Dispersion Polymerization of Styrene in Supercritical Carbon Dioxide: Importance of Effective Surfactants

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ABSTRACT: The dispersion polymerization of styrene in supercritical CO_2 using amphiphilic diblock copolymers to impart steric stabilization was investigated. Lipophilic, CO_2-insoluble materials can be effectively emulsified in carbon dioxide using amphiphilic diblock copolymer surfactants. The resulting high yield (>90%) of polystyrene is obtained in the form of a stable polymer colloid comprised of submicron-sized particles. The particle diameter and distribution of sizes were shown to be dependent on the nature of the stabilizing block copolymer.

Introduction

Carbon dioxide is rapidly becoming an attractive alternative to liquid solvents traditionally used in separations, coating applications, and polymerizations since it is an environmentally benign medium which has the potential to eliminate the production of organic and aqueous waste streams in manufacturing facilities.[1,2] Because CO_2 has a critical temperature (T_c) of 31.1 °C and a critical pressure (P_c) of 73.8 bar,[3] it presents an interesting and easily accessible medium in which to explore the advantages of supercritical fluids. As an illustration, one of the primary advantages of employing a supercritical fluid as the reaction medium lies in the ability to manipulate the solvent strength (dielectric constant) by simply varying the temperature or pressure of the system. When CO_2 is used as the continuous phase for a polymerization reaction, the partition coefficient of the reagents and products between the solvent and the dispersed phase is of primary importance. To begin with, CO_2 has a low dielectric constant; by varying temperature and density, Keyes and Kirkwood reported values ranging from 1.01 to 1.45 for gaseous CO_2 and 1.60−1.67 for liquid CO_2.[4] It has been noted that CO_2 behaves very much like a hydrocarbon solvent with respect to its capability to dissolve small molecules, and thus many monomers exhibit high solubility in CO_2.[5] Even though it constitutes a medium with a relatively low dielectric constant, CO_2 has a strong quadrupole moment that allows it to dissolve some polar molecules such as methanol. In contrast, other polar molecules such as water, amides, ureas, urethanes, and azo dyes exhibit very poor solubility in CO_2.[5] Bartle and coworkers have compiled the solubilities of a large number of compounds of low volatility in supercritical CO_2.[6] In contrast to the high solubility of many small molecules in CO_2, it is an exceedingly poor solvent for most high molar mass polymers. In fact, the only classes of polymers which have been shown to demonstrate good solubility in CO_2 are fluoropolymers and silicones. Our group has previously demonstrated the successful synthesis of high molecular weight fluoropolymers through the use of homogeneous free-radical solution polymerizations in CO_2.[7] However, the relative insolubility of many industrially important polymers in supercritical CO_2 necessitates the use of heterogeneous polymerization techniques.

Dispersion polymerization constitutes one heterogeneous technique which has proven useful thus far for CO_2-based systems. In 1994, we reported the successful dispersion polymerization of methyl methacrylate (MMA) in CO_2 using a fluorinated acrylate homopolymer, poly(1,1-dihydroperfluorooctyl acrylate) [poly(FOA)], as the stabilizer.[8] Dispersion polymerizations are characterized by the solubility of both the monomer and the initiator in the continuous phase, but the insolubility of the resulting polymer in the continuous phase. Because the polymer is stabilized as a colloid, the polymerization continues to higher degrees of polymerization than the analogous precipitation reaction in the absence of stabilizer. In addition, the product from a dispersion polymerization exists as spherical particles that typically range in size from 100 nm to 10 μm.[9] Barrett has published a general review of heterogeneous dispersion polymerizations.[10] Numerous investigators have employed free-radical dispersion polymerization methods for the preparation of monodisperse polystyrene (PS) particles in the micron size range using organic solvents as the dispersing medium.[11−16] In these experiments, homopolymers such as hydroxypropyl cellulose, poly(*N*-vinylpyrrolidone), poly(acrylic acid), and poly(vinyl alcohol) were used to sterically stabilize the PS colloids in alcoholic media. However, research has revealed that amphiphilic block and graft copolymers are generally the best steric stabilizers.[17,18] Dawkins and Taylor have shown that diblock copolymers of PS and poly(dimethylsiloxane) are effective as stabilizers for the dispersion polymerization of styrene in aliphatic hydrocarbons.[19−21] In more recent work, Winnik and co-workers have employed diblock copolymers of PS and poly(ethylene oxide) to stabilize the dispersion polymerization of styrene in methanol.[22]

Although we have shown that poly(FOA) is an effective stabilizer for the polymerization of MMA in CO_2, it was not an effective stabilizer for the polymerization of other monomers such as styrene. This was thought to be derived from ineffective anchoring of the fluorinated acrylate stabilizer to a growing PS particle. To remedy this situation, herein we employ a strategy that improves the anchoring efficiency of the polymeric stabilizer: we use block copolymers containing a PS segment, which should readily partition into the lipophilic core and anchor itself to a growing PS particle, and a poly(FOA) block which is readily solubilized in CO_2 and should serve to stabilize the growing PS particle through a steric stabilization mechanism. We also demonstrate

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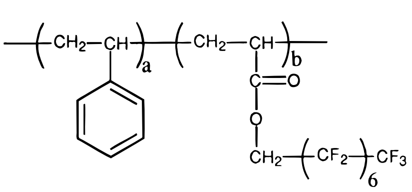
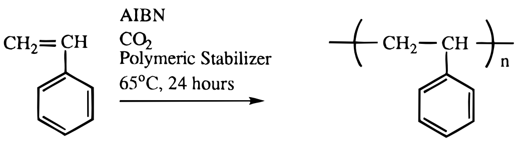


Figure 1. Poly(styrene-*b*-FOA) structure;[24] the fluorinated alkyl chain contains ca. 25% CF_3 branches.

Scheme 1. Polymerization of Styrene in Supercritical CO_2



that this block copolymeric surfactant stabilizes the *in situ* generation of a polymer colloid during the dispersion polymerization of styrene monomer in CO_2.

Experimental Section

Materials. Styrene (Aldrich) and 1,1-dihydroperfluorooctyl acrylate (FOA, 3M) monomers were purified by passage through an alumina column and were deoxygenated by argon purge prior to use. Tetraethylthiuram disulfide (TD, Aldrich) was recrystallized twice from methanol. 2,2′-Azobisisobutyronitrile (AIBN, Eastman Kodak) was recrystallized twice from methanol. Tetrahydrofuran (Mallinckrodt, HPLC grade) was used as received. Carbon dioxide (SFC/SFE grade with a helium head pressure) was generously provided by Air Products and Chemicals and was used as received.

Diblock Copolymers. Polystyrene-*b*-poly(FOA) [PS-*b*-poly(FOA)] diblock copolymers (Figure 1) were synthesized using the "iniferter" technique developed by Otsu.[23]

The synthesis of these specific block copolymers has been previously described.[24] The styrene block was synthesized first using tetraethylthiuram disulfide as the initiator. The telechelic PS block was then used as a 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 of the blocks, $<M_n>_{\text{styrene}}/<M_n>_{\text{FOA}}$.[25]

Dispersion Polymerizations. Polymerizations were conducted in supercritical CO_2 in a 10-mL, high-pressure view cell equipped with sapphire windows which permit visual observation of the reaction mixture.[26] In both the precipitation polymerizations without added stabilizer and dispersion polymerizations with added stabilizer, AIBN was employed as the free-radical initiator (Scheme 1). The decomposition kinetics and initiator efficiencies of AIBN in supercritical CO_2 have been previously reported.[7,27] The reactor was charged with initiator and the desired amount of surfactant and purged with a flow of argon prior to the addition of monomer. The styrene monomer was then added to the system under argon using a glass syringe. An Isco Model No. 260D automatic syringe pump was used to pressurize the reactor with CO_2 to approximately 70 bar, and the reaction mixture was heated to 65 °C. As the reaction vessel was heated, the remaining CO_2 was slowly added to the system until the desired temperature and pressure were reached. The initial reaction conditions were 65 °C and either 204 or 345 bar, and the reaction was allowed to proceed for 24 h while being stirred. At the end of the reaction, the reactor was cooled, the CO_2 was slowly vented from the cell, and the polymer product was removed from the cell.

Characterization. The molecular weight data for the PS samples were determined using a Waters 150-CV gel permeation chromatograph (GPC) with Ultrastyragel columns of 100, 500, 10^3, and 10^4 Å porosities using THF as the eluent and PS standards (Showa Denko). The morphology of the polymers was determined using a JEOL 6400 FE scanning electron microscope (SEM). The mean particle size and particle size distributions were determined by measuring the diameter of 100 particles. These data were also used to construct particle-size histograms. ^{1}H NMR spectra were obtained from a Bruker WM250 spectrometer.

Results and Discussion

Data for the polymerizations of styrene in supercritical CO_2 with and without added stabilizer are summarized in Tables 1−3. All polymerizations were initially homogeneous due to the solubility of both the styrene monomer and the initiator in CO_2 at the reaction conditions employed. The polymerizations conducted in the absence of stabilizer resulted in precipitation of the resulting polymer, which fouled the reactor, and proceeded to undesirably low conversions forming low molecular weight product. In contrast, the reactions which were carried out in the presence of added stabilizer started out homogeneously, but, instead of precipitating, formed a remarkably stable colloidal dispersion of PS. The successful stabilization of the polymerization simultaneously resulted in both higher yields and higher molecular weight PS.

The mechanism for particle formation in these polymerizations may involve both homogeneous nucleation and micellar nucleation since these block copolymers associate to form micelles in a CO_2 continuous phase.[28] Regardless of which nucleation mechanism is operative, clearly the resultant PS particles become effectively stabilized since the solution exhibited 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 PS obtained from these successful dispersion polymerizations was in the form of spherical particles with a broad particle size distribution. The broad particle size distribution for the product obtained from these polymerizations is analogous to the results obtained by Dawkins and Taylor for dispersion polymerizations of styrene in *n*-alkanes using diblock copolymers as stabilizers.[19] They attributed the resulting relatively broad particle size distributions in their systems to the fairly high solubility of oligomeric polystyryl radicals in the dispersion medium; this decreases the tendency for the polystyryl radical to adsorb onto existing particles and allows significant nucleation to occur throughout the course of the polymerization. The similarity of our findings with their results is interesting since CO_2 and hexane have similar solvating power for small molecules. Moreover, the presence of large amounts of styrene monomer in the continuous phase at low degrees of polymerization also increases the threshold molecular weight for precipitation and association of the PS oligomers.

As the length of both the anchoring PS block and the soluble poly(FOA) block was increased, the mean particle diameter (D_n) and the particle size dispersity (PSD) simultaneously decreased (see Table 1). The PSD for the polystyrene particles which result when the 3.7K/17K stabilizer is employed is extremely broad; the resulting particles range in size from 100 nm to 4.0 μm. The range in particle size narrows considerably when the slightly larger stabilizing copolymers are employed. Indeed, the 4.5K/25K stabilizer yields particles in the size range of 70 nm to 1.6 μm while the 6.6K/35K stabilizer yields particles in the size range of 150 nm to 1.0 μm. These results parallel findings in conventional liquid solvents where an increase in the size of the

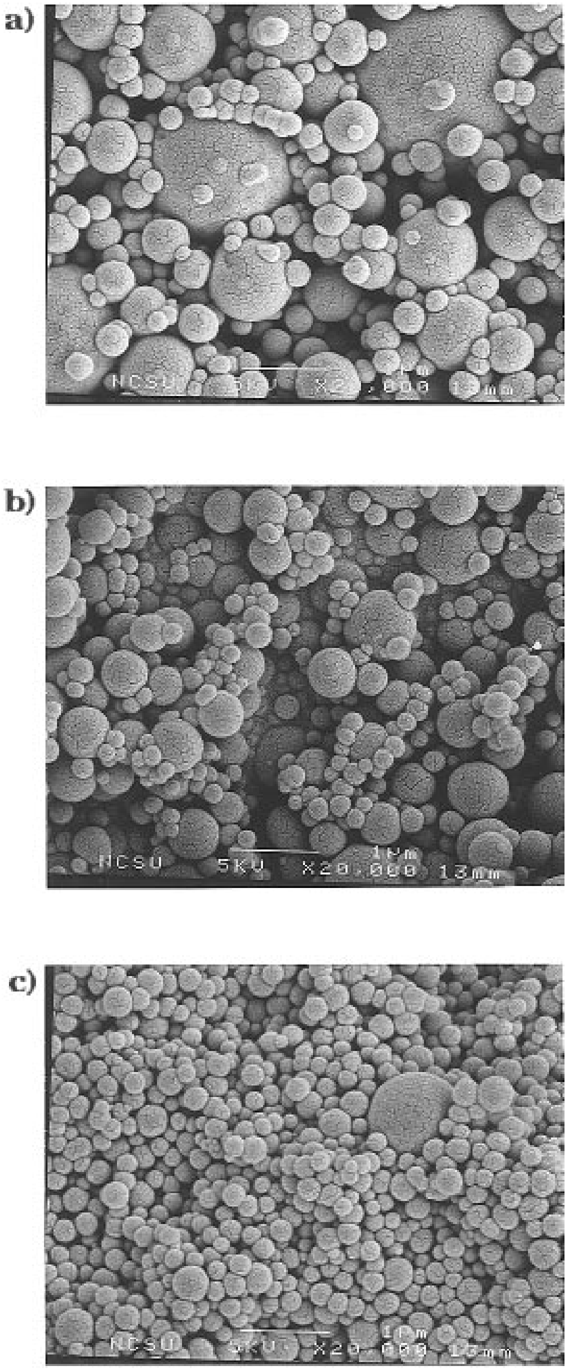


Figure 2. Scanning electron micrographs of PS particles synthesized by dispersion polymerization utilizing (a) 3.7K/17K, (b) 4.5K/25K, and (c) 6.6K/35K PS-*b*-poly(FOA) stabilizer.

polymeric stabilizing moiety typically provides more effective stabilization and creates smaller particles.[18] Scanning electron micrographs of the PS produced in these reactions are shown in Figure 2. In addition, an illustrative histogram constructed from the particle diameter data is shown in Figure 3.

The use of poly(FOA) homopolymer as the stabilizing moiety seems to afford some degree of stabilization, giving intermediate values for the yield and molecular weight. This partial stabilization of the PS particles either may be the result of a very weak physical adsorption of the poly(FOA) to the particle surface or may result from the poly(FOA) becoming chemically grafted to the particles by chain transfer reactions to the backbone of the stabilizer.[29] Since poly(FOA) has a positive second virial coefficient in CO_2,[30,31] when it covers the surface of a colloidal particle, it provides an excellent steric barrier that prevents aggregation. In addition, the unsuccessful dispersion polymerization of styrene monomer using poly(FOA) homopolymer as a stabilizer stands in contrast to the successful dispersion polymerization of MMA using poly(FOA) homopolymer as a stabilizer.[8,29] These findings suggest that the adsorption of the stabilizer onto the PS particles is greatly enhanced by the presence of the styrenic block.

Table 1. Results of Styrene Polymerizations in CO_2 at 204 bar and 65 °C with AIBN Initiation (2.0 g of styrene, 2.4×10^{-2} M AIBN

stabilizer	stabilizer concn (w/v %)	yield[b] (%)	$\langle M_n \rangle$ (10^{-3} g/mol)	PDI[c]	D_n[d] (µm)	PSD[e]
none	0	22.1	3.8	2.3	na[f]	na
poly(FOA)[a]	4	43.5	12.8	2.8	na	na
(3.7K/17K)	4	72.1	19.2	3.6	0.40	8.3
(4.5K/25K)	4	97.7	22.5	3.1	0.24	1.3
(6.6K/35K)	4	93.6	23.4	3.0	0.24	1.1

[a] Poly(FOA) homopolymer stabilizer was made homogeneously in CO_2 with AIBN initiation. [b] Yields were determined gravimetrically. Yields from separate duplicate runs are within +7%. [c] PDI = polydispersity index of molecular weight distribution, M_w/M_n. [d] D_n = mean particle diameter. [e] PSD = particle size distribution, D_w/D_n. [f] na = not applicable.

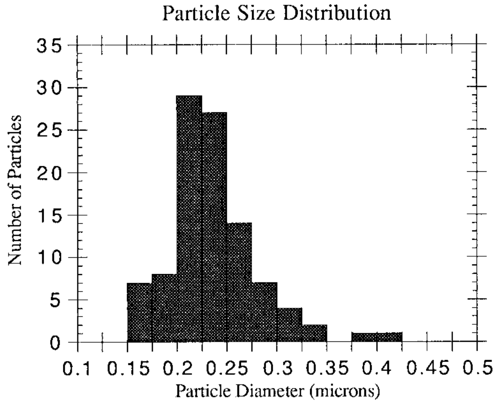


Figure 3. Particle size distribution histogram for PS particles stabilized by 6.6K/35K PS-*b*-poly(FOA) stabilizer.

Table 2. Effect of Variation in Initiator Concentration and Stabilizer (4.5K/25K) Concentration (CO_2 at 204 bar and 65 °C for 24 h)

[stabilizer] (w/v %)	[AIBN] (10^3 M)	yield[a]	$\langle M_n \rangle$ (10^{-3} g/mol)	PDI[b]	D_n[c] (µm)	PSD[d]
0	6.1	10.3	8.5	1.6	na[e]	na
0	12	14.6	7.4	1.6	na	na
0	24	26.0	4.1	2.8	na	na
2	6.1	79.5	84.3	3.4	0.26	1.6
2	12	89.6	55.3	3.1	0.31	2.2
4	12	95.1	53.1	3.6	0.21	3.6

[a] Yields were determined gravimetrically. Yields from separate duplicate runs are within +7%. [b] PDI = polydispersity index of molecular weight distribution, M_w/M_n. [c] D_n = mean particle diameter. [d] PSD = particle size distribution, D_w/D_n. [e] na = not applicable (no particles were present in the unstabilized PS products).

As anticipated, when the concentration of the initiator was decreased, the molar mass of the resulting polystyrene product increased (see Table 2). At the lowest initiator concentration studied, the presence of the block copolymeric surfactant increased the resulting molar mass of the product by an order of magnitude over that achieved in the absence of stabilizer. When the amount of stabilizer is doubled, the amount of PS particle surface area which can be covered by the protective

Table 3. Effect of Variation in Length of CO_2-Soluble Segment of Stabilizer (2.0 g of Styrene, 1.2×10^{-2} M AIBN, CO_2 at 345 bar and 65 °C for 24 h)

stabilizer	stabilizer concn (w/v %)	yield[a] (%)	$\langle M_n \rangle$ (10^{-3} g/mol)	PDI[b]	D_n[c] (μm)
none	0	12.0	8.2	1.4	na[d]
(3.7K/14K)	2	75.9	41.2	3.9	0.16
(3.7K/28K)	2	83.9	39.2	4.8	0.22
(3.7K/40K)	2	81.4	54.9	3.6	0.19
(3.7K/61K)	2	53.5	43.6	3.5	0.21
(3.7K/245K)	2	76.4	33.8	5.3	0.31

[a] Yields were determined gravimetrically. Yields from separate duplicate runs are within +7%. [b] PDI = polydispersity index of molecular weight distribution, M_w/M_n. [c] D_n = mean particle diameter. [d] na = not applicable (no particles were present in these particles).

poly(FOA) steric barrier increases and as a result the PS particles produced are smaller.

The results of a study in which the length of the CO_2-soluble poly(FOA) segment was systematically varied while the length of the anchoring PS segment was kept contstant are summarized in Table 3. For all of the reactions in which a diblock copolymer was employed as the steric stabilizer, the resulting yields and molecular weights are higher that those reactions run in the absence of this type of stabilizer. The results do not, however, show any discernible trend in yield, molecular weight, or particle size as a function of the length of the soluble block. It is very likely that all of the block copolymers employed in this study are outside the limit for the anchor-soluble balance (ASB) which is required to efficiently prevent flocculation of the smaller particles. If the anchoring PS segment of the stabilizer is too small, the equilibrium favors unadsorbed single or associated stabilizer molecules in the continuous phase over adsorbed stabilizer at the particle surface and as a result the stabilization is inefficient.[10]

Conclusion

Block copolymers which exhibit amphiphilicity in a CO_2 continuous phase have been synthesized and employed as polymeric stabilizers for the successful dispersion polymerization of styrene. These reactions yield spherical PS particles with broad particle size distributions and the product can be isolated in the form of a dry, free-flowing powder. Increasing the length of the stabilizing moiety results in the narrowing of the particle size distribution. The amphiphilic activity exhibited by the block copolymers suggests that environmentally responsible CO_2 is a viable replacement for the solvents traditionally used in heterogeneous polymerizations and lays the foundation for surfactant-modified, CO_2-based separations processes. It is now possible to contemplate the general design of other interfacially active molecules for CO_2 in a strategy that exploits the use of environmentally benign CO_2 for other solvent-intensive processes such as cleaning, separations, and extractions.

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