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Preparation of Highly Cross-Linked, Monodisperse Poly(methyl methacrylate) Microspheres by Dispersion Polymerization; Part II. Semi-continuous Processes

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Abstract: In our previous publication, the problem of particle deformation and coagulation at the nucleation stage in the presence of cross-linker was intensely studied by seeded batch dispersion polymerization of methyl methacrylate (MMA). In the present work, highly cross-linked, monodisperse PMMA particles were prepared under various reaction conditions by seeded semi-continuous process. Monodisperse, 6.5 μm-diameter PMMA particles containing up to 8 wt% of DVB or EGDMA were successfully made by seeded semi-continuous process and multi-semi-continuous addition process, respectively. Therefore, this study shows that seeded semi-continuous process is more effective and efficient to prepare highly cross-linked, monodisperse particles than non-seeded and seeded batch processes.

Keywords: highly cross-linked, monodisperse poly(MMA) microspheres, dispersion polymerization, semi-continuous process.

Introduction

Micron-sized monodisperse polymer particles are used in a wide variety of scientific and technological applications.[1-4] Especially, there have been strong demands for highly cross-linked polymer beads with superior heat resistance, solvent resistance, mechanical strength to serve as spacer for display panel, slip property improvers for plastic film, conductive ball for anisotropic conductive film, etc.[5-9] Micron-sized uniform particles can be made by the successive seeded emulsion polymerization developed by Vanderhoff[10] or the activated swelling and suspension polymerization methods developed by Ugelstad.[11] However, these processes are complex, time-consuming and difficult to implement in large scale. Another technique used in the preparation of monodisperse beads with micrometer diameter is dispersion polymerization, which has been extensively studied.[12-24] This process is very attractive for large-scale preparation for such particles. However, there are many citations[5-7,19,23,25] in the literature to attest to the fact that dispersion polymerization failed when cross-linking agents are present. One often finds flocculation or coagulation of the product. When the reaction appears to succeed, one finds odd-shape particle and a broad size distribution of the product. Recently, many studies have reported methods to overcome flocculation and deformation by dispersion polymerization in the presence of cross-linker.[5-7,19,23,25] It is widely believed that cross-linking agents interfere with the sensitive particle nucleation step causing flocculation and deformation.[5,25-30] The immobilization of steric stabilizer due to cross-linking agent causes instability of the polymerization.[6] In addition to this cross-linking suppresses the monomer swelling into particle. Thomson *et al.*[6] reported that monodisperse particles could be possibly obtained with less than 0.02 wt% of DVB in the initial charge. However larger amounts of DVB (1 wt% of DVB, based on total monomer) could be incorporated only by incremental addition 7 h after the start of the polymerization. Winnik[25] and co-worker also reported that cross-linked monodisperse PS particles could be obtained by the addition of DVB or EGDMA at the end of the nucleation stage.

In our previous study,[28] cross-linked monodisperse smooth surface PMMA particles containing up to 5 wt% DVB could be prepared by seeded batch processes.

This study focuses on the seeded semi-continuous processes in the dispersion polymerization using the PMMA seed particle after nucleation stage. We examined the effect of methanol/water ratio as polymerization medium, cross-linker concentration, feeding time of cross-linker, reaction temperature and seed/monomer ratio at second stage on the final particle morphology.

Experimental

Materials. Methyl methacrylate (MMA, Junsei) was washed with 10 wt% aqueous sodium hydroxide solution to remove

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the inhibitor. Divinylbenzene (DVB-55, Sigma) and ethylene glycol dimethacrylate (EGDMA, Sigma) were passed through an activated aluminum oxide column to remove inhibitor. 2,2'-azobis(isobutyronitrile) (AIBN, Junsei) purified by recrystallization in methanol. All other materials were used without further purification, including methanol (MeOH, Daejung chemical), and poly(vinyl pyrolidone) (PVP K-30, Junsei).

Batch Process (Preparation of PMMA Seed). The standard recipe for preparation of PMMA particles by batch process is given in Table I. All ingredients were weighed and mixed in 2 oz glass bottle, purged with nitrogen, capped, and sealed. The mixtures were then placed in a shaker, operating at 120 cycles per min in a constant temperature water bath at 55 °C for 48 h.

Semi-continuous Process. The standard recipe for preparation of PMMA particles by semi-continuous process is given in Table I. MeOH and PVP K-30 were weighed and mixed in 250 mL four-neck reaction flask equipped with a condenser and a gas inlet. The mixture was mechanically stirred at 120 rpm and deoxygenated by bubbling nitrogen gas at room temperature for at least 30 min, and temperature was gradually raised. When the temperature reached 55 °C, monomer mixture [9 g of MMA, 0.09 g of AIBN] was added continuously for 6 h in the flask and the reaction was continued for 18 h. Most of the polymerization carried out in this study showed more than 95 wt% conversion.

Table I. Batch Process (Preparation of PMMA Seed) and Semi-continuous Process (Amount in grams)

Ingredients	Batch Process[a]	Semi-Continuous Process[b]	
		1st Stage	2nd Stage[c]
MMA	3	-	9
MeOH	25.8	77.4	-
PVP K-30	1.2	3.6	-
AIBN	0.03	-	0.09
Total	30.03	101	9.09

[a]Bottle polymerization, 55 °C, 120 cycle/min for 48 h.
[b]Flask polymerization, 55 °C, 120 rpm for 48 h. [c]Feeding time: 6 h.

Seeded Semi-continuous Process. The standard recipe for preparation of cross-linked PMMA particles by seeded semi-continuous dispersion polymerization is listed in Table II. The following procedure was used: 11 g of water and PMMA seed mixture were added to a 250 mL four-neck reaction flask equipped with a condenser and a gas inlet. The mixture was mechanically stirred at 120 rpm and deoxygenated by bubbling nitrogen gas at room temperature for at least 30 min, and temperature was gradually raised. When the temperature reached 70 °C, the monomer mixture [3 g of MMA, 25.8 g of methanol, 11 g of water, 0.03 g of AIBN, DVB (0~100 wt% based on total amount of seed and monomer)] was added continuously for 6 h in the PMMA seed mixture and reaction was continued for 18 h. Most of the polymerization carried out in this study showed more than 95 wt% conversion.

Seeded Multi-Semi-continuous Process. The recipe and procedure were the same as that seeded semi-continuous process, except that a first aliquot of EGDMA (1~2 wt% based on total amount of seed and MMA, dissolved in MeOH) was added continuously for 1 h to the reaction while the monomer mixture was added continuously for 6 h at the same time. After 6 h, a second aliquot of 5~7 wt% of EGDMA was added continuously for another 6 h and the reaction was continued for 18 h.

Characterization of Cross-linked PMMA Particles. Particle size, size distribution and morphology of the resulting dispersion were analyzed using a scanning electron microscopy (SEM, JEOL JSM 6400). The sample was prepared by taking one drop of the final dispersion diluted in about 2~3 mL of MeOH and one drop of the diluted dispersion was coated on the aluminum stud and dried overnight at room temperature. The sample was sputter-coated with gold, and examined at 15 kV. The particle size of the latexes was measured with photographs and the particle size distri-

Table II. Standard Recipe for Seeded Semi-continuous & Seeded Multi-Semi-continuous Processes (Amounts in Grams)

Ingredients	Seeded Semi-continuous		Seeded Multi-Semi-continuous			
	1st Stage[c]	2nd Stage[d]	1st Stage[c]	2nd Stage[d]		
				Aliquot of MMA	1st Aliquot of EGDMA	2nd Aliquot of EGDMA
MMA	3	3	3	3	-	-
MeOH[a]	25.8	25.8	25.8	25.68	0.56	1.98
H_2O[a]	11[e]	11	11[e]	10.71	0.24	0.82
PVP K-30	1.2	-	1.2	-	-	-
DVB	-	0-100[b]	-	-	1-2[f]	5-7[f]
AIBN	0.03	0.03	0.03	0.03	0.002	0.007

[a]MeOH/Water = 7/3. [b]Wt % based on total amount of seed & monomer. [c]55 °C, 120 cycle/min for 48 h. [d]60~70 °C, 120 rpm for 24~48 h. [e]11 g of water was post-added to the PMMA seed mixture. [f]Wt % of EGDMA.

bution (PSD) was determined using the ratio of the number (D_n) and Weight (D_w) average diameters as follows:

$$\overline{D_n} = \frac{\sum_{i=0}^{N} D_i}{N} \tag{1}$$

$$\overline{D_w} = \frac{\sum_{i=0}^{N} D_i^4}{\sum_{i=0}^{N} D_i^3} \tag{2}$$

where N is the total number of particles counted and d_i is the diameter of particle i.

$$PSD = \frac{\overline{D_w}}{\overline{D_n}} \tag{3}$$

Results and Discussion

Batch and Semi-continuous Processes. Figures 1(A) and 1(B) show SEM micrographs of PMMA microspheres prepared by batch process and semi-continuous process, respectively as described in Table I. In batch process, the

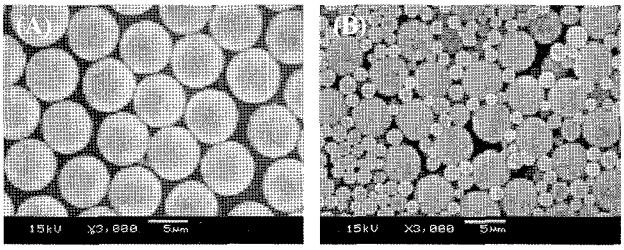

Figure 1. SEM photographs of PMMA particles prepared by (A) batch process and (B) semi-continuous process.

formation of monodisperse and smooth surface PMMA particles can be observed, whereas particles with broad particle size distribution have been observed in semi-continuous process, which can be attributed to the lengthy nucleation process.

Based on our previous study,[28] dispersion polymerization in the presence of DVB by batch and semi-continuous processes exhibited different morphologies due to effect of adding cross-linker at nucleation stage. Figure 2 shows the particle morphology of PMMA particles prepared by batch and semi-continuous dispersion polymerization processes at increasing concentrations of DVB. In the case of copolymerization of MMA and DVB, reactivity of DVB was

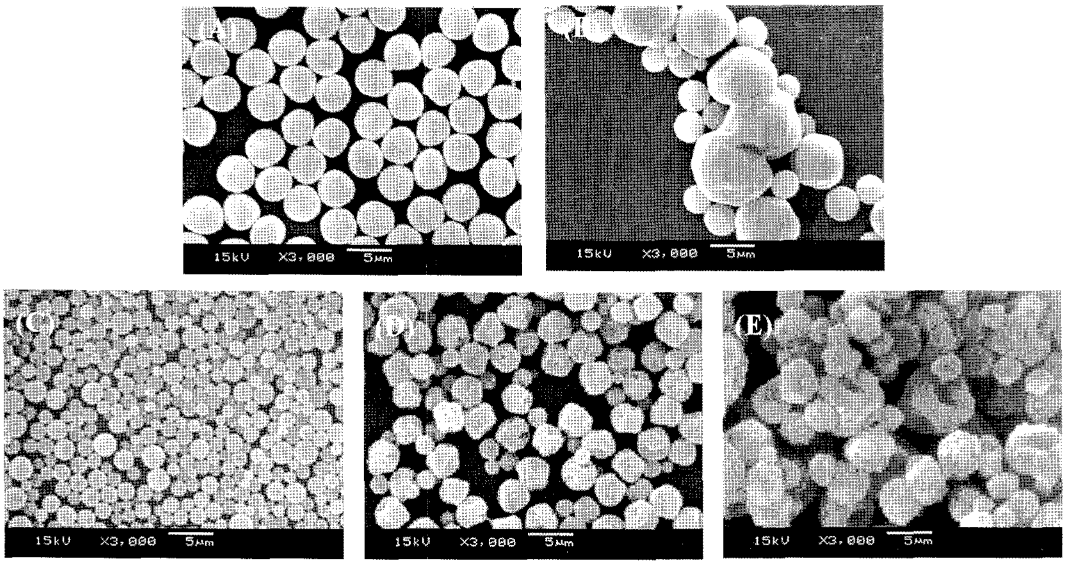

Figure 2. SEM photographs of cross-linked PMMA particles prepared at different DVB concentrations by batch and semi-continuous processes [batch process : (A) 0.1 wt%, (B) 0.15 wt%; semi-continuous process : (C) 0.5 wt %, (D) 1 wt%, (E) 2 wt%)].

Table III. Effect of MeOH/Water Ratio

	DVB (%)[a]	MeOH/Water (wt%)	$\overline{D_n}$(μm)	PSD	Particle Shape
A	3	100/0	6.3	1.07	Knobbly particle & secondary nucleated particle
B	6	100/0	7.3	1.1	Heavily wrinkled particle & secondary nucleated particle
C		70/30	6.5	1.04	Monodisperse & smooth surface particle
D	7	70/30	6.5	1.05	Deformed particle

[a]Based on total amount of seed and monomer 70 °C, 24 h, 120 rpm, feeding time : 6 h.

higher than MMA. Accordingly, when a very small amount of DVB (0.05 to 0.1 wt%) is present in the initial charge, nuclei of highly cross-linked structure and particle deformation occurs because DVB participates preferentially in the nucleation[6] [Figure 2(A)]. With higher DVB contents, coagulation and flocculation occurred in the dispersion [Figure 2(B)]. However, in semi-continuous process at DVB concentration of 0~0.5 wt%, smooth surface particles were obtained [Figure 2(C)]. But at higher content DVB, the deformation occurred [Figure 2(D)]. Further increase to 2 wt% of DVB resulted in flocculation of the dispersion [Figure 2(E)].

The difference between batch process and semi-continuous process is the timing of the formation of cross-links. In the batch process, the cross-link density of the nuclei is much higher than that of the semi-continuous process. Even though the total DVB incorporated into the polymers in the two reactions was the same, the stability of the dispersions during the copolymerization reaction was totally different. In semi-continuous process, more DVB could be incorporated into the polymer particles if it is added slowly to the reaction. Consequently, smooth surface particles without deformation could be prepared containing up to 0.5 wt% DVB by semi-continuous process. This result shows that the semi-continuous process is more effective than batch process to prepare highly cross-linked smooth surface particles by dispersion polymerization.

Seeded Semi-continuous Process. To prevent coagulation and particle deformation by cross-linker, Thomson *et al.*[6] reported that monodisperse polystyrene particles could be possibly obtained with 1 wt% of DVB and the crosslinking agent should be added continuously for 7 h after the start of the polymerization by slow-addition method. Winnik[25] and co-worker reported that cross-linked monodisperse particles without deformation could be obtained by semi-continuous addition of DVB during 12 h at the end of the nucleation stage. Also, many researchers tried to overcome the problem by long time addition method.[6,25,26] In our previous report,[28] preparation of cross-linked PMMA particles by batch process was described and smooth surface PMMA particles containing up to 5 wt% of DVB have been prepared by seeded batch process. This work is a continuation of the previous study but by seeded semi-continuous process in dispersion polymerization under various polymerization conditions as follows.

Effect of MeOH/Water Ratio. Generally, the swelling rate of monomer inside the particle increases as the polarity of polymerization media increases.[13,29-31] Consequently, we infer that as the water ratio increases, DVB diffusion into PMMA particle becomes easier and has more uniform cross-link structure inside the particle. However, when the MeOH/water ratio is 100/0 with more than 3 wt% of DVB, DVB could not be infiltrated sufficiently inside the particle due to low polarity of the medium, and cross-link structure was formed near the particle surface, thereby swelling of

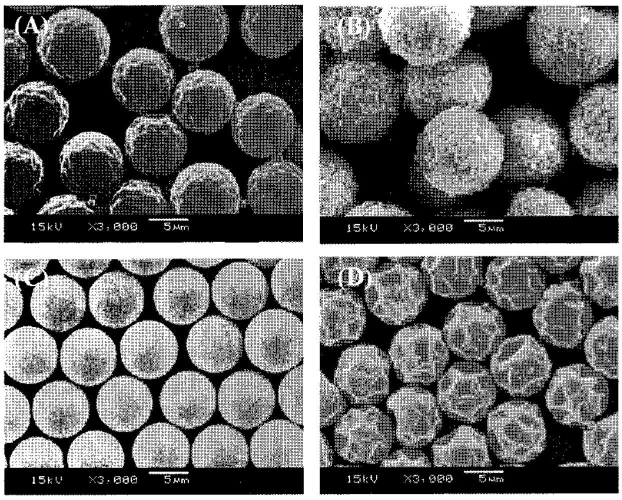

Figure 3. SEM photographs of cross-linked PMMA particles prepared at different MeOH/water weight ratios [(A) 100/0 at 3 wt% DVB, (B) 100/0 at 6 wt% DVB, (C) 70/30 at 6 wt% DVB, (D) 70/30 at 7 wt% DVB].

MMA was refrained and small secondary particles was formed due to high cross-link density on the particle surface [Figure 3(A)]. Furthermore, when concentration of DVB is 6 wt%, the inflated-wrinkled particles with 7 μm diameter was observed with lots of small sized secondary particles on the surface [Figure 3(B)]. From this result it can be inferred that deformation of particles occurs by localized cross-linking on the particle surface, resulting from the low polarity of the medium, and then some parts of monomer remaining in the medium formed secondary particles. These secondary particles and oligomers combine with vinyl group of DVB which exists on the cross-linked particle surface, or the precipitated oligomers were piled up on the sunken particle surface which covered with snow like. This phenomenon is similar to particle generation by precipitation polymerization reported by Stover *et al.*.[24] On the other hand, when the ratio of MeOH/water is from 70/30 to 60/40 with 6 wt% of DVB, monodisperse and spherical particles were achieved [Figure 3(C)]. The deformation was only observed at 7 wt% of DVB [Figure 3(D)]. When the ratio of MeOH/water is 50/50, the coagulation occurred even without DVB due to phase separation between MMA and polymerization media.

Effect of Feeding Time of DVB. Table IV and Figure 4 show the particle size, size distribution and morphology of particles prepared by seeded semi-continuous process with different feeding times of DVB. It was observed that for the 6 wt% DVB concentration, wrinkles on the particle surface appeared with feeding time of less than 6 h [Figures 4(A)~(E)]. The occurrence of wrinkles is due to phase separation caused by high cross-link density and rapid consumption of DVB at low conversion. However if the feeding time is raised to 6 h, monodisperse smooth surface particles could

Table IV. Effect of Feeding Time of DVB

	DVB (%)[a]	Feeding Time(h)	$\overline{D_n}$(μm)	PSD	Particle Shape
A	6	1	6.2	1.05	
B		2	6.3	1.05	
C		3	6.3	1.05	
D		4	6.5	1.06	Deformed particle
E		5	6.5	1.08	Slightly wrinkled particle
F		6	6.4	1.05	Monodisperse & smooth surface particle
G	7	6	6.3	1.1	Deformed particle
H		12	6.3	1.06	Monodisperse & smooth surface particle
I	9	12	Broad		Coagulum & secondary nucleated small particle

[a]Based on total amount of seed and monomer MeOH/water = 70/30, 24 h, 120 rpm.

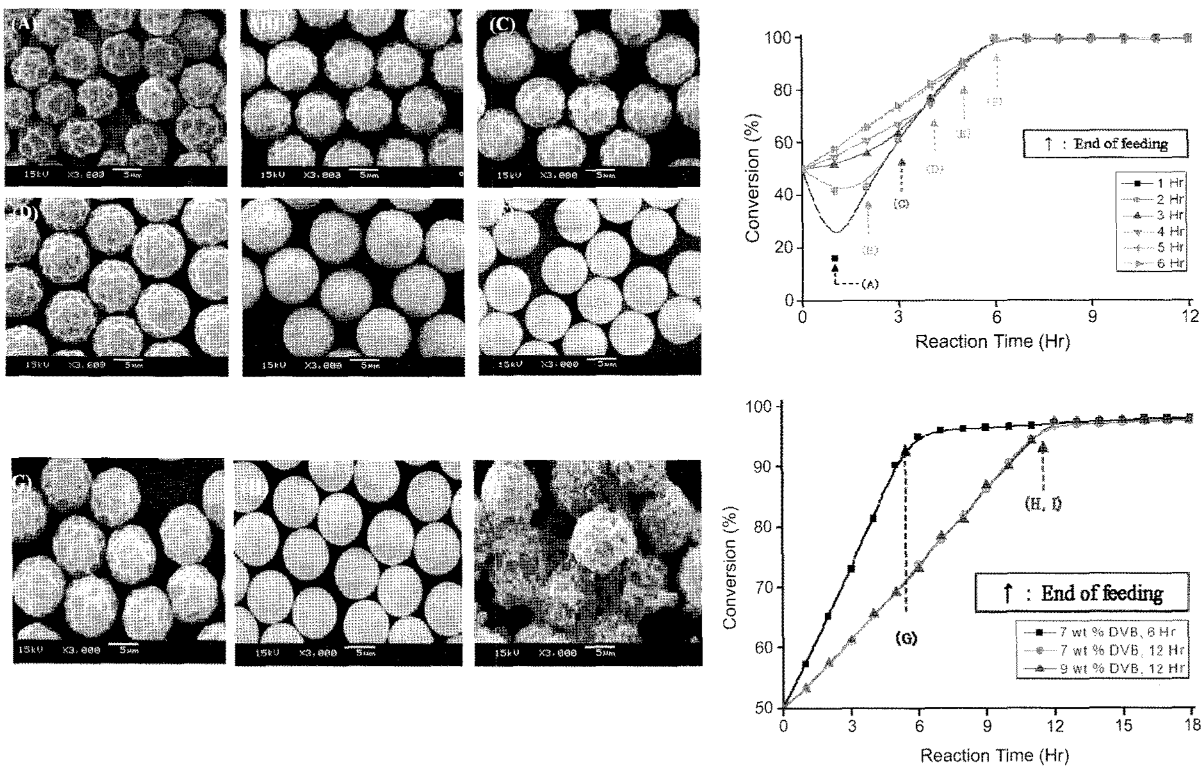

Figure 4. SEM photographs of cross-linked PMMA particles prepared at six different feeding time of DVB [(A) 1 h, (B) 2 h, (C) 3 h, (D) 4 h, (E) 5 h, (F) 6 h at 6 wt% of DVB, (G) 6 h at 7 wt% DVB, (H) 12 h at 7 wt% DVB, (I) 12 h at 9 wt% DVB] and the time-conversion curves.

be formed, as shown in Figure 4(F). This is due to gradual infiltration of cross-linker and MMA into the particle, thereby creating more uniform cross-link density inside the particle. On the other hand, wrinkled particles were produced for 7 wt% DVB concentration [Figure 4(G)]. With the same amount of DVB concentration but at increased feeding time of 9 h, smooth surface particles could also be created [Figure 4(H)]. However with further increase in DVB concentration to 9 wt% and feeding time of 12 h, particles were deformed and coagulated as shown in Figure 4(I).

Effect of Polymerization Temperature. Reaction temperatures of 60, 65 & 70 °C have been used in this study in order to investigate the effect of temperature on the morphology of PMMA particles. Figure 5 shows the morphology of PMMA particles prepared with 6~8 wt% DVB at 60~70 °C, respectively. Formation of monodisperse and smooth surfaced PMMA particles could be observed. When the DVB concentration is 7 wt%, formation of wrinkled surface PMMA

Table V. Effect of Polymerization Temperature

	DVB (%)[a]	Temp. (°C)	Feeding Time (h)	$\overline{D}_n$(μm)	PSD	Particle Shape
A	7	65	6	6.4	1.04	Monodisperse & smoothsurface particle
B		70		6.5	1.1	Deformed particle
C		70	12	6.5	1.07	Monodisperse & smoothsurface particle
D	8	65	6	6.4	1.09	Deformed particle
E		65	12	6.5	1.05	Monodisperse & smoothsurface particle
F		70		6.5	1.1	Deformed particle
G	9	65	12	Broad		Deformed particle & coagulation

[a]Based on total amount of seed and monomer. MeOH/Water = 70/30, 120 rpm.

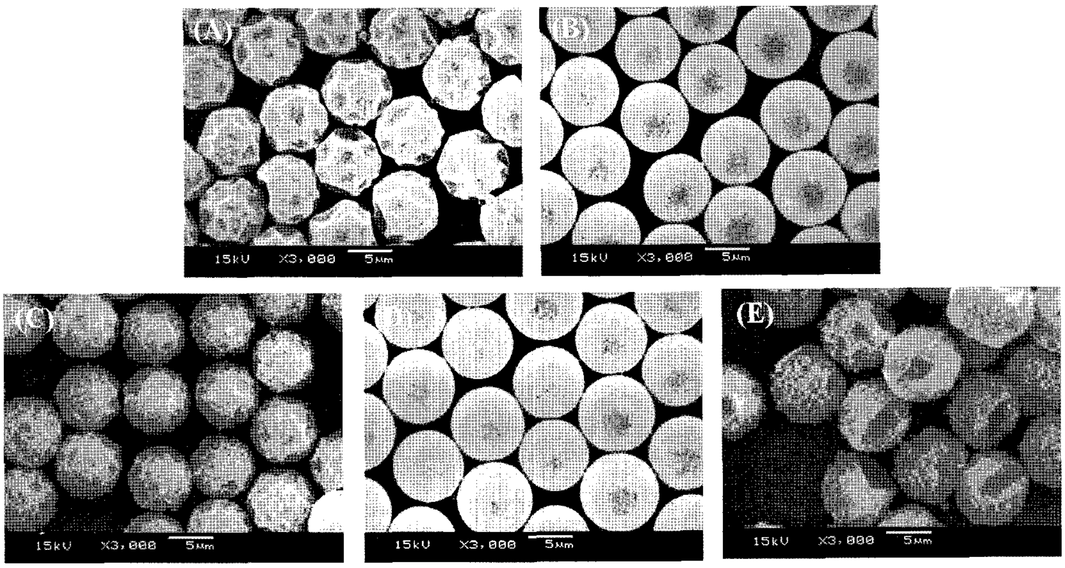

Figure 5. SEM photographs of cross-linked PMMA particles prepared at different polymerization temperatures [(A) 70 °C & 7 wt% at feeding time 6 h, (B) 65 °C & 7 wt% at 6 h, (C) 65 °C & 8 wt% DVB at 6 h, (D) 65 °C & 8 wt% DVB at 12 h, (E) 70 °C & 8 wt% DVB at 12 h].

particles has been observed at 70 °C [Figure 5(A)], but smooth surfaced particles were obtained at 60 and 65 °C due to the formation of more uniform cross-link structures throughout the particles [Figurre 5(B)]. Further increase in DVB concentration to 8 wt% but at increased feeding time of 12 h at 65 °C showed formation of smooth surfaced and monodisperse PMMA particles [Figure 5(D)] and highly deformed and non-spherical particles were obtained at 70 °C [Figure 5(E)]. For further increase of DVB concentration to 9 wt% deformed particles were observed at all reaction temperatures.

Effect of Seed/MMA Ratio. Table VI and Figure 6 show the particle size, size distribution and morphology of particles prepared by seeded semi-continuous process with three different seed/MMA ratios at 7~8 wt% of DVB concentrations. When the ratio of seed/MMA is 100/0 with 7 wt% of DVB, smooth surface particles could be prepared due to exclusion of phase separation [Figure 6(A)]. However, when the concentration of DVB is 8 wt%, although infiltration of cross-linker is good enough, wrinkles on the particle

Table VI. Effect of Seed/Monomer Ratio

	Seed/MMA(wt%)	DVB(%)[a]	$\overline{D}_n$(μm)	PSD	Particle Shape
A	100/0	7	5.5	1.05	Monodisperse & smooth surface particle
		8	6.1	1.07	Wrinkled particle
B	100/33	7	6.2	1.06	Deformed particle
C	100/100	7	6.4	1.1	Deformed particle

[a]Based on total amount of seed and monomer 70 °C, 120 rpm, feeding time : 6 h.

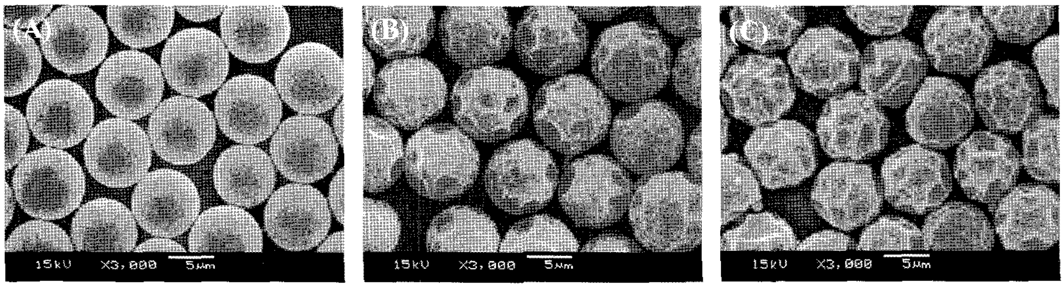

Figure 6. SEM photographs of cross-linked PMMA particles prepared at different seed/MMA weight ratios [(A) 100/0 & 7 wt% DVB, (B) 100/0 & 8 wt%, (C) 100/33 & 7 wt%].

surface occurred due to high DVB concentration causing phase separation [Figure 6(B)]. For the samples with 100/33 and 100/100 ratios at 6 wt% DVB, the secondary particles and deformation were not observed. On the other hand, at 7 wt% DVB deformation of particle surface was occurred [Figure 6(C)]. With further increase of DVB concentration, the formation of secondary particle and coagulation was observed.

Seeded Multi-Semi-continuous Process. To prepare highly cross-linked particles without deformation, Winnik[25] and co-worker reported that by multi-addition method of EGDMA at the end of the nucleation stage, monodisperse PS particles containing 6 wt% EGDMA could be obtained. In our previous report,[28] we could produce monodisperse PMMA particles containing up to 7 wt% EGDMA by seeded multi-batch process. In this study, we tried to prepare highly cross-linked PMMA particle by seeded multi-semi-continuous process as follows.

Two-Step Addition in Seeded Multi-Semi-continuous Process. Figure 7 shows the schematic diagram of preparation of cross-linked PMMA particles by two-step addition of EGDMA in seeded multi-addition process. At 70 °C, a first aliquot of EGDMA with concentration in the range of 1~2 wt% was added at one time into the reaction, and after 6 h, a second aliquot of 5~7 wt% EGDMA was added continuously for 6 h. Then, the reaction was continued for 12 h. Table VII and Figure 8 show the particle size, size distribution and morphology of particles prepared by two-step addition method. In case of addition of 1 wt % EGDMA and MMA to the first step, easy infiltration of MMA was achieved due to low concentration of cross-linker, and monodisperse particles with 6.5 μm diameter were prepared. After 6 h reaction, 6 wt% of EGDMA was added continuously for 6 h as the second step, monodisperse, smooth surface, cross-linked particles were obtained [Figure 8(A)]. On the other hand, when the concentration of EGDMA was

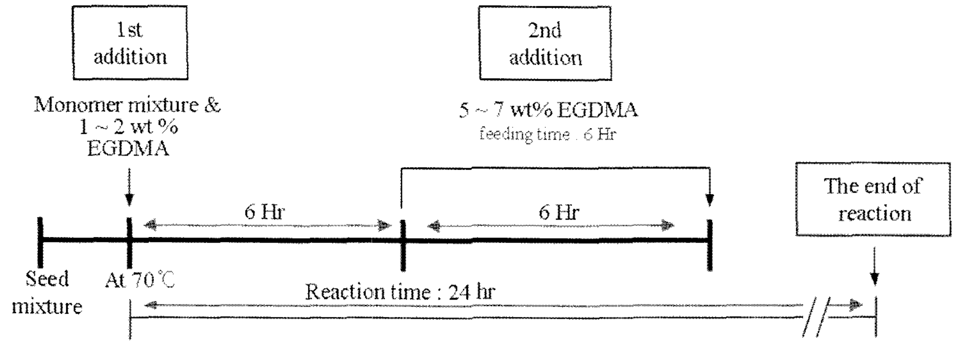

Figure 7. Schematic diagram of seeded multi-addition process.

Table VII. Seeded Multi-Addition Process

	EGDMA (wt%)[a]		$\overline{D}_n(\mu m)$	PSD	Particle Shape
	1st Addition	2nd Addition			
A	1	6	6.5	1.05	Monodisperse & smooth surface particle
B	1	7	6.8	1.08	Wrinkled surface particle
C	2	5	6.7	1.1	Knobbly particle & new nucleatedsmall particle
D	2	6	6.5	1.12	

[a]Based on total amount of seed and monomer 70 °C, 24 h, 120 rpm.

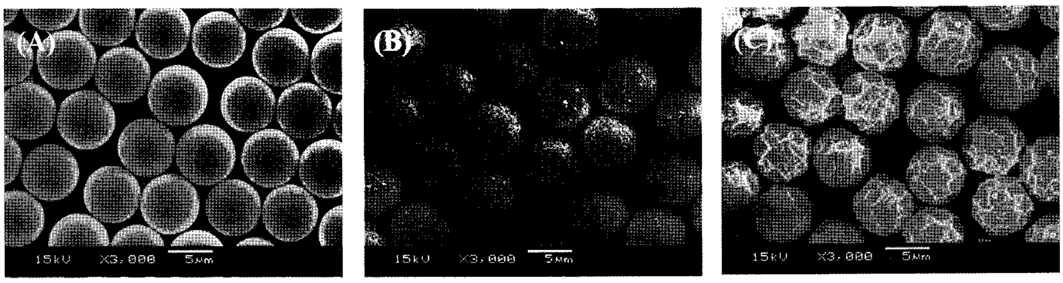

Figure 8. Scanning electron micrographs of cross-linked PMMA particles prepared by seeded multi-addition process [(A) 1→6 wt%, (B) 1→7 wt%, (C) 2→5 wt% EGDMA].

increased to 7 wt% in second aliquot, EGDMA was not sufficiently infiltrated inside the particle due to high cross-link density on the particle surface, and deformation of particle and formation of small secondary particle were observed [Figure 8(B)]. When 2 wt% EGDMA was added to the reaction at first aliquot, deformation of the particles was observed due to the high cross-link density, resulting in occurrence of phase separation [Figure 8(C)]. Consequently, for 1→6 wt% EGDMA, monodisperse, smooth surface particles were prepared and thereby 1 wt% of EGDMA at first aliquot is found to be the most suitable.

Figure 9 shows schematic diagram of preparation of cross-linked PMMA particles by two-step addition of EGDMA by seeded multi-semi-continuous process. At 70 °C, a first aliquot of EGDMA in the range of 1~2 wt% was each added from 1 to 6 h to the reaction and MMA mixture was added continuously over 6 h at the same time, then a second aliquot of EGDMA with concentration in the range 5~7 wt% was added continuously over 6 h to the reaction, and reaction was continued for 12 h. Table VIII and Figure 10 show the particle size, size distribution and morphology of particles prepared by this method. When the first aliquot of EGDMA is 1 wt% and second aliquot of EGDMA is 6 wt %, monodisperse and smooth particles were obtained for all feeding time range. However, in case of 1→7 wt% EGDMA, when the first aliquot was added for less than 3 h and then the second aliquot was added for 6 h, wrinkles on the particle surface were observed after the end of the reaction

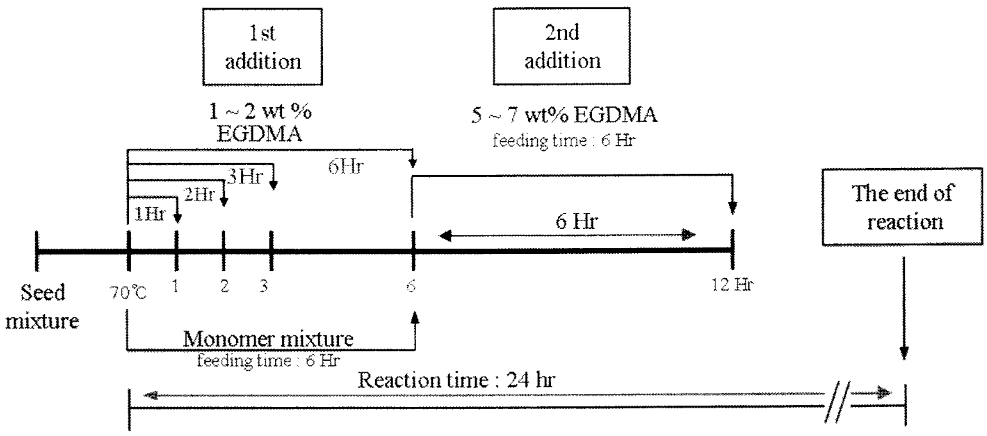

Figure 9. Schematic diagram of seeded multi-semi-continuous process.

Table VIII. Seeded Multi-Semi-continuous Process

	EGDMA (wt%)[a]		$\overline{D}_n(\mu m)$	PDI	Particle Shape
	1st Addition(feeding time (h))	2nd Addition(feeding time (h))			
A	1 (1~2)	6 (6)	6.5	1.07	Monodisperse & smoothsurface particle
B	1 (2)	7(6)	Broad		wrinkled surface & newnucleated small particle
C	1 (3)		6.8	1.05	Monodisperse & smoothsurface particle
D	2 (3)	5 (6)	Broad		Knobbly particle & new nucleated small particle
E	2 (6)	6 (6)	Broad		Deformed particle & Coagulum

[a]Based on total amount of seed and monomer 70 °C, 24 h, 120 rpm.

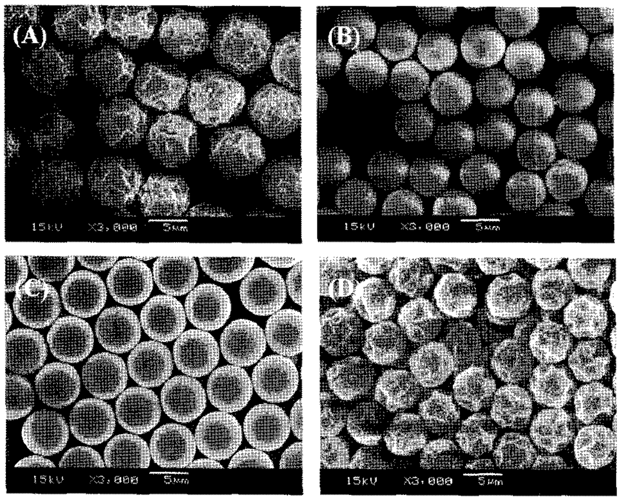

Figure 10. Scanning electron micrographs of cross-linked PMMA particles prepared by two times addition in multi-semi-continuous process [(A) 1(1)→7(6) wt%, (B) 1(2)→7(6) wt%, (C) 1(3)→7(6) wt%, (D) 2(6)→6(6) wt% of EGDMA].

[Figures 10(A) and (B)]. However, when the first aliquot was added for more than 3 h, monodisperse smooth surface particles were obtained [Figure 10(C)]. On the other hand, if EGDMA concentration is 2→5 wt%, particles were deformed over all the range of feeding time, and for 2→6 wt% EGDMA, wrinkle and coagulation of the secondary small particles were formed [Figure 10(D)].

Alternative Addition in Seeded Multi-Semi-continuous Process. We also tried to make more highly cross-linked and spherical particles by alternate semi-continuous-addition of MMA and EGDMA into the reaction as shown in Figure 11. At the second stage of reaction, 10~20 wt% of thw MMA mixture was added continuously for 2 h to the reaction as for the first step, and then 1 wt% of EGDMA was added continuously over 1 h at the second step, and this process was repeated until all MMA and EGDMA were consumed. To minimize the accumulation of unreacted monomer, the reaction time was extended for 48 h, and the initiator was mixed with each aliquots of MMA and EGDMA before it was added into the reaction. Most of the polymerization carried out in this study showed more than 95 wt% conversion.

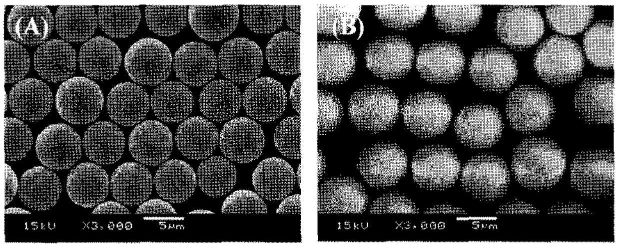

Figure 12. Scanning electron micrographs of cross-linked PMMA particles prepared at alternative addition in multi-semi-continuous process [(A) 8 wt% and (B) 9 wt% EGDMA].

Figure 12 shows SEM micrographs of the cross-linked PMMA particles prepared by alternative semi-continuous-addition process. The particles with 8 wt% EGDMA [Figure 12(A)] are monodisperse and have smooth surface indicating more uniform cross-link structure throughout the particles. However at higher EGDMA concentration (9 wt%), the particles are wrinkled on the surface [Figure 12(B)].

Conclusions

This study describes the preparation of highly cross-linked, monodisperse PMMA particles by various seeded semi-continuous dispersion polymerization processes using the PMMA seed particles after nucleation stage. Various semi-continuous processes such as semi-continuous, seeded semi-continuous, seeded multi-semi-continuous process and various polymerization reaction parameters such as methanol/water ratio, concentrations of DVB, polymerization temperature, seed/MMA ratio are reported. Smooth surface particles containing 7 wt% DVB was able to obtain for more than 9 h feeding time. Furthermore by decreasing the polymerization temperature to 60~65 °C and increasing feeding time to more than 12 h, monodisperse particles with smooth surface could be formed for 8 wt% of DVB. In addition, the smooth surface particles containing up to 8 wt% of EGDMA could be prepared by two-step semi-continuous-addition process and alternative addition process. In our previous report,

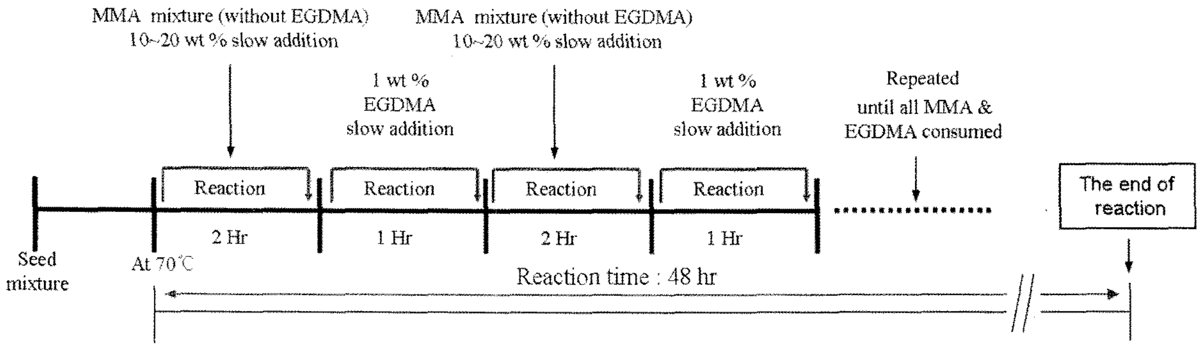

Figure 11. Schematic diagram of alternative addition in seeded multi-semi-continuous process.

monodisperse smooth surface particles containing up to 5 wt% of DVB could be prepared by seeded batch process.[28] Consequently, we conclude that seeded semi-continuous process is more effective and versatile to prepare highly cross-linked monodisperse PMMA particles than non-seeded and seeded batch processes due to gradual infiltration of cross-linker and MMA into the PMMA seed particles.

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References

(1) J. Uglestad, A. Berg, T. Ellingsen, R. Schmid, T. N. Nilsen, P. C. Mork, P. Stenstad, E. Horns, and O. Olsvik, *Prog. Polym. Sci.*, **17**, 87 (1992).
(2) E. D. Sudol, in *Polymeric dispersions: principles and applications*, J. M. Asua, Ed., Kluwer, Doedrecht, 1997, pp 375.
(3) C. Pichot, T. Delair, and A. Elaissari, in *Polymeric dispersions: principles and applications*, J. M. Asua, Ed., Kluwer, Dordrecht, 1997, pp 515.
(4) S. Arnold, C. T. Liu, and W. B. Whitten, *Opt. Lett.*, **16**, 420 (1991).
(5) M. Hattori, E. D. Sudol, and M. S. El-asser, *J. Appl. Polym. Sci.*, **50**, 2027 (1993).
(6) B. Thomson, A. Rudin, and G. Lajoie, *J. Polym. Sci.*; *Part A: Polym. Chem.*, **33**, 345 (1995).
(7) S. W. Hong, K. H. Kim, and J. Huh, *Macromol. Res.*, **13**, 397 (2005).
(8) M. Mahkam, M. Assadi, and R. Mohammadzadeh, *Macromol. Res.*, **14**, 34 (2006).
(9) J. Y. Kwon and H. D. Kim, *Macromol. Res.*, **14**, 373 (2006).
(10) E. B. Branford and J. W. Vanderhoff, *J. Appl. Phys.*, **26**, 684 (1995).
(11) J. Ugelstad, K. H. Kaggerud, F. K. Hansen, and A. Berge, *Makromol. Chem.*, **180**, 737 (1979).
(12) Y. Almog, S. Reich, and M. Levy, *Br. Polym. J.*, **14**, 131 (1982).
(13) A. Tuncel, R. Kahraman, and E. Piskin, *J. Appl. Polym. Sci.*, **50**, 303 (1993).
(14) K. P. Lok and C. K. Ober, *Can J. Chem.*, **63**, 209 (1985).
(15) C. K. Ober and H. L. Hair, *J. Polym. Sci.; Part A: Polym. Chem.*, **25**, 1395 (1987).
(16) C. K. Ober and K. P. Lok, *Macromolecules*, **20**, 268 (1987).
(17) A. J. Paine, *J. Polym. Sci., Polym. Chem. Ed.*, **28**, 2485 (1990).
(18) S. Shen, E. D. Sudal, and M. S. El-Aasser, *J. Polym. Sci.*; *Polym. Chem. Ed.*, **31**, 1393 (1993).
(19) S. Shen, E. D. Sudol, and M. S. El-Aasser, *J. Polym. Sci.*; *Part A: Polym. Chem.*, **32**, 1087 (1994).
(20) R. Hu, V. L. Dimonie, E. D. Sudal, and M. S. El-Aasser, *J. Appl. Polym. Sci.*, **55**, 1411 (1995).
(21) J. M. Saenz and J. M. Asua, *J. Polym. Sci., Polym. Chem. Ed.*, **33**, 1511 (1995).
(22) D. Horak, F. Svec, and J. M. J. Frechet, *J. Polym. Sci.*, *Polym. Chem. Ed.*, **33**, 2329 (1995).
(23) C. M. Tseng, Y. Y. Lu, M. S. El-Aasser, and J. W. Vanderhoff, *J. Polym. Sci.*, *Polym. Chem. Ed.*, **24**, 2985 (1986).
(24) W. H. Li and H. D. H. Stover, *J. Polym Sci.*; *Part A: Polym. Chem.*, **36**, 1543 (1998).
(25) J. S. Song and M. A. Winnik, *Macromolecules*, **38**, 8300 (2005).
(26) H. T. Zhang, J. X. Huang, and B. B. Jiang, *J. Appl. Polym. Sci.*, **85**, 2230 (2002).
(27) J. Choi and S. Y. Kwak, *J. Polym Sci.*; *Part A: Polym. Chem.*, **40**, 4368 (2002).
(28) K. C. Lee and S. Y. Lee, *Macromol. Res.*, **15**, 244 (2007).
(29) J. W. Kim and K. D. Suh, *Colloid Polym. Sci.*, **276**, 870 (1998).
(30) M. Okubo, *J. Appl. Polym. Sci.*, **83**, 2013 (2002).
(31) D. G. Yu and J. H. An, *Macromolecules*, **38**, 7485 (2005).