA, 70 °C, 24 h, with stirring
[a] Determined by FE-SEM
[b] Particle size distribution

Conclusion

Using compressed liquid DME, monodispersed poly(acrylonitrile) particles in a size range of 0.35–0.50 μm were generated via dispersion polymerization at a lower pressure than was required with supercritical carbon dioxide. The morphology of the polymer particles was determined principally by the type of surfactant used. Additionally, the particle size was controlled by alterations in the concentrations of the monomer, surfactant, and initiator. However, the polymerization temperature and pressure exerted no observable effects on the polymer particle size.

Acknowledgments This work was supported by the BK21 project of the Ministry of Education, Korea Gas Corporation and the National Research Laboratory (NRL) program of the Korea Institute of Science & Technology Evaluation and Planning.

Reference

1. Hans-Georg Hicke PBmMBHSMU (1996) J Appl Polym Sci 60 (8):1147–1161
2. Bilgili E, Hamey R, Scarlett B (2004) China Particuology 2 (3):93–100
3. Mulholland GW, Bauer BJ (2000) J Nanopart Res 2(1):5–15
4. Niall Behan CB (2001) Macromol Rapid Commun 22(1):41–43
5. Saxena V, Sadoqi M, Shao J (2004) Int J Pharm 278(2):293–301
6. Venier-Julienne MC Beno JP (1996) Pharm Acta Helv 71(2):121–128
7. Boguslavsky L, Baruch S, Margel S (2005) J Colloid Interface Sci 289(1):71–85
8. Zhang C, Du Z, Li H, Ruckenstein E (2002) Polymer 43 (20):5391–5396
9. Cao K, Yu J, Li B-G, Li B-F, Pan Z-R (2000) Chem Eng J 78(2–3):211–215
10. O'Neill ML, Yates MZ, Johnston KP, Smith CD, Wilkinson SP (1998) Macromolecules 31(9):2838–2847
11. Shiho H, DeSimone JM (2000) Macromolecules 33(5):1565–1569
12. DeSimone JM, Maury EE, Menceloglu YZ, McClain JB, Romack TJ, Combes JR (1994) Science 265(5170):356–359
13. Wang Z, Yang YJ, Dong Q, Liu T, Hu CP (2006) Polymer 47 (22):7670–7679
14. Oh KS, Bae W, Kim H (2007) Polymer 48(6):1450–1454
15. Oh KS, Bae W, Kim H (2008) Eur Polym J 44(2):415–425
16. Semelsberger TA, Borup RL, Greene HL (2006) J Power Sources 156(2):497–511
17. Wu J, Liu Z, Wang F, Ren C (2003) J Chem Eng Data 48 (6):1571–1573
18. Poling BE, Prausnitz JM, O'Connell JP (2000) The properties of gases and liquid. McGraw-Hill, New York
19. Bae W, Shin H, Kim H (2004) Phys Chem Chem Phys 6(9):2295–2300
20. Shin J, Lee YW, Kim H, Bae W (2006) J Chem Eng Data 51 (5):1571–1575
21. Katharina Landfester MA (2000) Macromol Rapid Commun 21 (12):820–824
22. Masayoshi O, Syuji F, Hiroshi M, Hideto M (2003) Colloid Polym Sci 281(10):964–972
23. Paine AJ, Luymes W, McNulty J (1990) Macromolecules 23 (12):3104–3109
24. Tseng CM (1986) YYLMSE-AJWV. J Polym Sci A Polym Chem 24(11):2995–3007
25. Shen S (1994) EDSMSE-A. J Polym Sci A Polym Chem 32 (6):1087–1100
26. Shen S (1993) EDSMSE-A. J Polym Sci A Polym Chem 31 (6):1393–1402
27. Wu J, Liu Z, Wang B, Pan J (2004) J Chem Eng Data 49(3):704–708