Macromolecules **1997,** *30,* 5673−5682

Dispersion Polymerizations of Styrene in Carbon Dioxide Stabilized with Poly(styrene-*b*-dimethylsiloxane)

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Received April 25, 1997; Revised Manuscript Received July 11, 1997⊗

ABSTRACT: Herein we report the use of poly(styrene-*b*-dimethylsiloxane) block copolymers as steric stabilizers for dispersion polymerizations of styrene in a carbon dioxide continuous phase. It was demonstrated that the anchor-soluble balance (ASB) of the stabilizer has a dramatic effect on both the progress of the reaction and the morphology of the resulting polystyrene (PS) colloid. When a stabilizer with an appropriate ASB is employed, the initial concentrations of styrene, stabilizer, and helium have substantial effects on the resulting size and dispersity of the colloidal particles. Dispersion polymerizations carried out under a series of different pressures (143−439 bar) resulted in variations in the conversion, molecular weight, and PS particle diameter, suggesting that the reaction is extremely sensitive to the density of the continuous phase. An investigation of the progress of the reaction as a function of time at two different temperatures revealed that the average molecular weight increases gradually over the course of the reaction. Finally, control reactions in heptane solvent were not as successful as those conducted in CO_2 suggesting that the plasticization of the polymer particles by CO_2 facilitates diffusion of monomer to the growing chain ends.

Introduction

Carbon dioxide (CO_2) provides an environmentally benign, inexpensive, and nonflammable alternative to the aqueous and organic solvents traditionally employed by the polymer industry.[1,2] 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).[3−8] Conversely, most industrially important hydrocarbon based polymers are relatively insoluble in CO_2. As an illustration, polystyrene (PS) is insoluble in CO_2 even at 225 °C and 2100 bar.[9] However, CO_2 acts as a plasticizing agent for PS,[10−15] and this phenomenon facilitates the diffusion of monomer inside the swollen polymer phase during a heterogeneous polymerization.

Dispersion polymerization constitutes a valuable technique for the preparation of polymeric particles in the micrometer-size range.[16] In this technique, all of the components of the reaction mixture are initially miscible and form a homogeneous solution. The resulting polymer, however, is insoluble in the continuous phase and is stabilized as a polymer colloid. Steric stabilization is widely used in these reactions, and stabilizer architectures include homopolymers as well as block, graft, or random copolymers or copolymerizable stabilizers.[17,18] Most of the work in the area of styrene dispersion polymerizations has employed free radical propagation, although anionic[19−21] and cationic[22] systems, which exploit the various mechanisms amenable for the polymerization of styrene, have also been recently investigated. Several groups have explored the preparation of monodisperse polystyrene (PS) particles in the micrometer size range through dispersion polymerizations conducted in alcoholic media using homopolymers as stabilizers.[23−36] Others have examined the use of block copolymers[19−21,37,38] and reactive macromolecules[39−43] as stabilizers for this process in polar, alcoholic media. In contrast, Dawkins and Taylor have investigated the use of diblock copolymers as stabilizers for the dispersion polymerization of styrene in nonpolar solvents.[44,45] Because CO_2 has a low dielectric constant, the alkane solvents employed by Dawkins and Taylor provide the most comparable “conventional liquid” system to the CO_2-based system investigated herein.

Dispersion polymerization has recently been shown to be a useful heterogeneous technique for the preparation of monodisperse poly(methyl methacrylate) (PMMA) colloids in a CO_2 continuous phase.[46−50] Both fluorinated and siloxane-based polymers were employed as steric stabilizers, and it was demonstrated that these efficient stabilizing systems preclude coagulation and precipitation of the growing PMMA particles. Further investigations revealed that the stabilizers which work well for PMMA do not effectively prevent coagulation of PS colloidal particles in CO_2, presumably due to poor anchoring at the particle’s surface.[51] To circumvent this problem, amphiphilic diblock copolymeric stabilizers which contained a PS anchoring block and a fluorinated acrylate soluble block were employed to achieve high yields of high molecular weight PS in a CO_2 continuous phase.[51] Although these fluoropolymer-based stabilizers were extremely effective, they suffered from several drawbacks including broad molecular weight distributions, limited solubility in traditional liquid solvents (which made characterization of them difficult), and relatively high cost. Several important advantages are gained by changing to siloxane-based stabilizing systems including lower cost, straightforward anionic synthesis leading to blocks with narrow molecular weight distributions, and solubility in a variety of common organic solvents which facilitates characterization. The investigation of the scope and limitations of

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⊗ Abstract published in *Advance ACS Abstracts,* September 1, 1997.

S0024-9297(97)00579-2 CCC: $14.00 © 1997 American Chemical Society

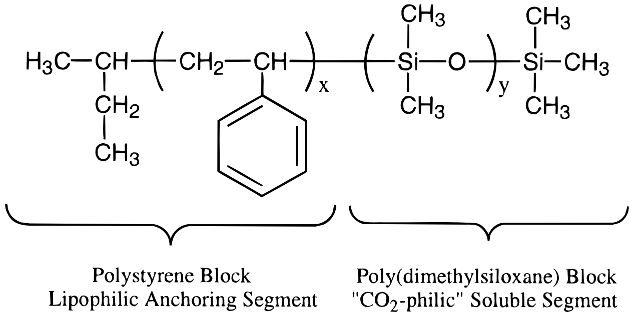

Figure 1. Structure of PS−PDMS diblock copolymer used as the stabilizer.

the use of siloxane-based diblock copolymers as stabilizers for the dispersion polymerization of styrene in a supercritical CO_2 continuous phase constitutes the goal of the work presented herein. The effect of the anchor-soluble balance (ASB) of the stabilizing block copolymer on the resulting styrene polymerization has been examined. In addition, the effects of the reaction time, stabilizer concentration, monomer concentration, reaction temperature, and CO_2 pressure on the resulting PS colloid have been explored.

Experimental Section

Materials. Styrene (Aldrich) was purified and deinhibited by passage through an alumina column and was deoxygenated by argon purge prior to use. Hexamethylcyclotrisiloxane (D_3, Acros) was kindly provided by Bayer and was purified via vacuum sublimation. Trimethylsiloxy terminated poly(dimethylsiloxane) homopolymer (PDMS, United Chemical Technologies) with a viscosity of 1000 cSt was used as received. 2,2′-Azobisisobutyronitrile (AIBN, Eastman Kodak) was recrystallized twice from methanol. *sec*-Butyllithium (1.3 M in cyclohexane, Aldrich) was used as received. Cyclohexane (Fisher) was stirred over concentrated sulfuric acid for ca. 2 weeks, decanted, and distilled over sodium under an argon atmosphere prior to use. Tetrahydrofuran (THF, Fisher) was distilled from a sodium/benzophenone solution under an argon atmosphere prior to use. Heptane (EM Science) and methanol (Mallinckrodt) were used as received. Carbon dioxide (SFC/SFE Grade with or without a helium head pressure) was kindly provided by Air Products and was used as received.

Diblock Copolymers. Poly(styrene-*b*-dimethylsiloxane) [PS−PDMS] copolymers (Figure 1) were synthesized via living anionic polymerization methods through sequential monomer addition following procedures described in the literature.[52,53] The molecular weights of the PS first blocks were determined by withdrawing a sample of the living PS anion prior to the addition of the second monomer, followed by quenching the aliquot with methanol and using gel permeation chromatography (GPC). After the formation of the block copolymers, the ratio of dimethylsiloxane repeat units to styrene repeat units was determined by ^{1}H NMR. The polydispersity index (PDI) for each block copolymer sample was determined using GPC relative to PS standards. For simplicity, these block copolymers will be referred to by listing the number average molecular weight (M_n) of the PS segment followed by the M_n of the PDMS segment. For example, the stabilizer which contains a PS segment with a M_n of 9.6×10^3 and a PDMS segment with a M_n of 2.4×10^4 will be abbreviated as 9.6K/24K.

Dispersion Polymerizations. Polymerizations were conducted in CO_2 in a 10 mL, high-pressure view cell equipped with sapphire windows which permit visual observation of the reaction mixture.[54] 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. Styrene 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 the desired temperature (50 or 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. Once the final reaction conditions were obtained, the reaction was allowed to proceed with magnetic stirring for reaction times which varied from 4 to 24 h. The reactions typically would begin as clear, colorless, homogeneous mixtures. For stabilized reactions, the solutions developed an orange color during the initial ca. 5 min, at which time the solutions gradually became slightly cloudy and deeper red-orange. The observed color results from the scattering of transmitted light by the growing PS particles, the Tyndall effect. Within 1 h, the solutions had developed the milky, white, opaque appearance characteristic of a latex. For unstabilized control reactions, the solutions became slightly cloudy but never became opaque, and the precipitated PS product coated the walls of the reactor.

At the end of the reaction, the CO_2 was slowly vented from the cell through a pressure let-down valve and was bubbled through methanol in order to collect any polymer particles which sprayed out during the venting process. The reactor was then quickly cooled in an ice water bath, and the polymer product was removed from the cell. The very small amount of polymer which was collected in the methanol during the venting process was collected by vacuum filtration over a Hirsch funnel. The product was then dried *in vacuo* at room temperature overnight. The yield of the dry polymer was determined gravimetrically, and all reactions were repeated at least twice with reproducible results. After determining the polymer yield, the PS product could be washed with *n*-heptane to remove excess stabilizer. The washing procedure involved the preparation of 1.0 w/v % solutions which were stirred at room temperature for 17 h.

For comparison, dispersion polymerizations were also conducted in *n*-heptane. In these reactions, the 10 mL high-pressure reaction vessel was charged with AIBN (1.2×10^{-2} M) and the desired amount of stabilizer (PS−PDMS 9.6K/24K) and purged with argon. Styrene monomer (2.0 g) and heptane (8.0 mL) were then added via a glass syringe. The system was closed and heated to 65 °C, and the reaction was allowed to proceed with stirring for 24 h. The pressure of the system remained below 2.5 bar during the course of the reaction. At the end of the reaction time, the cell was quickly cooled by immersion in an ice water bath and the product was precipitated into methanol. The product, which was a white powder, was collected by vacuum filtration over a Hirsch funnel, dried, and weighed as outlined above.

Characterization. A modular Waters 600E gel permeation chromatograph (GPC) with three Ultrastyragel columns of linear, 10^3, and 10^4 Å porosities and a 410 differential refractometer was used for the determination of the molecular weights and the molecular weight distributions. Dichloromethane was used as the mobile phase with a flow rate of 1.0 mL/min, and the instrument was calibrated using PS standards (Showa Denko). ^{1}H NMR spectra were obtained from a Bruker WM250 spectrometer. Polymer morphologies were determined using a JEOL 6400 FE scanning electron microscope (SEM) and a JEOL 100S transmission electron microscope (TEM). The TEM was calibrated with a germanium shadowed carbon replica made from a 28 800 lines in^{-1} diffraction grating. For TEM, samples were prepared by placing one drop of a dilute solution (1 w/v % in heptane) on a carbon coated copper grid and evaporating to dryness. Where particle sizes are reported, the mean particle sizes and particle size distributions were determined by measuring the particles' diameters. Number (d_n) and weight (d_w) average particle diameters were calculated from the particle size distribution histograms using the following equations:[34]

$$d_n = \frac{\sum_{i=1}^{N} d_i}{N} \quad (1)$$

$$d_w = \frac{\sum_{i=1}^{N} d_i^{4}}{\sum_{i=1}^{N} d_i^{3}} \quad (2)$$

where d_i is the diameter of particle i, and N is the total number of particles measured in that sample. As an illustration, a particle size distribution histrogram is shown in Figure 2.

Results and Discussion

Diblock Copolymers. The results from the synthesis of the amphiphilic diblock copolymers are summarized in Table 1. An investigation of the solubility of these materials revealed that they are insoluble in pure CO_2 at both liquid (T = 20 °C, P = 68 bar) and supercritical (T = 65 °C, P = 340 bar) conditions. When 20 w/v % styrene is present in the solution, however, 2 w/v % of any of the diblock copolymers utilized herein completely dissolved and the resulting mixture was homogeneous. Indeed, styrene acts as a cosolvent for the stabilizer in this system, increasing both the density and the Hildebrand solubility parameter (δ) of the medium. For example, pure CO_2 at 65 °C and 275 bar has a density of 0.792 g/mL and a δ value of 6.74 $(\text{cal/cm}^3)^{1/2}$, while a 20 w/v % solution of styrene in CO_2 at these conditions has a density of 0.935 g/mL and a δ value of 8.681 $(\text{cal/cm}^3)^{1/2}$.[55] Additionally, small angle neutron scattering studies reveal that these type of diblock copolymers, which contain a CO_2-philic soluble segment and a CO_2-phobic anchoring segment, self-assemble to form micelles in CO_2[56] and in a styrene/CO_2 mixture.[57]

Dispersion Polymerizations of Styrene in Heptane. Previous work by Dawkins and Taylor using PS−PDMS stabilizers for the free radical dispersion polymerization of styrene in *n*-alkanes resulted in a relatively low molecular weight polymer which was formed in low yield.[44] Moreover, the PS particles produced in their experiments had a very broad particle size distribution. They attributed these results to the relatively high solvency of the dispersion medium (*n*-heptane) for the growing chains which reduces the tendency for the polystyryl radicals to adsorb onto existing particles. As a result, secondary particle nucleation was prevalent, and consequently the particle size distributions were broad. They estimated that the threshold molecular weight for precipitation (J_{crit}) in their system is about 10 000.

We repeated their work using *n*-heptane and the PS−PDMS (9.6K/24K) stabilizer synthesized in our laboratory and obtained similar results (Table 2). Paralleling the results of Dawkins and Taylor, the recovered yield and molecular weights of PS from these reactions were low even when the stabilizer was present. In addition, the particles obtained from the dispersion polymerizations in *n*-heptane were very polydisperse in size, with diameters ranging from less than 0.5 μm to more than 100 μm.

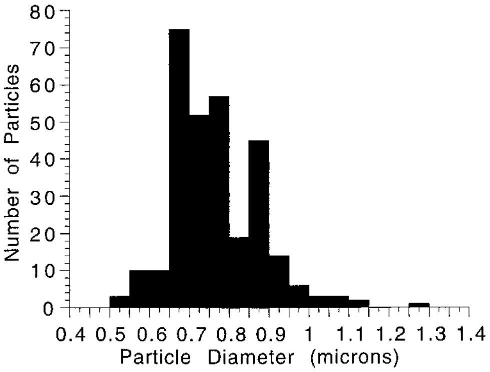

Figure 2. Illustrative particle size distribution histrogram.

Table 1. Summary of Characterization Data from the Synthesis of PS−PDMS Diblock Copolymers

PS anchor block		PDMS soluble block	copolymer
$\langle M_n\rangle \times 10^{-3}$ [a]	PDI[b]	$\langle M_n\rangle \times 10^{-3}$ [c]	PDI
4.3	1.07	25	1.38
4.3	1.07	65	1.68
9.6	1.08	24	1.16
9.6	1.08	64	1.41

[a] $\langle M_n\rangle$ = number average molecular weight. [b] PDI = polydispersity index of the molecular weight distribution, M_w/M_n. [c] Determined by ^{1}H NMR.

Table 2. Data for the Polymerizations of Styrene in *n*-Heptane

stabilizer	yield[a] (%)	$\langle M_n\rangle \times 10^{-3}$	PDI	d_n[b] (μm)	PSD[c]
none	23.8	24.0	1.6	none	
0.20 g PS−PDMS (9.6K/24K)[d]	39.2	19.9	2.1	0.5−100	broad

[a] Yields were determined gravimetrically. [b] d_n = mean particle diameter. [c] PSD = dispersity index of the particle size distribution, d_w/d_n. [d] (M_n PS segment/M_n PDMS segment).

Table 3. Data for the Polymerizations of Styrene in CO_2[a]

entry	stabilizer	yield[b] (%)	$\langle M_n\rangle \times 10^{-3}$	PDI	d_n[c] (μm)	PSD[d]
1	none	12.0	8.2	1.4	none	
2	PDMS homopolymer	15.4	8.5	1.4	none	
3	PS−PDMS (4.3K/25K)[e]	90.6	65	3.6	0.22	1.31
4	PS−PDMS (9.6K/24K)	91.7	56	4.3	0.46	1.08
5	PS−PDMS (4.3K/65K)	52.2	21	9.2	coag[f]	
6	PS−PDMS (9.6K/64K)	90.9	39	8.1	coag	

[a] Reaction conditions: 2.0 mL styrene, 1.2×10^{-2} M AIBN, 360 ± 10 bar, 65 °C, 24 h; for stabilized reactions (entries 2−6), 0.200 g of stabilizer was used. [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_n PS segment/M_n PDMS segment). [f] coag indicates that the latex collapsed during polymerization and particles were coagulated.

Dispersion Polymerizations of Styrene in CO_2. (1) Effect of Stabilizer ASB. The data for the polymerizations of styrene in CO_2 using several different stabilizers are summarized in Table 3. Precipitation polymerizations that were conducted in the absence of stabilizer (entry 1) resulted in both low conversions and low molecular weight PS. For comparison, polymerizations which were conducted in the presence of the CO_2-soluble homopolymer, PDMS, did not result in any improvement over the reactions run without added stabilizer (entry 2). Apparently, these poor results are due to the inefficient anchoring of the PDMS homopolymer to the surface of the PS particles. This result is not particularly surprising since the primary mechanisms by which homopolymeric stabilizers are effective is through either chemical grafting or physical adsorption to the surface of the growing polymer colloid. Although free radicals can chain transfer to siloxanes

Table 4. Conversion of Styrene as a Function of Time[a]

temp (°C)	reaction time, (h)	yield[b] (%)	$\langle M_n\rangle^c \times 10^{-3}$	PDI
65	4	8.5	13.7	1.9
65	8	30.3	22.1	2.3
65	12	54.3	30.4	2.5
65	16	69.4	35.6	2.8
65	20	87.8	48.9	3.0
65	24	93.2	47.1	3.1
50	8	5.2	13.5	1.8
50	16	18.0	21.3	2.3
50	24	34.4	26.8	2.5
50	32	62.5	37.2	2.6
50	40	88.2	56.5	3.6
50	48	98.0	58.1	3.7

[a] Reaction conditions: 20 (w/v) % styrene, 5% (based on styrene) PS−PDMS 9.6K/24K; 1.2×10^{-2} M AIBN; P = 360 ± 10 bar. [b] Yields were determined gravimetrically. [c] Samples were washed in *n*-heptane prior to GPC analysis to remove residual stabilizer.

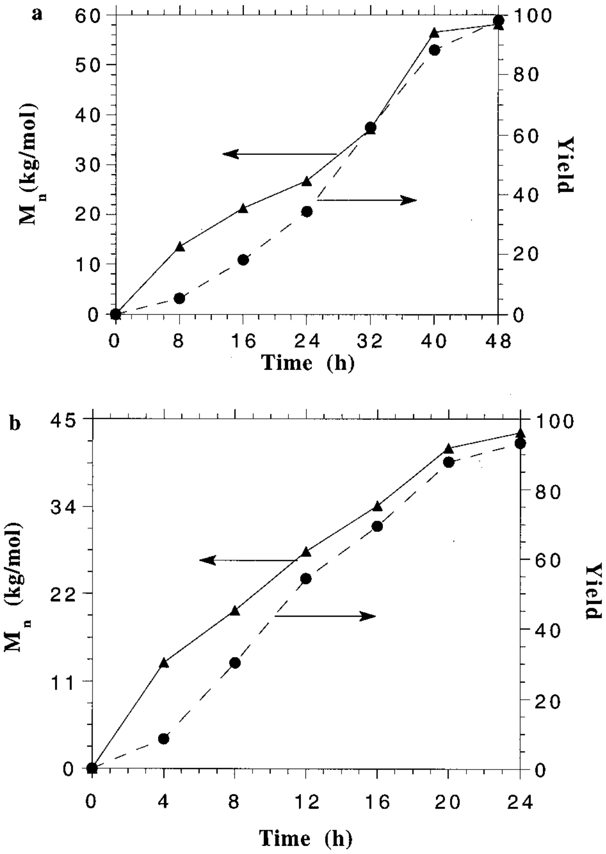

Figure 3. Yield and M_n as a function of time for reactions at (a) 50 °C and (b) 65 °C.

by hydrogen abstraction,[58] Pelton et al. have shown that the use of AIBN as the initiating species does not lead to chain transfer to PDMS, and therefore no chemical grafting takes place.[59] Other work by Harrison et al. has shown that PDMS homopolymer is not interfacially active in this system,[60] and so stabilization by physical adsorption of the homopolymeric stabilizer is also ineffective.

In contrast, polymerizations conducted in the presence of an amphiphilic diblock copolymer resulted in significantly higher conversions. The effect of the stabilizer composition, or ASB, was explored by using copolymers with varying ratios of block lengths. When the stabilizer contained a PDMS segment with a M_n of ca. 25 g/mol (entries 3 and 4), the polymerization resulted in high yields of high molecular weight PS. At the end of the reaction time, the reaction mixture was a stable latex which did not settle even when stirring was stopped. The products from these reactions were isolated directly from the reactor as dry, white, free-flowing powders. As the length of the PS segment of the stabilizer was increased, the resulting colloidal particles became larger and more monodisperse. On the other hand, when diblock copolymer stabilizers were used which had longer PDMS segments (entries 5 and 6), the resulting latex was unstable and settled during

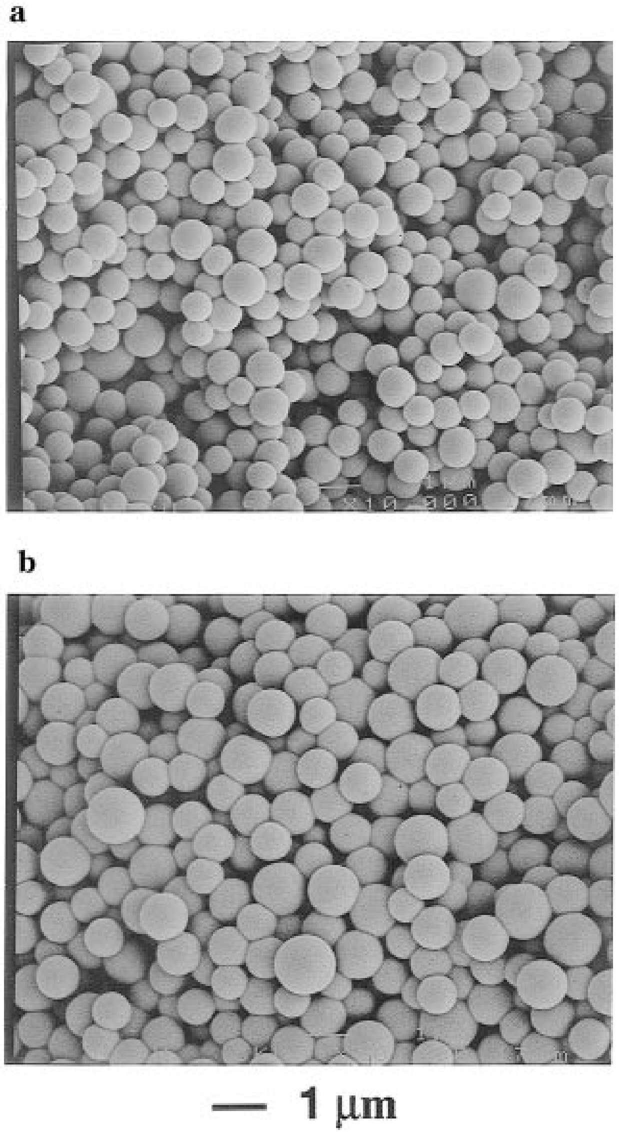

Figure 4. Scanning electron micrographs from the dispersion polymerizations of styrene at (a) 50 °C and (b) 65 °C.

Table 5. Effect of Stabilizer (9.6K/24K) Concentration on the Dispersion Polymerization of 20 w/v % Styrene in Supercritical CO_2 at 365 ± 7 bar[a]

entry	stabilizer concn (wt % to styrene)	yield[b] (%)	$\langle M_n\rangle \times 10^{-3}$	PDI	d_n^c (μm)	PSD[d]
1	2.5	81.8	38.9	4.2	1.15	1.19
2	5.0	95.7	41.1	3.3	0.76	1.06
3	7.5	95.4	50.1	2.9	0.43	1.03
4	10	84.7	50.3	2.7	0.37	1.04
5	15	81.6	57.5	2.7	0.31	1.04

[a] Reaction conditions: [AIBN] = 1.2×10^{-2} M; 24 h reaction time; T = 65 °C. [b] Yields were determined gravimetrically. [c] d_n = mean particle diameter. [d] PSD = dispersity index of the particle size distribution, d_w/d_n.

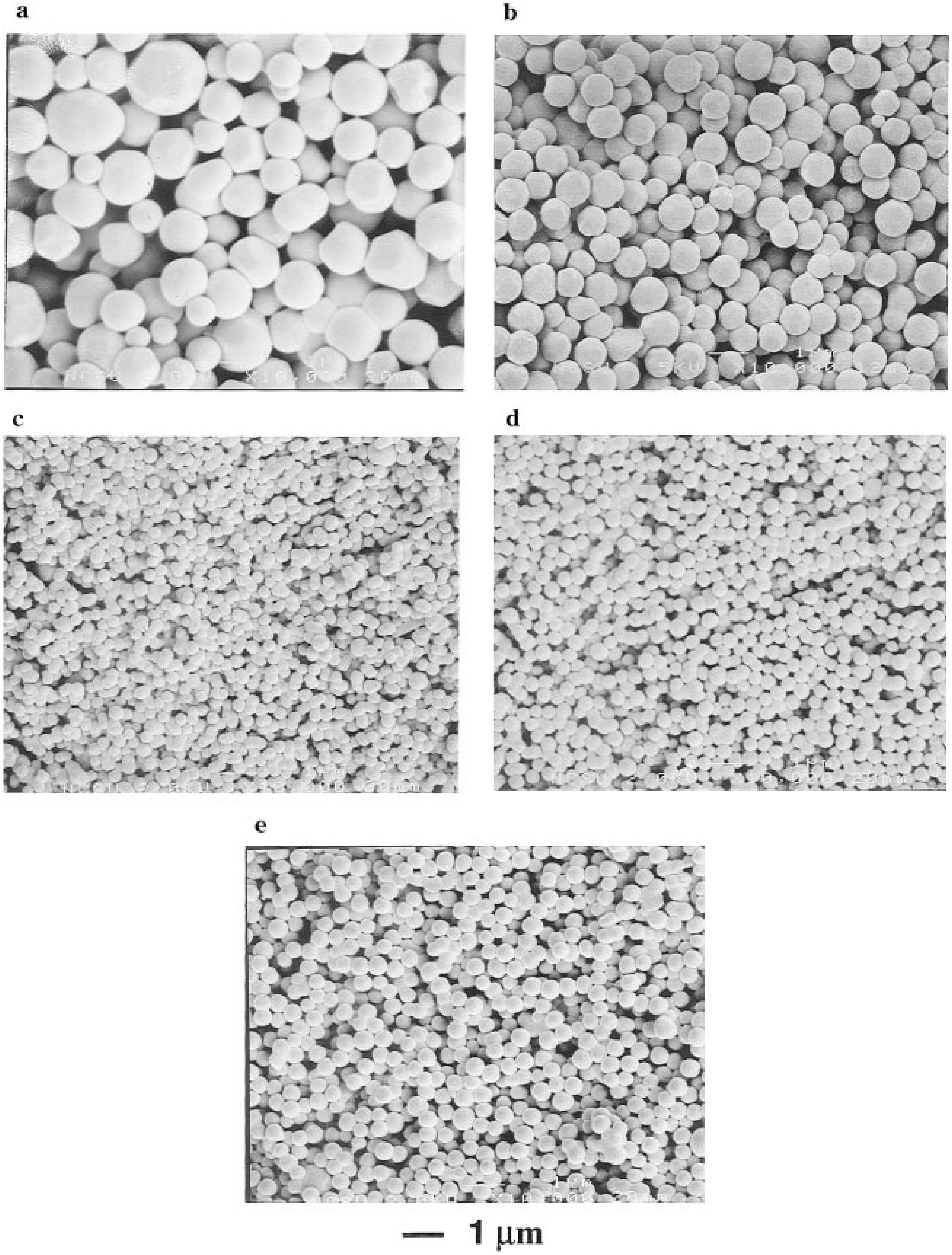

Figure 5. Scanning electron micrographs from reactions containing: (a) 2.5%, (b) 5.0%, (c) 7.5%, (d) 10%, and (e) 15% PS−PDMS (9.6K/24K) stabilizer; values are w/w % to styrene monomer.

the course of the reaction. These reactions yielded lower molecular weight PS having very broad molecular weight distributions. Two factors could account for this result: the lower ASB of these stabilizers and the limited solubility[61] of the longer PDMS segments in the CO_2. Barrett has shown that the ideal range for the ASB of the stabilizer in a dispersion polymerization is between 1:3 and 3:1.[16] The 9.6K/24K stabilizer, which falls within this range, gave the best results (high conversions and molecular weights, narrow particle size distributions, stable latexes) and was thus chosen for use in further studies.

(2) Conversion and Molecular Weight as a Function of Reaction Time and Temperature. In an

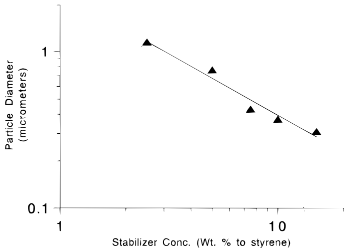

Figure 6. Particle diameter (μm) as a function of stabilizer concentration (w/w % to styrene monomer).

Table 6. Effect of the Percent Solids on the Dispersion Polymerization of Styrene[a]

styrene concn (w/v % in CO_2)	yield (%)	$\langle M_n \rangle \times 10^{-3}$	PDI
10	97.9	52	3.2
20	95.7	49	3.3
30	78.2	38	4.0

[a] Reaction conditions: 24 h reaction time; $P = 360 \pm 10$ bar; $T = 65$ °C.

effort to gain insight into the reaction progress as a function of time, samples were obtained by stopping the reactions at various intervals. Table 4 and Figure 3 depict the results from this study. At the temperatures studied, the plots show a fairly linear increase in both the molecular weight and the yield as a function of time. Ongoing investigations using a detailed analysis of the GPC trace as a function of time[62] suggest that the predominant mechanism of chain termination changes over the course of the reaction, and this could account for the trend observed.

When the conversion was low, difficulties arose in the isolation of the PS particles due to the high solubility of PS in the unreacted styrene monomer. Indeed, because of the large amount of unreacted monomer in the reactions which were stopped at conversions below 80%, no particles could be isolated from these experiments. Scanning electron micrographs of the particles obtained from high conversion reactions at the two different temperatures studied are shown in Figure 4. At high conversion, the particles resulting from reactions at 50 and 65 °C had number average particle diameters of 610 nm and 760 nm, respectively. In both cases, the polydispersity index of the particle size distribution was 1.05. It must be noted that changing the reaction temperature affects both the kinetics of the polymerization and the density and solubility parameter of the CO_2 continuous phase. The fact that the PS particle size increased with increasing temperature parallels the results in other solvents.[33,38] As expected, increasing the polymerization temperature also resulted in a decrease in the molecular weight of the PS formed.

(3) Effect of the Stabilizer Concentration. Polymerizations of styrene using various amounts of the (9.6K/24K) stabilizer were conducted in CO_2 at 65 °C and pressures of 365 ± 7 bar (Table 5). When stabilizer concentrations between 2.5 and 15 (wt % to styrene) were used, high yields were obtained in all cases with no apparent trend. The molecular weights and particle sizes were affected by the amount of stabilizer employed. As the concentration of stabilizer was increased, the molecular weight of the resulting PS increased and the MWD became narrower. The inverse correlation between the particle size and the molecular weight in this system has also been observed in other dispersion polymerizations, with the smallest particles having the highest molecular weights.[30,32] Paine et al. have rationalized this phenomenon by examining the locus of polymerization, which may be either in the continuous phase or in the monomer swollen polymer particle.[30] They suggest that particles represent the dominant proportion of the locus for polymerization in the case of

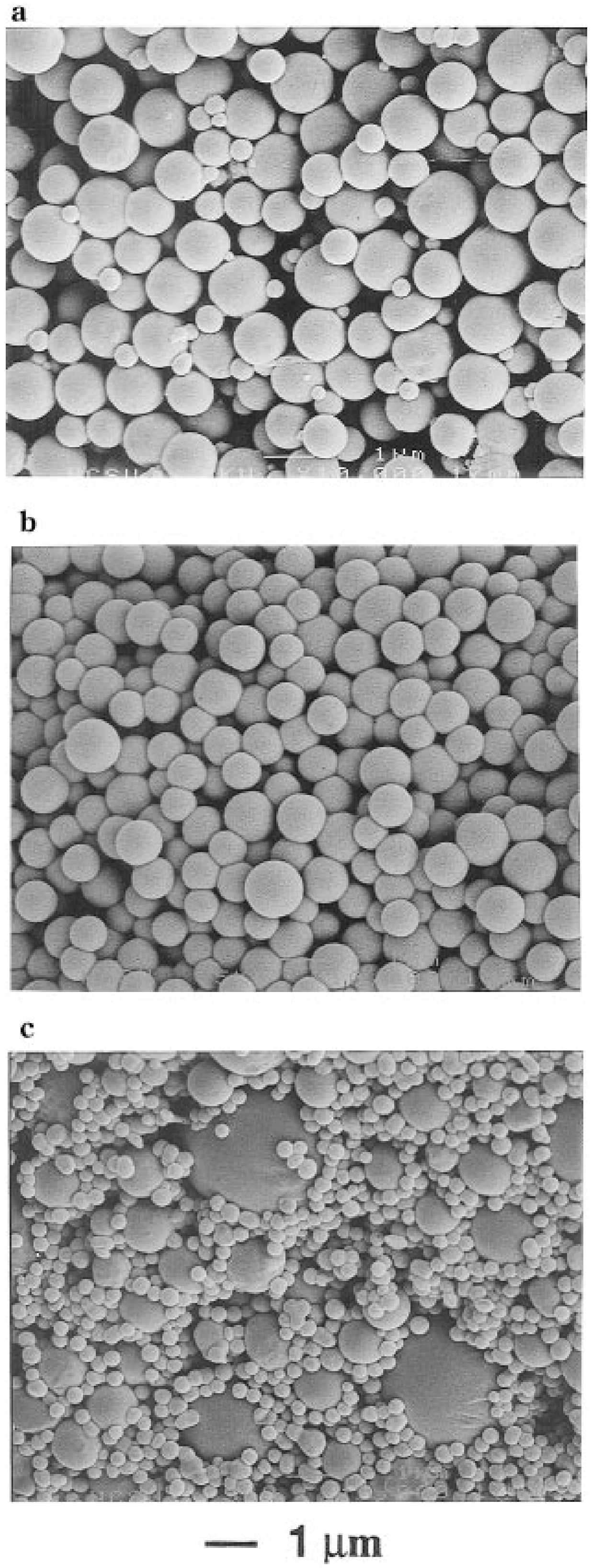

Figure 7. Scanning electron micrographs of PS particles obtained from reactions with (a) 10%, (b) 20%, and (c) 30% styrene (w/v % to total) in SFC/SFE grade pure CO_2 at 360 bar and 65 °C.

Table 7. Pressure Study for Styrene (20 w/v %) Polymerization Using 5% (wt % to Styrene) PS−PDMS (9.6K/24K) as the Stabilizer[a]

entry	P_i[b] (bar)	P_f[c] (bar)	ΔP[d] (bar)	yield (%)	$\langle M_n \rangle \times 10^{-3}$	PDI	d_n (μm)	d_w (μm)	PSD
1	143	151	+8	46.4	20.7	5.7			
2	225	244	+19	79.3	34.3	4.8			
3	287	297	+10	95.4	40.8	4.9	0.65	0.96	1.46
4	364	341	-23	93.2	44.7	3.3	0.63	0.78	1.24
5	418	385	-33	97.0	60.2	2.9	0.52	0.54	1.04
6	181	202	+21	65.9	26.7	4.9			
7	237	256	+19	95.7	43.9	3.6			
8	297	298	+1	89.3	44.6	3.2	0.66	0.70	1.06
9	368	293	-75	95.7	48.9	3.3	0.76	0.80	1.06
10	439	344	-95	90.1	49.0	3.0	0.85	0.89	1.05

[a] Reaction conditions [AIBN] = 1.2×10^{-2} M; 24 h reaction time; $T = 65$ °C. Entries 1−5: CO_2 with a helium head pressure. Entries 6−10: pure CO_2 (no helium). [b] P_i = initial pressure. [c] P_f = final pressure. [d] ΔP = change in pressure.

small particles, which have a large surface area, due to efficient capture of oligomeric radicals generated in solution. They argue that the molecular weights from polymer chains which propagate in the polymeric particles are usually higher that those which propagate in the solution due to the gel effect inside the particles, and thus the trend that we observed in our molecular weight data is consistent with their work. Additionally and more importantly in the CO_2 system, the smaller particles would have a fewer number of radicals per particle; thus, less bimolecular termination is expected in the smaller particles than in larger particles.

As expected from simple surface area arguments, increasing the stabilizer concentration resulted in smaller and more monodisperse PS particles. Scanning electron micrographs of these particles are shown in Figure 5. The particle diameter is proportional to the stabilizer concentration, and a log-log plot of the particle diameter as a function of the concentration of the stabilizer (Figure 6) shows a linear dependence with $d_n \propto [S]^{-0.782}$. Literature values for the slopes of these curves from the dispersion polymerization of styrene in alcohol media using homopolymers as stabilizers range from −0.12 to −0.32.[26,30,32,63] Uyama and Kobayashi made the observation that the absolute value of the slope from these plots decreases as the polarity of the solvent increases, with the effect of the stabilizer concentration on the particle size becoming smaller as the polarity of the solvent was increased.[32] This finding is in agreement with our results since CO_2, which has a density dependent dielectric constant ranging from ca. 1.0 to 1.6,[64] has the lowest dielectric constant of any common solvent studied.

(4) Effect of the Monomer Concentration. Dispersion polymerizations were also conducted at three different concentrations of styrene (Table 6). In all cases, the ratios of PS−PDMS (9.6K/24K) stabilizer and initiator to styrene monomer were kept constant at 5 and 0.5 w/w%, respectively. Figure 7 shows the scanning electron micrographs of the PS particles obtained from these reactions. Generally, results in the literature have shown that an increase in the particle diameter is observed when the monomer concentration is increased.[63] The phenomenon results from the fact that in most cases the monomer is a good solvent for the polymer, which leads to an increase in both the critical chain length for precipitation, J_{crit}, and the surface activity, z. However, in our system this trend in the particle size and distribution obtained with increasing monomer concentration was not observed. The particles produced at 10% solids have a bimodal size disbution, with a second crop of small particles being evident in the SEM photograph. Since renucleation is favored by low total solids, a low solvency medium, and low free monomer content,[16] the smaller particles in this case most likely result from a secondary nucleation process near the end of the reaction. At 20% solids the particles are fairly monodisperse in size, indicating a single nucleation stage which is fairly short in duration. Finally, at 30% solids the SEM photograph indicates a trimodal size distribution. Although no evidence exists to verify the exact cause for the trimodal distribution, it may be the result of a dispersant limited agglomeration process[16] at high conversion. Clearly the relationship between concentration and the resulting mechanism of nucleation and particle growth is extremely complex in this case, and further experiments are underway to investigate this phenomenom more thoroughly.

(5) 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 a styrene polymerization without having to add a cosolvent. The effects of pressure on the polymerizations are summarized in Table 7. In addition, Hsiao has recently shown that the small amount (ca. 4 mol %) of helium present in CO_2 which is charged from a cylinder which has a helium head pressure can have a profound effect on the morphology of PMMA prepared by dispersion polymerization.[65,66] To investigate this effect in the present system, pressure studies were undertaken using two different sources of solvent: CO_2 with a helium head pressure (entries 1−5) and pure CO_2 (entries 6−10).

The first set of experiments explored the use of CO_2 from a cylinder which had a helium head pressure which facilitates the delivery of the solvent; this type of cylinder results in approximately 3.7 mol %[66] helium in the CO_2 that is delivered to the reaction vessel. The experiments which had relatively low initial pressures of 143 and 225 bar did not lead to high conversion. In addition, because of the large amount of residual styrene present at the end of these reactions, we were not able to isolate and evaluate the PS particles. For the reactions with initial pressures of at least 287 bar in which particles could be isolated, the PS particles produced became more monodisperse as the pressure was increased. In this case, changing the density of the continuous phase by manipulating the pressure has a dramatic effect on the reaction.

Using pure CO_2 which did not contain any helium, the diameter of the resultant PS particles became 30% larger as the initial pressure was increased from 297 bar to 439 bar. Figure 8 shows the scanning electron micrographs of the PS particles which were produced

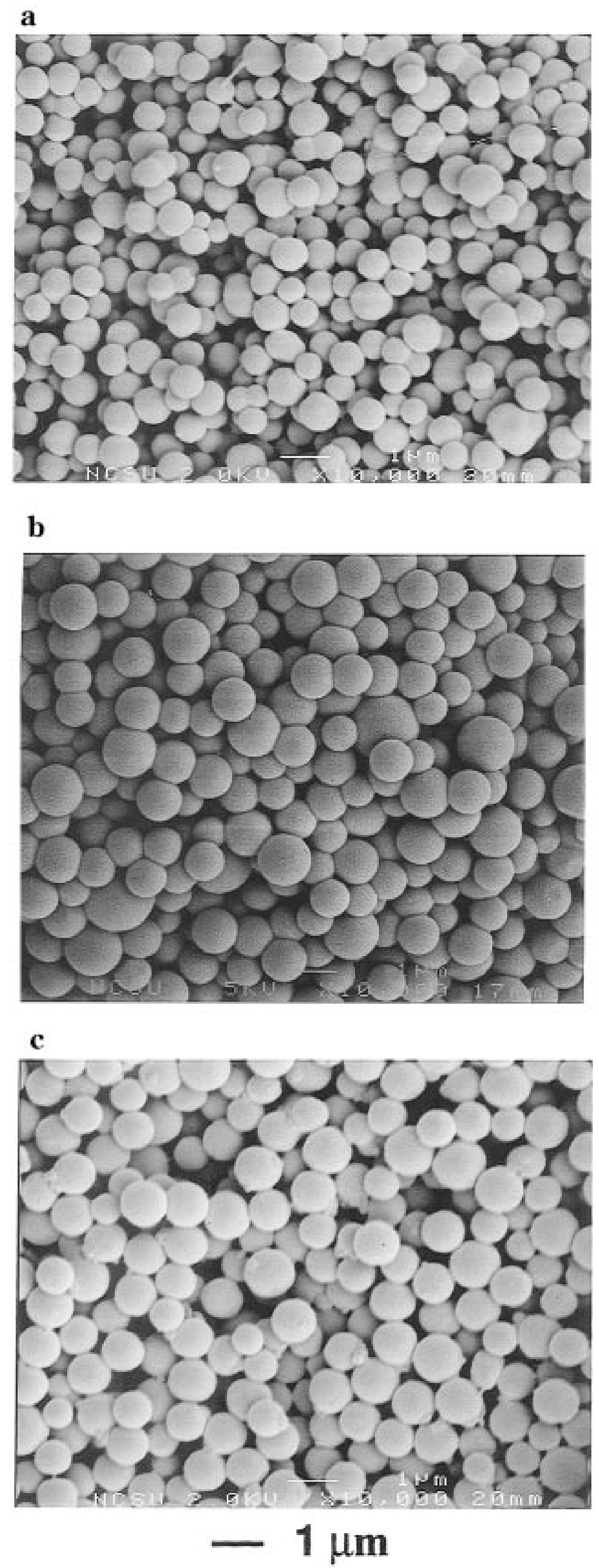

Figure 8. Scanning electron micrographs of PS particles obtained from reactions with initial pressure of (a) 297 bar, (b) 368 bar, and (c) 439 bar of SFC/SFE grade pure CO_2.

as a function of initial pressure. 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, J_{crit}, or for surface activity, z, of the growing oligomeric radicals which were initiated in solution.

Regardless of the source of CO_2, a general trend emerged that the molecular weights were found to increase with increasing pressure while the MWD's became narrower. Another interesting observation that was made during these experiments involved the change in pressure over the course of the reaction. Since styrene has a negative reaction volume,[67] a decrease in the pressure as the monomer converts to polymer is expected for homogeneous solution polymerization. However, for low initial pressures we observed an increase in pressure during the course of the reaction. This observation brings into question the use of pressure monitoring to calculate reaction rates. We believe that this effect arises from the thermodynamics of mixing, which favors expulsion of the CO_2 and monomer from the polymer phase at the lower pressures studied. Wissinger and Paulaitis have shown that the amount of CO_2 which swells the PS phase at 65 °C increases with increasing pressure.[12] However, the partitioning of the monomer between the particle phase and the continuous phase and its dependence on pressure are currently unknown. Ongoing studies designed to determine the monomer partitioning in these systems using pulsed electron beam polymerization[68] and diffusion ordered spectroscopy (DOSY),[69−71] a two-dimensional technique based on pulsed field gradient NMR, will shed light on this phenomenom.

(6) Effect of Venting Process on Product Morphology. One striking observation that was made in all of the diblock copolymer stabilized dispersion polymerizations of styrene in CO_2 was the formation of large multiparticle aggregates in the crude product. Figure 9 shows an example of these aggregates found in the dry product which is left in the reactor after the venting process. For a given reaction, these aggregates are fairly uniform in size, although the shape varies from spherical to ellipsoidal. Moreover, the size of these aggregates varied substantially from reaction to reaction, and we believe this effect may result from subtle changes in the time period of the venting process. However, when the reaction product was sprayed out of the reactor during venting, no secondary aggregate structure was observed. Although other possibilities for the formation of these aggregates certainly exist, we hypothesize that they are formed in the reactor during the venting process as the solvent-swollen, extended PDMS chains collapse. Future studies with more carefully controlled venting procedures are underway in an effort to understand and control this interesting particle aggregation process.

Conclusions

Through dispersion polymerizations in dense CO_2, high conversions of high molecular weight PS can be produced using siloxane-based block copolymers. The use of CO_2 as the continuous phase facilitates the isolation of the products as dry, white, free-flowing powders. This class of stabilizers offers several advantages over the fluorinated stabilizers previously used to produce PS in CO_2 including cost effectiveness and ease of preparation and characterization. The ASB of the stabilizer was found to be a crucial factor affecting both the stability of the resulting latex in CO_2 and the particle morphology. A kinetic study of the polymerization showed that the molecular weight and the conversion increase as a function of time. As expected, both the concentration of monomer and the concentration of stabilizer affected the morphology of the resulting

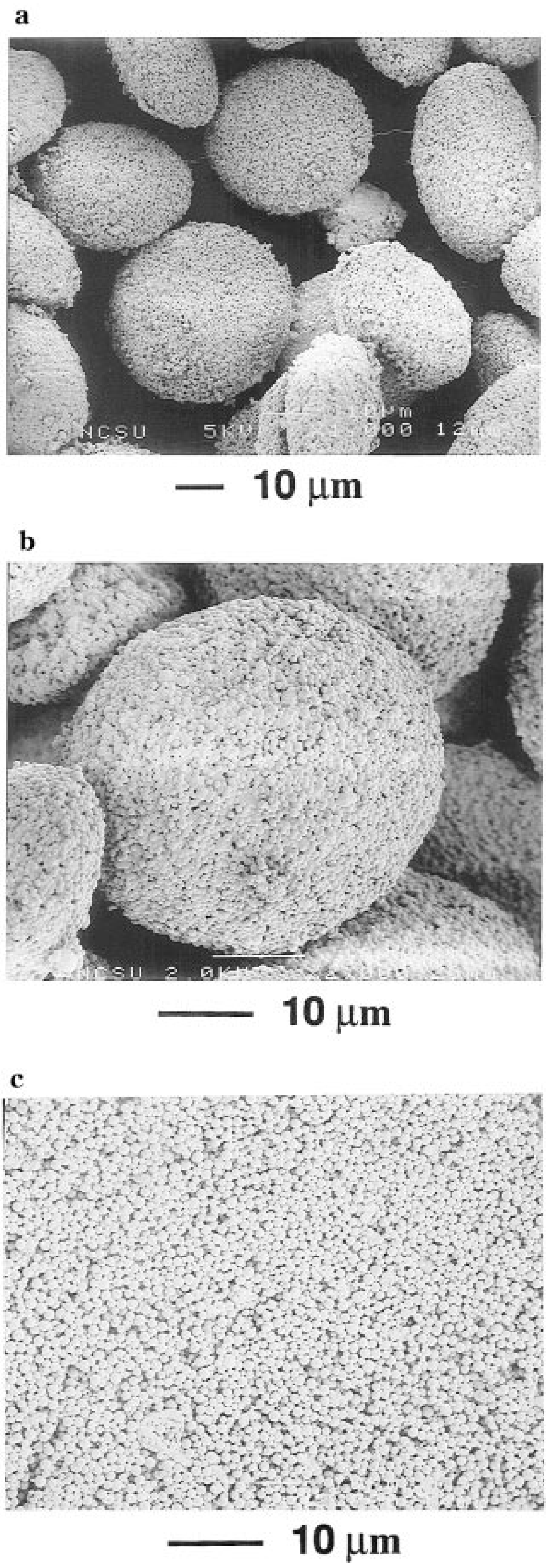

Figure 9. Scanning electron micrographs of aggregates of PS particles obtained using PS−PDMS stabilizers: (a) product from reactor, 1 k× magnification; (b) product from reactor, 2 k× magnification; (c) product sprayed out during venting process, 2 k× magnification.

PS particles. Additionally, the temperature and pressure of the reaction mixture was found to have a dramatic effect on the resulting PS product. The demonstration of the efficacy of siloxane materials as stabilizers for dispersion polymerizations opens the doorway to the design and synthesis of a variety of cost effective surfactants for use in CO_2.

Acknowledgment. At UNC, we gratefully acknowledge financial support from the NSF through a Presidential Faculty Fellowship (J.M.D., 1993−1997), the *Environmentally Benign Chemical Synthesis and Processing Program* sponsored by the NSF and the EPA, and the *Consortium for Polymeric Materials Synthesis and Processing in Carbon Dioxide* sponsored by Air Products and Chemicals, Bayer, B. F. Goodrich, DuPont, Eastman Chemical, Hoechst-Celanese, and Xerox. In addition, we thank Dale Batchelor, Valerie Knowlton, and John Mackenzie, Jr., at North Carolina State University for assistance with the electron microscopy and Isco for the use of their syringe pump.

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MA970579U