

## GMA-Functionalized Reactive Stabilizer for Polymerization of Methyl Methacrylate in Supercritical CO<sub>2</sub>: Effect of Stabilizer, Initiator and Monomer Concentrations

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Received July 30, 2007; Revised November 28, 2007

**Abstract:** Glycidyl methacrylate linked poly(dimethylsiloxane) (GMA-PDMS) was synthesized and used as a stabilizer for the dispersion polymerization of methyl methacrylate (MMA) in supercritical CO<sub>2</sub>. This study examined the effect of the concentrations of the stabilizer, 2,2'-azobisisobutyronitrile (AIBN) initiator, and MMA on the yield, molecular weight, and morphology of the poly(methyl methacrylate) (PMMA) product. PMMA was obtained in 94.6% yield using only 0.87 wt% GMA-PDMS. When the AIBN concentration was increased from 0.25 to 1.06 wt%, the molecular weight and particle size of the PMMA decreased from 56,600 to 21,600 and from 4.1 to 2.7  $\mu\text{m}$ , whereas the particle size distribution increased from 1.3 to 1.9. The  $M_n$  of the PMMA product ranged from 41,600 and 55,800 under typical polymerization conditions. The PMMA particle diameter ranged from 1.8 to 11.0  $\mu\text{m}$  and the particle size distribution ranged from 1.4 to 1.8.

**Keywords:** polymerization, supercritical CO<sub>2</sub>, macromonomer.

### Introduction

Many researches have used CO<sub>2</sub> as a polymerization medium.<sup>1-8</sup> Since carbon dioxide is a non-solvent for most monomers, elevated pressure is needed to increase the solubility of monomer in CO<sub>2</sub>. In the early stage of polymerization, the oligomers synthesized from the monomers might be dissolved in carbon dioxide at moderate pressures. However, the growing polymer particles fall out of carbon dioxide and precipitate on the bottom of the reactor. To produce the polymer in high yields, it is necessary that the growing polymer be well dispersed in the CO<sub>2</sub> during polymerization. Fluoropolymers and fluoro-copolymers were widely used to stabilize the growing PMMA in supercritical CO<sub>2</sub>. DeSimone *et al.* demonstrated that poly(1,1-dihydroperfluorooctyl acrylate) effectively stabilize the dispersion polymerization of MMA in CO<sub>2</sub>.<sup>9,10</sup> Block copolymers containing CO<sub>2</sub>-philic fluoro groups were also used to stabilize the dispersion polymerization of MMA.<sup>11,12</sup> Howdle *et al.* used acid-terminated perfluoropolyether (Krytox 157FSL, DuPont) as a stabilizer for PMMA polymerization.<sup>13,14</sup> They also demonstrated PMMA polymerization using the stabilizer grafted with fluorinated groups and containing carboxylic groups.<sup>15</sup>

Due to CO<sub>2</sub>-philic property of siloxane, poly(dimethylsiloxane)-based polymers and copolymers were also widely

used as stabilizers for the dispersion polymerization in supercritical CO<sub>2</sub>. In addition, PDMS macromonomers as a reactive stabilizer have been applied to the dispersion polymerization. PDMS macromonomers react with monomers during polymerization and enhance the stability of growing polymer in CO<sub>2</sub>. However, a small amount of the macromonomer was inevitably incorporated into the product polymer. The PMMA polymerized with PDMS macromonomers had a relatively high molar mass and the PMMA yield was fairly high.<sup>16-19</sup> Since CO<sub>2</sub>-philic PDMS macromonomers have the capability to polymerize with monomers, they were applied to stabilize dispersion polymerization of several types of vinyl monomers, such as styrene and 2-hydroxyethyl methacrylate.<sup>20,21</sup>

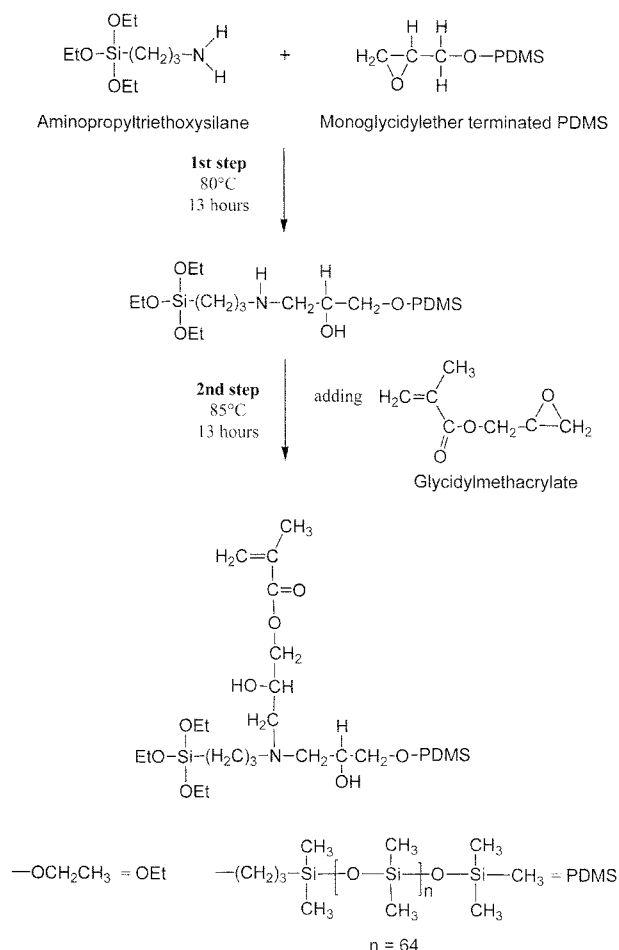
We synthesized a new reactive stabilizer having a vinyl group and CO<sub>2</sub>-philic PDMS for dispersion polymerization of vinyl monomers. Glycidyl methacrylate (2,3-epoxypropyl methacrylate) and mono-glycidyl ether terminated PDMS were linked using aminopropyltriethoxysilane. The synthetic procedure to make our stabilizer is quite simple, neither catalyst nor solvent is needed. The prepared stabilizer, glycidyl methacrylate linked PDMS (GMA-PDMS stabilizer), was used for dispersion polymerization of MMA in supercritical CO<sub>2</sub>. In this paper, we demonstrate the effects of the new stabilizer on the yield, molar mass, and morphology of the PMMA product at various conditions.

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## Experimental

**Materials.** Aminopropyltriethoxysilane (Degussa, A-1100, 98.5%+), glycidylmethacrylate (GMA) (Mitsubishi Rayon, 97%+), monoglycidylether terminated poly(dimethylsiloxane) (MG-PDMS) (Aldrich,  $M_n \approx 5,000$ ), monomethylether-hydroquinone (MeHQ) (Waco Pure, reagent grade, 98%+), Dichloromethane (DC Chemical Co., 99.5%+), acetic acid (DC Chemical Co., 99.5%+), tertiarybutylammoniumiodide (TBAI) (Fluka, 98%+), 0.1 M-perchloric acid (Riedel-deHaen, Germany, 99.8%+) were used as received. Methylmethacrylate (MMA) (Junsei Chemical Co., purity 99%+) was purified by vacuum distillation and stored at appropriate condition prior to use. 2,2'-Azobisisobutyronitrile (AIBN) (Otsuka Chemical Co. 99%+) was recrystallized twice from methanol. Hexane (Aldrich, HPLC grade), heptane (Aldrich, HPLC grade) and toluene (CP grade, 99%+) were used as received. CO<sub>2</sub>, with purity of 99.99%, was supplied by Korea Standard Gas.

**Synthesis of GMA-Functionalized Reactive Stabilizer.** The synthetic procedure of GMA-functionalized reactive stabilizer is shown in Scheme I. In the first step, MG-PDMS



**Scheme I.** Stabilizer synthesis for MMA polymerization in CO<sub>2</sub>.

and aminopropyltriethoxysilane were added in a 100 mL four-neck flask connected to condenser, thermometer and nitrogen inlet tube. The reaction mass was maintained at 80 °C for 13 h to complete the ring opening addition between the epoxide and the amine. Conversion of epoxy-amine addition was monitored by measuring epoxy-amine value (EPA)<sup>22</sup> using automatic titrator (Metrohm 798MPT Titrimo). After the desired EPA value was reached, the reaction mass was cooled down to room temperature. At the second step, the mixture of GMA and MeHQ was injected in the reactor. Then the mixture in the reactor was heated to 85 °C for 13 h to incorporate the reactive methacrylate group of GMA with the PDMS-amine through the ring opening addition of GMA.

**Polymerization of MMA.** Dispersion polymerization of MMA was carried out in a high-pressure, variable-volume cell, which has a working volume of ~28 cm<sup>3</sup>. The details of the cell and related devices are described in other references.<sup>23-25</sup> After AIBN is loaded in the high-pressure cell, the cell is purged with CO<sub>2</sub> at 2-3 bar several times to remove any entrapped air. The mixture of MMA and our reactive stabilizer is injected into the cell using a syringe. Then, balanced amount of CO<sub>2</sub> is transferred into the cell gravimetrically using a high-pressure cylinder. The pressure of the reaction mass is manipulated by changing the volume of the cell. After the desired time of polymerization, the cell is rapidly cooled using both dry ice and ice water. The CO<sub>2</sub> in the cell slowly vented to atmospheric pressure. PMMA product was washed with hexane/heptane solution to remove unreacted GMA-PDMS stabilizers and then was dried for further characterization.

**Characterization.** The molecular weight was determined using the titration method<sup>22</sup> and gel permeation chromatography (Waters 150-C) with a WATERS Styragel 3.8×300 mm column (HR2X1, HR3X1, HR4X1). For the GPC analysis, tetrahydrofuran was used as the eluent and PS standards were used. A differential refractive index detector from Precision Detector Inc. was used to monitor the column output. Both the sample analysis and the calibration were conducted at a flow rate of 1 mL/min. The structure of the expected GMA-PDMS stabilizer was confirmed by FT-IR (Digilab EXCALIBUR FTS-4000 infrared spectrometer). The morphology of the PMMA product was characterized with scanning electron microscopy (SEM) (HITACHI, S-2400). The average diameter of the PMMA particles was determined from one hundred individual particles in each SEM micrograph.

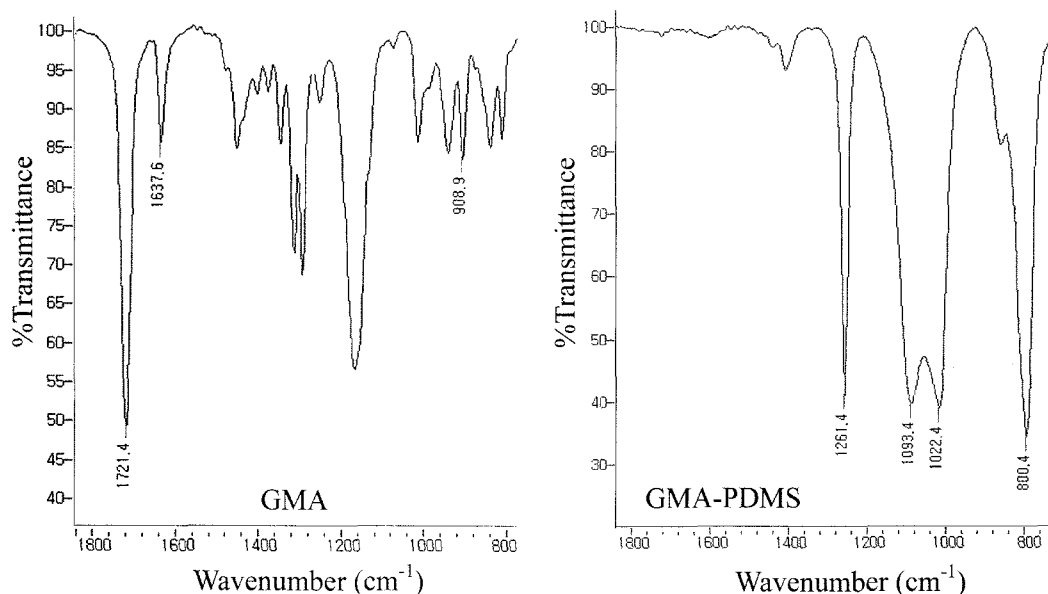
## Results and Discussion

We determined the molar mass of GMA-PDMS macromonomer using titration method and GPC. A molar mass of 5365 was calculated from the amine value of aminopropyltriethoxysilane and the EPA values of GMA and glycidyl

**Table I. Molecular Weight of Each Component Composed of GMA-PDMS Stabilizer**

Component	EPA Value (mmol/g)	Amine Value (mgKOH/g)	$M_n^a$ from Titration (g/mol)	$M_n$ from GPC (g/mol)
Glycidyl ether terminated PDMS	0.20	-	5,000	5,500
Aminopropyltriethoxysilane	-	250.43	224.01	221.37 <sup>c</sup>
Glycidyl methacrylate	7.07	-	141.44	142.16 <sup>c</sup>
GMA-PDMS			5,365.45 <sup>b</sup>	5,800

<sup>a</sup> $M_n$  is calculated from EPA and amine value. <sup>b</sup>Sum of the  $M_n$  values of glycidyl ether terminated PDMS, aminopropyltriethoxysilane, and glycidyl methacrylate. <sup>c</sup>Theoretical molecular weight.



**Figure 1.** FT-IR spectrum of GMA and GMA-PDMS stabilizer: 1721.4  $\text{cm}^{-1}$  (C=O), 1637.6  $\text{cm}^{-1}$  (C=C), 1261.4  $\text{cm}^{-1}$  ( $\text{Si}(\text{CH}_3)_2$ ,  $\text{Si}(\text{CH}_3)_3$  stretching), 1093.4  $\text{cm}^{-1}$ , 1022.4  $\text{cm}^{-1}$  (Si-O-Si), 800.4  $\text{cm}^{-1}$  ( $\text{Si}-\text{OCH}_2\text{CH}_3$ ,  $\text{Si}(\text{CH}_3)_2$ ,  $\text{Si}(\text{CH}_3)_3$  bending), 908.9  $\text{cm}^{-1}$  (glycidyl ether).

ether terminated PDMS. The  $M_n$  and polydispersity of GMA-PDMS measured using GPC were 5,800 and 1.1, respectively. The details of the molar mass data are listed in Table I. The FT-IR spectrum of the stabilizer is shown in Figure 1. In the GMA spectrum, carbonyl peak at 1721.4  $\text{cm}^{-1}$ , C=C peak at 1637.6  $\text{cm}^{-1}$  and glycidyl ether peak at 908.9  $\text{cm}^{-1}$  are shown. After the epoxy-amine addition is completed, the peaks corresponding to siloxane intensively appear at 1261.4 ( $\text{Si}(\text{CH}_3)_2$ ,  $\text{Si}(\text{CH}_3)_3$  stretching), 1093.4, and 1022.4 (Si-O-Si), and 800.4  $\text{cm}^{-1}$  ( $\text{Si}-\text{OCH}_2\text{CH}_3$ ,  $\text{Si}(\text{CH}_3)_2$ ,  $\text{Si}(\text{CH}_3)_3$  bending) in the stabilizer spectrum whereas the intensity of the carbonyl, C=C, and ether peaks apparently reduced. The dispersion polymerization of MMA was carried out at 80 °C and 207 bar. The reaction was typically maintained for 4 h. Table II lists the polymerization conditions of each experiment and the properties of the PMMA products.

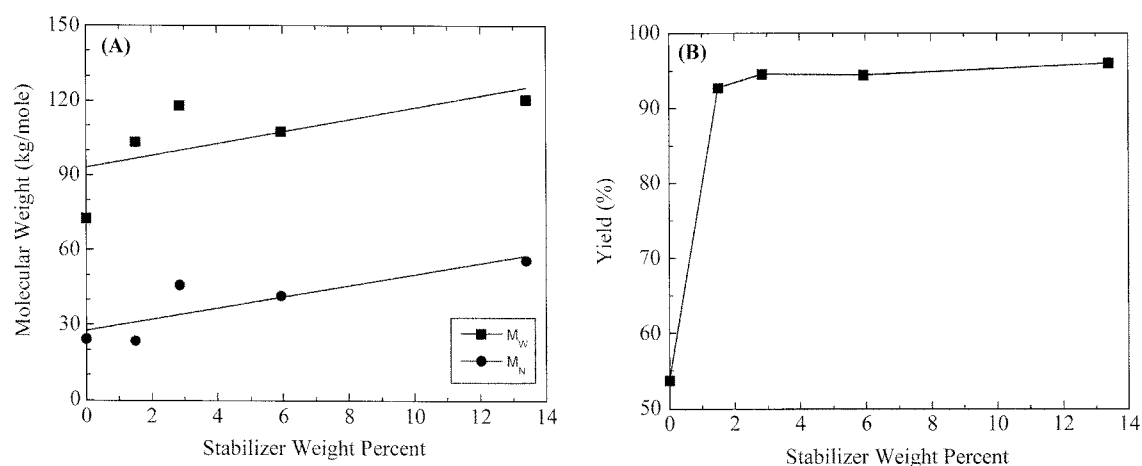
**Effect of Stabilizer Concentration.** Using the data in Table II (Run No 1~5), we plotted Figure 2 showing the effects of stabilizer concentration on the molecular weight

and the yield of PMMA products. The reactions were carried out at  $0.51 \pm 0.03$  wt% AIBN and  $28.8 \pm 1.4$  wt% MMA. At the stabilizer concentrations between 0 and 13.4 %, the molecular weight of PMMA gradually increased with the amount of the stabilizer added into the reactor. Except the case using 1.5 wt% stabilizer, the polydispersity of the PMMA decreased with increasing stabilizer concentration, suggesting that MMA dispersion in  $\text{CO}_2$  became more stable as the stabilizer concentration in the reactant increased. At the beginning of the polymerization, MMA and PMMA growing chains of low molecular weight were dissolved in supercritical  $\text{CO}_2$  at 207 bar. As the polymerization proceeds, the growing chains increases and precipitates from the MMA- $\text{CO}_2$  solution. The precipitation prevents the growing PMMA chains from reacting with MMA. The high molar mass of PMMA is limited and broad molecular weight distribution is obtained. Increasing amount of the stabilizer makes the growing PMMA chains more stable in MMA-PMMA chian- $\text{CO}_2$  mixture. With sufficient stabilizer, the polymerization is carried out in the

**Table II. Dispersion Polymerization of MMA with GMA-Linked PDMS Stabilizer in CO<sub>2</sub><sup>a</sup>**

Run No.	AIBN (wt%)	Stabilizer (wt%) <sup>b</sup>	Monomer (wt%)	Yield (%)	$M_n^c$	PDI <sup>d</sup>	$D_n^e$ (μm)	PSD <sup>f</sup>	Morphology
1	0.48	0.0	30.2	53.7	24,300	3.0	-	-	non powder
2	0.54	1.5	30.0	92.7	23,600	4.4	19.3	-	powder
3	0.51	2.9	30.1	94.6	46,000	2.6	11.0	-	powder
4	0.48	5.9	29.4	94.4	41,600	2.6	3.5	1.4	powder
5	0.54	13.4	27.4	96.0	55,800	2.2	1.8	1.5	powder
<sup>g</sup> 6	0.14	6.6	29.5	15.9	4,800	18.2	-	-	non powder
<sup>h</sup> 7	0.25	5.5	28.6	92.9	56,600	2.9	4.1	1.3	powder
4	0.48	5.9	29.4	94.4	41,600	2.6	3.5	1.4	powder
8	1.06	5.4	30.1	92.8	21,600	3.2	2.7	1.9	powder
9	0.51	6.1	19.4	48.6	9,700	8.0	2.9	1.7	hard solid and powder
4	0.48	5.9	29.4	94.4	41,600	2.6	3.5	1.4	powder
10	0.51	6.3	42.0	97.4	58,500	1.9	3.7	1.7	powder
11	0.51	5.5	50.6	92.4	56,500	2.0	3.5	1.8	powder
12	0.51	4.7	58.5	-	29,400	3.7	-	-	hard solid and powder

<sup>a</sup>Reactions were performed at 80 °C and 207 bar for 4 h. <sup>b</sup>GMA linked PDMS was used as stabilizer (Scheme 1). The stabilizer wt% based on the MMA weight in the reactor. <sup>c</sup>Molecular weight was determined with PS standard. <sup>d</sup>PDI is polydispersity ( $M_w/M_n$ ). <sup>e</sup> $D_n$  represent number average diameter. <sup>f</sup>PSD represents particle size distribution ( $D_w/D_n$ ). <sup>g</sup>Reactions were performed at 80 °C and 207 bar for 8 h. <sup>h</sup>Reactions were performed at 80 °C and 207 bar for 6 h.

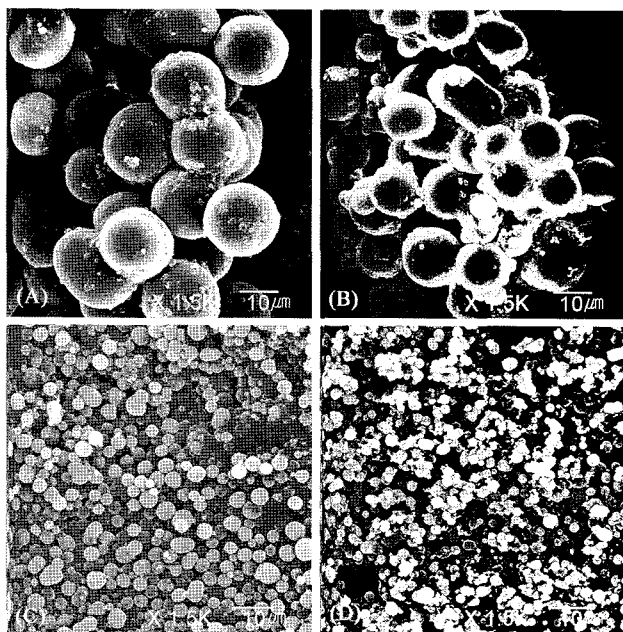


**Figure 2.** Variation of (A) PMMA molecular weight and (B) yield with respect to the stabilizer concentrations. The stabilizer weight percent was based on the MMA weight in the reactor. The concentrations of AIBN and MMA were  $0.51 \pm 0.03$  wt% and  $28.8 \pm 1.4$  wt%, respectively.

well dispersed phase. As the consequence, the molecular weight of PMMA increases and the polydispersity decreases with the amount of the stabilizer. Figure 2(B) shows the effect of the stabilizer concentration on the PMMA yield. Without using the stabilizer, the PMMA was obtained in the low yield of 53.7%. Adding 1.5 wt% the stabilizer increases the PMMA yield to 92.7%. The yield increased to 94.6% when the stabilizer concentration was raised to 2.9 wt%. However, adding more than 3 wt% stabilizer did not increase much of the PMMA yield. At the sta-

bilizer concentration of 13.4 wt%, the PMMA yield increases to 96.0 wt%. In the absence of the stabilizer, PMMA oligomer or low molecular weight PMMA was not stable in CO<sub>2</sub> continuous phase. The PMMA particles formed in the initial stage of polymerization precipitated and had a little chance to react with MMA dispersed in CO<sub>2</sub>. Therefore, the PMMA with low molecular weight ( $M_n$  24,300) was synthesized in low yield (53.7%).

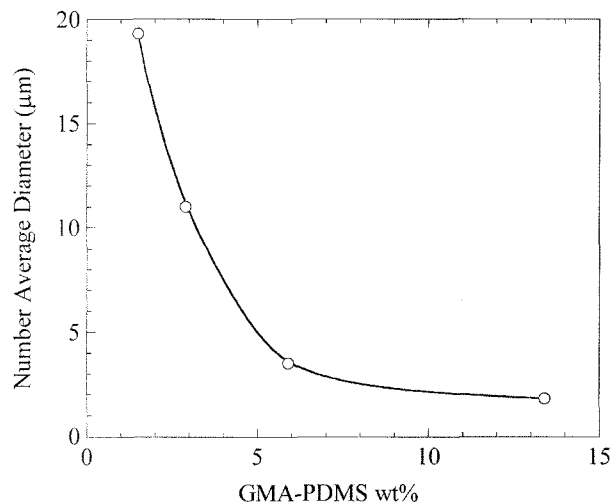
Figure 3 is SEM images showing the effect of the stabilizer concentration on the morphology of the PMMA prod-



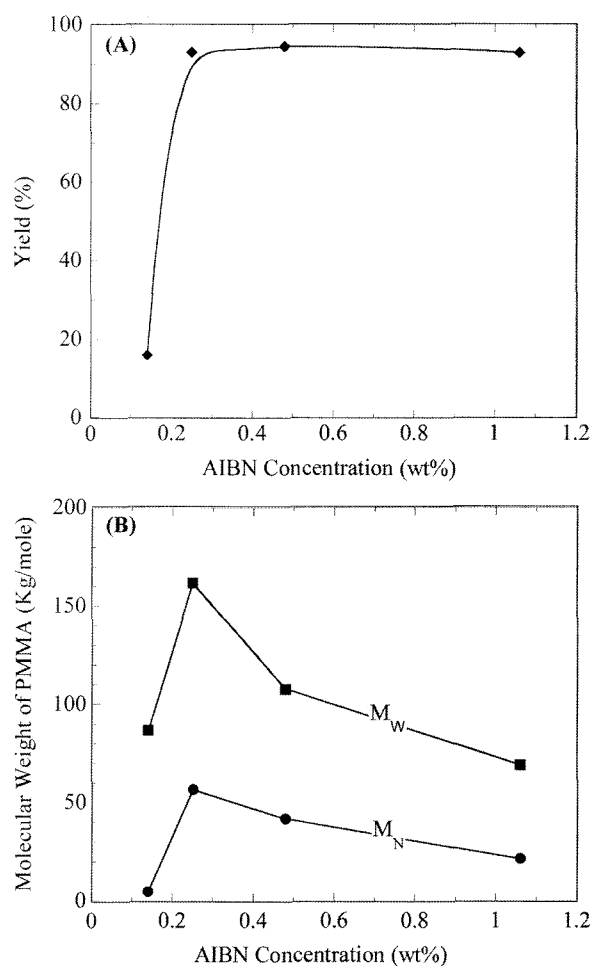
**Figure 3.** SEM images of PMMA product synthesized in  $\text{CO}_2$  with (A) 1.5 wt%, (B) 2.9 wt%, (C) 5.9 wt%, and (D) 13.4 wt% GMA-PDMS stabilizer. The stabilizer weight percent was based on the monomer weight. The concentrations of AIBN and MMA were  $0.51 \pm 0.03$  wt% and  $28.8 \pm 1.4$  wt%, respectively.

uct. The PMMA synthesized without the stabilizer was transparent and non-powdery. When MMA was polymerized with 1.5 wt% GMA-PDMS stabilizer, PMMA was obtained in the powder form. The average diameter of the PMMA particles was 19.3  $\mu\text{m}$ . Increasing the stabilizer concentration to 2.9 wt% reduced the particle size to 11.0  $\mu\text{m}$ . Some particles had small diameters less than 1  $\mu\text{m}$ , which broadened the particle size distribution (Figure 3(B)). At 5.9 wt% GMA-PDMS stabilizer the particle size was considerably reduced to 3.5  $\mu\text{m}$  and the fairly regular size of PMMA particles (PSD=1.4) were obtained. Increasing the stabilizer concentration from 5.9 to 13.4 wt% reduced the particle size to 1.8  $\mu\text{m}$  whereas the PSD value did not change. Figure 4 demonstrated that at high GMA-PDMS concentrations over 5.9 wt% the diameter of the PMMA became smaller than 3  $\mu\text{m}$ . This phenomenon was also observed in other stabilizer systems.<sup>7-10,13,16,20</sup> The particle size of PMMA synthesized using GMA-PDMS stabilizer was similar with the size of PMMA prepared with fluoro and fluoro copolymer stabilizer, which had a range of 2-5  $\mu\text{m}$ .<sup>8,12,13,15,16</sup>

**Effect of Initiator Concentration.** Figure 5(A) and 5(B), prepared with the data in Table II (Run No 4, 6–8), show the effect of AIBN concentration on the yield and molecular weight of the PMMA product. The reaction was carried out for 4 h at 0.5 wt% AIBN as a reference. At AIBN concentration of 0.14 wt%, the PMMA yield was only 15.9%. The yield of PMMA significantly increased once the amount of AIBN added into the reactant exceeded 0.25 wt%. Since the



**Figure 4.** Effect of GMA-PDMS concentration on the number average diameter of the PMMA particles.



**Figure 5.** Effect of AIBN concentration on (A) the PMMA yield and (B) molecular weight. The concentrations of MMA were  $29.4 \pm 0.8$  wt%. GMA-PDMS stabilizer concentrations based on the monomer weight were  $6.0 \pm 0.6$  wt%. The polymerization conditions and the product properties were listed in Table II.

rate of free radical polymerization decreases with initiator concentration, the reactions using 0.14 and 0.25 wt% AIBN were extended from 4 to 8 h and from 4 to 6 h, respectively. It was found that the yield and molecular weight of the PMMA polymerized at AIBN concentration of 0.14 wt% increased slowly with time. We will report the effect of reaction time in a separate article. Figure 5(B) shows that the number average molecular weight of PMMA increased from 21,600 to 56,600 as the concentration of AIBN decreased from 1.06 to 0.25 wt%. Christian *et al.*<sup>13</sup> also observed that the molecular weight of PMMA increased with decreasing AIBN concentrations between 0.5 and 2.5 wt%. However, we found that further decrease of AIBN concentration to 0.14 wt% reduced the molecular weight to 4,800 although the reaction time was extended to 8 h. Our results suggest that at extremely low concentration of initiator, the formation of PMMA active chain was limited, and then the PMMA of low molecular weight was obtained in low yield.

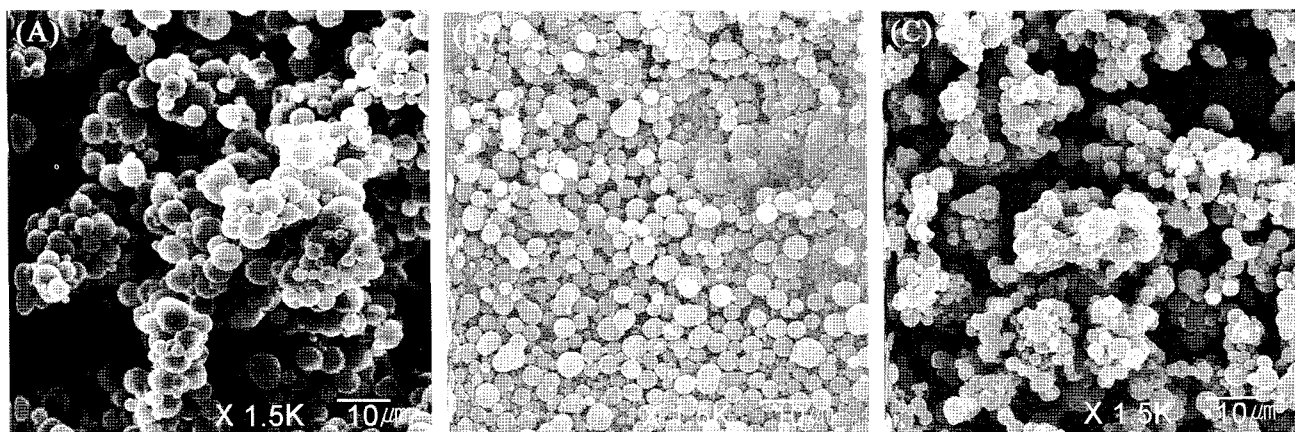
Figure 6 shows the morphology of the PMMA particles synthesized at different AIBN concentrations. It is easily expected that the particle size decreases with increasing an initiator concentration since the number of monomer molecules per an initiator reduces. The PMMA with a diameter of 4.1  $\mu\text{m}$  was obtained at 0.25 wt% AIBN. Increasing AIBN concentration to 1.06 wt% reduced the particle size to 2.7  $\mu\text{m}$ . At 0.14 wt% AIBN we could not obtain PMMA particles but sticky oil-like PMMA product was obtained in a low yield although the reaction time was extended to 8 h.

**Effect of Monomer Concentration.** To investigate the effect of monomer concentration on the MMA polymerization using GMA-PDMS stabilizer, MMA concentration was varied between 19.4 and 58.5 wt%. It is expected that MMA acts as a cosolvent for PMMA-CO<sub>2</sub> mixture. Lora and McHugh<sup>26</sup> reported that at 80 °C, PMMA ( $M_n=46,400$ ,  $M_w=93,300$ ) was soluble at pressures higher than 920 bar in the PMMA (5.1 wt%) – MMA (28.9 wt%) – CO<sub>2</sub> (66.0 wt%)

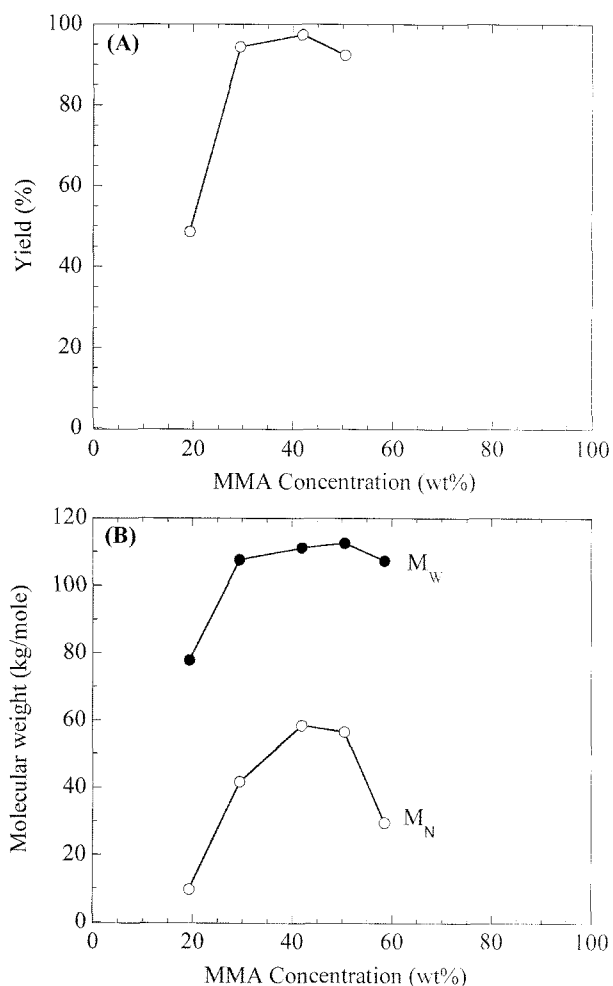
mixture. At the initial stage of the polymerization, the growing PMMA chains can be dissolved in MMA – CO<sub>2</sub> solution at low concentrations of low molar mass PMMA. However, from Lora and McHugh's data,<sup>26</sup> it is apparent that at 207 bar, the PMMA chains will be separated from the homogenous mixture of PMMA – MMA – CO<sub>2</sub>. Therefore, the cosolvent effect of MMA is supposed to be greatly limited in our experimental conditions.

At 19.4 wt% MMA, oily PMMA was produced. The final PMMA product was obtained in low yield of 48.6 %. The low PMMA yield was caused by the slow reaction rate at low monomer concentration. At 19.4 wt% MMA, the four hour reaction time was so short that the MMA was not completely converted to PMMA. Figure 7(A) shows that increasing MMA concentration to 29.4 wt% increased the yield to 94.4%. Additional increasing of MMA concentration to 42.0% slightly increased the PMMA yield to 97.4%. However, further increasing the monomer concentration to 50.6 wt% reduced the PMMA yield to 92.4%. We used a magnetic stirrer to mix the reactant, which was not strong enough to fully mix the viscous fluid. One possible reason for the low yield is the weak mixing due to the high viscosity of the reactant containing high MMA concentration. When MMA concentration was 58.5 wt%, we failed to fully recover the whole PMMA product since some of the product was stuck to the bottom of the reactor.

Figure 7(B) shows the effect of MMA concentration on the molecular weight of the PMMA product. The lowest  $M_n$  (9,700) and  $M_w$  (77,900) were obtained at 19.4 wt% MMA. The  $M_n$  increased to 41,600 when MMA concentration changed from 19.4 to 29.4 wt%. The molecular weights of the PMMA increased with the monomer concentrations. The PMMA with the highest  $M_n$  (58,500) was produced at 42.0 wt% MMA. It is well known that in free radical polymerization the molar mass of the polymer increases with the monomer concentration. However, our experimental results

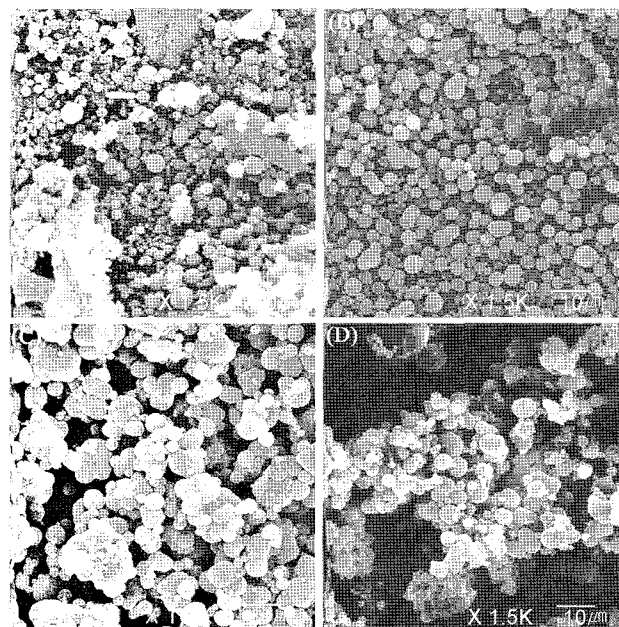


**Figure 6.** SEM images of PMMA product synthesized in CO<sub>2</sub> at (A) 0.25 wt%, (B) 0.48 wt%, and (C) 1.06 wt% AIBN. The concentrations of MMA were  $29.4 \pm 0.8$  wt%. GMA-PDMS stabilizer concentrations based on the monomer weight were  $6.0 \pm 0.6$  wt%. The reaction conditions and the product properties were listed in Table II.



**Figure 7.** Effect of MMA concentration on (A) the PMMA yield and (B) molecular weight. The concentrations of AIBN were  $0.5 \pm 0.01$  wt%. The stabilizer concentrations based on the monomer weight were  $5.5 \pm 0.8$  wt%. The reaction conditions and the product properties were listed in Table II.

show that increasing MMA concentration over 50.6 wt% rapidly reduced the  $M_n$ . At 58.5 wt% MMA, where the monomer concentration was higher than the  $\text{CO}_2$ , the  $M_n$  of the PMMA product decreased to 29,400. It is interesting that the molar mass and yield of the PMMA reached maximum when 40 wt% MMA was used. Lora and McHugh's data<sup>26</sup> show that PMMA is soluble only at 300 bar in the PMMA (5 wt%) – MMA (48.4 wt%) –  $\text{CO}_2$  (46.6 wt%) mixture. If the high molar mass and yield of the PMMA is derived from the cosolvent effect, the PMMA synthesized at 50.6 wt% MMA should have higher molar mass and yield than the PMMA polymerized at low MMA concentrations. However, our experiment showed opposite results. When the MMA concentration increases from 19.4 to 42.0 wt%, the increase in molar mass and yield of PMMA results from the increasing monomer concentration, not from the cosolvent effect of MMA. At MMA concentrations higher



**Figure 8.** SEM images of PMMA product synthesized in  $\text{CO}_2$  at (A) 19.4 wt%, (B) 29.4 wt%, (C) 42.0 wt%, and (D) 50.6 wt% MMA. The concentrations of AIBN were  $0.5 \pm 0.01$  wt%. The stabilizer concentrations based on the monomer weight were  $5.5 \pm 0.8$  wt%. The reaction conditions and the product properties were listed in Table II.

than 50.6 wt%, where the amount of  $\text{CO}_2$  is less than MMA, the continuous phase is possibly unstable for the dispersion polymerization. Similar result was reported in non- $\text{CO}_2$  system by Klein *et al.*<sup>27</sup> They reported that colloidal stability of PMMA polymerization in MMA – hexane system became unstable as MMA concentration increased from 26.3 to 47.2 wt%. We suggest that the tendency to reach maximum yield and molecular weight at 42 wt% MMA might be the consequence of the balance determined by two factors. One is the effect of MMA concentration and the other is the stability of the dispersion phase that was influenced by the mixing and the composition between MMA and  $\text{CO}_2$ . We need further study to clarify how to vary the stability of the MMA –  $\text{CO}_2$  – PMMA dispersion phase with MMA concentration.

Figure 8 shows the SEM images of the PMMA particles synthesized at various monomer concentrations. At 19.4 wt% MMA the PMMA was produced in the form of a hard solid with some powders. To investigate the morphology of the hard solid PMMA, we broke the PMMA and took the SEM image of the particle area of the solid PMMA (Figure 8(A)). The average diameter of the particles of the hard solid PMMA measured to 2.9  $\mu\text{m}$ . When MMA concentration increased to 29.4 wt% the PMMA was entirely produced in a particle shape with the average diameter of 3.5  $\mu\text{m}$ . Increasing MMA concentration to 42.0 wt% did not change the average particle diameter (3.7  $\mu\text{m}$ ). However, the PSD of the PMMA increased from 1.4 to 1.7. We found

that further increasing MMA concentration to 50.6 wt% little influenced the particle diameter (3.5  $\mu\text{m}$ ) and PSD (1.8) of the PMMA product (Figure 8(D)).

## Conclusions

We demonstrated the synthesis and usage of GMA-PDMS macromonomer as a stabilizer for the dispersion polymerization of MMA in CO<sub>2</sub>. Solvent and catalyst are not needed to synthesize GMA-PDMS stabilizer. Therefore processes to separate and purify the stabilizer from reactant medium are not required, which is a great advantage for commercial production. PMMA was produced in high yield over 94% using only 0.87 wt% (2.9 wt% based on monomer weight) GMA-PDMS. Typically, the  $M_n$  of the PMMA product ranged between 41,600 and 55,800. The particle diameter of the PMMA was between 1.8 and 3.5  $\mu\text{m}$  and the PSD ranged between 1.4 and 1.8.

**Acknowledgements.** This paper was supported by Dong-A University research fund in 2005.

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