Dispersion Polymerization of MMA in Supercritical CO_2 in the Presence of Copolymers of Perfluorooctylethylene Methacrylate and Poly(propylene glycol) Methacrylate

Lunhan Ding and Susan V. Olesik*

Department of Chemistry, Ohio State University, 100 West 18th Ave., Columbus, Ohio 43210

Received December 30, 2002; Revised Manuscript Received April 8, 2003

ABSTRACT: A series of random copolymers, poly(perfluorooctylethylene methacrylate)−poly(propylene glycol) methacrylate, were synthesized as dispersants for dispersion polymerizations of methyl methacrylate in CO_2. The results show that the composition of copolymeric dispersants has a dramatic effect on the polymerization yield and on the morphology of the resulting poly(methyl methacrylate) particles. The effect of varying the dispersant concentration, monomer concentration, and the initial medium pressure on the resultant polymerization was also investigated.

Introduction

Increasingly, CO_2 is recognized as an attractive replacement for aqueous and organic solvents that are traditionally used in separations,[1] extractions,[2] and polymerizations.[3−10] This can be attributed to the fact that CO_2 is nontoxic, nonflammable, inexpensive, and readily available. In addition, CO_2 can be easily separated from other components. CO_2 is often used as a supercritical fluid due to its readily accessible critical point ($T_c = 31.8$ °C; $P_c = 75.8$ bar). For both supercritical and liquid CO_2 the dielectric constant varies from 1.2 to 1.5, and its viscosity is also low under both supercritical and liquid conditions.[11] Accordingly, liquid and supercritical CO_2 are good solvents for nonionic compounds with low to moderate molecular weight but are poor solvents for most macromolecules except for some fluoropolymers,[12] poly(siloxanes),[13] and poly(ether−carbonate) copolymers.[14] Poly(methyl methacrylate) (PMMA) is insoluble in both liquid and supercritical CO_2. However, CO_2 can act as a plasticizing agent for PMMA[16] and thus is capable of facilitating the diffusion of monomer inside the swollen polymer phase during a heterogeneous polymerization, such as dispersion polymerization. Consequently, high polymerization conversion can be easily obtained in dispersion polymerizations of MMA using CO_2 as the medium.

Dispersion polymerization involves having the monomer and initiator soluble in the reaction medium, while the polymer formed is insoluble and thus dispersed in the medium through polymeric dispersant which is dissolved in the medium prior to the polymerization. Monodisperse or nearly monodisperse latex particles that are sterically stabilized by the polymeric dispersant can be produced with diameters ranging from submicrons to tens of microns. Since CO_2 is a good solvent for most liquid vinyl monomers and a poor solvent for most polymers, recent studies have shown that CO_2 can be used as a successful medium for dispersion polymerization of various monomers including styrene,[17] methyl methacrylate,[3−5] vinyl acetate,[18] vinylpyrrolidone,[19] acrylonitrile,[20] and glycidyl methacrylate,[21] and free-flowing powders of polymers can be produced directly by simply venting the reactor.

The primary challenge for dispersion polymerization in CO_2 is the choice of the dispersants that can sterically stabilize the polymer particles as they form. Those dispersants should contain both "CO_2-philic" segment (s) that are highly soluble in CO_2 and "hydrocarbon polymer anchor" segment(s) that are absorbed on the surface of the polymer particles. The "CO_2-philic" group extends out from the surface of the polymer particles into the CO_2 phase, acting as steric barriers to prevent flocculation. The successful dispersants for dispersion polymerizations in CO_2 have been block copolymers that incorporated either a siloxane[4] (e.g., poly(dimethylsiloxane)) or a fluorinated polymer[3,21] [e.g., poly(fluorooctyl acrylate)] as the CO_2-soluble segment. DeSimones et al. also showed that the homopolymer of fluorooctyl acrylate (PFOA) can be an effective polymeric dispersant for dispersion polymerization of styrene[22] and MMA.[3] However, synthesis of block copolymers can be complex and may not be economically viable. Homopolymeric dispersants, i.e., poly(1,1-dihydrofluorooctyl acrylate), are expensive perfluoro polymers and cannot be characterized in usual solvents due to their poor solubility. DeSimone et al.[23] employed copolymers of fluoroacrylate and styrene as dispersion agents for dispersion polymerizations of styrene in CO_2, in which the amount of styrene incorporated in copolymers, however, is very limited (below 16%), and no evident improvement is observed. Beckman et al.[5] synthesized a series of graft copolymers, poly(methyl methacrylate-*co*-hydroxyethyl methacrylate)-*g*-poly(perfluoropropyl oxide), which are proven to be effective stabilizers for the dispersion polymerization of MMA in CO_2.

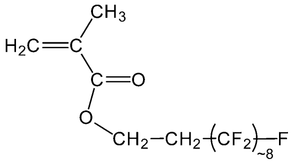
In this study, an alternative approach for dispersion polymerization of MMA in CO_2 is demonstrated that involves using random copolymers of two commercially available monomers as the dispersants: a monomer with a large CO_2-philic group, i.e., perfluorooctylethylene methacrylate, and another monomer with a large "hydrocarbon polymer anchor" group, i.e., poly(propylene glycol) methacrylate. The impacts of different comonomer ratios, dispersant concentrations, MMA

---

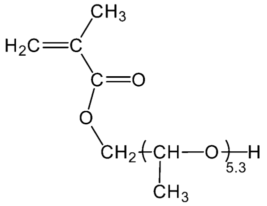
* Corresponding author.

10.1021/ma026015u CCC: $25.00

concentrations, and pressure variation of CO_2 on MMA polymerization were also investigated.



2-(perfluorooctyl)ethyl methacrylate (FOEMA)



poly(propylene glycol) methacrylate (PPGMA)

Experimental Section

Materials. Methyl methacrylate (MMA) was distilled under reduced pressure to remove the inhibiltors. Poly(propylene glycol) methacrylate with molecular weight 395 g/mol and Zonyl TM fluoromonomer (2-(perfluorooctyl)ethyl methacrylate) with molecular weight 534 g/mol were purified by passing through an basic alumina column. 2,2′-Azobis(isobutyronitrile) (AIBN) was recrystallized from methanol. All the chemicals above were purchased from Aldrich. Carbon dioxide (Chromatographic grade, 99.995 %) was obtained from Praxair and was used as received.

Preparation of Copolymeric Dispersants. Random copolymers of FOEMA and PPGMA (poly(FOEMA-*co*-PPGMA) with various monomer ratios were prepared using radical polymerization. With 0.05 g of AIBN as the initiator, 2.5 g of FOEMA and 2.5 g of PPGMA were dissolved in 2.5 mL of toluene. The solution was heated to 65 °C, and the polymerization was found to be complete after 24 h. The product was dissolved in 5 mL of acetone and precipitated in 200 mL of pentane, followed by rinsing with pentane three times and drying in a vacuum.

Dispersion Polymerizations of MMA in CO_2. The polymerization reactions were conducted in CO_2 in a 10 mL, high-pressure stirred reaction vessel. The reactor was charged with the desired amount of dispersant, MMA and AIBN. Next it was connected to an ISCO model 260D syringe pump that allowed adding CO_2 to the reactor at a pressure of approximately 70 bar. The reaction vessel was then heated to 65 °C. As the reaction vessel was heated, the remaining CO_2 was added into the reaction mixture until the desired pressure was reached. Then the reactor was sealed and allowed to continue the polymerization with stirring for 12 h. At the end of the reactions, the reactor was cooled in cold water, and the CO_2 was slowly vented. The polymer product was collected. To quantify the reaction yield, the reaction vessel was rinsed with acetone to collect any residual PMMA. The polymerization yield was determined gravimetrically.

Polymer Characterization. Comonomer ratios incorporated in the copolymeric dispersant were determined by ^1H NMR spectra using a Bruker DPX-250 MHz NMR spectrometer with $CDCl_3$ as the solvent. Microscopic images of PMMA particles were obtained from a JEOL JSM-800 scanning electron microscope. The molecular weights of the copolymeric dispersants and PMMA were determined using a multiangle light scattering equipment combined with miniDAWN light scattering detector from Wyatt Technology Corp. and Shimadzu high-performance liquid chromatography with THF as the solvent at 40 °C using two Polymer Laboratories PLGel Mixed-D columns in series (300 × 7.5 mm with 5 μm particles) and a refractive index detector.

Table 1. Properties of Copolymeric Dispersants Based on FOEMA and PPGMA

FOEMA % (wt) feed	FOEMA % (wt) measd	solubility (g/mL) in CO_2 at 330 bar and 65 °C	M_n, PDI[a]
30	31	insoluble	87 000, 4.78
50	52	0.0016	74 000, 3.33
67	67	0.0030	92 000, 3.52
75	75	0.0040	
100	100	0.0060	

[a] PDI = polydispersity index of the molecular weight distribution (M_w/M_n). As polymer with 75% FOEMA and PFOEMA cannot dissolve in THF, M_n and PDI for those two polymers were not obtained.

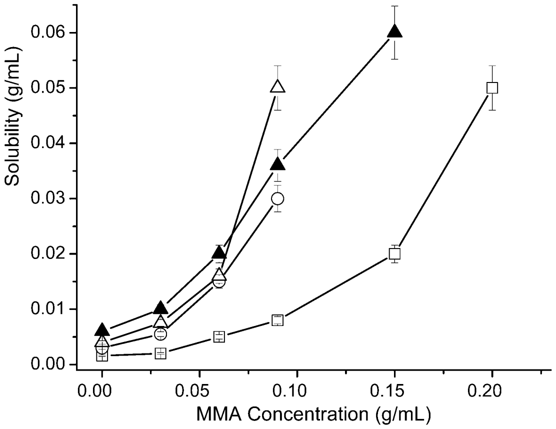


Figure 1. Solubility of copolymers in the mixture of CO_2 and MMA at 65 °C and 330 bar: (□) 52% FOEMA; (O) 67% FOEMA; (△) 75% FOEMA; (▲) 100% FOEMA.

Results and Discussion

Copolymeric Dispersants. The copolymeric dispersants were synthesized by radical polymerization of FOEMA and PPGMA in toluene at 65 °C. Because of the presence of PPGMA units, the resultant copolymers are unlike poly(FOEMA) in that they dissolved in chloroform and other organic solvents. Accordingly, ^1H NMR spectra of the copolymers were recorded using an NMR spectrometer, and the proportion of FOEMA in the copolymers was thus calculated from ^1H NMR spectra of the copolymers. Table 1 shows the results of ^1H NMR measurements. As expected, the proportion of FOEMA incorporated in the copolymers is similar to the feed ratios of the comonomers.

The solubility of the copolymers in the mixtures of CO_2 and MMA at 65 °C and 330 bar was determined and is shown in Figure 1. The solubility of the copolymers in the mixture of CO_2 and MMA decreased gradually as the amount of CO_2-philic monomer (FOEMA) decreased in the copolymers. The copolymer containing 52% poly(propylene glycol) methacrylate still remained soluble in CO_2 at 65 °C and 330 bar. This may be due to the fact that the poly(propylene glycol) ester itself is quite miscible with CO_2.[15] Figure 1 also shows that the solubility of copolymers in pure CO_2 is very limited. The solubility of the copolymers increases dramatically when a small amount of MMA is mixed with CO_2. Consequently, polymerization mixtures always started with a homogeneous phase even when a large amount of copolymeric dispersants was used. CO_2-philic groups on the copolymers are perfluorooctyl groups ($-(CF_2)_8-F$), and "hydrocarbon polymer anchor" groups are poly(propylene glycol) containing more than five of the propylene glycol units. During the dispersion polymerization, the copolymer dispersant may gradually

Table 2. Characterization of PMMA Particles Prepared at 30% MMA/CO$_2$ (w/v), 1% AIBN/MMA (w/w), and 65 °C with the Initial Pressure of 330 bar

no.	position in Figures	copolymeric dispersant (% of MMA (wt/wt))	yield (%)	D_n (μm)	M_n, PDI
1		31% FOEMA at 2%	78		217 000, 2.25
2		52% FOEMA at 2%	92	3.30	311 000, 1.80
3		67% FOEMA at 2%	90	3.50	117 000, 1.90
4		75% FOEMA at 2%	92	5.31	296 000, 1.76
5		100% FOEMA at 2%	42		84 000, 2.64
6	Figure 2a	31% FOEMA at 5%	86		213 000, 2.17
7	Figure 2b	52% FOEMA at 5%	91	2.68	243 000, 1.58
8	Figure 2c	67% FOEMA at 5%	93	3.10	208 000, 1.96
9	Figure 2d	75% FOEMA at 5%	91	3.67	283 000, 1.56
10	Figure 2e	100% FOEMA at 5%	48		78 000, 2.45
11		31% FOEMA at 10%	87		210 000, 2.15
12		52% FOEMA at 10%	93	2.77	260 000, 1.50
13		67% FOEMA at 10%	93	3.44	234 000, 1.66
14		75% FOEMA at 10%	92	3.71	240 000, 1.64
15		100% FOEMA at 10%	51		154 000, 2.52

be absorbed on PMMA particles with its poly(propylene glycol) anchors and prevent particle aggregation with its perfluorooctyl groups that stretch out in CO$_2$ as MMA is consumed in the polymerization.

Effect of Different Copolymeric Dispersants. The data for dispersion polymerizations of MMA in CO$_2$ using different copolymeric dispersants are summarized in Table 2. Figure 2 shows representative electron micrographs. For the purpose of comparison, five dispersant copolymers with differing proportions of FOEMA to PPGMA (31%, 52%, 67%, 75%, and 100% FOEMA) were studied. Three concentration levels (2%, 5%, and 10%) of these dispersants were employed in the polymerization of MMA.

The polymerizations using the copolymer with 31% FOEMA or less as the dispersant were not successful. At all the three dispersant concentrations, the polymerization reaction started out homogeneously and then formed a colloidal dispersion of PMMA that flocculated later during the polymerization. The polymerizations gave high conversions of PMMA, but the polydispersivity of molecular weight was high. Because of the large proportion of PPGMA structural units in the copolymer chains, this copolymeric dispersant is quite miscible with MMA and even with PMMA, which makes it an unacceptable dispersant in the later portion of the polymerization reaction. Therefore, the SEM images (Figure 2a) of these particles showed significant aggregation.

The dispersion polymerizations carried out in the presence of the copolymer with 52% FOEMA started out slightly translucent and formed stable colloidal dispersion of PMMA at all three concentrations for the course of polymerization reaction. High conversions with low polydispersivity of molecular weight were observed under these conditions. The mechanism for particle formation in the polymerizations may involve nucleation by aggregation of oligomeric radicals with the copolymeric dispersant and nuclei growth as monomers continuously diffuse into nuclei and are polymerized while new oligomeric radicals are absorbed onto the particles.[24] The polymerization reactions were completed in 12 h and gave free-flowing polymer powders upon venting the CO$_2$.

The polymerization reactions using the copolymers with 67% and 75% FOEMA as the dispersants were able to produce spherical PMMA particles at similar high conversions. However, the particle size increased compared to the use of 52% FOEMA. These copolymers contain higher amounts of FOEMA structural units and thus are more soluble in CO$_2$. During the polymerizations, the copolymers may be either absorbed onto polymer particles or dissolved in the reaction medium. The competition between absorption and dissolution caused the dispersants to be less efficient, and polymer particles formed were larger in size.

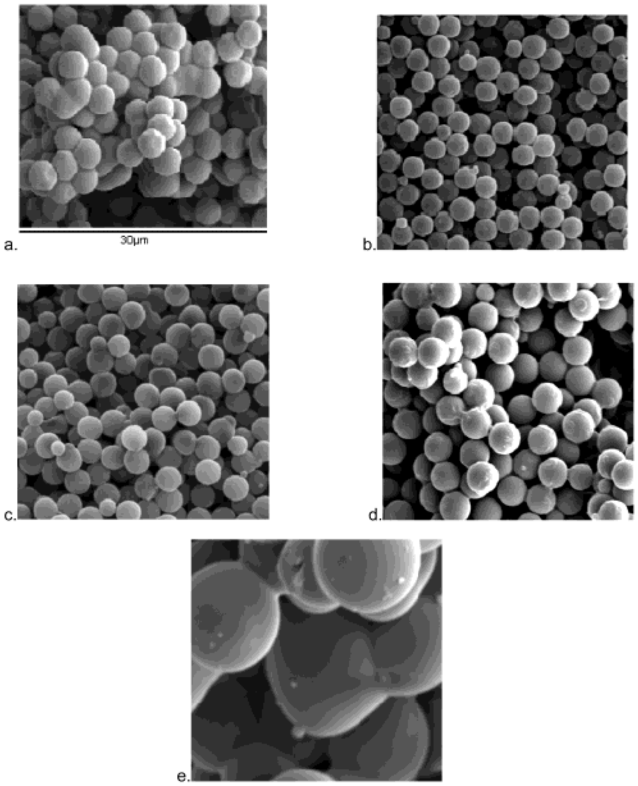


Figure 2. Scanning electron micrographs of PMMA particles prepared with various copolymeric dispersants at the concentration of 5%: (a) 31% FOEMA; (b) 52% FOEMA; (c) 67% FOEMA; (d) 75% FOEMA; (e) PFOEMA. Reaction conditions: 3.0 g of MMA, 0.03 g of AIBN, 65 °C, 330 bar, 12 h.

PFOEMA (100% FOEMA) without "hydrocarbon polymer anchor" groups seemed to be too soluble in the mixture of CO$_2$ and MMA and thus was not a good dispersant for the polymerization of MMA. The reactions at all three concentrations produced aggregated polymers with poor conversions. Molecular weights of PMMA in this case were low and the polydispersity of molecular weight was high compared with those of the products using other copolymeric dispersants.

Therefore, the copolymeric dispersant with 52% FOEMA seemed optimal. The use of the dispersants with 67% and 75% FOEMA also can produce high yields of polymer beads with nearly monodispersity in size. Since almost half of the nonfluoro monomer was incorporated in the copolymer, the 52% dispersant should be inexpensive compared with PFOA that structurally is very similar to PFOEMA and has been successfully used as the dispersant for the polymerizations of styrene[22] and MMA in CO$_2$.[3]

Effect of Copolymeric Dispersant Concentrations. Dispersion polymerizations of MMA using various amounts of the copolymeric dispersant that contained 52% FOEMA were conducted in CO$_2$ at 65 °C and a pressure of 330 bar (Table 3). When 1% of the copolymeric dispersant was used, precipitation was observed after 6 h, and thus the yield of the polymeri-

Table 3. Characterization of PMMA Particles Prepared at Different Concentrations of the Copolymeric Dispersant (52% FOEMA), 30% MMA/CO_2 (w/v), 1% AIBN/MMA (w/w), and 65 °C with the Initial Pressure of 330 bar

position in Figures	concn of the dispersant (52% FOEMA) (wt/wt % to MMA)	yield (%)	D_n (μm)	M_n, PDI
Figure 3a	1	74		124 000, 2.37
Figure 3b	2	92	3.30	311 000, 1.80
Figure 3c	5	91	2.68	243 000, 1.58
Figure 3d	10	93	2.77	260 000, 1.50
Figure 3e	16.7	92	2.46	293 000, 1.76

zation was low. For the higher copolymeric dispersant concentrations (2−16.7%), the polymerization reaction always gave the products as freely flowing powders with over 90% yields, and the particles did not agglomerate as shown in Figure 3. The particle sizes were affected by the amount of the copolymeric dispersant used in the polymerization reaction. Typically, an increase in the dispersant concentration produces smaller particles.[21] Figure 3 and Table 3 illustrate that particle sizes generally changed from 3.30 to 2.46 μm as the dispersant concentration was varied from 2% to 16.7%. However, this regulation was not followed as can be seen by comparing parts c and d of Figure 3. This phenomenon may indicate that the particles size control is not strong for the 5−10% copolymeric dispersant level. Similar results were observed by others[4] in the dispersion polymerization of MMA with CO_2 as the reaction medium.

A high yield of polymer was obtained when the polymerization produces spherical particles with nearly homogeneous size distribution (Figure 2b−d; Figure 3b−e). Additionally, under the same conditions, the molecular weight of the product was higher and molecular weight distribution was narrower, whereas a poor conversion corresponded to a nondescript morphology, as can be seen in the polymerizations using PFOEMA and the copolymer with 31% FOEMA as the dispersants (Table 2 and Figure 2a,e and Figure 3a). This phenomenon suggests that successful stabilization of the nuclei is crucial for the polymerization to reach high yields. Because the monomers are miscible with both its polymers and CO_2, the polymerization system should contain two phases, i.e., PMMA particle phase swollen with MMA and CO_2 and CO_2/MMA continuous phase. The polymerization takes place in both the continuous phase and particle phase.[23] In most cases the latter is more important because the gel effect in polymer particles can substantially increase the rate and yield of polymerization. The extent to which each of these reaction pathways occurs depends on the partitioning of the monomer, initiator, and free radicals between the two phases.[24] The initiator (AIBN) is more soluble in the PMMA particle phase. As particles are formed, a larger portion of AIBN may transfer into the PMMA particle phase. If the polymer particles in the initial stage of polymerization cannot be stabilized well, they may aggregate together and form large chunks of polymers, and thus AIBN in the PMMA particle phase may be buried deeply and not be able to act as the initiator efficiently because monomers need to penetrate inside the polymers to reach the new formed radicals in the polymer phase. Additionally, oligomeric radicals that are formed from AIBN remaining in the CO_2/MMA continuous phase may be adsorbed on the surface of polymer chunks and soon covered or terminated by other oligomeric radicals due to small surface areas of polymer chunks. In contrast, if polymer particles in the initial stage are stabilized perfectly by the dispersant, particle sizes can be very small—in the submicron range. In this case, the monomers in the CO_2/MMA phase may be able to continuously diffuse inside polymer particles that are in the micron range and further be polymerized by reactions with the radicals in the particles until all the monomers in the CO_2 continuous phase are consumed. Because the polymerization system contains a large number of polymer particles with large surface areas, newly formed oligomeric radicals in the reaction medium may also easily be absorbed on polymer particles and further react with monomers. Therefore, the polymerization reactions always gave high yields of polymers.

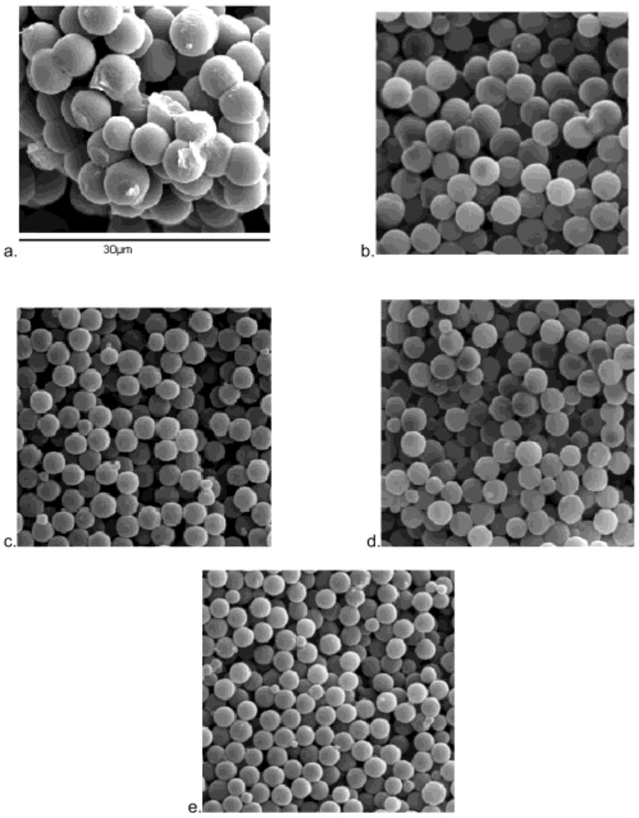


Figure 3. Scanning electron micrographs of PMMA particles prepared with various concentrations (w/w % to MMA) of the copolymeric dispersant (52% FOEMA): (a) 1%; (b) 2%; (c) 5%; (d) 10%; (e) 16.7%. Reaction conditions: 3.0 g of MMA, 0.03 g of AIBN, 65 °C, 330 bar, 12 h.

Effect of Monomer Concentrations. The dispersion polymerizations were carried out at five different concentrations of MMA, and the results are summarized in Figure 4 and Table 4. The copolymer with 52% FOEMA structural units was used as the dispersant in all the cases, and its concentration was maintained at 2% (w/w) relative to MMA for all the polymerizations. In the first reaction (Figure 4a) with 10% (w/v) of MMA, only irregular PMMA particles were obtained perhaps because the concentration of the dispersant was low in the reaction medium (0.2% w/v). PMMA particles with diameters in the micron range with nearly homogeneous size distribution were produced using 20%, 30%, and 40% (w/v) of MMA concentrations. As a variety of factors, such as the monomer/CO_2 ratio, stirring rate, concentration, of dispersant can affect particle size, it is reasonable that the sizes of PMMA particles in above

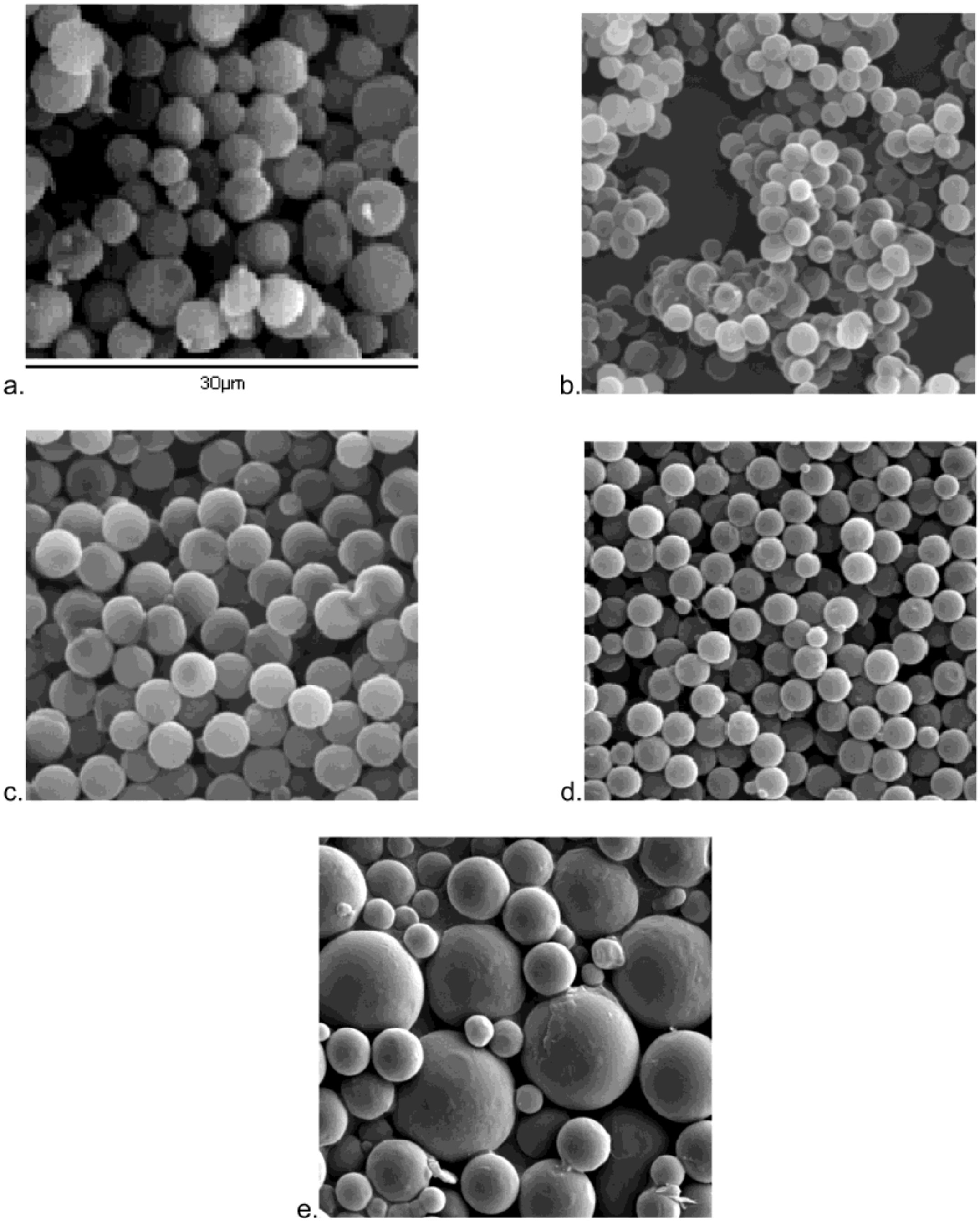


Figure 4. Scanning electron micrographs of PMMA particles prepared with various MMA concentrations (w/v%): (a) 10%; (b) 20%; (c) 30%; (d) 40%; (e) 50%. Reaction conditions: 2% (w/w to MMA) of copoly(52% FOEMA−48% PPGMA), 1% AIBN (w/w to MMA), 65 °C, 330 bar, 12 h.

Table 4. Characterization of PMMA Particles Prepared at 2% (w/w to MMA) of Copolymeric Dispersant (52% FOEMA), 1% AIBN/MMA (w/w), and 65 °C with the Initial Pressure of 330 bar

position in Figures	MMA/CO_2 (w/v %)	yield (%)	D_n (μm)	M_n,PDI
Figure 4a	10	79		204 000, 2.05
Figure 4b	20	90	2.43	294 000, 1.68
Figure 4c	30	92	3.30	311 000, 1.80
Figure 4d	40	92	2.65	254 000, 1.71
Figure 4e	50	91		197 000, 1.83

three cases are different from each other. When the concentration of MMA reached 50% (w/v), PMMA particles with various sizes were found in the polymerization product. Dispersion polymerization is expected to produce monodisperse polymer particles because the number of nuclei should remain constant in the entire polymerization reaction after the initial period of nucleation, and then the nuclei continue to grow and become polymer particles as more monomers are polymerized. However, perhaps in this case, the solvent strength of the reaction medium changed significantly during the polymerization, resulting in multiple nucleation mechanisms and polymer beads with different sizes. Hsiao et al.[25] noted increasing particle diameters with increasing monomer concentration when poly(FOA) was used as the dispersant. No trend in particle diameter with monomer concentration was observed in this study.

Effect of Initial Reaction Pressure. To monitor the effect of the initial pressure of the reaction medium, the

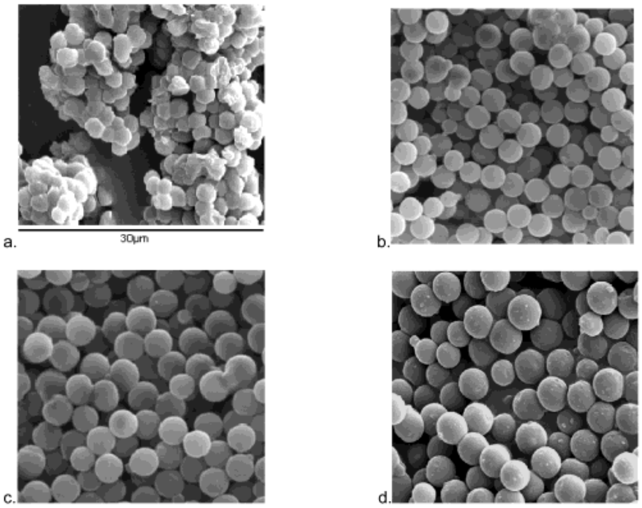


Figure 5. Scanning electron micrographs of PMMA particles prepared with various initial pressures: (a) 110, (b) 210, (c) 330, and (d) 410 bar. Reaction conditions: 3.0 g of MMA, 0.03 g of AIBN, 0.06 g of copoly(52% FOEMA−48% PPGMA), 65 °C, 12 h.

Table 5. Characterization of PMMA Particles Prepared at 30% MMA/CO_2 (w/v), 1% AIBN/MMA (w/w), 2% (w/w to MMA) of Copolymeric Dispersant (52% FOEMA) and 65 °C

position in Figures	initial press. (bar)	yield (%)	D_n (μm)	M_n, PDI
Figure 5a	110	64		126 000, 2.61
Figure 5b	210	91	2.74	271 000, 1.74
Figure 5c	330	92	3.30	311 000, 1.80
Figure 5d	420	90	3.50	265 000, 1.66

polymerization conditions for monomer and initiator concentrations, temperature, and stirring rate were held constant. The copolymeric dispersant with 52% FOEMA was chosen for this study, and its concentration was held constant at 2% monomer. The initial reaction pressure was varied from 110 to 420 bar. The results of polymerizations are shown in Figure 5 and Table 5. At 110 bar, although the polymerization started in one homogeneous phase, large agglomerates were formed with a yield of 64%. In contrast, a freely flowing powder was obtained with a conversion of over 90% at pressures > 110 bar, and the diameters for those polymer particles increased modestly as the initial pressure increased. This result is similar to the observations by DeSimone et al.[21]

Reaction Kinetics. Figure 6 shows the conversion rate vs the reaction time for all five copolymeric dispersants (5%). Curve shapes for polymerizations stabilized by 52% FOEMA, 67% FOEMA, and 75% FOEMA copolymeric dispersants were very similar to each other. At the beginning, the polymerization proceeds slowly as the reaction mainly occur in the bulk solution. When more PMMA particles are formed in the reaction mixture (between 4 and 5 h), the main location of polymerization shifts to the interior of the particles, and thus the reaction rate increases steeply due to the "gel effect" which occurs inside the latex particles. This strong rate increase is typically observed in dispersion polymerizations.[24] A similar "gel effect" rate increase also occurs in the polymerization stabilized by 31% FOEMA copolymeric dispersant. However, the polymerization rate decreases in the post period of polymerization, perhaps because flocculation of latex particles takes place as shown in SEM micrographs. No gel effect is observed for polymerization using PFOEMA as the dispersant which caused the resulting low yield of PMMA.

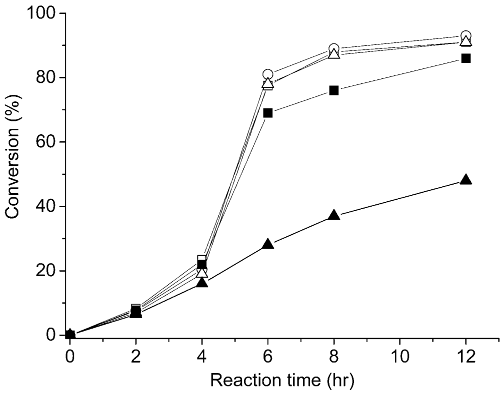


Figure 6. Conversion as a function of the reaction time for dispersion polymerizations of MMA in CO_2 at 65 °C and 330 bar stabilized with various copolymeric dispersants at the concentration of 5%: (□) 52% FOEMA; (O) 67% FOEMA; (△) 75% FOEMA; (■) 31% FOEMA; (▲) 100% FOEMA.

Conclusion

The dispersion polymerization of MMA in CO_2 was successfully conducted using random copolymers of FOEMA and PPGMA as the dispersants. Generally spherical PMMA particles with high conversions can be produced when the copolymers containing 50−75% FOEMA are chosen as the dispersants for the polymerizations. Slight adjustment of particle size was possible by varying the concentrations of dispersants and monomers as well as the initial pressures of the reaction medium.

Acknowledgment. Financial support for this work by the National Science Foundation is gratefully acknowledged. We thank Sreenivas Bhattiprolu in the Microscopic and Chemical Analysis Research Center at The Ohio State University for the SEM images. We also thank Jon Parquette and Noel Paul for assistance with the molecular weight measurements.

References and Notes

(1) Paulaitis, M. E.; Krukonis, V. J. *R. C. Rev. Chem. Eng.* **1983**, *1*, 179−250.
(2) Hubert, P.; Vitathum, O. G. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 710−715.
(3) DeSimone, J. M.; Maury, E. E.; Menceloglu, Y. Z.; McClain, J. B.; Romack, T. J.; Combes, J. R. *Science* **1994**, *265*, 365−359.
(4) Li, G.; Yates, M. Z.; Johnston, K. P.; Lim, K. T.; Webber, S. E. *Macromolecules* **2000**, *33*, 1606−1612.
(5) Lepilleur, C.; Beckman, E. J. *Macromolecules* **1997**, *30*, 745−756.
(6) Fehrenbacher, U.; Ballauff, M. *Macromolecules* **2002**, *35*, 3653−3661.
(7) Baradie, B.; Shoichet, M. S. *Macromolecules* **2002**, *35*, 3569−3575.
(8) Berger, T.; McGhee, B.; Scherf, U.; Steffen, W. *Macromolecules* **2000**, *33*, 3505−3507.
(9) Cooper, A. I.; Hems, W. P.; Holmes, A. B. *Macromolecules* **1999**, *32*, 2156−2166.
(10) Christian, P.; Giles, M. R.; Griffiths, R. M. T.; Irvine, D. J.; Major, R. C.; Howdle, S. M. *Macromolecules* **2000**, *33*, 9222−9227.
(11) Vesovic, V.; Wakehan, W. A.; Olchowy, G. A.; Sangers, J. V.; Watson, J. T. R.; Millat, J. *J. Phys. Chem. Ref. Data* **1990**, *19*, 763−808.

(12) DeSimone, J. M.; Guan, Z.; Elsbernd, C. S. *Science* **1992**, *257*, 945−947.
(13) Hoefling, T. A.; Newman, D. A.; Enick, R. M.; Beckman, E. J. *J. Supercrit. Fluids* **1993**, *6*, 165−171.
(14) Sarbu, T.; Styranec, T.; Beckman, E. J. *Nature (London)* **2000**, *405*, 165−168.
(15) Mawson, S.; Yates, M. Z.; O'Neil, M. L.; Johnston, K. P. *Langmuir* **1997**, *13*, 1519−1528.
(16) Wang, W. C. V.; Kramer, E. J.; Sachse, W. H. *J. Polym. Sci., Polym. Phys. Ed.* **1982**, *20*, 1371−1384.
(17) Canelas, D. A.; DeSimone, J. M. *Macromolecules* **1997**, *30*, 5673−5682.
(18) Canelas, D. A.; Betts, D. E.; DeSimone, J. M.; Yates, M. Z.; Johnston, K. P. *Macromolecules* **1998**, *31*, 6794−6805.
(19) Carson, T. J.; Lizotte, J.; DeSimone, J. M. *Macromolecules* **2000**, *33*, 1917−1920.
(20) Shiho, H.; DeSimone, J. M. *Macromolecules* **2000**, *33*, 1565−1569.
(21) Shiho, H.; DeSimone, J. M. *Macromolecules* **2001**, *34*, 1198−1203.
(22) Shiho, H.; DeSimone, J. M. *J. Polym. Sci., Part A: Polym. Chem.* **1999**, *37*, 2429−2437.
(23) Shiho, H.; DeSimone, J. M. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 1146−1153.
(24) Sudol, D. Dispersion polymerization. In *Polymeric Dispersions: Principles and Applications*; *NATO ASI Ser. E 335*, 1997, 141−153.
(25) Hsiao, Y.-L.; Maury, E. E.; DeSimone, J. M.; Mawson, S.; Johnston, K. P. *Macromolecules* **1995**, *28*, 8159−8166.

MA026015U