

Synthesis of Fluorinated Diblock Copolymer by ATRP and Its Application of PAVAc Polymerization in ScCO₂

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ABSTRACT: A series of fluorinated diblock copolymers consisting of poly(styrene-*r*-acrylonitrile) (PSAN) and poly(1,1,2,2-tetrahydroperfluorooctyl methacrylate) (PFOMA) were prepared by atom transfer radical polymerization (ATRP). The copolymers with well-controlled molecular weight and narrow molecular weight distribution (PDI < 1.2) were characterized by ¹H NMR, GPC, and FTIR. With the amphiphilic diblock copolymers as stabilizers, acrylonitrile-vinyl acetate random copolymers were synthesized by dispersion polymerization in supercritical carbon dioxide (ScCO₂). Compared with precipitation polymerization, the products prepared via dispersion polymerization possess of

higher yield and higher molecular weight. In addition, via dispersion polymerization, the particle morphology of the product is spherical. And the dispersity index of the particle size distribution is very narrow. At the same reaction condition, the particle morphology of the product prepared by precipitation polymerization is irregular. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 1146–1151, 2006

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

INTRODUCTION

In the past decade, more and more attention was paid to controlled/living radical polymerization (CRP) techniques. Compared with traditional free-radical polymerization, one of the advantages of controlled radical polymerizations is the control of the molecular weight and terminal group.¹ It has been proven that a well-controlled block copolymer can be synthesized by a sequential two-step or one-pot method without any transformation or protection of initiating sites. ATRP, one of the most robust CRP techniques, has been applied for the controlled polymerization of various monomers such as styrenes,^{2–4} acrylates,^{5–8} methacrylates,^{9–11} acrylamides,^{12,13} and acrylonitrile.^{14–16} In addition, compared with other controlled radical polymerizations, the reaction condition of ATRP is relatively mild. Through referring to plenty of literatures, poly(styrene-*r*-acrylonitrile) (PSAN)-*b*-poly(1,1,2,2-tetrahydroperfluorooctyl methacrylate) (PFOMA) has been not reported. A key issue for the synthesis of well-controlled block copolymers in ATRP is the

nature and quantity of the terminal group of the first block that controls both the initiation and the blocking efficiency during the polymerization of a second monomer. Moreover, producing fully functionalized chains requires the suppression of termination and transfer reactions and can be achieved by adjusting the ratio of ($k_{\text{deact}}/k_{\text{act}}$) in ATRP.¹⁷ In this field, a lot of investigations are required to be done.

In this article, the synthesis of well-controlled PSAN-*b*-PFOMA by ATRP is investigated. The structures of PSAN-Br macroinitiator and PSAN-*b*-PFOMA diblock copolymer were described in Figure 1.

Recently, the application of the supercritical fluid technique, especially, supercritical carbon dioxide, as a green chemical method for synthesizing polymers has been emphasized.^{18–21} Unfortunately, most industrially important hydrocarbon-based polymers are relatively insoluble in ScCO₂. The polymers prepared early in ScCO₂ possess of lower yield and smaller molecular weight. Therefore, the application of ScCO₂ cannot attract adequate attention early. Lately, dispersion polymerization was found and proven useful for ScCO₂ based systems. In this article, we adopt dispersion copolymerization of acrylonitrile-vinyl acetate with PSAN-*b*-PFOMA as a stabilizer. It is potential to improve the yields and molecular weights of the copolymers. PSAN-*b*-PFOMA can form a reverse micelle structure in ScCO₂,²² because the PFOMA block

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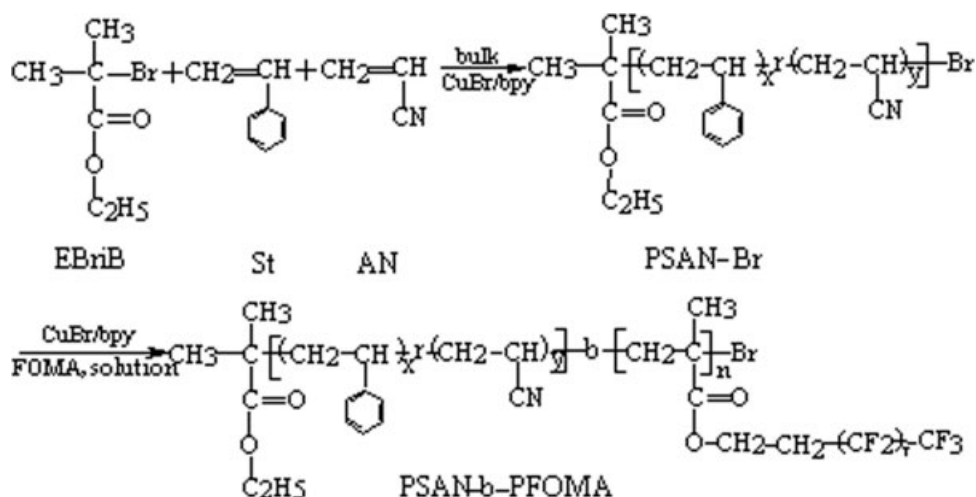


Figure 1 The synthesizing route of the macroinitiator and block polymer.

of PSAN-*b*-PFOMA can dissolve in ScCO_2 , and the PSAN block cannot dissolve in it. We presume that monomers can enter into the micell and react in it. Therefore, the micelle structures can prevent acrylonitrile-vinyl acetate-based colloidal particles from aggregation. In this article, with the diblock copolymers as stabilizers, poly(acrylonitrile-*r*-vinyl acetate) (PAVAc) colloid particles were prepared successfully by dispersion polymerization in ScCO_2 .

EXPERIMENTAL

Materials

1,1,2,2-Tetrahydroperfluorooctyl methacrylate (FOMA, Dupont) was purified by passage through a neutral alumina column at 40°C . Acrylonitrile (AN, Shanghai Chemical Reagent Company, CP, Shanghai, China) was purified by passage through a neutral alumina column at room temperature. Styrene (St, Shanghai Chemical Reagent Company, CP, Shanghai, China) was stirring in the presence of CaH_2 for 24 h and was distilled prior to use. Tetrahydrofuran (THF, Shanghai Chemical Reagent Company, AR, Shanghai, China) was

refluxed for 24 h in the presence of sodium wire. α,α,α -Trifluorotoluene (TFT, Shanghai Chemical Reagent Company, CP, Shanghai, China) was distilled under atmospheric pressure. CuBr (Shanghai Chemical Reagent Co., LTD., AR, Shanghai, China) was purified as described in the literature.²³ 2,2'-Bipyridine (bpy, Shanghai Chemical Reagent No. 1 Plant, AR, Shanghai, China) was recrystallized from hexane three times. Ethyl α -bromoisobutyrate (EBriB, Lancaster, 98+%) was used as received. Vinyl acetate (VAc, Shanghai Chemical Reagent Company, CP, Shanghai, China) was purified by passage through a neutral alumina column at room temperature. 2,2'-Azobisisobutyronitrile (AIBN, Shanghai Chemical Reagent Company, AR, Shanghai, China) was recrystallized from methanol three times. Carbon dioxide (CO_2 , Shanghai Wugang Gas Co., Shanghai, China 98+%) and nitrogen (N_2 , Shanghai Wugang Gas Co., Shanghai, China 99.9%) were used as received.

Atom transfer radical polymerization of PSAN-*b*-PFOMA

As a typical monofunctional PSAN-Br polymerization via ATRP (sample PSAN-Br-3 in Table I), CuBr

TABLE I
The Results of PSAN-Br and PSAN-*b*-PFOMA Prepared via ATRP

Sample	Feed ratio ^a (10^4 mol)	Time (h)	Yield (%)	M_n^b (theo)	M_n^c ($^1\text{H-NMR}$)	GPC	
						M_n	M_w/M_n
PSAN-Br-1	318/187/8.68	6	76.0	3,960	4,520	6,560	1.13
PSAN- <i>b</i> -PFOMA-1	42.4/1.08	65	65.9	17,730	18,160	8,340	1.14
PSAN-Br-2	347/204/8.68	7	82.0	4,630	4,750	6,790	1.09
PSAN- <i>b</i> -PFOMA-2	39.5/1.08	82	88.2	21,800	21,790	8,560	1.18
PSAN-Br-3	382/224/8.68	8	83.3	5,150	5,180	8,280	1.14
PSAN- <i>b</i> -PFOMA-3	50.3/1.08	88	83.8	25,920	25,990	8,950	1.13

^a PSAN-*b*-PFOMA, the feed ratio is $[\text{FOMA}]/[\text{PSAN-Br}]$.

^b M_n (theo) = yield % $\times \Sigma$ {[monomer]/[initiator] $\times M_n$ (monomer)} + M_n (initiator).

^c M_n ($^1\text{H-NMR}$) was calculated from the molar ratio of the monomer to initiator obtained from $^1\text{H-NMR}$ spectra.

(4.34×10^{-4} mol), and bpy (1.30×10^{-3} mol) were added into a dry 20 mL flat-bottom flask equipped with a stir bar. After sealing it with a rubber tube, the flask was degassed and backfilled with nitrogen three times and then left it under nitrogen. At the same time, the system was stirred. After 30 min, CuBr and bpy were well mixed. Styrene (3.82×10^{-2} mol) and AN (2.24×10^{-2} mol) were added successively, both of which were deoxygenated and added via syringes that had been purged with nitrogen. After the mixture became homogeneous, EBriB (8.68×10^{-4} mol) was added to the flask via a syringe, which had been purged with nitrogen. Then, the flask was placed in a 100°C oil bath for 8 h. The flask was cooled and diluted by THF after the reaction had been finished, and then the mixture was precipitated with excessive hexane. The yield was determined by gravimetry. The weight of the catalyst was subtracted from the total mass of the product to obtain the weight of polymer product. The mixture was purified by dissolving in THF and passed through a neutral alumina column to remove catalyst. The polymer was precipitated using excessive hexane, collected by filtration, and then dried in vacuum at 30°C for 24 h. The synthesis of the diblock copolymer PSAN-*b*-PFOMA was like that of synthesis of the macroinitiator. The difference lies in that the synthesis of macroinitiator was performed in bulk, while the block copolymerization needed to be carried out in solution. And, the reaction needed more time. In addition, when PSAN-*b*-PFOMA was synthesized, PSAN-Br was used as an initiator instead of EBriB. The solvent consisted of TFT and THF (4 : 1, v/v). The ratio of the total volume of the solvent added to the total mass of macroinitiator and fluoromonomer added was 2 : 1. The synthesise route of the macroinitiator and diblock polymer is shown by Figure 1.

Dispersion polymerization of AN-VAc in ScCO₂

Polymerization was conducted in ScCO₂ in a 20 mL, stainless steel autoclave equipped with a stir bar. In a typical polymerization, the reactor was charged with the desired amount of AIBN and stabilizer (PSAN-*b*-PFOMA) (0–0.20 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 purged with a flow of carbon dioxide slowly for three times to replace the air. The reactor was pressurized with CO₂, with a 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 prior to removal of the polymer product. To quantify the reaction product, the reaction cell was

rinsed with DMF to remove any residual polymer product and stabilizer. The polymer conversion was 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 ¹H NMR and a Waters 150 gel permeation chromatography (GPC). ¹H NMR was carried out on a Bruker-500 spectrometer with CDCl₃ as solvent. And the GPC consists of a waters 510-HPLC pump and a waters 410 differential refractometer. THF was used as solvent for PSAN-Br and PSAN-*b*-PFOMA, with calibrations based on standard polystyrene. FTIR spectra of the macroinitiators and diblock copolymers were recorded on a Nicolet 550 Series II spectrometer. The morphology of the polymers 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 100 particles chosen at random. The viscosity average molecular weights (M_v) were determined with an Ubbelohde capillary viscometer at 30°C using DMF as solvent.

RESULTS AND DISCUSSION

Characterizations of PSAN-Br and PSAN-*b*-PFOMA

Polymerizations of PSAN-Br and PSAN-*b*-PFOMA were carried out at 100°C in bulk and in solution,

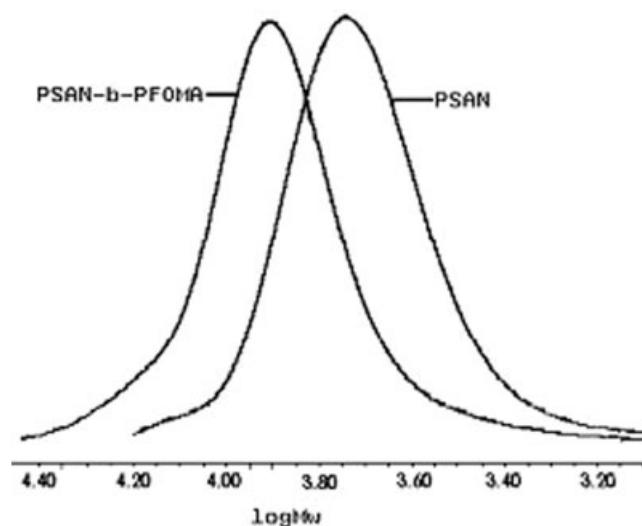


Figure 2 GPC traces of PSAN and PSAN-*b*-PFOMA: PSAN-Br (PSAN-Br-3 in Table I, M_n (GPC) = 8280, M_w/M_n = 1.14), PSAN-*b*-PFOMA (PSAN-*b*-PFOMA-3 in Table I, M_n (GPC) = 8950, M_w/M_n = 1.13).

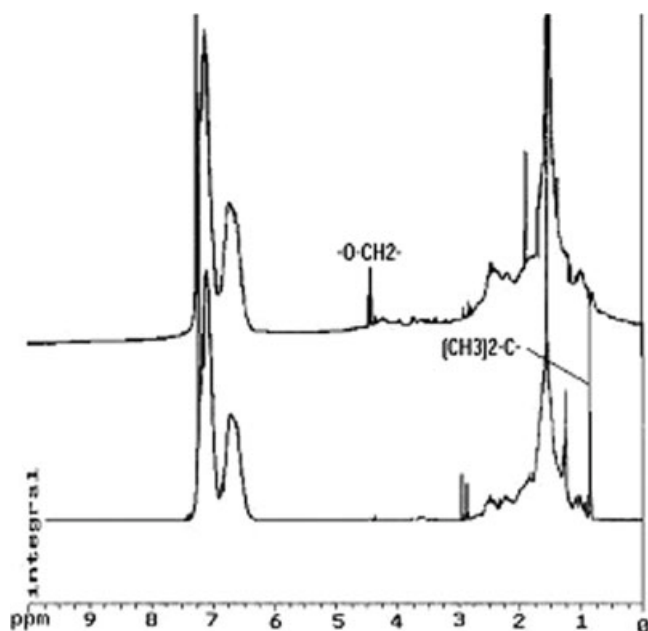


Figure 3 ^1H NMR spectra of PSAN-Br-3 (lower side) and PSAN-*b*-PFOMA-3 (upside) in CDCl_3 .

respectively. The results are listed in Table I. It is shown that the molecular weights of PSAN-Br and PSAN-*b*-PFOMA calculated by ^1H NMR is very close to the theoretical values. At the same time, the molecular weight distribution of PSAN-Br and PSAN-*b*-PFOMA suggested by GPC. From Table I, the molecular weight distribution of both PSAN-Br and PSAN-*b*-PFOMA is very narrow ($\text{PDI} < 1.2$). In addition, we noticed that the molecular weights given by GPC were different from the theoretical values. There may be two reasons: First, the macroinitiators and block copolymers are polar polymers, while the standard polystyrene is nonpolar one. Second, for PSAN-*b*-PFOMA, THF is not a good solvent for the PFOMA block. So the PFOMA block cannot stretch completely. Therefore, the molecular weights given by GPC may be not very accurate. According to the literature,²⁴ when applying of polystyrene calibration curves to GPC analysis of more polar leads to inaccurate M_w parameters.

Figure 2 shows the GPC traces of PSAN-Br and PSAN-*b*-PFOMA, both of which are with single peak, proving that there is no impurity in both

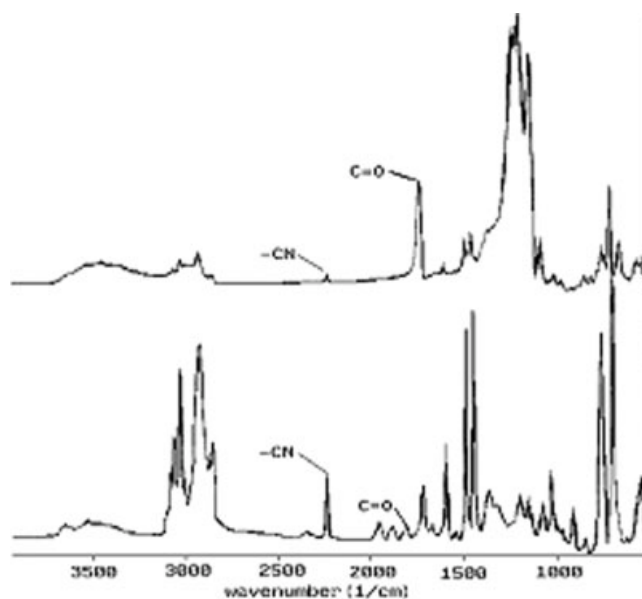


Figure 4 FTIR spectra of PSAN-Br-3 (lower side) and PSAN-*b*-PFOMA-3 (upside).

PSAN-Br and PSAN-*b*-PFOMA. Furthermore, it can be seen that the GPC trace of the block copolymer shifts to the higher molecular weight. Therefore, monomer FOMA is proven to be initiated by macroinitiator PSAN-Br successfully. ^1H NMR spectra of the macroinitiator and diblock copolymer are shown in Figure 3. Obviously, ^1H NMR spectrum of PSAN-*b*-PFOMA-3 shows diagnostic signals centered at 4.4 ppm, characteristics of the methylene in $-\text{O}-\text{CH}_2-$ of the ester group of FOMA. At the same time, it can be seen that the intensity of peaks of the methylene in $-\text{O}-\text{CH}_2-$ is relatively small, which may be ascribed to the poor solubility of the PFOMA block of PSAN-*b*-PFOMA in CDCl_3 . The PSAN-*b*-PFOMA may form a micelle structure with PSAN unit as shell and PFOMA unit as core,^{26–29} making the intensity relatively small. But we can calculate molecular weight of PSAN-*b*-PFOMA via other characteristic peaks from ^1H NMR spectrum.³⁰ For PSAN-Br, on the basis of the intensity of peaks at 6.3–7.2 ppm ($I_{6.3-7.2}$), 0.9–3.1 ppm ($I_{0.9-3.1}$) and 0.8–0.9 ppm ($I_{0.8-0.9}$) (lower side), the molar ratio of St/EBriB could be calculated according to eq. (1):

TABLE II
Effect of Stabilizer Concentration on the Yield

Sample	Stabilizer ^a	M_v	Yield (%)	D_n^b (μm)	PSD ^c	Particle Morphology
1	None	54,600	55.0	–	–	Irregular
2	PSAN- <i>b</i> -PFOMA-1	75,500	70.0	0.21	1.13	Spherical
3	PSAN- <i>b</i> -PFOMA-2	74,800	70.5	0.11	1.04	Spherical
4	PSAN- <i>b</i> -PFOMA-3	79,500	71.8	0.11	1.04	Spherical

^a The stabilizer concentration is 10 (w/w % to monomers) for Sample 2–Sample 4.

^b D_n , mean particle diameter.

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

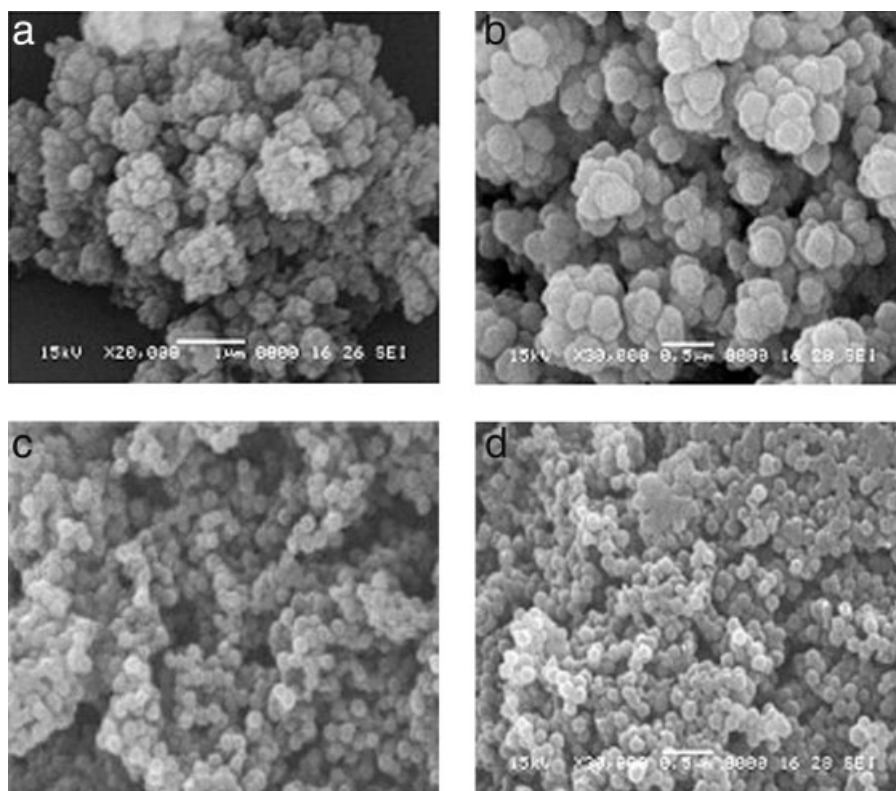


Figure 5 Scanning electron micrographs from reactions (a) sample 1 in Table II and (b)–(d) sample 2–4 in Table II.

$$\text{St/EBriB} = (I_{6.3-7.2}/5)/(I_{0.8-0.9}/6) \quad (1)$$

The molar ratio of AN/EBriB could be calculated according to eq. (2):

$$\text{AN/EBriB} = [I_{0.9-3.1} - (3I_{6.3-7.2}/5)]/(I_{0.8-0.9}/2) \quad (2)$$

So, the $M_n(^1\text{H NMR})$ of the PSAN-Br could be calculated to eq. (3):

$$M_n(^1\text{H NMR}) = \text{St/EBriB} \times M_{\text{St}} + \text{AN/EBriB} \times M_{\text{AN}} + M_{\text{EBriB}} \quad (3)$$

For PSAN-*b*-PFOMA, on the basis of the intensity of peaks at 6.3–7.2 ppm ($I_{6.3-7.2}$), 0.8–3.1 ppm ($I_{0.8-3.1}$) (lower side) and 6.3–7.2 ppm ($I_{6.3-7.2}^*$), 0.8–3.1 ppm ($I_{0.8-3.1}^*$) (upside), the molar ratio of FOMA/St could be calculated according to eq. (4):

$$\text{FOMA/St} = [(I_{0.8-3.1}^* - (I_{0.8-3.1})(I_{6.3-7.2}^*)/(I_{6.3-7.2}))]/(I_{6.3-7.2}^*) \quad (4)$$

So, the $M_n(^1\text{H NMR})$ of the PSAN-*b*-PFOMA could be calculated to eq. (5):

$$M_n(^1\text{H NMR}) = \text{FOMA/St} \times \text{St/EBriB} \times M_{\text{FOMA}} + M_{\text{EBriB}} - \text{Br} \quad (5)$$

According to eqs. (1) and (2), we can calculate the molar ratio of the St/AN from $^1\text{H NMR}$ spectrum of

PSAN-Br, and the result accords with azeotropic molar ratio.

There exists a little error that should be noted. The peak related to the initiator protons (CH_3- in $\text{CH}_3-\text{CH}_2-\text{O}-$) has also been appeared at region of 0.9–3.1 ppm. So, in eq. (2) there exists a little error.

The successful synthesis of diblock copolymerization PSAN-*b*-PFOMA is affirmed again by the FTIR spectra. In FTIR spectra of PSAN-Br and PSAN-*b*-PFOMA, compared with PSAN-Br, the diblock copolymer's characteristic peak of the ester group at 1735 cm^{-1} of becomes more intense, indicating the successful synthesis of the diblock copolymer.

Dispersion polymerization of acrylonitrile-vinyl acetate

Dispersion polymerizations of acrylonitrile-vinyl acetate with the diblock copolymers as stabilizers were conducted in ScCO_2 , and the results are shown in Table II. The precipitation polymerization that was conducted in the absence of stabilizer (Sample 1) resulted in the formation of irregular polymer particles [Fig. 5(a)]. In contrast, spherical particles can be observed resulted from the reactions carried out in the presence of the amphiphilic diblock copolymers (PSAN-*b*-PFOMA) [Fig. 5(b–d)]. The mechanism for particle formation in these polymerizations may involve micellar nucleation or surfactant adsorption to precipitating

polymer,³¹ although such aggregates have not yet been identified in the presence of a large amount of monomers. In addition, the yields and the molecular weights were found to be increased greatly by stabilizer addition. Therefore, the resultant PAVAc particles became effectively stabilized, which can be indicated by the yields and the molecular weights. The products prepared via dispersion polymerization possess milky white appearance, which was similar to that observed for conventional aqueous latex. Upon the venting of CO₂, a dry, white, free-flowing powder remained in the reaction vessel. From Figure 4, when the PFOMA block is shorter [$M_{\text{PFOMA}} = 13,890$ (calculated on the basis of ¹H NMR) (PSAN-*b*-PFOMA-1 in Table I)], the dispersion effect is not obvious [Fig 5(b)]. The aggregate phenomenon is relative patency. The dispersity index of the particle size distribution is also relatively wider. And, the diameter of the particle is relatively bigger. When the molecular weight of PFOMA block reaches over 17,360 (calculated on the basis of ¹H NMR) (PSAN-*b*-PFOMA-2 in Table I), the dispersion effect is very good [Fig. 5(c,d)]. The dispersity index of the particle size distribution is very narrow. And, the diameter of the particle is little. But, there is no obvious trend lying in particle morphology and the dispersity index of the particle size distribution by continuing to increase the molecular weight of the PFOMA block. So, we can draw a conclusion that when the molecular weight of PSAN block is about 4500 (see Table I), it is enough that the molecular weight of PFOMA block reach to 17,360. 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 the molecular weight of the diblock stabilizers with soluble PFOMA segments' molecular is much longer than that of the macroinitiator, which may make an inefficient adsorption of the stabilizer on the polymer.³¹ The M_v was calculated using the Mark-Houwink-Sakurada equation given by $[\eta] = KMv^a$, where the K and a values used in the calculation are 20.9×10^{-3} mL/g and 0.75, respectively.³³

CONCLUSIONS

Amphiphilic diblock copolymer, consisting of PSAN and PFOMA and with well-controlled molecular weight and narrow molecular weight distribution (PDI < 1.2), was successfully synthesized via ATRP. Using it as a stabilizer, dispersion copolymerization of acrylonitrile-vinyl acetate in supercritical carbon dioxide can be accomplished to provide micrometer-size spherical PAVAc particles. Compared with precipitation polymerization, PAVAc prepared by dispersion possesses of higher yield and higher molecu-

lar weight. In addition, the PAVAc particle morphology is spherical, and the dispersity index of the particle size distribution is very narrow.

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