Polymerization of Methyl Methacrylate in Carbon Dioxide Using Glycidyl Methacrylate Linked Reactive Stabilizer: Effect of Pressure, Reaction Time, and Mixing

Sang-Hun Han, Kyung-Kyu Park, and Sang-Ho Lee*

Department of Chemical Engineering, Dong-A University, Busan 604-714, Korea

Abstract: Using glycidyl methacrylate-linked poly(dimethylsiloxane), methyl methacrylate was polymerized in supercritical CO_2. The effects of CO_2 pressure, reaction time, and mixing on the yield, molecular weight, and molecular weight distribution (MWD) of the poly(methyl methacrylate) (PMMA) products were investigated. The shape, number average particle diameter, and particle size distribution (PSD) of the PMMA were characterized. Between 69 and 483 bar, the yield and molar mass of the PMMA products showed a trend of increasing with increasing CO_2 pressure. However, the yield leveled off at around 345 bar and the particle diameter of the PMMA increased until the pressure reached 345 bar and decreased thereafter. With increasing pressure, MWD became more uniform while PSD was unaffected. As the reaction time was extended at 207 bar, the particle diameter of PMMA decreased at $0.48 \pm 0.03\%$ AIBN, but increased at 0.25% AIBN. Mixing the reactant mixture increased the PMMA yield by 18.6% and 9.3% at 138 and 207 bar, respectively.

Keywords: polymerization, supercritical CO_2, macromonomer, pressure effect, mixing.

Introduction

Since Sumitomo Chemical Company disclosed polymerization process of vinyl monomers in carbon dioxide in 1968,[1] great number of studies have been focused on polymerization of methyl methacrylate (MMA) in liquid and supercritical CO_2.[2-7] CO_2 is fundamentally non-solvent for most polymers. For instance, poly(methyl methacrylate) (PMMA) is insoluble in CO_2 even at 255 °C and 2,550 bar, whereas MMA and its oligomers are dissolved at decent pressures.[8,9] As the polymerization proceeds, PMMA active chains are synthesized. Once the molar mass of the active chains exceeds a certain limit, they fall out of the homogenous solution of CO_2-MMA. Therefore, PMMA is synthesized via precipitation polymerization without stirring and surfactant that make the growing chains stable in the continuous phase. Generally, the surfactants for the dispersion polymerization in CO_2 consist of two parts. One part contains CO_2-philic fluoro or silicone repeat units in the backbone or pending structures, whereas the other part has compatible components to growing polymers.[10-13] Some researches used cosolvents with surfactants to enhance the stability of the dispersion polymerization in CO_2.[14,15]

Using a reactive surfactant is another approach for the polymerization of vinyl monomers in supercritical CO_2. Since

Shaffer et al.[16] used poly(dimethylsiloxane) monomethacrylate as a surfactant for polymerization of MMA and styrene in supercritical CO_2, PDMS macromonomers have been widely used as a reactive stabilizer for the dispersion polymerization in liquid and supercritical CO_2. For instance, commercially supplied PDMS macromonomers, such as PDMS monomethacrylate,[7,14,16-19] monocarbinol-terminated PDMS,[14] PDMS-g-pyrrolidone carboxylic acid,[6] methacryloxypropyl-terminated PDMS,[20] and vinyldimethylsiloxy PDMS,[21] were used for the dispersion polymerization of MMA and styrene. Instead of using commercially available macromonomer stabilizer, Giles et al. synthesized a PDMS monomethacrylate surfactant from hexamethylcyclotrisiloxane and 3-(methacryloxy)propyldimethylchlorosilane using a lithium catalyst.[19] They demonstrated the effect of the molar mass of their own surfactants on the dispersion polymerization of MMA in CO_2.

We prepared a new reactive stabilizer by linking glycidyl methacrylate (GMA) and monoglycidyl ether terminated PDMS (MG-PDMS) using aminopropyltriethoxysilane. The synthetic procedure requires no use of both a solvent and catalyst. Since our procedure does not make any by-product, additional pretreatment or purification process is not required. The resulted product, glycidyl methacrylate linked poly(dimethylsiloxane) (GMA-PDMS) has both a vinyl group and CO_2-philic group. Figure 1 shows the structure of GMA-PDMS. The details to synthesize and characterize GMA-

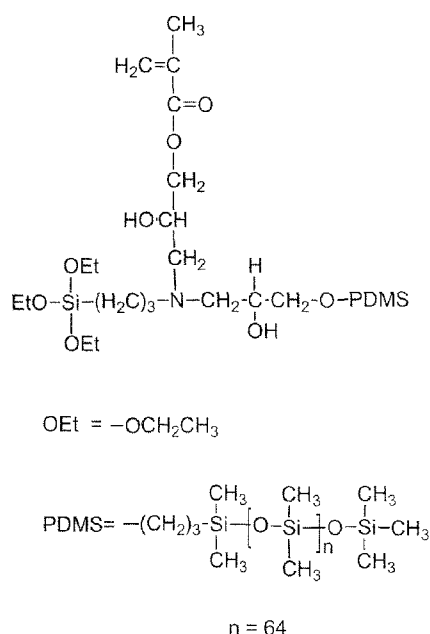*Corresponding Author. E-mail: sangho@dau.ac.kr

Figure 1. The structure of GMA-PDMS stabilizer.

PDMS are described in our previous paper.[22]

Using GPC, the molar mass of MG-PDMS and GMA-PDMS were determined to 5,500 and 5,800, respectively. By adding the molar mass of aminopropyltriethoxysilane and GMA to the M_n of MG-PDMS, the M_n of GMA-PDMS stabilizer was calculated to 5,884, which is almost identical to the M_n measured from GPC. The prepared GMA-PDMS was used for dispersion polymerization of MMA in supercritical CO_2. Our previous studies were focused on synthesizing GMA-PDMS and investigating the effect of the stabilizer, initiator, and monomer concentrations on dispersion polymerization of MMA in supercritical CO_2. In this paper, we demonstrated the effect of CO_2 pressure, reaction time, and mixing on the yield, molar mass, and morphology of the PMMA products.

Experimental

Materials. MMA with minimum purity of 99% was obtained from Junsei Chemical Co. and purified by vacuum distillation.

2,2'-Azobisisobutyronitrile (AIBN) with minimum purity of 99% (Otsuka Chemical Co. 99%+) was recrystalized twice from methanol. Hexane (Aldrich, HPLC grade) and toluene (CP grade, 99%+) were used as received. Carbon dioxide with purity of 99.99% was obtained from Korea Standard Gas.

Polymerization of MMA. Dispersion polymerization of MMA in supercritical CO_2 was carried out using a high-pressure, variable-volume cell with working volume of 28 cm^3. The details of experimental apparatus,[23,24] and the polymerization procedure are described in other references.[22] After the polymerization was conducted for a desired reaction time, the cell was cooled in a dry ice bath. Then, the CO_2 in the cell was completely released to atmospheric pressure. To remove unreacted GMA-PDMS, PMMA product was agitated in hexane for 24 h and filtered. The filtered PMMA was thoroughly dried for further analysis.

Characterization. The molecular weight of PMMA product was measured using gel permeation chromatography (Waters 150-C) with WATERS Styragel 3.8×300 mm column (HR2X1, HR3X1, HR4X1). Tetrahydrofuran was used as the eluent. PS standards (Waters) were used to calibrate molecular weight. A differential refractive index detector (Precision Detector Inc.) was used to monitor the column output and the data were processed using WATERS GPC software (Millennium 2000). Scanning electron microscopy (SEM) images were collected using HITACHI S-2400 SEM to characterize the morphology of PMMA product. The particle diameters of the PMMA product were averaged from around one hundred individual particles of each SEM micrograph.

Results and Discussion

Effect of Pressure. The dispersion polymerization of MMA in CO_2 is influenced by the solubility of MMA and growing PMMA chains in CO_2. PMMA is not dissolved even at pressures greater than 2,500 bar, whereas MMA is soluble in CO_2 pressure of 120 bar at 80 °C.[9] The solubility of MMA in supercritical CO_2 can be tuned by changing CO_2 pressure that is directly related to CO_2 density. Therefore, the properties of the PMMA product are dependent on the CO_2 pressure. To investigate the effect of CO_2 pressure on

Table I. Effect of Pressure on Dispersion Polymerization of MMA

No	AIBN(wt%)	Pressure (bar)	Yield (%)	M_n^a (g/mol)	PDI^b	D_n^c (μm)	PSD^d	Morphology
1	0.49	69.0	87.4	10,300	17.2	-	-	non-powder
2	0.51	138.0	93.4	56,500	2.4	2.8	1.4	powder
3	0.48	207.0	94.4	41,600	2.6	3.5	1.4	powder
4	0.50	345.0	99.0	52,000	2.0	4.8	1.5	powder
5	0.53	483.0	98.8	77,000	1.9	4.5	1.4	powder

^{a}Number average molecular weight was determined using GPC with PS standard. ^{b}PDI is polydispersity index (M_w/M_n). ^{c}D_n represents number average diameter of the PMMA particle. ^{d}PSD represents particle size distribution (D_w/D_n).
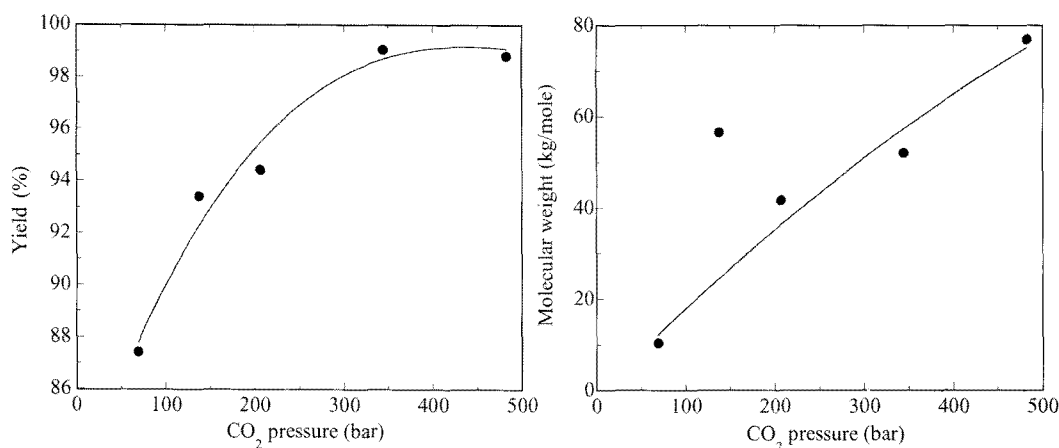
Figure 2. Effect of pressure on the yield and number average molecular weight of the PMMA products polymerized in CO_2. The concentrations of AIBN and MMA were 0.51 ± 0.02 wt% and 29.4 ± 0.7 wt%, respectively. The stabilizer concentration was 5.4 ± 0.5 wt% based on the monomer weight.

the PMMA product, the dispersion polymerization of MMA was performed at various pressures between 69 and 483 bar. The polymerizations were carried out at 80 °C for 4 h using 0.51 ± 0.02 wt% AIBN and 29.4 ± 0.7 wt% MMA. The concentration of GMA-PDMS stabilizer was 5.4 ± 0.5 wt% based on the monomer weight. Table 1 summarizes the variation of the yield, molar mass, and morphology of the PMMA products with CO_2 pressures.

Using the data in Table I (Run No 1~5), we plotted Figure 2 showing the effects of reaction pressure on the yield and the molecular weight of PMMA products.

MMA (30 wt%) - CO_2 (70 wt%) binary mixture separates into two phases, MMA- and CO_2-rich phase, at 80 °C and pressures lower than 105 bar.[9] At pressures lower than 105 bar, the two phases exist in the reactor at the initial stage of polymerization. As the polymerization proceeds there are three phases in the reactor: MMA-rich phase, CO_2-rich phase, and the growing PMMA solid phase. Since most MMA exists in a MMA-rich phase located at low position of the reactor, precipitation polymerization mainly occurs during the reaction. Thus, stable dispersion is not formed in the mixture of MMA, CO_2, and the growing PMMA chain. It is expected that the yield and M_n of PMMA product are low when the reaction is carried out at pressures lower than 105 bar. Also the molecular weight distribution will be wide. Table I shows that at 69 bar, the PMMA with M_n of 10,300 was obtained in the yield of 87.4%. The M_n and the yield at 69 bar were the lowest values in our experiments. The PMMA product was recovered in non-powder form whereas the other ones at pressures higher than 138 bar were in powder form. Notice that the PMMA synthesized at 69 bar has broad molecular weight distribution.

Since MMA is completely soluble in CO_2 at 138 bar, MMA-CO_2 mixture is homogeneous at the initial stage of the polymerization. As the polymerization proceeds, growing PMMA chains or low molecular weight PMMA are pro-

duced. Although PMMA is fundamentally insoluble in CO_2, the solubility of the growing chain can be enhanced by high CO_2 pressures. The growing PMMA will finally fall out of the homogenous solution of MMA-CO_2-PMMA when the molar mass of the PMMA chain exceeds a certain value. However, the mixture in the reactor forms the stable dispersions composed of MMA-CO_2 fluid phase and the growing PMMA solid phase. Different from the PMMA product at 69 bar, PMMA was thoroughly obtained in a micro-spherical powder form. Figure 2 well demonstrates that the yield and M_n of the PMMA increase with the reaction pressure. As the reaction pressure increased from 69 to 483 bar, the yield increased from 87.4 to 98.8 %. The M_n also increased from 10,300 to 77,000, except the case at 138 bar. Compared with the polydispersity of PMMA polymerized at 69 bar, the polydispersity changed a little at pressures higher than 69 bar. With the pressure increasing from 138 to 483 bar, the polydispersity reduced from 2.4 to 1.9, suggesting that the effect of CO_2 pressure on the molecular weight distribution is limited once the reaction pressure exceeds the critical pressure of CO_2.

Figure 3 shows the SEM images of the PMMA particles synthesized at different CO_2 pressures. The PMMA microsphere with a diameter of 2.8 μm was obtained at the pressure of 138 bar. As the pressure increased to 207 and 345 bar, the number average particle size enlarged to 3.5 and 4.8 μm, respectively. However, further increasing the pressure to 483 bar reduced the PMMA particle size a little to 4.5 μm. While the average particle size increased with CO_2 pressure, the particle size distributions (PSD) of the PMMA products were constant at 1.4~1.5, suggesting that the PSD is not influenced by CO_2 pressure.

Effect of Reaction Time. To investigate the effect of reaction time on the yield, molar mass, and morphology of PMMA products, PMMA were polymerized for different periods at various AIBN concentrations. The polymeriza-
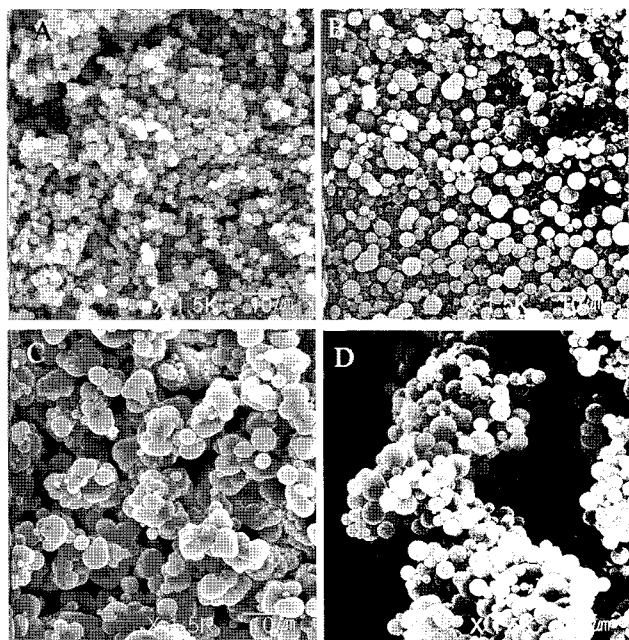
Figure 3. SEM images of PMMA products synthesized at various CO_2 pressure. (A) 138 bar, (B) 207 bar,[22] (C) 345 bar, and (D) 483 bar. The GMA-PDMS concentration was 5.4 ± 0.5 wt% based on the monomer weight. The concentrations of AIBN and MMA were 0.51 ± 0.02 wt% and 29.4 ± 0.7 wt%, respectively. The SEM image at 207 bar, (B), was obtained by Han *et al.*.[22]

tions were carried out at 80 °C and 207 bar using 28.9 ± 1.6 wt% MMA and 5.7 ± 0.9 wt% GMA-PDMS. Since the rate of free radical polymerization is proportional to the square root of initiator concentration, the polymerization is extended to longer periods at low AIBN concentrations. Table II summarizes the polymerization conditions and the properties of the PMMA products.

As the reaction time increased from 3 to 8 h, the PMMA yield increased from 85.6 to 97.7% at 0.48 wt% AIBN. The

increase of the yield leveled off around 95~97% after 4 h of the reaction time. The M_n of PMMA products shows a similar pattern with respect to the reaction time. When the polymerization was maintained for 3 h, the low molar mass PMMA ($M_n = 17,000$) was produced in the low yield of 85.6%. The low yield and M_n were the consequence of the low extent of the reaction, which indicates 3 h was not enough to complete the polymerization. When the reaction time was extended to 4 h, the yield and M_n of PMMA product increased to 94.4% and 41,600, respectively. However, the polydispersity of the PMMA decreased with increasing reaction time. When the reaction time was extended from 3 to 4 h, the polydispersity significantly reduced from 7.1 to 2.5. The polydispersity leveled off around 2.2~2.4 when the polymerization time exceeded 5 h.

Figure 4, plotted using the data listed in Table II, demonstrates the effects of reaction time on the yield and molecular weight of PMMA products. When 0.48 wt% AIBN was used, the yield and M_n of PMMA products were not influenced by the reaction time once the reaction time extended beyond 5 h.

The yield of PMMA products decreased when AIBN concentration decreased from 0.48 to 0.25 wt%. At 0.25 wt% AIBN, the yield of PMMA polymerized for 4 h was 66% which was much lower than the yield of PMMA polymerized at 0.48 wt% AIBN. To compensate the slow reaction rate at 0.25 wt% AIBN, we extended the reaction time to 6 h. Due to the longer reaction time, the PMMA yield increased to 92.9%. However, this yield was still lower than the yield obtained from the polymerization carried out for 4 h at 0.48 wt% AIBN. Increasing reaction time to 8 h enhanced the PMMA yield to 95.6%, which was almost identical to the yield at 0.48 wt% AIBN. When the polymerization was carried out for same period, the M_n of PMMA product at 0.25 wt% was 1.6~1.8 times higher than the M_n of the PMMA at 0.48 wt% AIBN, which well agreed with our

Table II. Effect of Reaction Time on Dispersion Polymerization of MMA

Run No	Reaction Time (h)	AIBN (wt%)	Yield (%)	M_n^a (g/mol)	PDI[b]	D_n^c (μm)	PSD[d]	Morphology
6	3	0.46	85.6	17,000	7.1	5.6	1.5	powder
3	4	0.48	94.4	41,600	2.5	3.5	1.4	powder
7	5	0.48	97.4	58,600	2.0	3.0	1.4	powder
8	6	0.48	95.0	55,800	2.2	2.8	1.3	powder
9	8	0.51	97.7	54,700	2.4	2.5	2.0	powder
10	4	0.26	66.2	75,700	2.1	2.0	1.9	powder
11	6	0.25	92.9	91,500	1.9	3.5	1.4	powder
12	8	0.25	95.6	82,500	4.9	3.7	1.2	powder
13	8	0.14	15.9	4,800	18.2	-	-	non-powder
14	16	0.12	21.4	6,800	13.1	-	-	few powder

[a]Number average molecular weight was determined using GPC with PS standard. [b]PDI is polydispersity index (M_w/M_n). [c]D_n represents number average diameter of PMMA. [d]PSD represents particle size distribution (D_w/D_n).
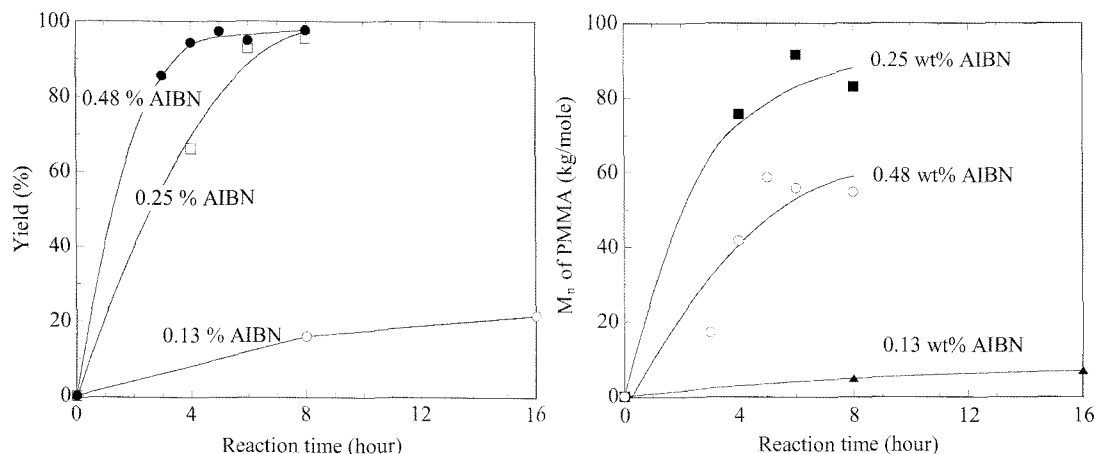
Figure 4. Effect of reaction time on the yield and molecular weight of the PMMA products polymerized at 207 bar of CO_2. The concentrations of MMA were 28.9 ± 1.6 wt%. The stabilizer concentration was 5.7 ± 0.9 wt% based on the monomer weight.

expectation at low initiator concentration. We further reduced AIBN concentration to 0.13 wt%. Although the reaction time was extended to 16 h, the PMMA yield decreased to 21.4%. This decrease in the PMMA yield was consistent with the results observed at 0.48 and 0.25 wt% AIBN. If the reaction is carried out for long period at 0.13 wt% AIBN, the highest molar mass of PMMA is expected to be produced. However, our experiment showed opposite results. The M_n was only 6,800 and the polydispersity was 13.1. These results suggest that at extremely low concentrations of AIBN, the formation of PMMA active chain is limited and thus low molecular weight of the PMMA is obtained in low yield.

Figures 5 and 6 show the variations of PMMA morphology with the reaction time at 0.25 and 0.48 wt% AIBN. All PMMA products were obtained in a powder form. At 0.25 wt% AIBN, the particle diameter increased from 2.0 to 3.5 μm when the reaction time increased from 4 to 6 h. At low AIBN concentration, a few PMMA active chains are formed. Therefore, one growing PMMA chain reacts with many MMA and the diameter of each PMMA chain becomes larger. As the reaction time was extended from 6 to 8 h the particle diameter increased from 3.5 to 3.7 μm. This increase was only 13.3% of the increase for extending the reaction time from 4 to 6 h. After 6 h of reaction time, more than 92.9% of MMA was converted and small amount of MMA was left in the reactor. Due to the small amount of MMA, the increase of the particle diameter was not apparent.

At 0.48 wt% AIBN, the average diameter of PMMA product is expected to be smaller than at 0.25 wt% AIBN, since the number of MMA per one growing PMMA chain is smaller than at 0.25 wt% AIBN. The average diameter of PMMA was 5.6 μm when the polymerization was conducted for 3 h. Figure 6 shows that as the reaction was proceeding, the particle diameter decreased and became smaller than the diameter at 0.25 wt% AIBN. Since the M_n and yield of the PMMA had increased until the reaction time reached
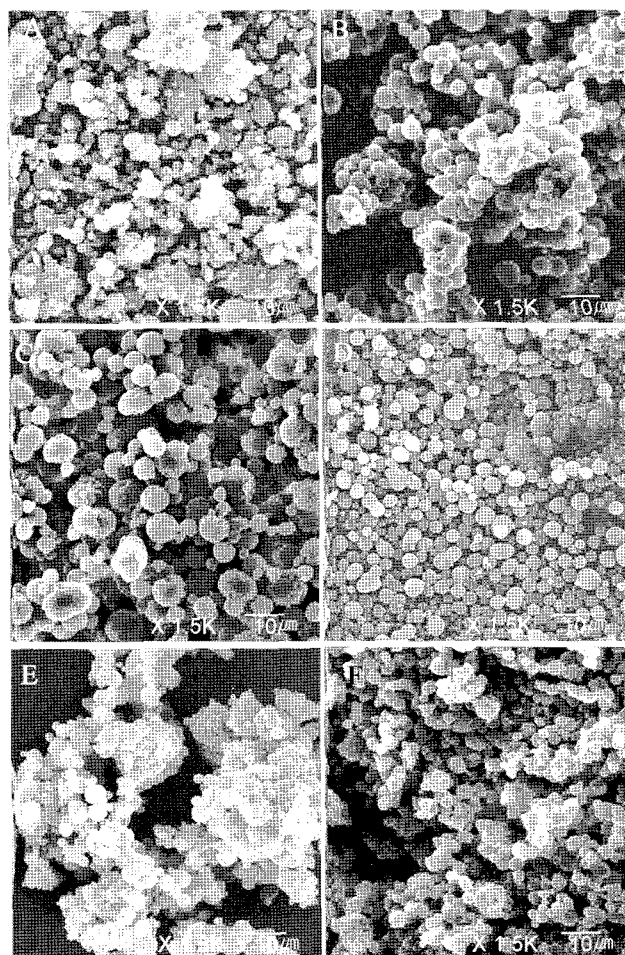

Figure 5. SEM images of PMMA products synthesized for (A) 4 h at 0.25 wt% AIBN, (B) 6 h at 0.25 wt% AIBN,[22] (C) 3 h at 0.46 wt% AIBN, (D) 4 h at 0.48 wt% AIBN,[22] (E) 5 h at 0.48 wt% AIBN, and (F) 6 h at 0.48 wt% AIBN. The polymerization conditions and the product properties are listed in Table II. The SEM images, (B) and (D), were obtained by Han et al..[22]
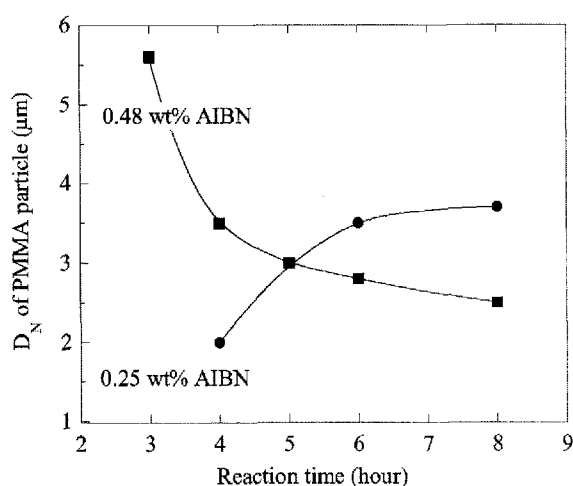
Figure 6. Effect of reaction time on the number average particle diameter (D_n) of the PMMA products polymerized at 207 bar. The concentrations of MMA were 28.9 ± 1.6 wt%. The stabilizer concentration was 5.7 ± 0.9 wt% based on the monomer weight.

5 h (Figure 4), we presupposed that the particle size would increase or be constant with the reaction time. However, the average particle size gradually reduced from 5.6 to 2.5 μm as the reaction time increased from 3 to 8 h. The decrease in the particle size leveled off after the reaction time exceeded 5 h. We were unable to figure out the reason for this reduction at 0.48 wt% AIBN. Further investigation is required to clarify this issue. When PMMA was polymerized at 0.25 and 0.48 wt% AIBN, the PSD decreased with the reaction time except the case that the reaction was extended to 8 h at 0.51 wt% AIBN. The PSD reduced from 1.9 to 1.2 and from 1.5 to 1.3 at 0.25 and 0.48 wt% AIBN, respectively. With the leveled-off particle diameter, the relatively constant PSD values indicate that the particle size of the PMMA becomes uniform with the reaction time.

Mixing Effect. In order to produce PMMA of uniform property, it is required to maintain stable dispersion between growing PMMA chains and MMA-CO_2 mixture. Not only a stabilizer but also mixing plays an important role to make stable dispersion of the materials in the reactor. At the

beginning of the polymerization, MMA is dissolved at moderate pressures. However, as the polymerization proceeds, growing PMMA chains are separated from the MMA-CO_2 solution. Efficient mixing is needed to prevent the produced PMMA from precipitation and coagulation. Table III summarizes the effect of mixing on the yield and properties of PMMA products at two different CO_2 pressures.

At CO_2 pressure of 138 bar, when the reaction was performed without mixing, PMMA was obtained in a mixed form of powder and solid mass. Most of the products were composed of the solid mass. The portion of powdery PMMA was less than 5% of the total products. The M_n of the solid and powdery PMMA products were 102,900 and 39,200, respectively. As polymerization proceeded without mixing, growing PMMA chains fell out of the solution and settled down on the bottom of the reactor. The PMMA chains reacted through precipitation polymerization with MMA and other PMMA chains. Therefore PMMA product had high M_n (102,900) and broad molecular weight distribution (3.2). The powdery PMMA had lower molar mass (39,200) and PDI (2.8). The total yield of the PMMA product was 74.8 wt%. When the reactant was mixed during the polymerization, PMMA product was obtained entirely in a powder form. The yield increased to 93.4%. Mixing the reactant increased the PMMA yield by 18.6%. The M_n and PDI were 56,500 and 2.4, respectively. The PMMA product had lower M_n than the solid mass, but higher than the powdery PMMA polymerized without mixing. It is obvious that mixing leads the PMMA product to have uniform molar mass in high yield. When polymerized without mixing at 207 bar, the PMMA product had M_n of 57,900 and was obtained in the yield of 85.1%. Similar to the PMMA at 138 bar without mixing, the PMMA product was a mixed form of a powder and solid mass. However, most of the PMMA were powders. When polymerized with mixing at 207 bar, powdery PMMA was produced and the yield increased to 94.4%. Mixing increased the yield by 9.3% at 207 bar. The increase in yield at 207 bar was half of the increase at 138 bar. At high CO_2 pressure, growing PMMA chains are more soluble than at low pressure. The high solubility enhances the stability of dispersion between the PMMA chains and

Table III. Effect of Mixing on Dispersion Polymerization^a of MMA

No	Mixing	Pressure (bar)	Yield (%)	M_n^b (g/mol)	PDI^c	D_n^d (μm)	PSD^e	Morphology
15	x	138	74.8	39,200^f 102,900^g	2.8 3.2	-	-	a few powder and solid mass
2	o	138	93.4	56,500	2.4	2.8	1.4	powder
16	x	207	85.1	57,900^h	4.0	-	-	powder and a few solid mass
3	o	207	94.4	41,600	2.5	3.5	1.4	powder

^{a}Reactions were performed for 4 h at 80 °C using 0.5 ± 0.02 wt% AIBN and 29.7 ± 0.3 wt% MMA. The concentration of GMA-PDMS was 5.4 ± 0.5 wt% based on the monomer weight. ^{b}Number average molecular weight was determined using GPC with PS standard. ^{c}PDI is polydispersity index (M_w/M_n). ^{d}D_n represents number average diameter. ^{e}PSD represents particle size distribution (D_w/D_n). ^{f}M_n of the powdery PMMA. ^{g}M_n of the solid mass PMMA. ^{h}M_n of the powdery PMMA.

MMA-CO_2 mixture, with the consequence that the PMMA is produced in high yield. At low CO_2 pressure, the PMMA chains are less soluble and the dispersion is less stable than at high pressure. Therefore, mixing is more required at low pressure than high pressure, which indicates the mixing effect on the yield is more distinguished at low CO_2 pressures than high pressures.

Summary

We prepared a new reactive stabilizer by linking GMA and MG-PDMS using aminopropyltriethoxysilane. The synthetic procedure requires no use of both a solvent and catalyst. In addition, there is no by products, which means any pretreatment or purification process is not needed. These characteristics could be beneficial to commercial process for dispersion polymerization in CO_2.

Between 69 and 483 bar of CO_2, the yield, molar mass and particle diameter of PMMA products increased with CO_2 pressures. The yield and particle diameter leveled off around at 345 bar. As reaction time was extended from 4 to 8 h, the particle diameter of PMMA decreased from 5.6 to 2.5 μm at 0.49 wt% AIBN, whereas the diameter increased from 2.0 to 3.7 μm at 0.25% AIBN. The particle diameters all leveled off around 6 h reaction time. The mixing effect on the yield is more remarkable at low CO_2 pressures than high pressures. Mixing the reactant increased the PMMA yield by 18.6% and 9.3% at 138 and 207 bar, respectively.

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