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Dispersion Polymerization of Acrylonitrile in Supercritical Carbon Dioxide

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ABSTRACT: Herein we report the successful dispersion polymerization of acrylonitrile in carbon dioxide using a block copolymer consisting of polystyrene and poly(1,1-dihydroperfluorooctyl acrylate) as a stabilizer. Submicron-sized polyacrylonitrile particles were obtained. The initial concentrations of acrylonitrile and the stabilizer and the reaction pressure had some effects on the resulting size of the colloidal particles.

Introduction

Carbon dioxide provides an environmentally benign, inexpensive, and nonflammable alternative to the aqueous and organic solvents traditionally employed by the polymer industry.[1−3] The primary challenge in extending the use of CO_2 as a solvent for polymer synthesis arises from the fact that silicones and fluoropolymers constitute the only classes of polymeric materials that have been shown to demonstrate high solubility in CO_2 at easily accessible temperatures and pressures ($T <$ 100 °C, $P <$ 350 bar).[4−9] Conversely, most industrially important hydrocarbon-based polymers are relatively insoluble in CO_2. Therefore, the production of such polymers in CO_2 necessitates the use of heterogeneous polymerization techniques.

Dispersion polymerization constitutes one of the heterogeneous polymerization techniques which has proven useful thus far for polymerizations in CO_2. Dispersion polymerizations are characterized by the solubility of the monomer, initiator, and surfactant in the continuous phase but the insolubility of the resulting polymer. Typically, the product from a dispersion polymerization exists as spherical particles that range in size from 0.1 to 10 μm.[10] Dispersion polymerizations are governed by a delicate interplay which includes the partitioning and interactions of all of the reaction mixture components.[11] The effectiveness of the surfactant represents a key component in the preparation of a stable latex.[12] Successful dispersion polymerizations of methyl methacrylate,[13−20] styrene,[21−24] divinylbenzene,[25] and vinyl acetate[26] in CO_2 have been reported. The stabilizers studied in these experiments were carefully selected and synthesized on the basis of their high solubility in CO_2 and the established criteria for steric stabilizer effectiveness. We have studied five different types of stabilizers: CO_2-soluble homopolymers, random copolymers, grafted copolymers, amphiphilic diblock copolymers, and copolymerizable macromonomers. While all of these general types of stabilizer architectures have been shown to be effective in a CO_2 continuous phase, their efficacy in protecting acrylonitrile-based latex particles from coagulation has yet to be established.

Herein some of the above-mentioned surfactants have been compared and contrasted in homopolymerization studies of acrylonitrile in CO_2. As a result of the research, the effectiveness of the block copolymer consisting of polystyrene (PS) and poly(1,1-dihydroperfluorooctyl acrylate) (PFOA) on the resulting submicron-sized polyacrylonitrile (PAN) particles has been discovered. In addition, the influence of the stabilizer concentration, monomer concentration, anchor-soluble balance (ASB) of the stabilizing block copolymer, and the pressure on the resulting PAN colloidal particles have also been investigated.

Experimental Section

Materials. 1,1-Dihydroperfluorooctyl acrylate (FOA, 3M) was purified by passage through an alumina column. 2,2′-Azobis(isobutyronitrile) (AIBN, Aldrich) and tetraethylthiuram disulfide (TD, Aldich) were recrystallized from methanol. Acrylonitrile (Aldrich), styrene (Aldrich), α,α,α-trifluorotoluene (TFT, Aldrich), *N*,*N*-dimethylacetamide (DMA, Aldrich), 2,3-dihydroperfluoropentane (PFP, SynQuest), methylene chloride (Mallinckrodt), and methanol (Mallinckrodt) were used as received. Carbon dioxide (SFC/SFE Grade) was kindly provided by Air Products and was used as received.

Fluorinated Acrylic Homopolymer. PFOA was synthesized using radical polymerization in bulk. A 5 g sample of FOA was polymerized with 0.025 g of AIBN as an initiator at 65 °C for 20 h in a nitrogen atmosphere, then dissolved in a mixture of PFP and methylene chloride (90/10 v/v %), and reprecipitated in methanol. The obtained polymers were filtered and dried in vacuo. The structure of this fluorinated acrylic homopolymer is shown in Figure 1a.

Diblock Copolymer. Diblock copolymer consisting of PS and PFOA (PS-*b*-PFOA) was synthesized using the "iniferter" technique developed by Otsu.[27] The synthesis of the specific block copolymers has been previously described.[28] The styrene block was synthesized first using tetraethylthiuram disulfide as the initiator. The telechelic PS block was then used as a

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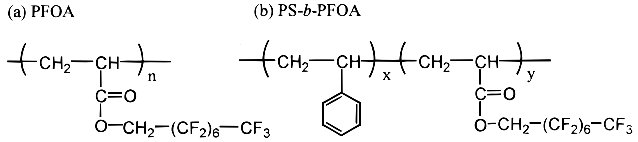

Figure 1. Structures of PFOA homopolymer and PS-*b*-PFOA diblock copolymer used as the stabilizer.

Table 1. Data for the Polymerizations of Acrylonitrile in CO_2[a]

entry	stabilizer	yield[b] (%)	Dn[c] (μm)	PSD[d]	particle morphology
1	none	70			irregular
2	PS-*b*-PFOA (4.2K/19.7K)	68	0.45	1.15	spherical
3	PS-*b*-PFOA (4.2K/30.0K)	72	0.44	1.05	spherical
4	PS-*b*-PFOA (4.2K/37.5K)	69	0.46	1.14	spherical
5	PFOA	65			irregular

[a] Reaction conditions: 2 g of acrylonitrile, 0.025 g of AIBN, 375 ± 5 bar, 65 °C, 20 h; for stabilized reactions (entries 2−5), 0.2 g of stabilizer was used. [b] Yields were determined gravimetrically. [c] Dn = mean particle diameter. [d] PSD = dispersity index of the particle size distribution, Dw/Dn.

macroinitiator in the photopolymerization of the second monomer, FOA, 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, $\langle M_n\rangle_{\text{styrene}}/\langle M_n\rangle_{\text{FOA}}$. The M_n of the PS was determined by GPC prior to the addition of FOA monomer. After the formation of the PFOA block, the ratio of FOA repeat units to styrene repeat units was determined by ^{1}H NMR. The structure of this diblock copolymer is shown in Figure 1b.

Dispersion Polymerizations. Polymerizations were conducted in CO_2 in a 25 mL, high-pressure view cell equipped with sapphire windows which permit visual observation of the reaction mixture. The reactor was charged with AIBN and the desired amount of surfactant (except control reactions in which no surfactant was used), and then the system was purged with a flow of argon prior to the addition of monomer. Monomer was then added to the system under an argon blanket. An ISCO model no. 260D automatic syringe pump was used to pressurize the reactor with CO_2 to approximately 70−120 bar, depending on the final pressure desired, and the reaction mixture was heated to 65 °C. As the reaction vessel was heated, the remaining CO_2 was added to the system, if needed, until the desired pressure was reached. Once the final reaction conditions were obtained, the reactions were allowed to proceed with stirring by a magnetic stir bar for 20 h. At the end of the reactions, the reactor was cooled, the CO_2 was slowly vented from the cell, and then the polymer product was removed from the cell. To quantify the reaction yields, the reaction cell was rinsed with DMA to remove any residual polymer product and stabilizer. The polymer conversion was determined gravimetrically. The weight of the stabilizer was subtracted from the total mass of the product to obtain the weight of polymer product.

Characterization. Molecular weights of the telechelic PS block were determined by a Waters 150-CV gel permeation chromatograph (GPC) with Ultrastyragel columns of 100, 500, 10^3, and 10^4 Å porosity, using tetrahydrofuran as the eluent against polystyrene standards at a flow rate of 1.1×10^{-3} dm^3 min^{-1} at 35 °C. A refractometer was used for the detection. The morphology of the polymers was determined using a JEOL 6400FE scanning electron microscope (SEM). The number-average particle size and particle size distribution were determined by measuring the diameter of 100 particles. ^{1}H NMR spectra were obtained from a Varian 300 MHz NMR.

Results and Discussion

Comparison of Stabilizers. The data for the polymerization of acrylonitrile in CO_2 using several different stabilizers are summarized in Table 1. The precipitation polymerization that was conducted in the absence of stabilizer (entry 1) resulted in the formation of nonspherical polymer particles (Figure 2a). In contrast, the reactions that were carried out in the presence of PS-*b*-PFOA amphiphilic diblock copolymers started out translucent and then formed a stable colloidal dispersion of PAN that showed no settling of polymer in the absence of stirring. The successful stabilization of the polymerization resulted in spherical particles (Figure 2b). The mechanism for particle formation in these polymerizations may involve micellar nucleation or surfactant adsorption to precipitating polymer,[29] although such aggregates have not yet been identified in the presence of a large amount of acrylonitrile monomer. The resultant PAN particles became effectively stabilized since the reaction mixture exhibited

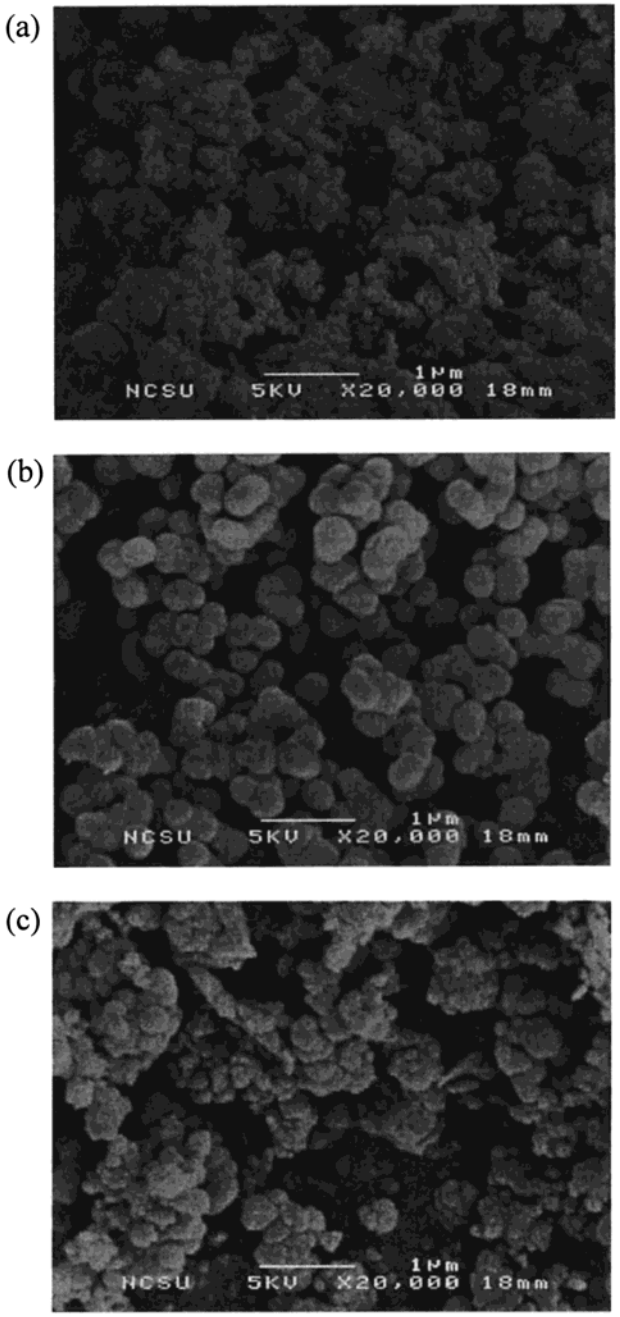

Figure 2. Scanning electron micrographs from reactions containing (a) none, (b) PS-*b*-PFOA (4.2K/30.0K), and (c) PFOA stabilizer.

Table 2. Effect of the Percent Solids on the Dispersion Polymerization of Acrylonitrile in CO_2[a]

entry	acrylonitrile conc (w/v % in CO_2)	yield[b] (%)	Dn[c] (μm)	PSD[d]	particle morphology
6	6	70	0.21	1.03	spherical
7	8	76	0.27	1.03	spherical
8	10	77	0.37	1.03	spherical
9	14	81			irregular

[a] Reaction conditions: 0.025 g of AIBN, 0.5 g of PS-*b*-PFOA (4.2K/30.0K), 375 ± 5 bar, 65 °C, 20 h. [b] Yields were determined gravimetrically. [c] Dn = mean particle diameter. [d] PSD = dispersity index of the particle size distribution, Dw/Dn.

a milky white appearance, which was similar to that observed for a conventional aqueous latex. Upon venting the CO_2, a dry, white, free-flowing powder remained in the reaction vessel.

The results of a study in which the length of the CO_2-soluble PFOA segment was varied while the length of the anchoring PS segment was kept constant are summarized in Table 1. For all of the reactions in which diblock copolymer was employed as the steric stabilizer, the dispersion polymerization of acrylonitrile was successfully carried out, although some aggregates were observed by SEM. One possible explanation for this agglomeration is that since diblock stabilizers with soluble PFOA segments as long as 20K−38K and a short anchor segment of 4.2K were employed, there may be inefficient adsorption of the stabilizer onto the polymer. The results did not, however, show any discernible trend in yield, particle size, and particle size distributions as a function of the length of the soluble block.

For comparison, the polymerization conducted in the presence of the CO_2-soluble homopolymer, PFOA, did not result in any improvement over the reaction run without added stabilizer (Figure 2c). This poor result is considered to be due to the inefficient anchoring of PFOA homopolymer to the surface of the PAN particles. This result is not particularly surprising since the primary mechanism by which homopolymeric stabilizers are effective is through either chemical grafting or physical adsorption to the surface of the growing polymer colloid. During the polymerization of acrylonitrile, PFOA may not become chemically grafted onto the PAN particles, or the physical adsorption could be ineffective due to the little tendency of PFOA to adsorb to the high-polarity surface. Similarly, PFOA has been shown to adsorb only very weakly at the interface between polar poly(ethylene glycol) and CO_2.[30] The unsuccessful dispersion polymerization of acrylonitrile using PFOA homopolymer as a stabilizer stands in contrast to the successful dispersion polymerizations of methyl methacrylate[13,14] and styrene.[23]

Effect of the Monomer Concentration. Dispersion polymerizations were also conducted at four different concentrations of acrylonitrile (Table 2). In all cases the contents of PS-*b*-PFOA (4.2K/30.0K) stabilizer and initiator added to the system were kept constant at 2 and 0.1 w/v %, respectively. Figure 3 shows the scanning

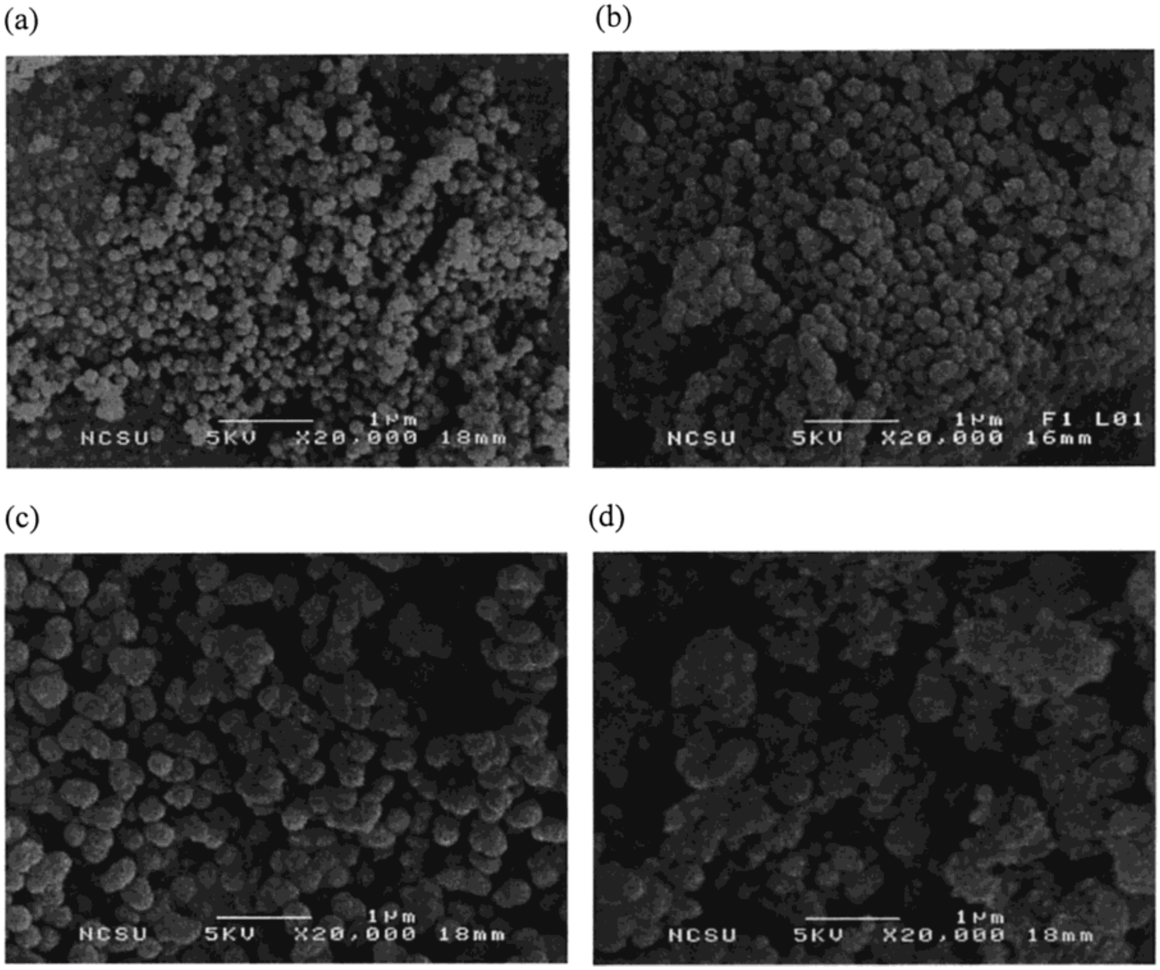

Figure 3. Scanning electron micrographs from reactions with (a) 6%, (b) 8%, (c) 10%, and (d) 14% acrylonitrile (w/v % in CO_2) in CO_2 at 375 ± 5 bar and 65 °C.

Table 3. Effect of Stabilizer (PS-*b*-PFOA(4.2K/30.0K)) Concentration on the Dispersion Polymerization of Acrylonitrile in CO_2[a]

entry	stabilizer conc (w/w % to monomer)	yield[b] (%)	Dn[c] (μm)	PSD[d]	particle morphology
10	10	87			irregular
11	15	76	0.44	1.03	spherical
12	20	77	0.37	1.03	spherical
13	30	77	0.33	1.02	spherical

[a] Reaction conditions: 2.5 g of acrylonitrile, 0.025 g of AIBN, 383 ± 14 bar, 65 °C, 20 h. [b] Yields were determined gravimetrically. [c] Dn = mean particle diameter. [d] PSD = dispersity index of the particle size distribution, Dw/Dn.

electron micrographs of the PAN obtained from these reactions. Generally, results in the literature for dispersion polymerization have shown that an increase in the particle diameter is observed when the monomer concentration increases and when the surfactant concentration decreases. Such an expected trend in the particle size was observed in this system where the monomer concentration was increased 6−14 w/v % while the surfactant/monomer ratio simultaneously decreased (surfactant amount remained constant at 0.5 g). When the monomer concentration was over 10 w/v %, the dispersion formed was initially stable, but flocculation during polymerization occurred and the morphology of the resulting polymer was found by SEM to be nonspherical. As the monomer concentration increased, the solvency of the medium for growing polymer chain also increased, and this resulted in an increase of critical molecular weight for precipitation or surface activity of the growing oligomeric radicals. Compared with other systems, the possibility of preparing a stable PAN dispersion with a higher PAN content is rather limited by the comparatively poor solubility of PAN in its monomer, the high polarity of PAN, and the strong attractive forces between nitrile groups on the surface of the polymer particles.

Effect of the Stabilizer Concentration. As shown in Table 3, the particle diameter was slightly affected by the concentration of the stabilizer. Figure 4 shows the scanning electron micrographs of the PAN obtained from these reactions. The diameter of the particles decreased from 0.44 to 0.33 μm when the concentration of PS-*b*-PFOA increased 15 to 30 w/w % (to monomer). In the presence of a large amount of PS-*b*-PFOA, it is believed that the oligomeric PAN 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.[23,24,31] The particle diameters were thus determined by the relative contribution of the anchoring modes of adsorption and chemical grafting. When the stabilizer concentration was lowered to 10 w/w %, the dispersion formed was initially stable, but flocculation occurred and the morphology of resulting polymer was found by SEM to be nonspherical. This indicates that for dispersion polymerizations of acrylonitrile in CO_2 15 w/w % stabilizer is needed to prevent coagulation of the

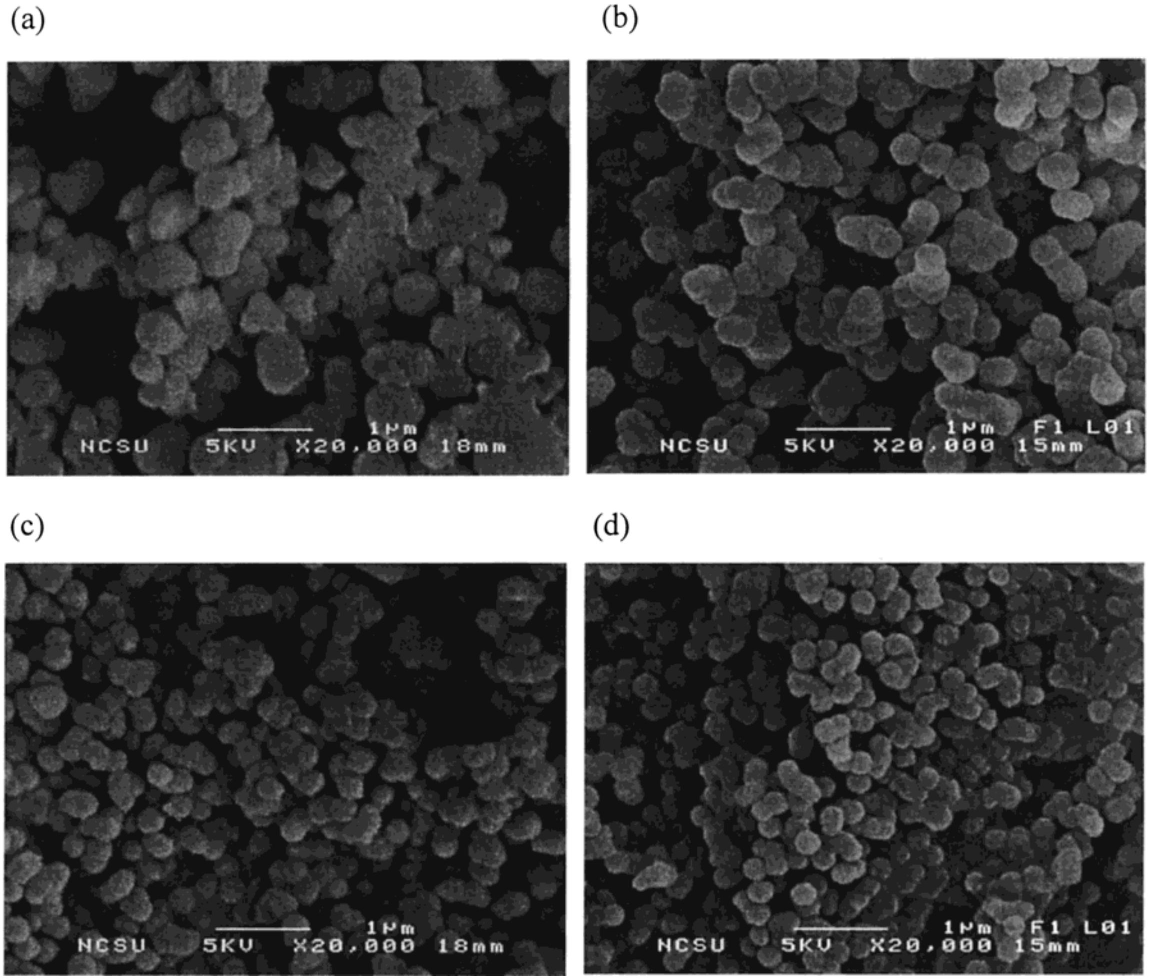

Figure 4. Scanning electron micrographs from reactions with (a) 10%, (b) 15%, (c) 20%, and (d) 30% stabilizer (w/w to acrylonitrile).

Table 4. Pressure Study for Acrylonitrile Polymerization in CO_2 Using PS-*b*-PFOA as the Stabilizer[a]

entry	P_i[b] (bar)	P_f[c] (bar)	yield[d] (%)	Dn[e] (μm)	PSD[f]
14	444	426	76	0.43	1.04
15	375	371	77	0.37	1.03
16	294	300	79	0.34	1.02
17	207	284	89	0.27	1.03

[a] Reaction conditions: 2.5 g of acrylonitrile, 0.025 g of AIBN, 0.5 g of PS-*b*-PFOA(4.2K/30.0K), 65 °C, 20 h. [b] P_i = initial pressure. [c] P_f = final pressure. [d] Yields were determined gravimetrically. [e] Dn = mean particle diameter. [f] PSD = dispersity index of the particle size distribution, Dw/Dn.

polymer particles at 10 w/v % PAN content. This is thought to be the result of less effective anchoring of the PS-*b*-PFOA stabilizer to a growing PAN particle. However, at 8 w/v % PAN content, a stable dispersion of PAN was generated even at 10 w/v % of stabilizer (based on monomer) (Table 1, entry 3). The minimum stabilizer concentration for a stable dispersion of PAN may depend on the total solid content of PAN.

Effect of CO_2 Pressure. A primary advantage of employing supercritical CO_2 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 an acrylonitrile polymerization without having to add a cosolvent. The effects of pressure on the polymerizations are summarized in Table 4. The diameter of the resultant PAN particles became 60% larger as the initial pressure was increased from 207 to 444 bar. As the pressure is increased, the solvency of the medium for the growing polymer chains increases, and this results in an increase in the critical molecular weight for precipitation or surface activity of the growing oligomeric radicals. Previous reports have demonstrated that, for the dispersion polymerization of styrene in CO_2 using PS-*b*-PDMS as the stabilizer, the diameter of the resultant PS particles also became 30% larger as the initial pressure was increased from 297 to 439 bar.[22]

Another interesting observation that was made during these experiments involved the change in pressure over the course of the reaction. For low initial pressures ($P < 300$ bar) we observed an increase in pressure during the course of the reaction. The same observation was made in styrene[22,23] and MMA[13] polymerization in CO_2. We believe that this effect arises from the thermodynamics of mixing, which favors expulsion of CO_2 and monomer from the polymer-rich phase at low CO_2 pressures.

Conclusions

Dispersion polymerization of acrylonitrile in supercritical carbon dioxide can be accomplished using a block copolymer consisting of PS and PFOA as a stabilizer to provide submicron-size spherical PAN particles. The particle diameter can be slightly controlled by the amount of the stabilizer, the monomer concentration, and the reaction pressure.

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