

Dispersion Copolymerization of Acrylonitrile-Vinyl Acetate in Supercritical Carbon Dioxide

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ABSTRACT: Dispersion copolymerization of acrylonitrile-vinyl acetate (AN-VAc) had been successfully performed in supercritical carbon dioxide (ScCO₂) with 2,2-azobisisobutyronitrile (AIBN) as a initiator and a series of lipophilic/CO₂-philic diblock copolymers, such as poly(styrene-*r*-acrylonitrile)-*b*-poly(1,1,2,2-tetrahydroperfluorooctyl methacrylate) (PSAN-*b*-PFOMA), as steric stabilizers. In dispersion copolymerization, poly(acrylonitrile-*r*-vinyl acetate) (PAVAc) was emulsified in ScCO₂ effectively using PSAN-*b*-PFOMA as a stabilizer. Compared with the precipitation polymerization (absence of stabilizer), the products prepared by dispersion polymerization possessed of higher yield and higher molecular weight. In addition, the particle morphol-

ogy of precipitation polymerization was irregular, but the particle morphology of dispersion polymerization was uniform spherical particles. In this study, the effects of the initial concentrations of monomer and the stabilizer and the initiator, and the reaction pressure on the yield and the molecular weight and the resulting size and particle morphology of the colloidal particles were investigated. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 5640–5648, 2006

Key words: atom transfer radical polymerization; fluorinated diblock copolymer; dispersion polymerization; acrylonitrile; vinyl acetate; supercritical carbon dioxide

INTRODUCTION

In the past decade, prominent progress has been made in defining the range and limitations of supercritical carbon dioxide (ScCO₂) as an inert polymerization medium.^{1–3} On the basis of the environmental advantages of ScCO₂, combined with its ability to be used as a solvent/dispersing medium for a variety of chemical reactions, it may become an important solvent in future polymer industry. The primary challenge in extending the use of ScCO₂ as a solvent for polymerization arises from the fact that, so far only two kinds of polymers have been found with high solubility in ScCO₂ at easily accessible temperatures and pressures ($T < 100^\circ\text{C}$, $P < 350$ bar), i.e., silicones and fluoropolymers.^{4–9} The fluoropolymers have been synthesized homogeneously in ScCO₂ by free radical methods.^{7,8,10–14} Unfortunately, most industrially important hydrocarbon-based polymers are relatively insoluble in ScCO₂. Therefore, polymerization has to be heterogeneous when hydrocarbon-based polymers are pro-

duced in ScCO₂. Among heterogeneous techniques, dispersion polymerization has been proven useful for ScCO₂-based systems. Since 1994, the successful dispersion polymerizations of methyl methacrylate,^{15–20} vinylidene fluoride,^{21–22} 2-hydroxyethyl methacrylate,²³ styrene,^{24–27} vinyl acetate,²⁸ acrylonitrile,²⁹ and vinyl pyrrolidinone³⁰ in ScCO₂ have been reported. Dispersion polymerizations are governed by a delicate interplay, which includes the separations and interactions of all components.³¹ The efficiency of the stabilizer also represents a key factor in the preparation of a stable latex.³² The stabilizers studied in earlier literatures were carefully selected and synthesized on the basis of their known solvency in ScCO₂ and the established criteria for steric stabilizer effectiveness. DeSimone et al. have previously demonstrated the amphiphilicity of fluorinated acrylate homopolymers, such as poly(1,1-dihydroperfluorooctyl acrylate) (PFOA), which contains a lipophilic acrylate backbone and a CO₂-philic, fluorinated side chain.¹⁶ Another approach to the stabilization of CO₂-phobic polymer colloids is the use of fluorocarbon–hydrocarbon block copolymers, with PS-*b*-PFOA as a famous example.²⁹ The fluorinated stabilizers are effective for dispersion polymerizations of lipophilic monomers in ScCO₂.^{23,24,30} In this study, the efficiency of PSAN-*b*-PFOMA in

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preventing acrylonitrile-vinyl acetate-based colloidal particles from aggregation has yet to be established. The synthesis of well-controlled diblock copolymer PSAN-*b*-PFOMA by ATRP has been previously described in another paper.³³ The structures of macroinitiator and diblock copolymer are described in Figure 1.

Dispersion polymerization of AN-VAc in ScCO₂ with PSAN-*b*-PFOMA as a stabilizer has been studied. It is potential to improve the yields and the molecular weights of the products. Because the PFOMA block of PSAN-*b*-PFOMA can dissolve in ScCO₂, but the PSAN block cannot dissolve in it, so PSAN-*b*-PFOMA can form a reverse micelle structure.³⁴ We presume that monomers can enter into the micelle and react in it. Therefore, the micelle structures can prevent acrylonitrile-vinyl acetate-based colloidal particles from aggregation. The influence of the initial concentration of monomer and the stabilizer and the initiator and the reaction pressure on PAVAc colloidal particle morphology and the yield and the molecular weight has been also investigated.

EXPERIMENTAL

Materials

1,1,2,2-tetrahydroperfluorooctyl methacrylate (FOMA, 99+%, Dupont) was purified by passage through a neutral alumina column at 40°C. Acrylonitrile (AN, Shanghai Chemical Reagent Company, Chemically Pure) and vinyl acetate (VAc, Shanghai Chemical Reagent Company, Chemically Pure) were purified by passage through a neutral alumina column at room temperature. Styrene (St, Shanghai Chemical Reagent Company, Chemically Pure) was stirred in the presence of CaH₂ for 24 h and was distilled before use. Tetrahydrofuran (THF, Shanghai Chemical Reagent Company, Analytical Reagent) was refluxed for 24 h in the presence of sodium wire. α, α, α -Trifluorotoluene (TFT, Shanghai Chemical Reagent Company, Chemically Pure Reagent) was distilled under atmospheric pressure. 2,2'-Bipyridine (bpy, Shanghai Chemical Reagent No. 1 Plant, Analytical Reagent) was recrystallized thrice from hexane. 2,2'-Azobisisobutyronitrile (AIBN, Shanghai Chemical Reagent Company, Analytical Reagent) was recrystallized thrice from methanol. CuBr (Shanghai Chemical Reagent Company Limited, Ana-

lytical Reagent) was purified as described in the literature.³⁵ Ethyl α -bromoisobutyrate (EBriB, 98+%, Lancaster), carbon dioxide (98+%, Shanghai Wugang Gas Company) and nitrogen(99.9+% Shanghai Wugang Gas Company) were used as received.

Diblock copolymer

Diblock copolymer consisting of PSAN and PFOMA (PSAN-*b*-PFOMA) was synthesized via atom-transfer radical polymerization (ATRP). ATRP technique was developed by Matyjaszewski et al. in 1995.³⁶⁻³⁷ The synthesis of the specific block copolymers has been previously described.³³ The PSAN-Br was synthesized first using ethyl α -bromo-isobutyrate as an initiator. It was then used as a macroinitiator in the polymerization of the second monomer, FOMA, to form the second block of the diblock copolymer. For simplicity, the block copolymers will be henceforth referred to by listing the number-average molecular weights (M_n) of the blocks, $\langle M_n \rangle_{\text{PSAN}} / \langle M_n \rangle_{\text{PFOMA}}$. The all of M_n were determined by ¹H-NMR. The structure of the diblock copolymer is shown in Figure 1.

Dispersion copolymerizations of AN-VAc

Polymerizations were conducted in ScCO₂ in a 20-mL stainless steel autoclave equipped with a stirring bar. In a typical polymerization, the reactor was charged with the desired amount of AIBN and the desired amount of stabilizer (0–0.30 g), and then the desired monomers, which were deoxygenated, were added to the system by degassed syringes. After that, the reactor was fastened and was put into an ice and salt bath for 30 min. Then, the reactor was slowly purged with a flow of carbon dioxide and was slowly vented for three times to replace the air. The reactor was pressurized with CO₂, and the pressurizing period depends on the final pressure desired. Then, the reaction mixture was heated to 65°C. Once the final reaction conditions were obtained, the reaction was allowed to proceed with stirring for 18 h. At the end of the reaction, the reactor was cooled, and the CO₂ was slowly vented from the cell before removal of the polymer product. To quantify the reaction yields, the reaction cell was rinsed with DMF to remove any residual polymer product and stabilizer. The polymer conversion was

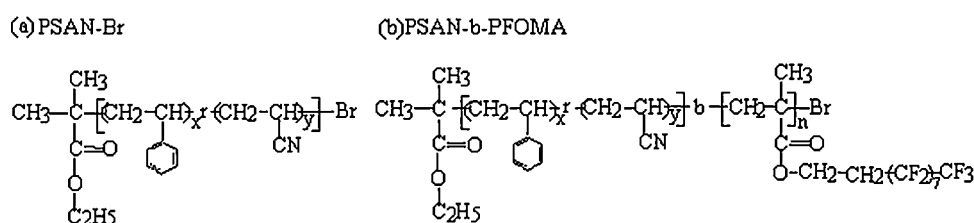


Figure 1 The structures of the macroinitiator and diblock polymer.

determined gravimetrically in each case. The weight of the stabilizer was subtracted from the total mass of the product to obtain the weight of polymer product.

Characterization

Molecular weights and molecular weight distributions of macroinitiators and block copolymers were determined by a Waters 150 gel-permeation chromatography (GPC) consisting of a waters 510-HPLC pump and a waters 410 differential refractometer. THF was used as solvent for PSAN and PSAN-*b*-PFOMA, with calibrations based on standard polystyrene. The molecular weights of PSAN and PSAN-*b*-PFOMA were calibrated by ¹H-NMR, which was done on a Bruker-500 spectrometer with CDCl₃ as solvent. The morphology of the polymers prepared in ScCO₂ was determined using a JEOL 6360LV scanning electron microscope (SEM), and number-average particle size and particle size distribution were determined by the measurement of 1000 particles chosen at random. Molecular weights of the PAVAc were determined with an Ubbelohde capillary viscometer at 30°C, using DMF as solvent.

RESULTS AND DISCUSSION

Effect of different stabilizers on dispersion polymerization

The results for the copolymerization of acrylonitrile and vinyl acetate in ScCO₂ using several different stabilizers are summarized in Table I. The precipitation polymerization that was conducted in the absence of stabilizer (Sample 1) resulted in the formation of irregular polymer particles [Fig. 2(a)]. In contrast, the reactions that were carried out in the presence of amphiphilic diblock copolymers started out spherical and

stable colloidal dispersion of PAVAc particles. The successful stabilization of the polymerization resulted in spherical particles [Figs. 2(b)–2(d)]. The mechanism for particle formation in these polymerizations may involve micellar nucleation or stabilizer adsorption to precipitating polymer,²⁹ although such aggregates have not yet been identified in the presence of a large amount of monomers. In addition, the molecular weight increased greatly in the presence of amphiphilic diblock copolymers. Furthermore, along with the increase of the content of acrylonitrile in the anchor block of amphiphilic diblock copolymer, the dispersion efficiency was obviously improved. The particle morphology became more regular, and the dispersity index of the particle size distribution became more narrow [Fig. 2(b–d)]. This may be due to the affinity of the anchor block and the PAVAc augments when the content of acrylonitrile in the anchor block increases. But, when compared with the dispersion efficiency using PSAN-*b*-PFOMA (stabilizer used in Sample 3) as a stabilizer, the dispersion efficiency using PSAN-*b*-PFOMA (stabilizer used in Sample 4) as a stabilizer has no obvious enhancement. Furthermore, along with the increase of the content of acrylonitrile in anchor block, there has difficulty in the purification of diblock copolymer because it cannot dissolve in many of traditional solvents. So, we only need add adequate the content of acrylonitrile in the anchor block. For all of the reactions in which diblock copolymer was employed as the steric stabilizer, the dispersion copolymerization of acrylonitrile and vinyl acetate was successfully carried out except some aggregates observed by SEM. One possible explanation for this agglomeration is that, since the molecular weight of the diblock stabilizers with soluble PFOMA segments is up to 20,000, only a short anchor segment of 5000 is employed, which may make an inefficient

TABLE I
Effect of Different Stabilizers on Dispersion Polymerization^a

Sample	Stabilizer	Yield ^b (%)	D_n^c (μm)	PSD ^d	M_v^e (10^{-4})	Particle morphology
1	None	55.0	—	—	5.43	Irregular
2	PS- <i>b</i> -PFOMA (4.9/20.6 K)	60.5	0.16	1.16	7.65	Spherical
3	PSAN- <i>b</i> -PFOMA ^f (5.0/21.0 K)	70.0	0.11	1.03	7.78	Spherical
4	PSAN- <i>b</i> -PFOMA ^g (5.1/21.3 K)	72.5	0.11	1.03	8.57	Spherical

^a In all cases, the contents of initiator, acrylonitrile, and stabilizer added to the system were kept constant at 1 (w/w% to monomers), 10 (w/v% in CO₂), and 10 (w/w% to monomers) respectively. The mass ratio of acrylonitrile to vinyl acetate is 9 : 1. All the reactions were performed at 65°C and 250 ± 5 bar for 18 h.

^b Yields were determined gravimetrically.

^c D_n = mean particle diameter.

^d PSD = dispersity index of the particle size distribution, D_w/D_n .

^e M_v was determined with an Ubbelohde capillary viscometer.

^f The mole ratio of styrene to acrylonitrile of the PSAN block is 63 : 37 (calculated from ¹H-NMR).³⁸

^g The mole ratio of styrene to acrylonitrile of the PSAN block is 50 : 50 (calculated from ¹H-NMR).

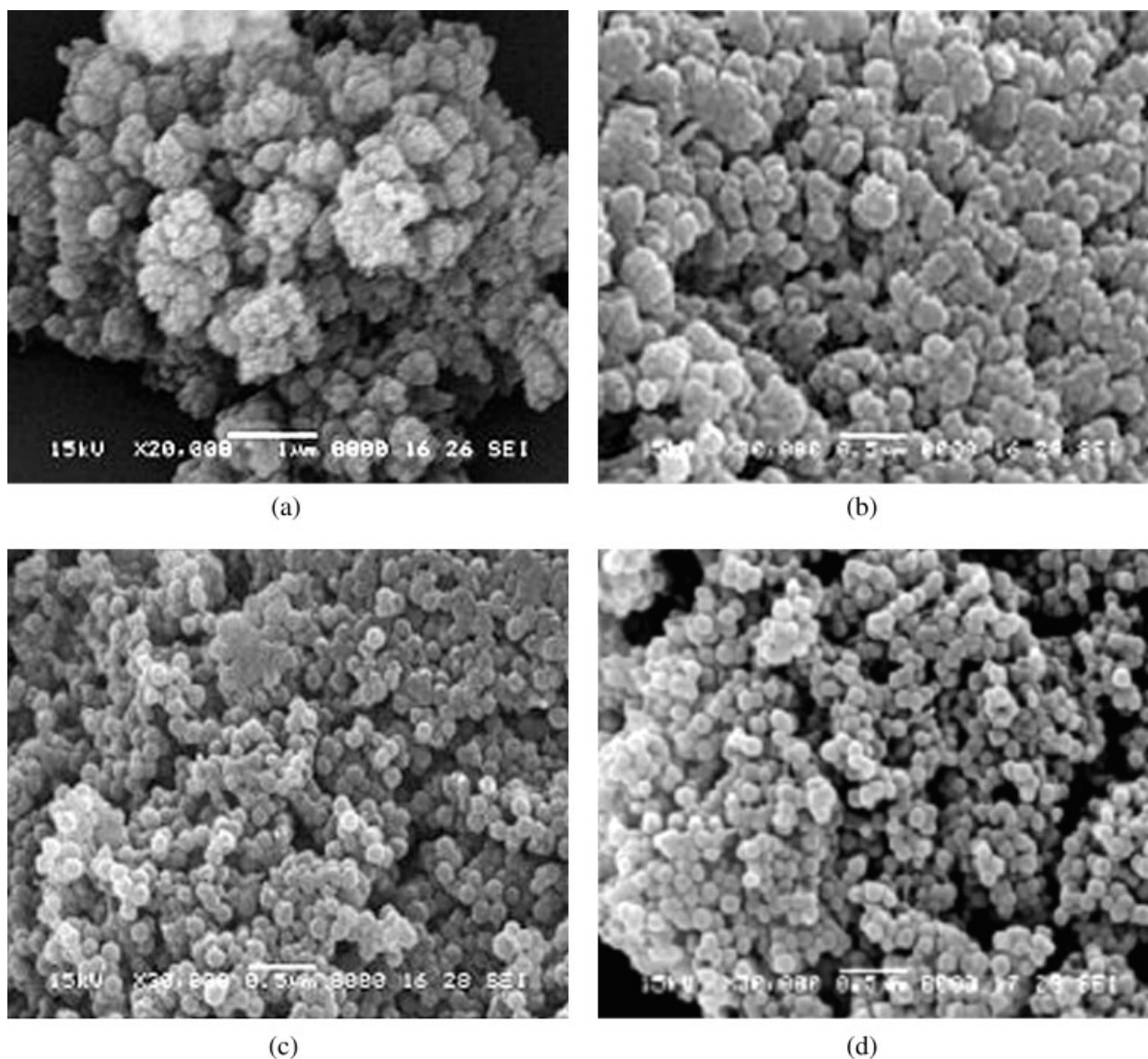


Figure 2 Scanning electron micrographs from reactions containing (a) no stabilizer (Sample 1 in Table I), (b) PS-*b*-PFOMA (4.9/20.6 K) (Sample 2 in Table I), (c) PSAN-*b*-PFOMA (5.0/21.0 K) (Sample 3 in Table I), (d) PSAN-*b*-PFOMA (5.1/21.3 K) (Sample 4 in Table I) in ScCO₂ at 65°C and 250 ± 5 bar for 18 h.

adsorption of the stabilizer on the polymer.²⁹ The resultant PAVAc particles became effectively stabilized since the reaction mixture exhibited a milky white appearance, which was similar to that observed for a conventional aqueous latex. Upon venting the CO₂, a dry, white, free-flowing powder remained in the reaction vessel. The M_v was calculated using the Mark-Houwink-Sakurada equation given by $[\eta] = KM_v^a$, where the K and a values used in the calculation are 20.9×10^{-3} mL/g and 0.75, respectively.³⁹

Effect of the stabilizer concentration on dispersion polymerization

Dispersion polymerizations were conducted at four different concentrations of stabilizer (Table II). The

yield was found to be obviously increased when the stabilizer concentration increased from 3 to 5 (w/w% to monomers). And, when the stabilizer concentration exceeds 5 (w/w% to monomers), the results show no obvious trend in yield. The diameter of the particles and the dispersity index of the particle size distribution decreased from 0.17 to 0.09 μm and 1.16 to 1.02 μm respectively, when the concentration of PSAN-*b*-PFOMA increased from 3 to 15 (w/w% to monomers). In the presence of a large amount of PSAN-*b*-PFOMA, it is believed that the oligomeric PAVAc radicals could rapidly adsorb the stabilizer prior to aggregation with other particles. As a result, there was an increase of the number of stable nuclei with higher stabilizer concentration, and correspondingly smaller particles were produced. We could get similar conclu-

TABLE II
Effect of Stabilizer Concentration on Dispersion Polymerization^a

Sample	Stab. Conc. ^b (w/w% to monomers)	Yield ^c (%)	D_n^d (μm)	PSD ^e	M_v^f (10^{-4})	Particle morphology
5	3	63.0	0.17	1.16	7.35	Spherical
6	5	72.5	0.13	1.05	7.85	Spherical
7	10	70.0	0.11	1.03	7.78	Spherical
8	15	71.8	0.09	1.02	7.81	Spherical

^a In all cases, the contents of initiator and acrylonitrile added to the system were kept constant at 1 (w/w% to monomers) and 10 (w/v % in ScCO_2) respectively. The mass ratio of acrylonitrile to vinyl acetate is 9 : 1. The stabilizer is PSAN-*b*-PFOMA (5.0/21.0 K) (same as Sample 3 in Table I). All the reactions were performed at 65°C and 250 ± 5 bar for 18 h.

^b Stab. Conc. = stabilizer concentration.

^c Yields were determined gravimetrically.

^d D_n = mean particle diameter.

^e PSD = dispersity index of the particle size distribution, D_w/D_n .

^f M_v was determined with an Ubbelohde capillary viscometer.

sions from literature.^{23,24,29} The particle diameters may be determined by the relative contribution of the anchoring modes of adsorption or chemical grafting. When the stabilizer concentration was lowered to 3 (w/w% to monomers), the dispersion polymerization was initially stable, but flocculation occurred and the morphology of resulting polymer was found by SEM to be anomalistic spherical. This indicates that the stabilizer was too little to prevent the polymer particles from agglomeration. From the Table II, when the stabilizer concentration was above 5 (w/w% to monomers), the role of the stabilizer concentration was completely negligible on yield and M_v and weakly positive on PSD. This is because the polymerization takes place in two loci, the supercritical continuous phase and the polymer-rich phase.^{38,40} When the stabilizer concentration is above 5 w/w%, the stabilizer reaches saturation in the supercritical continuous phase. So further increasing the stabilizer content has negligible effect on yield and M_v . But it can enable more surface area of the polymer particle stabilization. Therefore, it has positive effect on PSD. Generally speaking, for dispersion polymerizations of PAVAc in ScCO_2 , five (w/w% to monomers) stabilizers are needed to prevent coagulation of the polymer particles at 10 (w/v% in ScCO_2) monomers content. So, we can draw a conclusion that we must add adequate stabilizer to get preferable dispersion effect. Figure 3 shows the scanning electron micrographs of the four different stabilizer concentration.

Effect of the monomers concentration on dispersion polymerization

Dispersion polymerizations were also conducted at four different concentrations of acrylonitrile (Table III). In all cases, the contents of PSAN-*b*-PFOMA (5.0/21.0 K) (same as Sample 3 in Table I) stabilizer and initiator

added to the system were kept constant at 5 and 1 (w/w% to monomers), respectively. It is shown in the table that the yield increased from 37.9% to 75.1% when the monomer concentration increased from 6% to 12% (Fig. 4), just like the trend described in literature, being in accordance with theory of free-radical polymerization.⁴¹ In addition, when the monomer concentration was lower, the molecular weight of the product was smaller. This may be that the lower monomer concentration result in the lower reaction rate.

Effect of the initiator concentration on dispersion polymerization

As shown in Table IV, the yield increased from 53.9% to 75.5% when the initiator concentration increased from 0.5 to 1.5 (w/w% to monomer). And the molecular weights of the products decreased from 123,300 to 54,300 when the initiator concentration increased from 0.5 to 1.5 (w/w% to monomers). These trends are also in accordance with theory of free-radical polymerization.⁴¹ However, according to free-radical polymerization with dominant bimolecular terminations, the expected dependences of polymerization rate and number average molecular weight upon the initiator concentration are expressed as power laws with exponent 0.5 and -0.5 , respectively. But, data in Table IV indicate quite different values (about 0.3 and -0.75 , respectively). There may exist an explanation that the polymerization takes place in two loci, the supercritical continuous phase and the polymer-rich phase, all over the reaction, especially, mainly in the latter. And, the initiator concentration in the polymer-rich phase may be lower than apparent initiator concentration. The polymerization rate in the polymer-rich phase initially increases to a maximum value and then slowly decreases with reaction time.⁴² There needs a lot of work to find out the reaction mechanism.

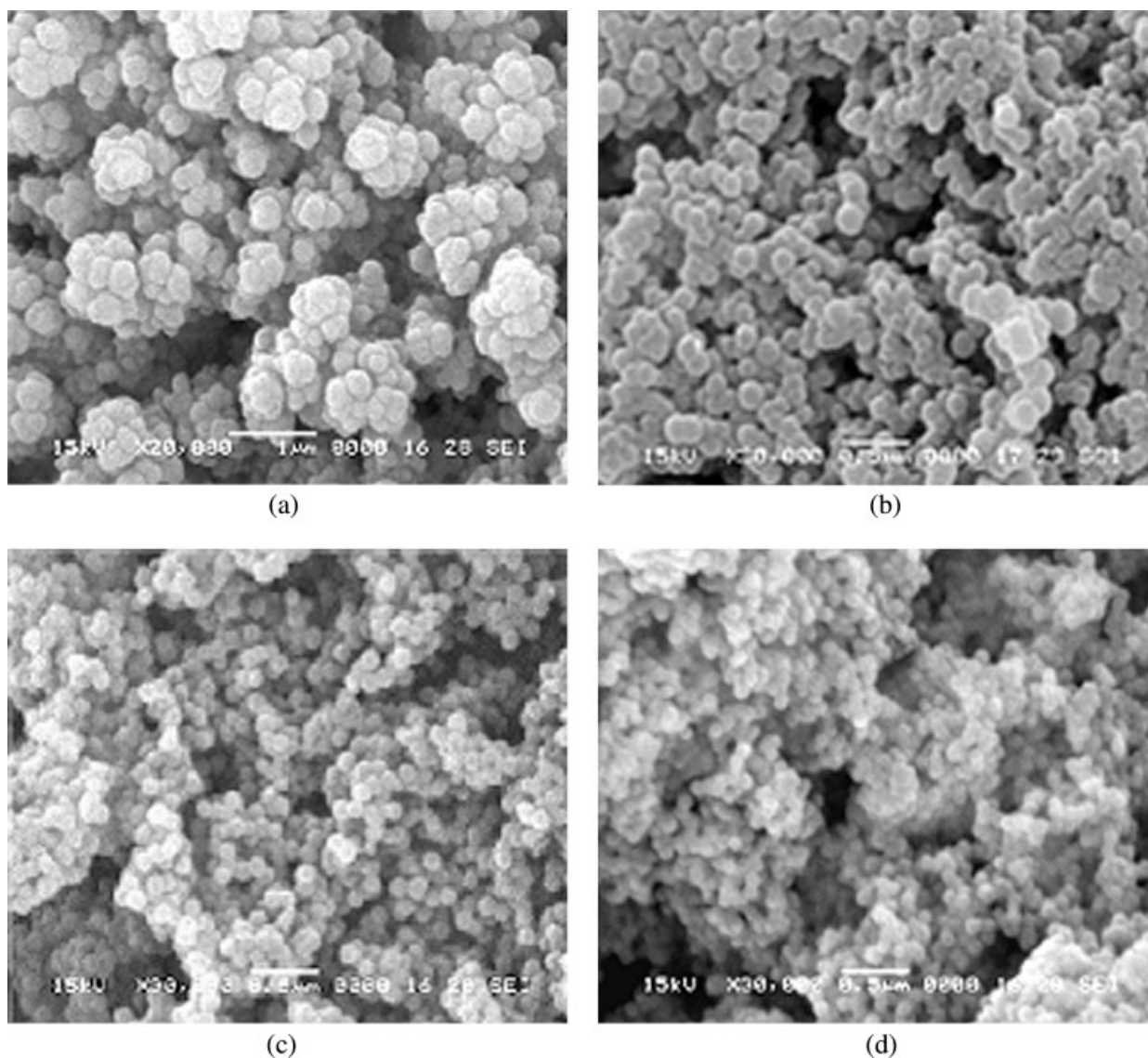


Figure 3 Scanning electron micrographs from reactions containing (a) 3%, (b) 5%, (c) 10%, (d) 15% stabilizer (w/w to monomers) in ScCO₂ at 65°C and 250 ± 5 bar for 18 h.

TABLE III
The Effect of the Monomer Concentration on Dispersion Polymerization^a

Sample	Mono. Conc. ^b (w/v% in CO ₂)	Yield ^c (%)	D_n ^d (μm)	PSD ^e	M_v ^f (10 ⁻⁴)	Particle morphology
9	6	37.9	–	–	4.47	Irregular
10	8	57.0	0.18	1.13	7.61	Spherical
11	10	70.0	0.11	1.03	7.78	Spherical
12	12	75.1	0.10	1.03	8.00	Spherical

^a In all cases, the contents of initiator and stabilizer (PSAN-*b*-PFOMA (5.0/21.0 K)) added to the system were kept constant at 1 (w/w% to monomers) and 5 (w/w% to monomers), respectively. The mass ratio of acrylonitrile to vinyl acetate is 9 : 1. All the reactions were carried out at 65°C and 250 ± 5 bar for 18 h.

^b Mono. Conc. = monomer concentration.

^c Yields were determined gravimetrically.

^d D_n = mean particle diameter.

^e PSD = dispersity index of the particle size distribution, D_w/D_n .

^f M_v was determined with an Ubbelohde capillary viscometer.

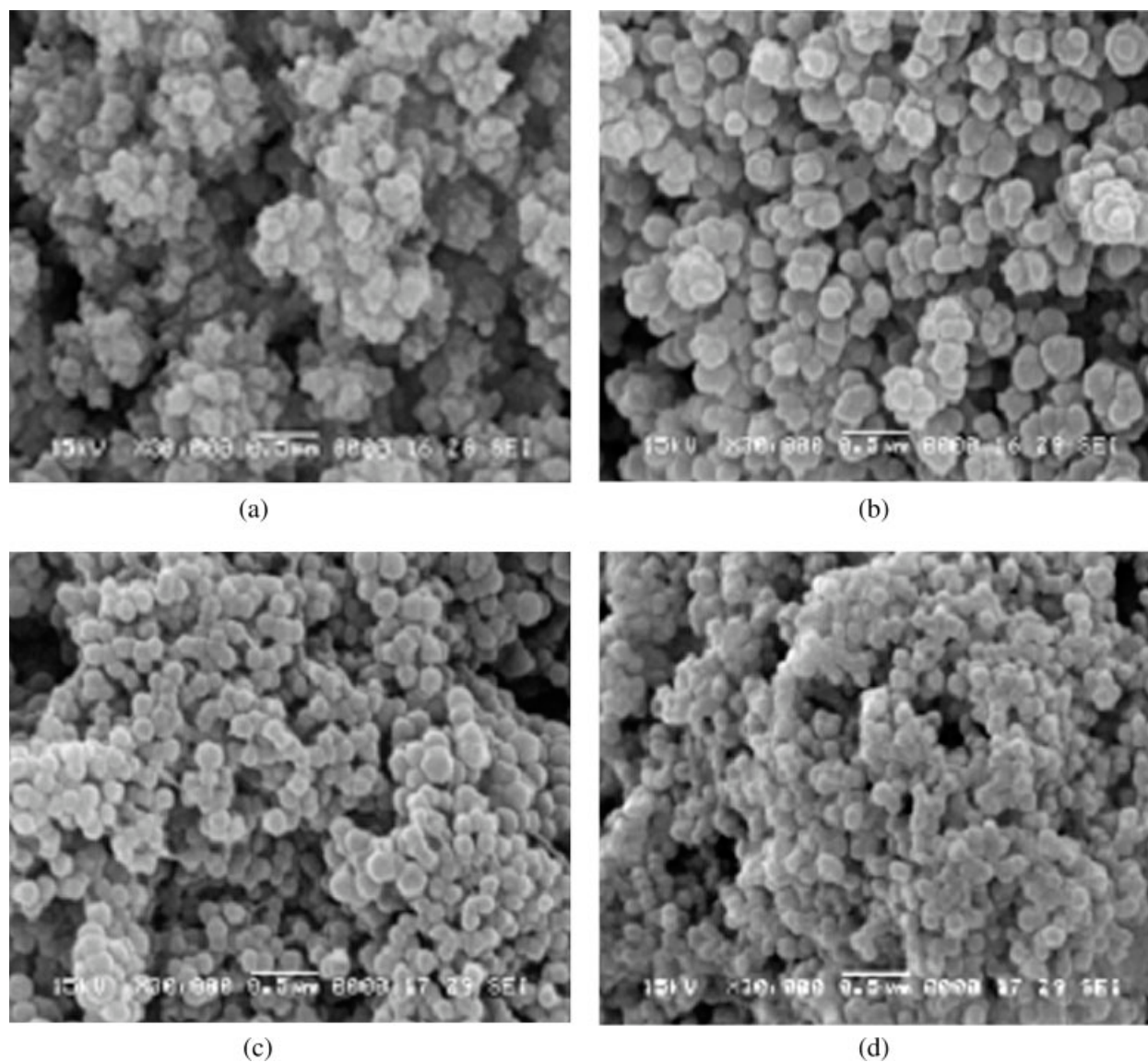


Figure 4 Scanning electron micrographs from reactions containing (a) 6, (b) 8, (c) 10, (d) 12 (w/v% in ScCO₂) monomer in ScCO₂ at 65°C and 250 ± 5 bar for 18 h.

TABLE IV
The Effect of the Initiator Concentration on Dispersion Polymerization^a

Sample	Ini. Conc. ^b	Yield ^c (%)	D_n ^d (μm)	PSD ^e	M_v ^f (10 ⁻⁴)	Particle morphology
13	0.5	53.9	0.20	1.04	12.33	Spherical
14	0.8	63.0	0.16	1.04	10.82	Spherical
15	1.0	70.0	0.11	1.03	7.78	Spherical
16	1.5	75.5	0.08	1.03	5.43	Spherical

^a In all cases, the contents of acrylonitrile and stabilizer (PSAN-*b*-PFOMA (5.0K/21.0K)) added to the system were kept constant at 10 (w/v% in ScCO₂) and 5 (w/w % to monomers), respectively. The mass ratio of acrylonitrile to vinyl acetate is 9 : 1. All the reactions were performed at 65°C and 250 ± 5 bar for 18 h.

^b Ini. Conc. = initiator concentration, w/w% to monomers.

^c Yields were determined gravimetrically.

^d D_n = mean particle diameter.

^e PSD = dispersity index of the particle size distribution, D_w/D_n .

^f M_v was determined with an Ubbelohde capillary viscometer.

TABLE V
Effect of CO₂ Pressure on Dispersion Polymerization^a

Sample	Initial pressure (bar)	Final pressure (bar)	Yield ^b (%)	D_n^c (μm)	PSD ^d	M_v^e (10 ⁻⁴)	Particle morphology
17	154	175	55.3	–	–	5.71	Irregular
18	209	230	68.5	0.14	1.03	7.42	Spherical
19	242	251	69.0	0.13	1.04	7.75	Spherical
20	316	310	70.0	0.13	1.04	8.81	Spherical

^a In all cases, the contents of acrylonitrile, initiator and stabilizer (PSAN-*b*-PFOMA (5.0/21.0 K)) added to the system were kept constant at 10 (w/v% in ScCO₂), 1 (w/w% to monomers), and 5 (w/w% to monomers), respectively. The mass ratio of acrylonitrile to vinyl acetate is 9 : 1. All the reactions were performed at 65°C and 250 ± 5 bar for 18 h.

^b Yields were determined gravimetrically.

^c D_n = mean particle diameter.

^d PSD = dispersity index of the particle size distribution, D_w/D_n .

^e M_v was determined with an Ubbelohde capillary viscometer.

Effect of CO₂ pressure on dispersion polymerization

A primary advantage of employing ScCO₂ lies in the ability to tune the solvent density and dielectric constant by simply changing either temperature or pressure. This property allows the exploration of solvent effects on acrylonitrile and vinyl acetate copolymerization without having to add a cosolvent. The effects of pressure on the copolymerizations are summarized in Table V. It can be seen that, when pressure is about 160 bar, the yield is close to the yield from precipitation polymerization. So does the molecular weight. One possible explanation is that, under lower pressure, the reaction condition does not arrive at the cloudpoint (defined as the reversible onset of a fully opaque solution) of the stabilizer.⁴³ Therefore, the stabilizer does not exhibit its function during reaction. Once the reaction condition arrives at the cloud-point, the increase of ScCO₂ pressure has no clear effect on yield. But, the molecular weight of the PAVAc increased from 74,200 to 88,100. There exists two possible explanation that the stabilizer's solubility in ScCO₂ increased along with increasing pressure.⁴³ The fluorinated block can stretch adequately to result in heightening critical precipitation molecular weight. The critical precipitation molecular weight means that polymers with a molecular weight larger than a certain critical value precipitate and begin to coagulate to form unstable particles.⁴⁴ Moreover, along with increasing pressure, the transport rates (from the supercritical continuous phase to the polymer-rich phase) of the reactants increase, and so the reactants' partition in the polymer-rich phase increases.⁴⁵ Another interesting observation that was made during these experiments involved the change in pressure over the course of the reaction. For lower initial pressures ($P < 300$ bar), it was observed that the reaction pressure increased during the course of the reaction. While, for higher initial pressures ($P > 300$ bar), it was observed that the reaction pressure decreased during

the course of the reaction. The phenomena are consistent with the reported literature.^{13,22,23,29} It is believed that this effect arises from the thermodynamics of mixing, which favors expulsion of CO₂ and monomer from the polymer-rich phase at low CO₂ pressures.

CONCLUSIONS

Using PSAN-*b*-PFOMA as a stabilizer, dispersion copolymerization of acrylonitrile and vinyl acetate in ScCO₂ can be accomplished to provide uniform submicron-size spherical PAVAc particles. Compared with the precipitation, the yield and the molecular weight are both greatly increased. And particle morphology becomes more regular. In addition, the yield and the molecular weight and the particle diameter can be slightly controlled by changing the initial concentration of monomer and the different stabilizers and the stabilizer concentration and the initiator concentration and the reaction pressure.

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