1198 *Macromolecules* **2001,** *34,* 1198−1203

Dispersion Polymerization of Glycidyl Methacrylate in Supercritical Carbon Dioxide

Hiroshi Shiho[†] and Joseph M. DeSimone*[,‡]

JSR Corporation, Fine Electronic Research Laboratories, Specialty Materials Laboratory, 100, Kawajiri-cho, Yokkaichi, Mie, 510-8552, Japan; Department of Chemistry, CB#3290, Venable and Kenan Laboratories, University of North Carolina at Chapel Hill, Chapel Hill, North Carolina 27599-3290; and Department of Chemical Engineering, North Carolina State University, College of Engineering, P.O. Box 7905, Raleigh, North Carolina 27695-7905

Received June 8, 2000

ABSTRACT: Herein we report a successful dispersion polymerization of glycidyl methacrylate (GMA) in carbon dioxide using a block copolymer consisting of polystyrene and poly(1,1-dihydroperfluorooctyl acrylate) (PFOA) as a stabilizer. Poly(GMA) was effectively emulsified in carbon dioxide using the amphiphilic diblock copolymer surfactant. Spherical particles were produced, although PFOA homopolymer was not particularly effective as a stabilizer. The initial concentrations of the monomer and stabilizer and the reaction pressure had substantial effects on the resulting size of the colloidal particles.

Introduction

In the past few years, remarkable progress has been made in defining the scope and limitations of carbon dioxide (CO_2) as an inert polymerization medium.[1−3] On the basis of the environmental advantages of CO_2 combined with its ability to be used as a solvent/dispersing medium for a wide variety of chemical reactions, CO_2 may be the solvent of the future for the polymer industry. 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 high solubility in CO_2 at easily accessible temperatures and pressures ($T < 100$ °C, $P < 350$ bar).[4−9] The fluoropolymers have been synthesized homogeneously in CO_2 by free radical methods.[7,8,10−14] Conversely, most industrially important hydrocarbon-based polymers are relatively insoluble in CO_2. Therefore, the polymerization techniques are heterogeneous when hydrocarbon-based polymers are produced in CO_2.

A dispersion polymerization constitutes one heterogeneous technique that has proven useful thus far for CO_2-based systems. Since 1994, the successful dispersion polymerizations of methyl methacrylate,[15−22] 2-hydroxyethyl methacrylate,[23] styrene,[24−27] vinyl acetate,[28] acrylonitrile,[29] and vinyl pyrrolidinone[30] in CO_2 have been reported. Dispersion polymerizations are governed by a delicate interplay which includes the partitioning and interactions of all of the reaction mixture components.[31] The effectiveness of the surfactant also represents a key component in the preparation of a stable latex.[32] The stabilizers studied in these experiments were carefully selected and synthesized on the basis of their known solvency in CO_2 and the established criteria for steric stabilizer effectiveness. We have previously demonstrated the amphiphilicity of fluorinated acrylate homopolymers, such as poly(1,1-dihydroperfluorooctyl acrylate) (PFOA), which contains a lipophilic acrylate backbone and a CO_2-philic, fluorinated side chain.[16] Another approach to the stabilization of CO_2-phobic polymer colloids is the use of fluorocarbon−hydrocarbon block copolymers, specifically PFOA and polystyrene (PS). While these fluorinated stabilizers are effective for dispersion polymerizations of lipophilic monomers in CO_2,[23,24,29,30] their efficiency in preventing glycidyl methacrylate (GMA)-based colloidal particles from aggregation has yet to be established.

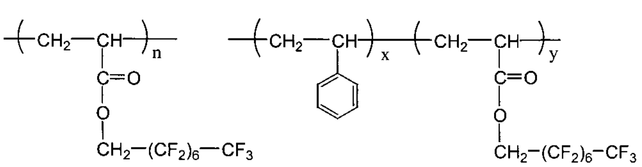

Figure 1. Structures of PFOA homopolymers and PS-*b*-PFOA diblock copolymer used as the stabilizer.

Herein this surfactant has been examined in the dispersion polymerization of GMA in CO_2. The influence of the stabilizer and monomer concentrations and the reaction pressure on the resulting poly(GMA) colloid have also been investigated.

Experimental Section

Materials. 1,1-Dihydroperfluorooctyl acrylate (FOA, 3M) was purified by passage through an alumina column. 2,2′-Azobisisobutyronitrile (AIBN, Aldrich) and tetraethylthiuram disulfite (TD, Aldrich) were recrystallized from methanol. Glycidyl methacrylate (GMA, 97%, Aldrich), styrene (99%, Aldrich), α,α,α-trifluorotoluene (TFT, 99%, Aldrich), 2,3-dihydroperfluoropentane (PFP, 98%, SynQuest), methylene chloride (99%, Mallinckrodt), and methanol (99%, 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. By use of 0.05 g (3.0×10^{-4} mol) of AIBN as the initiator, 10 g (2.2×10^{-2} mol) of FOA was polymerized at 65 °C for 20 h under a nitrogen atmosphere. The product was dissolved in a mixture of PFP and methylene chloride and then precipitated in methanol. The obtained polymers were filtered and dried in vacuo. The structure of this fluorinated acrylic homopolymer is shown in Figure 1a.

---

* To whom correspondence should be addressed.

[†] JSR Corporation.

[‡] North Carolina State University and University of North Carolina at Chapel Hill.

10.1021/ma0010074 CCC: $20.00

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

entry	stabilizer	yield[b] (%)	Dn[c] (μm)	PSD[d]	product morphology
1	none	92			bulky solids
2	PS-*b*-PFOA (4.2K/19.7K)	90	1.50	1.01	spherical particles
3	PFOA	92	4.31	1.17	spherical particles (flocculated)

[a] Reaction conditions: 5 g of GMA, 0.025 g of AIBN, 392 ± 10 bar, 65 °C, 20 h; for stabilized reactions (entries 2 and 3), 0.5 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.

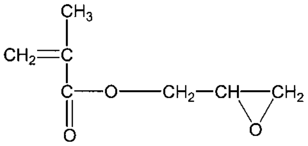

Figure 2. Structure diagram of GMA.

Diblock Copolymer. A diblock copolymer consisting of PS and PFOA (PS-*b*-PFOA) was synthesized using the "iniferter" technique developed by Otsu.[33] The synthesis of the specific block copolymers has been previously described.[34] The styrene block was synthesized first using TD as the initiator. The telechelic PS block was then used as a macroinitiator during the photopolymerization of the second monomer (FOA) to form 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, $<M_n>_{PS}$ / $<M_n>_{PFOA}$. 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 1.5×10^{-4} mol of AIBN and the desired amount of surfactant (0−0.75 g), and then the system was purged with a flow of argon prior to the addition of monomer. The desired amount of GMA ($1.8-5.3 \times 10^{-2}$ mol) 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 100 bar or below, 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 reaction was allowed to proceed with stirring for 20 h. At the end of the reaction, the reactor was cooled, and the CO_2 was slowly vented from the cell before removal of the polymer product. To quantify the reaction yields, the reaction cell was rinsed with methylene chloride to remove any residual polymer product and stabilizer. The polymer conversion determined gravimetrically was more than 90% in each case. The weight of the stabilizer was subtracted from the total mass of the product to obtain the weight of polymer product.

Polymer Characterization. Molecular weight of the telechelic PS block was determined by using 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. The morphology of the polymers was determined using a JEOL 6400FE scanning electron microscope (SEM). The number-average particle size and particle size distributions were determined by measuring the diameter of 100 particles. ^{1}H NMR spectra were obtained from a Varian 300 MHz NMR.

Results and Discussion

1. Comparison of Stabilizers. The structure diagram of GMA is shown in Figure 2, and the data for the polymerization of GMA in CO_2 using two different stabilizers is summarized in Table 1. The polymerization that was conducted in the absence of stabilizer (entry 1) resulted in the formation of a precipitated polymer with a nondescript morphology. In contrast, the polymerizations carried out in the presence of an amphiphilic diblock copolymer started out slightly translucent and then formed a remarkably stable colloidal dispersion of poly(GMA). The successful stabilization of the polymerization simultaneously gave spherical particles in the micron-size range (Figure 3a). The mechanism for particle formation in these polymerizations may mainly involve micellar nucleation since PS-*b*-PFOA copolymers associate to form micelles in a CO_2 continuous phase,[35] although such aggregates have not yet been identified in the presence of large amounts of GMA monomer. Grafting of PFOA blocks on the poly(GMA) particles could also occur in the solution phase early in the polymerization process possibly through chain transfer of the growing poly(GMA) chain to the backbone of the stabilizer to generate secondary or tertiary carbon radicals. The methylene linkage on the side chain of PFOA is less susceptible to hydrogen abstraction by a free-radical mechanism due to the

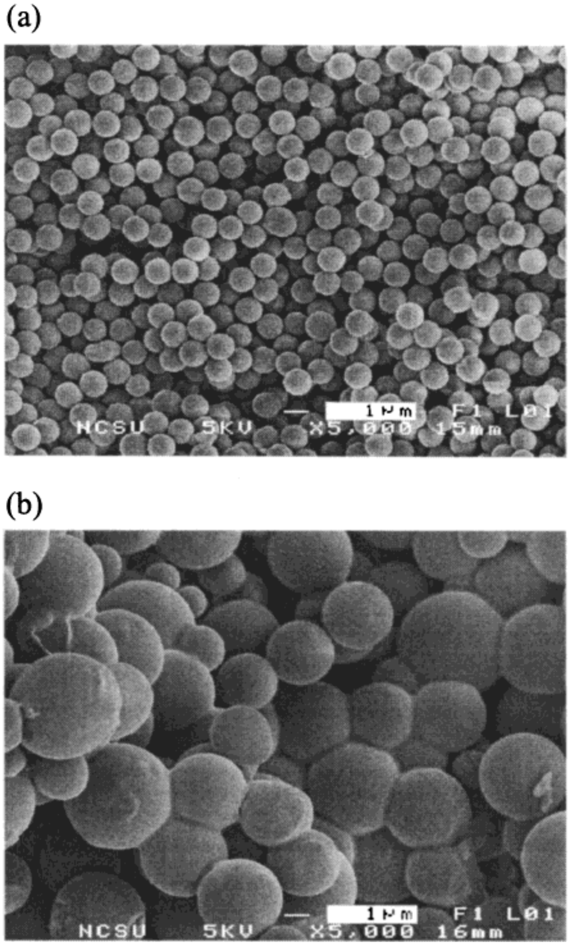

Figure 3. Scanning electron micrographs from reactions containing (a) PS-*b*-PFOA and (b) PFOA stabilizer.

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

entry	GMA concn (w/v % in CO_2)	yield[b] (%)	Dn[b] (μm)	PSD[b]	particle morphology	calcd stabilizer surace coverage[c] (nm^2 molecule^{-1})
4	10	93	0.28	1.05	spherical	4.3
5	14	94	0.43	1.03	spherical	3.9
6	20	90	1.50	1.01	spherical	1.6
7	30	95	4.78	1.01	spherical	0.7

[a] Reaction conditions: 0.025 g of AIBN, 0.5 g of PS-*b*-PFOA (4.2K/19.7K), 390 ± 12 bar, 65 °C, 20 h. [b] Yields, Dn, and PSD are defined in footnotes to Table 1. [c] Surface coverage was calculated based on the particle diameter and the amount of PS-*b*-PFOA added to the system.

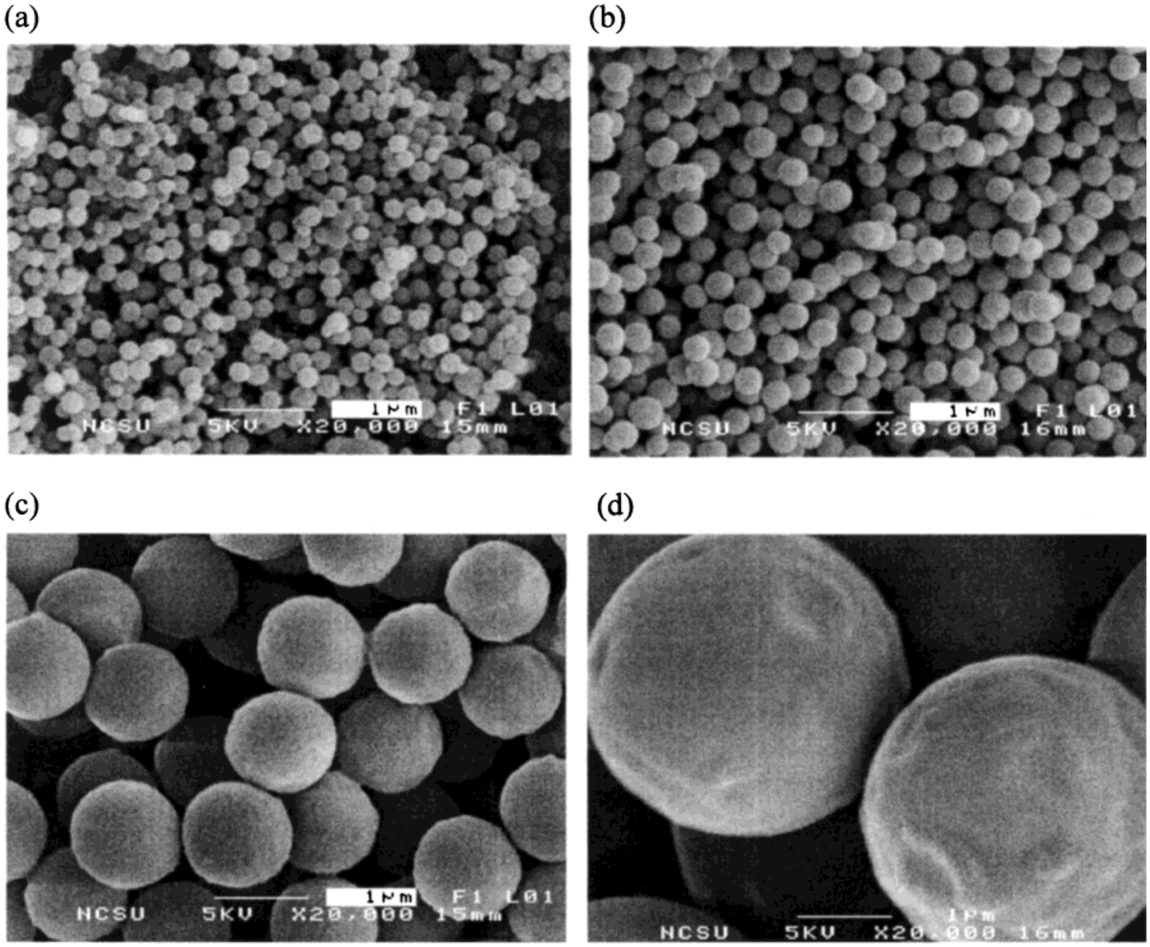

Figure 4. Scanning electron micrographs of poly(GMA) particles obtained from reactions with GMA concentrations of (a) 10, (b) 14, (c) 20, and (d) 30 w/v %.

strong electronegativity of the adjacent CF_2 units. As sufficient graft copolymers were generated, more stable nuclei were formed through association of oligomeric radicals with the graft copolymers or homopolymers. The resultant poly(GMA) particles presumably became effectively stabilized since the reaction mixture exhibited a milky white appearance which was similar to that observed for a conventional aqueous latex. Upon venting of the CO_2, a dry, white, free-flowing powder remained in the reaction vessel.

For comparison, the polymerization conducted in the presence of the CO_2-soluble homopolymer of PFOA resulted in a less effective stabilizing system than the block copolymer. The reaction started out homogeneously and then formed a colloidal dispersion of poly(GMA), but flocculated later during the course of the reaction (Figure 3b). The reaction conditions were modified by changing the stabilizer concentration, monomer concentration, and the reaction pressure, but these changes resulted in little improvement. Apparently, this poor stability is due to the inefficient anchoring of PFOA homopolymer to the surface of the poly(GMA) particles. In addition, the unsuccessful dispersion polymerization of GMA using PFOA homopolymer as a stabilizer stood in contrast to the successful dispersion polymerization of methyl methacrylate[15,16] and styrene[26] using PFOA homopolymer as a stabilizer. These findings suggest that the adsorption of the stabilizer onto the poly(GMA) particles is enhanced by the presence of the styrenic block.

2. Effect of the Monomer Concentration. The dispersion polymerizations were also conducted at four different concentrations of GMA (Table 2). In all cases, the contents of PS-*b*-PFOA (4.2K/19.7K) stabilizer and initiator added to the system were kept constant at 2 and 0.1 w/v %, respectively. Figure 4 shows the scanning electron micrographs of the poly(GMA) obtained from these reactions. Generally, dispersion polymerization

Table 3. Effect of Stabilizer Concentration on the Dispersion Polymerization of GMA in CO_2[a]

entry	stabilizer concn (w/w% to monomer)	yield[b] (%)	Dn[b] (μm)	PSD[b]	particle morphology	calcd stabilizer surface coverage[b] (nm^2 molecule^{-1})
8	3	94	1.92	1.01	spherical	4.1
9	5	96	1.79	1.01	spherical	2.7
10	7.5	95	1.72	1.01	spherical	1.8
11	10	90	1.50	1.01	spherical	1.6
12	15	95	1.39	1.01	spherical	1.1

[a] Reaction conditions: 5 g of GMA, 0.025 g of AIBN, 392 ± 11 bar, 65 °C, 20 h. [b] Yields, Dn, PSD, and surface coverage are defined in footnotes to Tables 1 and 2.

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

entry	P_i[b] (bar)	P_f[c] (bar)	yield[d] (%)	Dn[d] (μm)	PSD[d]	calcd stabilizer surface coverage[d] (nm^2 molecule^{-1})
13	451	449	95	1.94	1.01	1.2
14	402	411	90	1.50	1.01	1.6
15	327	358	94	1.01	1.02	2.4
16	262	311	95	0.59	1.02	4.0
17	193	280	98	0.46	1.03	5.2
18[e]	126	174	97	2.41	1.08	0.99

[a] Reaction conditions: 5 g GMA, 0.025 g AIBN, 0.5 g PS-*b*-PFOA(4.2K/19.7K), 65 °C, 20 h. [b] P_i = initial pressure. [c] P_f = final pressure. [d] Yields, Dn, PSD, and surface coverage are defined in footnotes to Tables 1 and 2. [e] Flocculated during the course of the reaction.

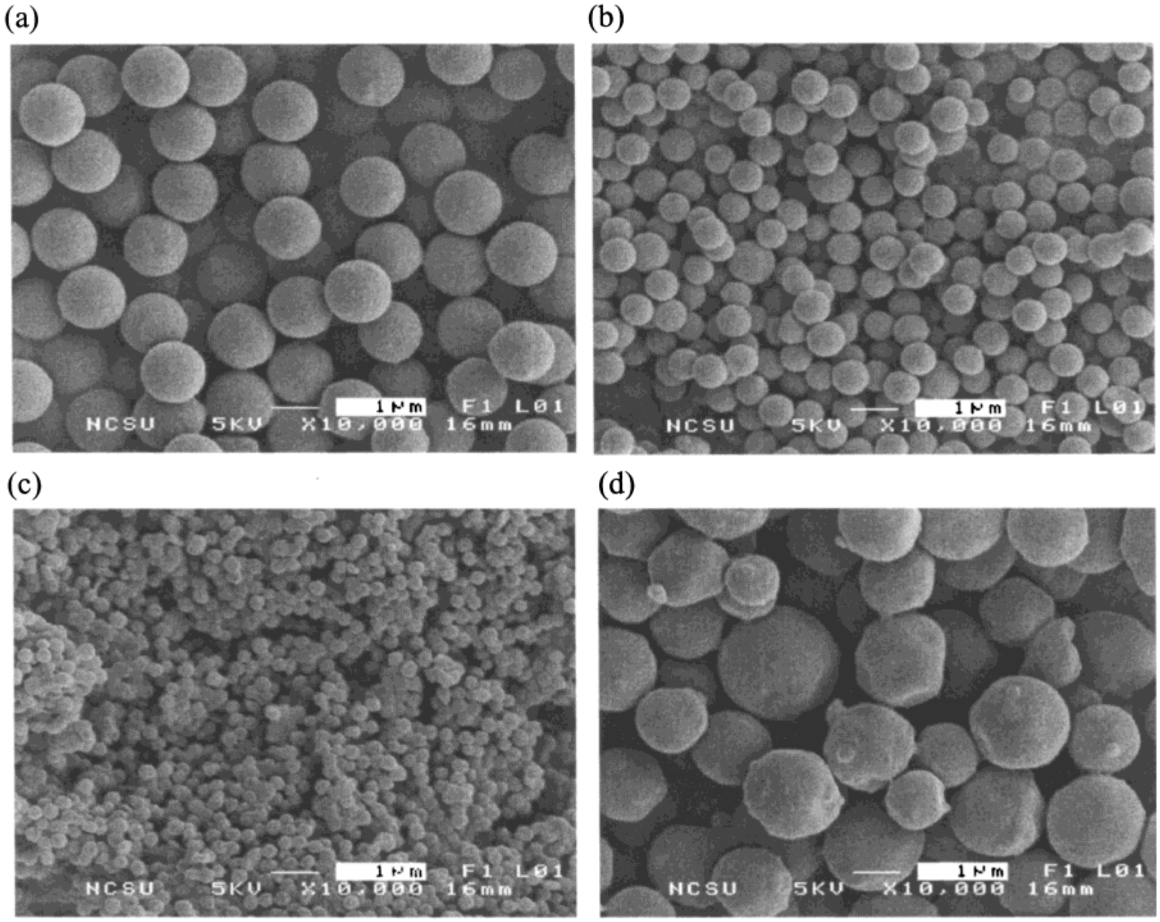

Figure 5. Scanning electron micrographs of poly(GMA) particles obtained from reactions with initial pressures of (a) 451, (b) 327, (c) 193, and (d) 126 bar in CO_2.

results in the literature show that the particle diameter increases when the monomer concentration increases because of a solvent effect.[36] This trend was also seen in our system. The diameter of the particles increased from 0.28 to 4.78 μm and the particle size distribution decreased from 1.05 to 1.01 when the monomer concentration increased from 10 to 30 w/v % (in CO_2). The increase in solvency at higher monomer concentration could influence the final particle size and particle size distribution in various ways. Since non-cross-linked poly(GMA) is soluble in its own monomer, the critical degree of polymerization at which the oligomeric radicals precipitate from solution is increased. The calculated coverage of the steric stabilizer based on the particle diameter and the amount of stabilizer added to the system decreases as the monomer concentration increases. This apparently results in the formation of fewer nuclei and, hence, larger particles. The locus of the polymerization as well as the partitioning of the monomer in the particle phase versus the solution phase also changes with the solvency of the dispersion medium. This changes the polymerization kinetics of the system. Since nucleation is favored by low total solids, a low solvency medium, and low free monomer content,[31] the wider particle size distributions in this case most likely result from a secondary nucleation process near the end of the reaction. At more than 20 w/v % solids, the particles are fairly monodisperse in size, indicating a single nucleation stage which is fairly short in duration.

3. Effect of the Stabilizer Concentration. As shown in Table 3, the particle diameter was affected by the concentration of the stabilizer. The particles, though retaining narrow particle size distributions, showed decreases in diameter from 1.92 to 1.39 μm when the concentration of PS-*b*-PFOA increased from 3 to 15 w/w % (to monomer). We believe that in the presence of PS-*b*-PFOA the oligomeric poly(GMA) radicals could rapidly adsorb the stabilizer prior to aggregation with other particles. The calculated coverage of the steric stabilizer based on the particle diameter and the amount of stabilizer added to the system decreases as the stabilizer concentration increases. As a result, there was an increase of the number of stable nuclei with higher stabilizer content and correspondingly smaller particles were produced.[37]

4. Effect of CO_2 Pressure. A primary advantage of employing $scCO_2$ as a reaction medium lies in the ability to tune the solvent density and dielectric constant by simply changing either temperature or pressure.[4] This property allows the exploration of solvent effects on a GMA polymerization without having to add a cosolvent. The effects of pressure on the polymerizations are summarized in Table 4 and Figure 5. In this case, changing the density of the continuous phase by manipulating the pressure has a dramatic effect on the reaction. The diameter of the resultant poly(GMA) particles increased and the particle size distribution narrowed as the initial pressure increased. In addition, the calculated coverages of the steric stabilizer decreased as the reaction pressure increased when the initial pressure was more than 193 bar. As the pressure increased, the solvency of the medium for the growing polymer chains increased, and this resulted in an increase in the critical molecular weight for precipitation or surface activity of the growing oligomeric radicals. When the initial pressure was 126 bar, the dispersion that formed was initially stable, but flocculation occurred during the course of the reaction, and the resulting polymer was found to be agglomerated by SEM.

An increase in pressure during the course of the reaction was observed when the initial pressure was less than 402 bar in contrast with a slight decrease in pressure during the course of the reaction when the initial pressure was 451 bar. Similar observations were made in styrene[25,26] and MMA[15] polymerizations 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 phase at low initial pressures.

Conclusions

Dispersion polymerization of GMA in supercritical carbon dioxide was successfully conducted using an amphiphilic diblock copolymer consisting of PS and PFOA as the stabilizer. Spherical poly(GMA) particles were produced with relatively narrow particle size distributions. The particle diameter was controlled by the amount of stabilizer and monomer, as well as the reaction pressure.

Acknowledgment. Financial support of this work by JSR is gratefully acknowledged. This material is based upon work supported in part by the STC Program of the National Science Foundation under Agreement No. CHE-9876674. We also thank the Kenan Center for the Utilization of Carbon Dioxide in Manufacturing for the use of its equipment and lab space. In addition, we thank ISCO for the use of their syringe pump. We thank Terri Carson for carrying out GPC analysis.

References and Notes

(1) Shaffer, K. A.; DeSimone, J. M. *Trends Polym. Sci.* **1995**, *3*, 146.

(2) Canelas, D. A.; DeSimone, J. M. *Adv. Polym. Sci.* **1997**, *133*, 103.

(3) Kendall, J. L.; Canelas, D. A., Young, J. L.; DeSimone, J. M. *Chem. Rev.* **1999**, *99*, 543.

(4) McHugh, M. A.; Krukonis, V. J. *Supercritical Fluids Extraction: Principles and Practice*, 2nd ed.; Butterworth-Heineman: Stoneham, MA, 1993.

(5) Yilgor, I.; McGrath, J. E.; Krukonis, V. J. *Polym. Bull.* **1984**, *12*, 499.

(6) Krukonis, V. J. *Polym. News* **1985**, *11*, 7.

(7) DeSimone, J. M.; Guan, Z.; Eisbernd, C. S. *Science* **1992**, *257*, 945.

(8) Guan, Z.; Combes, J. R.; Menceloglu, Y. Z.; DeSimone, J. M. *Macromolecules* **1993**, *26*, 2663.

(9) Hoefling, T. A.; Newman, D. A.; Enrick, R. M.; Beckman, E. J. *J. Supercrit. Fluids* **1993**, *6*, 165.

(10) Guan, Z.; Combes, J. R.; Eisbernd, C. S.; DeSimone, J. M. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1992**, *33* (2), 329.

(11) Ehrich, P. *Chemtracts: Org. Chem.* **1993**, *6*, 92.

(12) DeSimone, J. M. International Patent Application PCT/US93/01626 1993.

(13) Guan, Z.; Eisbernd, C. S.; DeSimone, J. M. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1993**, *34(1)*, 446.

(14) Kappellen, K. K.; Mistele, C. D.; DeSimone, J. M. *Polym. Mater. Sci. Eng.* **1996**, *74*, 256.

(15) Hsiao, Y.-L.; Maury, E. E.; DeSimone, J. M.; Mawson, S. M.; Johnston, K. P. *Macromolecules* **1995**, *28*, 8159.

(16) DeSimone, J. M.; Maury, E. E.; Meuceloglu, Y. Z.; McClain, J. B.; Romack, T. J.; Combes, J. R. *Science* **1994**, *265*, 356.

(17) Hsiao, Y.-L.; DeSimone, J. M. *J. Polym. Sci., Part A: Polym. Chem.* **1997**, *35*, 2009.

(18) Shaffer, K. A.; Jones, T. A.; Canelas, D. A.; DeSimone, J. M.; Wilkinson, S. P. *Macromolecules* **1996**, *29*, 2704.

(19) O'Neill, M. L.; Yates, M. Z.; Johnston, K. P.; Smith, C. D.; Wilkinson, S. P. *Macromolecules* **1998**, *31*, 2848.

(20) O'Neill, M. L.; Yates, M. Z.; Johnston, K. P.; Smith, C. D.; Wilkinson, S. P. *Macromolecules* **1998**, *31*, 2838.

(21) Lepilleur, C.; Beckman, E. J. *Macromolecules* **1997**, *30*, 745.

(22) Yong, T.-M.; Hems, W. P.; van Nunen, K. L. M.; Holmes, A. B.; Steinke, J. H. G.; Taylor, P. L.; Segal, J. A.; Friffin, D. A. *Chem. Commun. (Cambridge)* **1997**, *18*, 1811.

(23) Shiho, H.; DeSimone, J. M. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, in press.

(24) Canelas, D. A.; Betts D. E.; DeSimone, J. M. *Macromolecules* **1996**, *29*, 2818.

(25) Canelas, D. A.; DeSimone, J. M. *Macromolecules* **1997**, *30*, 5673.

(26) Shiho, H.; DeSimone, J. M. *J. Polym. Sci., Part A: Polym. Chem.* **1999**, *37*, 2429.

(27) Shiho, H.; DeSimone, J. M. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 1146.

(28) Canelas, D. A.; Betts, D. E.; DeSimone, J. M.; Yates, M. Z.; Johnston, K. P. *Macromolecules* **1998**, *31*, 6794.

(29) Shiho, H.; DeSimone, J. M. *Macromolecules* **2000**, *33*, 1565.
(30) Carson, T. J.; Lizotte, J.; DeSimone, J. M. *Macromolecules*, **2000**, *33*, 1917.
(31) Barrett, K. E. J. *Dispersion Polymerization in Organic Media*; John Wiley and Sons: New York, 1975.
(32) Napper, D. H. *Polymeric Stabilization of Colloidal Dispersions*; Academic Press: New York, 1983.
(33) Otsu, T.; Yoshida, M. *Makromol. Chem. Rapid Commun.* **1982**, *3*, 127.
(34) Guan, Z.; DeSimone, J. M. *Macromolecules* **1994**, *27*, 5527.
(35) Yates, M. Z.; O'Neill, N. L.; Johnston, K. P.; Webber, S.; Canelas, D. A.; Betts, D. E.; DeSimone, J. M. *Macromolecules* **1997**, *30*, 5060.
(36) Sudol, E. D. *In Polymeric Dispersions: Principles and Applications*; Asua, J. M., Ed.; Kluwer Academic: Boston, MA, 1997; p 141.
(37) Winnik, M. A.; Lukas, R.; Chen, W. F.; Furlong, P.; Croucher, M. D. *Macromol. Chem. Macromol. Symp.* **1987**, *10/11*, 483.

MA0010074