

Preparation of Highly Cross-linked, Monodisperse Poly(methyl methacrylate) Microspheres by Dispersion Polymerization; Part I. Batch Processes

Ki-Chang Lee* and Sang-Yun Lee

Department of Polymer Sci. & Eng., Engineering Research Institute, Gyeongsang National University, Jinju 660-701, Korea

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Abstract: Nucleation is the most sensitive stage in the preparation of highly cross-linked, monodisperse microspheres by dispersion polymerization, since the addition of a small amount of cross-linker results in particle deformation and coagulation. To overcome these problems, 5 μm poly(methyl methacrylate) seed particles prepared by dispersion polymerization were used in the preparation of monodisperse, cross-linked PMMA particles containing up to 7 wt% divinylbenzene by seeded batch dispersion polymerization. Spherical particles with a narrow size distribution containing up to 8 wt% of EGDMA were prepared by seeded multi-batch dispersion polymerization processes. These particles were identified by scanning electron microscopy and DSC.

Keywords: cross-linked particle, dispersion polymerization, seeded batch process, MMA.

Introduction

Micron-sized monodisperse polymer particles are used in a wide variety of scientific and technological applications with high-value-added materials, such as separation media, ion-exchangers, support materials, toners, coatings, calibration standards, biomedical and clinical examinations, catalyst carriers, information storage materials.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, etc.⁵⁻⁹ Micron-sized uniform particles can be made by the successive seeded emulsion polymerization developed by Vanderhoff¹⁰ 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 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. Tseng and co-worker²⁵ described in their experiment that small

amount of divinylbenzene (DVB) was mixed with styrene for dispersion polymerization. When the amount of DVB is 0.3 wt% based on the total monomer, the particle size has changed and the size distribution was significantly broadened. However, with further increases in DVB concentration, coagulation was observed. Shen *et al.*¹⁸ reported that cross-linked poly(methyl methacrylate) (PMMA) particle was prepared by dispersion polymerization with ethylene glycol dimethacrylate (EGDMA). It was stated in his work that 0.3 wt% EGDMA concentration gave partial flocculation of the dispersion and the total flocculation was observed at 0.6 wt%. Recently, many studies on how to overcome flocculation and deformation of cross-linking dispersion polymerization have been extensively reported. Generally, the cross-linking agent interfere with the sensitive particle nucleation step causing flocculation and deformation.^{5,18,27} The immobilization of steric stabilizer due to cross-linking agent causes instability of the polymerization.⁶ In addition, the cross-link formation decreases the monomer swelling into particle. In the work of Thomson *et al.*⁶ it was reported that monodisperse particles could be possibly obtained with small amount of DVB in the initial charge. However larger amounts could be incorporated only by incremental addition of DVB 7 h after the start of the polymerization. Winnik²⁵ and co-worker discovered that addition of DVB or EGDMA at the end of the nucleation stage, cross-linked monodisperse particles could be obtained. Also, many researchers tried to overcome the problem due to the presence of cross-linker by long time addition method^{6,25,26} and addition of swelling agent method.^{27,28} Although a large number of studies

*Corresponding Author. E-mail: kcleee@gsnu.ac.kr

have been reported on the cross-linked polystyrene by dispersion polymerization, little is known about cross-linked PMMA.

This study focuses on the dispersion polymerization using the PMMA seed particle after nucleation stage. We examined the effect of cross-linker concentration and methanol/water ratio as polymerization media, reaction temperature and seed/monomer ratio at second stage on the particle swelling and the final particle morphology. In addition, the highly cross-linked, monodisperse and smooth surface PMMA particles polymerized using different processes such as batch, seeded batch, seeded multi-batch process are reported.

Experimental

Materials. Methyl methacrylate (MMA, Junsei) was washed with 10 wt% aqueous sodium hydroxide solution to remove 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) was purified by recrystallization in methanol. All other materials were used without further purification, including methanol (MeOH, Daejung chemical), and poly(vinyl pyrrolidone) (PVP K-30, Junsei).

Preparation of PMMA Seed. The standard recipe used in the preparation of PMMA seed particle is given in Table I. All ingredients were weighed and mixed in 2 oz glass bottle, and then purged with nitrogen, capped, and sealed. The bottles were then placed in a shaker operating at 120 cycle/min in a constant temperature water bath at 55 °C for 48 h.

Seeded Batch Dispersion Polymerization Process. The standard recipe for preparation of cross-linked PMMA particle by seeded batch dispersion polymerization is listed in Table II. The following procedure was used: 12.9 g of methanol and 11 g of water were mixed and then blended with PMMA seed mixture, which was previously prepared in the first stage. The reaction media was adjusted to MeOH/Water ratio of 7 : 3. Then 1.5 g of MMA, 0.015 g AIBN, DVB (0-100 wt%, based on total amount of seed and monomer) were mixed with PMMA seed mixture in 2 oz glass bottle, purged with nitrogen, capped, and sealed. The bottle was then placed in a shaker operating at 120 cycle/min in a

Table I. Preparation of PMMA Seed*

Ingredients	wt (%)	Amount (g)
MMA	10	1.5
MeOH	85.9	12.9
PVP K-30	4	0.6
AIBN	0.1	0.015
Total	100	15.015

*Polymerization condition: 55 °C, 120 cycle/min for 48 h.

Table II. Standard Recipe for Seeded Batch Process & Seeded Multi-batch Process (Amounts in Grams)

Ingredients	Seeded Batch Process ^d		Seeded Multi-batch Process ^e	
	1st stage	2nd stage	1st stage	2nd stage
MMA	1.5	1.5	3	3
MeOH	12.9	12.9 ^a	25.8	25.8 ^a
H ₂ O	·	11 ^a	·	22 ^a
PVP K-30	0.6	·	1.2	·
DVB	·	0-100 ^b	·	0-9 ^c
AIBN	0.015	0.015	0.03	0.03

^aMeOH/Water = 7/3. ^bwt% based on total amount of seed & monomer. ^cEGDMA. ^d55-70 °C, 120 cycle/min for 24-48 h. ^e70 °C, 120 rpm for 24-48 h.

constant temperature water bath at 70 °C for 24 h at second stage.

Seeded Multi-batch Dispersion Polymerization Process. The recipe in Table II was used in the preparation of cross-linked PMMA particle by seeded multi-batch dispersion polymerization. All the ingredients (except for EGDMA and 10 wt% MeOH) 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 then gradually raised temperature. When the temperature reaches at 70 °C, a first aliquot of EGDMA (1 wt% based on total amount of seed and MMA, dissolved in MeOH) was added in the mixture. After 5 h, a second aliquot of 5 wt% of EGDMA was added to the reaction and continue the reaction for 19 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 taken 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 at room temperature overnight. The sample was sputter-coated with gold, and examine at 15 kV. The particle size of the latexes was measured with photographs and the particle size distribution (PSD) were determined the ratio of the number (\overline{D}_n) and Weight (\overline{D}_w) average diameters as follows:

$$\overline{D}_n = \frac{\sum_{i=0}^N D_i}{N} \quad (1)$$

$$\overline{D}_w = \frac{\sum_{i=0}^N D_i^4}{\sum_{i=0}^N D_i^3} \quad (2)$$

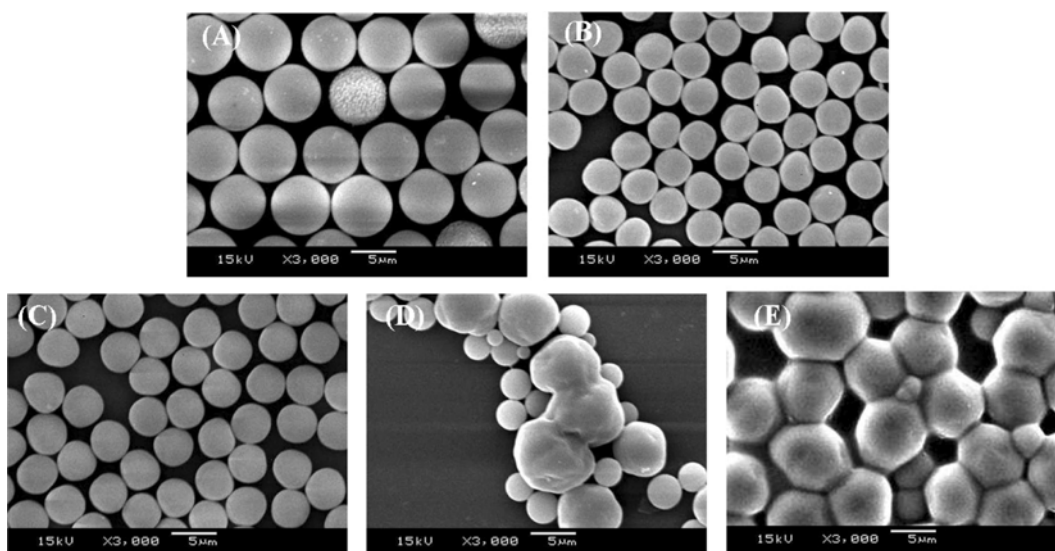


Figure 1. Scanning electron micrographs of cross-linked PMMA particles prepared with four different DVB concentrations ((A) 0 wt%, (B) 0.05 wt%, (C) 0.1 wt%, (D) 0.15 wt%, (E) 0.35 wt%).

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

$$PSD = \frac{\overline{D_w}}{\overline{D_n}} \quad (3)$$

The glass-transition temperatures (T_g) of the cross-linked PMMA particles were measured with a differential scanning calorimeter (DSC, TA Q-10, TA Instrument) at a heating rate 10 °C/min, from -50 to 200 °C.

Results and Discussion

Dispersion Polymerization by Batch Process. To determine the effect of DVB concentration on PMMA particles prepared by batch dispersion polymerization, SEM morphology was taken. Figure 1 shows SEM micrographs of particle with four different DVB concentrations. For the reactions with 0 wt% of DVB/monomer swelling is sufficient with 5 μ m diameter, monodisperse and smooth surface particle was obtained (Figure 1(A)). On the other hand, when a very small amount of DVB (0.05 to 0.1 wt%) was present in the initial charge, the nuclei of cross-linked structure was obtained but the particle was no longer spherical (Figures 1(B) and 1(C)). Particle deformation was occurred due to the monomer swelling from the localized cross-link density.²⁰ As the DVB concentration increases, coagulation occurred in the dispersion (Figure 1(D)) due to immobilization and lost of stability on the particle surface. Further increase in DVB concentration to 0.35% resulted in flocculation of the almost dispersion (Figure 1(E)). These results explained that dispersion polymerization is very sensitive to the change of reaction elements which influences the particle number, size, size distribution, and morphology.⁶ This

phenomenon occurred in the presence of cross-linking agent that refrain the swelling of monomer, thereby coagulation occurred due to nucleation of cross-linked structure.²³

In case of copolymerization of MMA and DVB, the particle nucleation was interfered by DVB since it is more reactive than MMA. In addition, when the DVB concentration increases, the immobilization of PVP as steric stabilizer was occurred, because the reaction irreversibly links the PVP-PMMA chain to the bulk particle PMMA-DVB phase.⁶

Dispersion Polymerization by Seeded Batch Process.

To prevent coagulation and particle deformation with addition of cross-linker after nucleation stage, seeded batch process of dispersion polymerization was carried out. Figure 2 shows SEM micrographs of PMMA seed particle according to the recipe shown in Table I. It was found to be monodis-

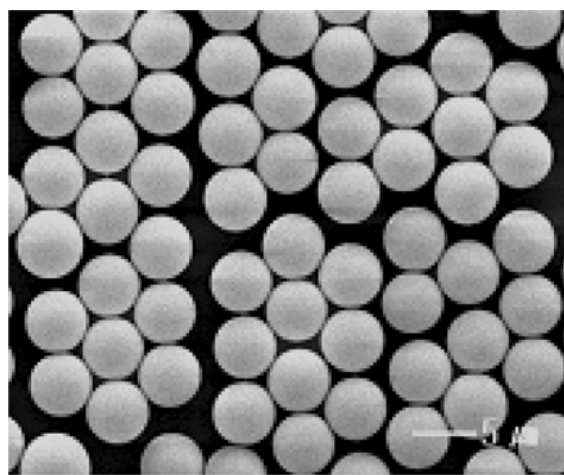


Figure 2. Scanning electron micrograph of PMMA seed particle.

perse particle with 5 μm diameter, greater than 97-98% conversion with negligible coagulum.

Effect of MeOH/Water Ratio. Table III and Figure 3 show the particle size, size distribution, and morphology prepared by seeded batch dispersion polymerization process with four different media ratio and 3-6 wt% of DVB concentration. When the polymerization media ratio of MeOH/water is 100/0, monodisperse and smooth surface particles

were obtained in 3 wt% DVB (Figure 3(A)) and, the generation of secondary small particle was found in 4-6 wt% DVB, as shown in Figure 3(B) and Figure 3(F). On the other hand, when the MeOH/water is from 70/30 to 60/40, monodisperse and clean particle was achieved with less than 5 wt% of DVB (Figures 3(C) and 3(D)), and the deformation was occurred with more than 5 wt% of DVB (Figures 3(G) and 3(H)). When the ratio of MeOH/water is 50/

Table III. Effect of MeOH/Water Ratio*

	MeOH/Water	DVB (%) ^a	\overline{D}_n (μm)	PDI	Particle Shape
A	100/0	3	6.1	1.04	Monodisperse & smooth surface particle
		4-5	6.3	1.05	Secondary nucleated small particle
		6	Broad		Coagulum & secondary nucleated small particle
B	70/30	0-5	6.2	1.08	Monodisperse & smooth surface particle
		6	5.9	1.2	Severely deformed particle
C	60/40	0-5	6.3	1.1	Monodisperse & smooth surface particle
		6	5.9	1.2	dented particle
D	50/50	0-6	Broad		Coagulum & secondary nucleated small particle

*70 °C, 24 h, 120 cycle/min. ^aBased on total amount of seed and monomer.

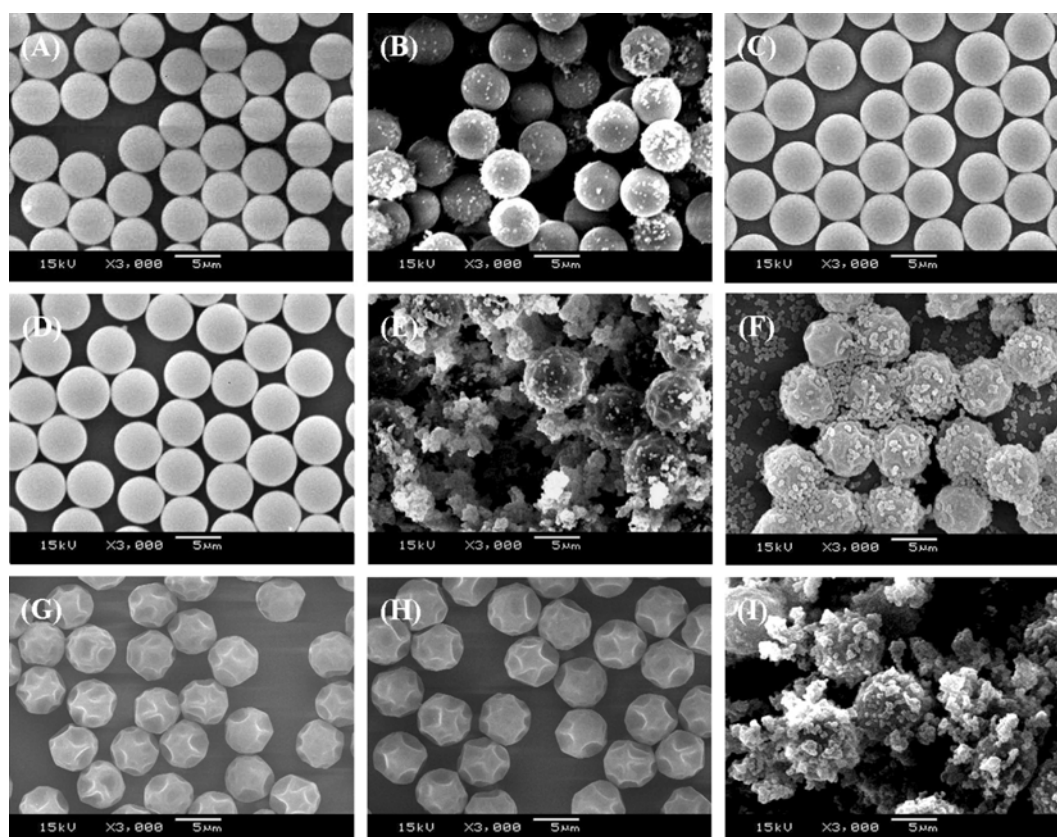


Figure 3. Scanning electron micrographs of cross-linked PMMA particles prepared with four different MeOH/water ratios by seeded batch dispersion polymerization ((A) MeOH/water : 100/0 & DVB 3 wt%, (B) 100/0 & 4 wt%, (C) 70/30 & 5 wt%, (D) 60/40 & 5 wt%, (E) 50/50 & 5 wt%, (F) 100/0 & DVB 6 wt%, (G) 70/30 & 6 wt%, (H) 60/40 & 6 wt%, (I) 50/50 & 6 wt%).

50, the coagulation was occurred without DVB concentration due to phase separation of between MMA and polymerization media (Figures 3(E) and 3(I)).

Generally, the swelling rate of monomer increases as the polarity of polymerization media increases.^{13,28,29,31} Consequently, we predicted that as the water ratio increases, DVB diffusion of the particle is quite easy and have more uniform particle inside cross-link structure. However, when the ratio is 100/0, DVB could not infiltrate sufficiently inside the particle thereby swelling of MMA was refrained and small secondary particles was formed due to highly cross-link density, which is generated at the surface of the particle. On the other hand, the ratio of 70/30 and 60/40, the infiltration of DVB is quite easy due to the increase of polarity of the polymerization media. Cross-linked and monodisperse particles are achieved without generation of secondary small particles.

Effect of DVB Concentration. Table IV and Figure 4 show the particle size, size distribution, and morphology prepared by seeded batch dispersion polymerization process with six different DVB concentrations. It was observed that when the amount of DVB is 5 wt% based on the total amount

of seed and monomer, monodisperse and smooth surface particle was obtained due to infiltration of MMA to surface of the particles (Figure 4(B)). However, when the concentration of DVB is more than 5 wt%, particle deformation was occurred because MMA could not infiltrate inside the particle sufficiently due to highly cross-link density of the particle surface. As shown in Figure 4(C) with 5.5 wt% of DVB, the cross-link structure is very dense and the infiltration of MMA is refrained thereby the deformation of the particle was observed due to the stress occurrence from the divergence of cross-link density in the particle.³⁰ With further increase the DVB concentration to 8 wt%, secondary small particle was generated (see Figure 4(D)). The polymerizations carried out in this study showed greater than 95 wt% conversion.

The glass transition temperatures (T_g) of the polymer prepared with varying amounts of DVB measured by DSC is shown in Figure 5. It can be seen in Table IV that T_g increases from 104 to 134°C with increasing up to 8 wt% of DVB content. However, with more than 8 wt% T_g did not show any increase at all. This result is also observed by other researcher.⁵

Table IV. Effect of DVB Concentration*

	DVB (%) ^a	T_g (°C)	\bar{D}_n (μm)	PDI	Particle Shape
A	0	104	6.5	1.07	Spherical particle
B	5	123	6.3	1.12	Spherical particle
C	5.5	132	6.3	1.13	Knobbly particle
D	8	134	Broad		Nucleated small article
E	20	-	Broad		Coagulum & secondary nucleated small particle
F	100	-	Broad		Coagulation

*70°C, 24 h, 120 cycle/min. ^aBased on total amount of seed and monomer.

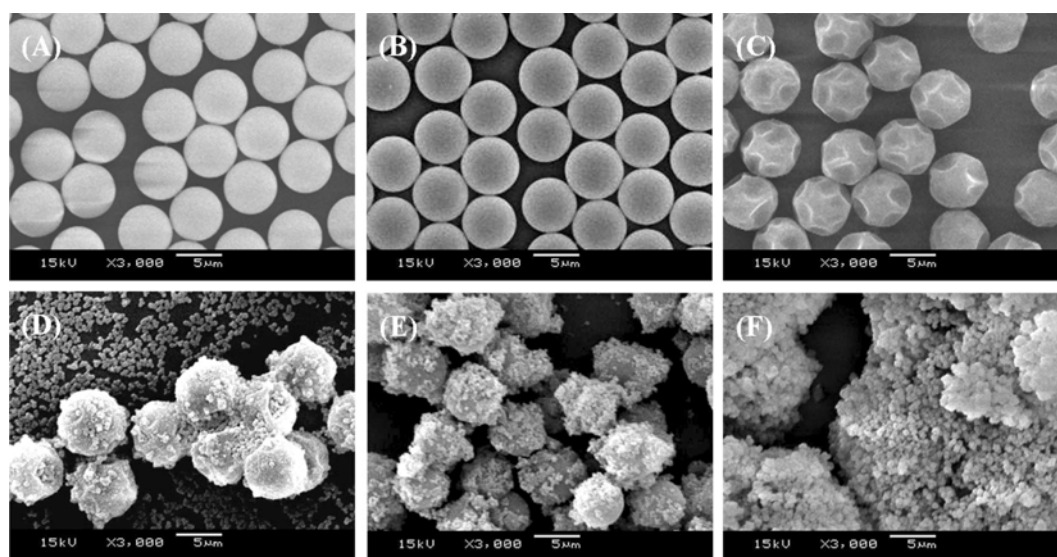


Figure 4. Scanning electron micrographs of cross-linked PMMA particles prepared with six different DVB concentrations by seeded batch dispersion polymerization ((A) 0 wt%, (B) 5 wt%, (C) 5.5 wt%, (D) 8 wt%, (E) 20 wt%, (F) 100 wt% of DVB).

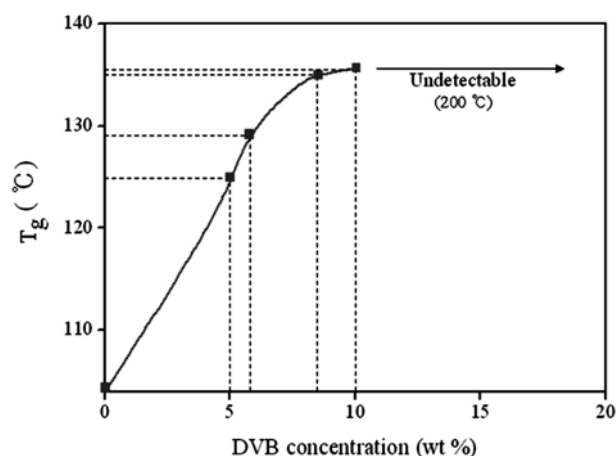


Figure 5. Graph of DVB concentration vs transition temperature.

Effect of Polymerization Temperature. Table V and Figure 6 show the particle size, size distribution and morphology prepared by seeded batch dispersion polymerization process with four different polymerization temperature and under 5-8 wt% of DVB concentration range. When polymerization temperature is between 55-60°C, monodisperse and smooth surface particle was obtained with less than 7 wt% of DVB (Figures 6(A-B), 6(E-F)). However, when the concentration of DVB is 8 wt%, the deformation was not occurred at 55°C (Figure 6(I)), however it was observed at 60°C (Figure 6(J)). On the other hand, at temperature between when 65-70°C, monodisperse and smooth surface particles were obtained for sample with less than 5 wt% of DVB, but at higher content DVB, the deformation was occurred (Figure 6(C-D), Figure 6(G-H)). Further increase to 8 wt% of DVB, the secondary small particle and coagulation were obtained (Figures 6(K) and 6(L)).

Generally, the reactivity of DVB increases as the temperature increases. In this study, the deformation of the particle was observed as polymerization temperature increase due to highly cross-link density on the particle surface. The phase separation was occurred due to divergence of the cross-link density. As mentioned earlier that MMA at lower temperature (less than 60°C) can easily infiltrate inside the particle due to more uniform cross-link density, monodisperse, smooth surface particle was prepared without deformation at higher DVB content (7 wt% of DVB).

Effect of Seed/MMA Ratio. Table VI and Figure 7 show the particle size, size distribution, and morphology prepared by seeded batch dispersion polymerization process with four different seed/MMA ratios and 6-8 wt% of DVB concentration range. In case of addition of less than 7 wt% of DVB without MMA at second stage, monodisperse and smooth surface particle was obtained (Figure 7(A) and 7(E)), with higher DVB content (8 wt% DVB), the wrinkle on the particle surface was observed (Figure 7(F)). When seed/MMA ratio is between 100/33-100/100 and with more than 6 wt% of DVB, the particle deformation was occurred (Figure 7(B)). With further increase in concentration of DVB to more than 8 wt%, nucleation of secondary small particle and coagulation were occurred (Figure 7(G) and 7(H)). However, when seed/MMA ratio is 100/150, the nucleation of secondary small particle and flocculation was observed with all of DVB range (Figures 7(D) and 7(I)).

When seed/MMA ratio is 100/0 with less than 7 wt% of DVB, uniform and smooth surface particle can be prepared due to easily infiltration of cross-linker. However, when the concentration of DVB is 8 wt%, although infiltration of cross-linker is enough, the wrinkle on the particle surface was occurred by phase separation due to highly DVB concentration. Samples with ratio 100/33 and 100/100 with less

Table V. Effect of Polymerization Temperature*

	DVB (%) ^a	Temp. (°C)	\bar{D}_n (μm)	PDI	Particle Shape	
A	6	55	6.2	1.05	Monodisperse & smooth surface particle	
B		60	6.3	1.07		
C		65	6.4	1.13		
D		70	6.4	1.13		Deformed particle
E	7	55	6.3	1.05	Monodisperse & smooth surface particle	
F		60	6.3	1.06		
G		65	6.4	1.2		Deformed particle
H		70	6.5	1.2		Deformed sphere with many small nodes
I	8	55	6.3	1.2	Monodisperse & smooth surface particle	
J		60	6.4	1.05		Wrinkled particle
K		65		Broad		Dented particle & secondary nucleated small particle
L		70		Broad		

*48 h, 120 cycle/min. ^aBased on total amount of seed and monomer.

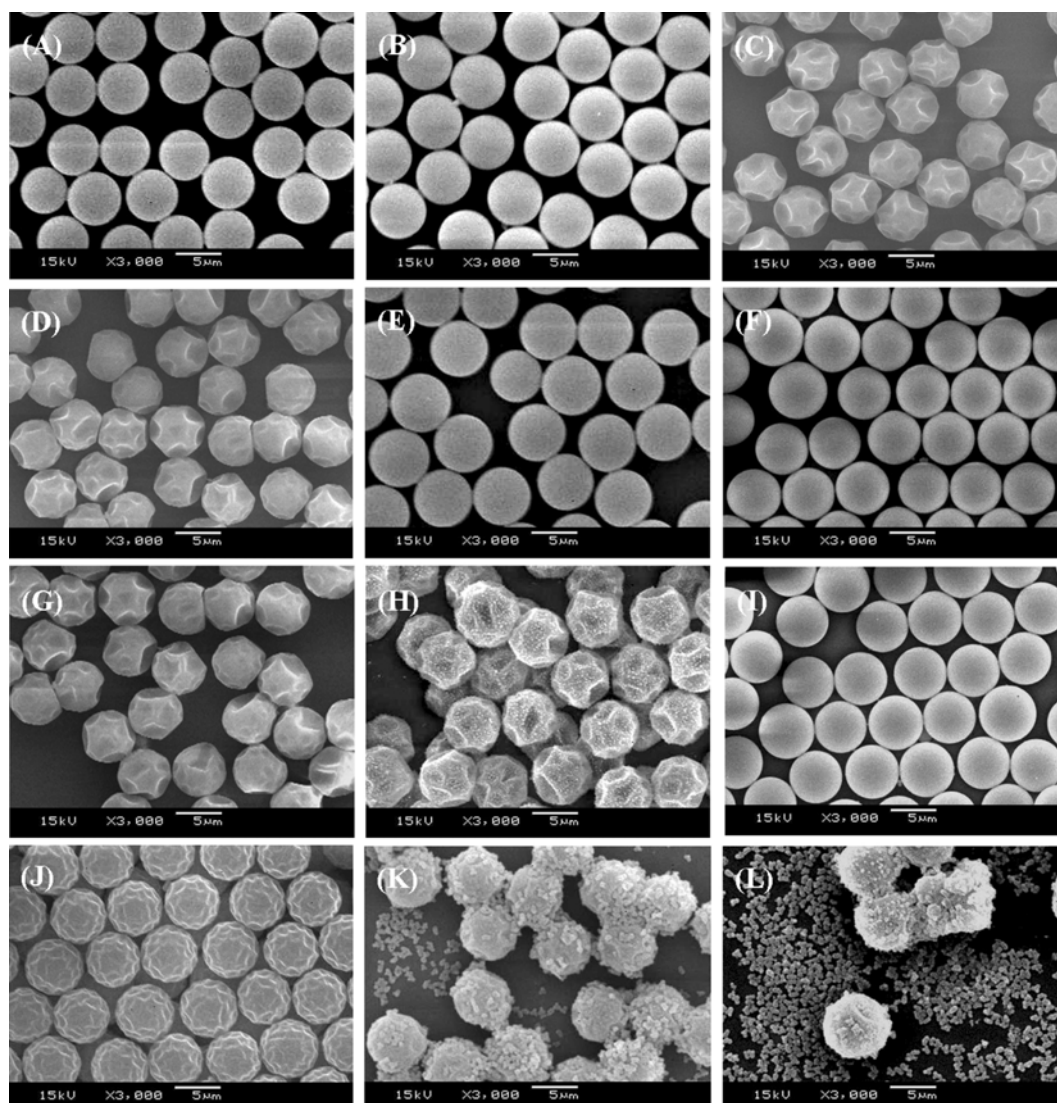


Figure 6. Scanning electron micrographs of cross-linked PMMA particles prepared with four different polymerization temperatures by seeded batch dispersion polymerization ((A) 55 °C, (B) 60 °C, (C) 65 °C, (D) 70 °C at 6 wt% of DVB. (E) 55 °C, (F) 60 °C, (G) 65 °C, (H) 70 °C at 7 wt% of DVB. (I) 55 °C, (J) 60 °C, (K) 65 °C, (L) 70 °C at 8 wt% of DVB).

than 5 wt% DVB although cross-link structure was formed and easily infiltration of MMA was achieved, however, the secondary particle and deformation were not observed. On other hand, higher content of DVB (for instance > 6 wt%), the DVB participated first in the reaction then infiltration of MMA was refrained due to highly cross-link density of the particle surface, and the remaining monomer in the polymerization media formed a secondary small particle. When 100/150, the infiltration of MMA cannot sufficiently performed due to highly concentration of MMA, thereby secondary small particle of PMMA was observed in polymerization media. These small secondary particles coagulated due to insufficient reaction of the steric stabilizer.

Dispersion Polymerization by Seeded Multi-batch Process. Another process we tried in the preparation of cross-

linked monodisperse particle by dispersion polymerization is by addition method of seed particles for multi-times at second stage and using EGDMA as cross-linker. Because of, compared with DVB, the reactivity of EGDMA is similar to MMA.^{32,33}

Two-Times Addition in Seeded Multi-batch Process.

Figure 8 is a schematic diagram of preparation of cross-linked PMMA particle by two-times addition of EGDMA in seeded multi-batch process. At temperature 70 °C, a first aliquot of EGDMA with concentration in the range of 1-3 wt% was added reaction, and a second aliquot of 5-6 wt% EGDMA was added to the reaction 5 h later. Then, the reaction was continued for 19 h. Table VII and Figure 9 show the particle size, size distribution, and morphology prepared by two times-addition method. In case of 1 → 5 wt% of

Table VI. Effect of Seed/Monomer Ratio*

	Seed/MMA (wt%)	DVB (%) ^a	\overline{D}_n (μm)	PDI	Particle Shape
A	100/0	6	5.2	1.05	Monodisperse & smooth surface particle
		7	5.3	1.07	
		8	5.3	1.15	Slightly Wrinkled particle
B	100/33	6	5.3	1.15	Deformed particle
		7	5.5	1.18	
		8	5.6	1.2	Knobbly particle & secondary nucleated particle
C	100/100	6	5.9	1.12	Deformed particle
		7	6.2	1.2	
		8	Broad		Dented particle & secondary nucleated particle
D	100/150	6			Coagulum & secondary nucleated particle
		7	Broad		
		8			

*70 °C, 24 h, 120 cycle/min. ^aBased on total amount of seed and monomer.

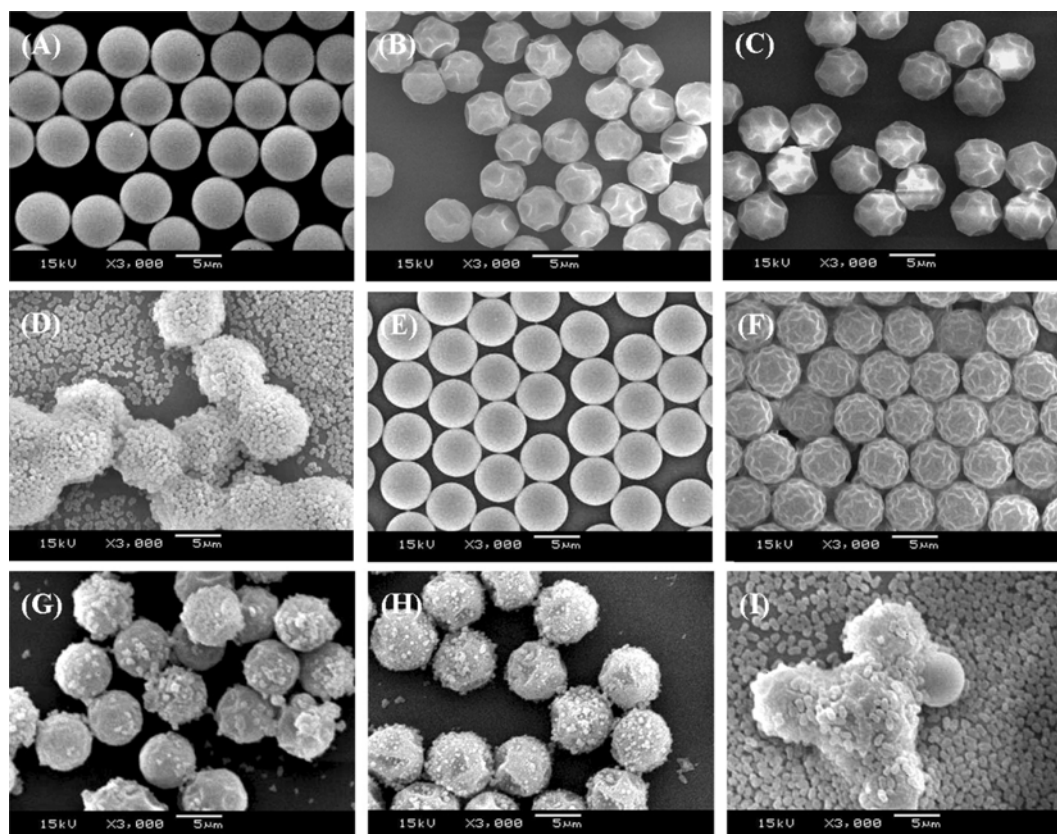


Figure 7. Scanning electron micrographs of cross-linked PMMA particles prepared with different seed/ MMA monomer ratios by seeded batch dispersion polymerization ((A) 100/0, (B) 100/33, (C) 100/100, (D) 100/150 at 6 wt% of DVB. (E) DVB 7 wt% & 100/0, (F) 8 wt% & 100/0, (G) 8 wt% & 100/33, (H) 8 wt% & 100/100, (I) 8 wt% & 100/150).

EGDMA, monodisperse, and smooth particle were obtained (Figure 9(A)), and when 1 → 6 wt% EGDMA was added, the wrinkle on the particle surface was observed (Figure

9(B)). With further addition from 2 → 5 wt% EGDMA, the deformation of particle was observed (Figure 9(C)), and for 3 → 5 wt% EGDMA, wrinkle and coagulation of the sec-

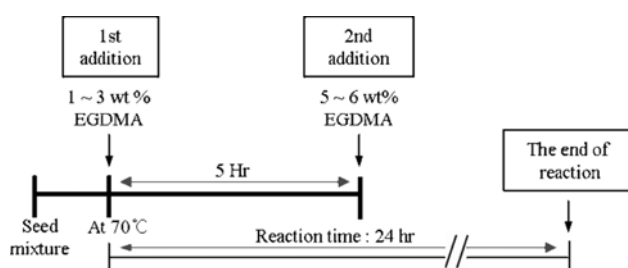


Figure 8. Schematic diagram of two-times addition in seeded multi-batch process.

ondary small particles were formed (Figure 9(D)).

In case of addition of 1 wt% EGDMA and MMA to the first step, easily infiltration of MMA was achieved due to low cross-link density, 6.5 μm diameter, monodisperse particles prepared. After 6 h reaction, 5 wt% of EGDMA was added to the reaction at the second step, monodisperse, smooth surface, cross-linked particle were obtained due to easily infiltration of EGDMA. On the other hand, if we increase the concentration to 6 wt% of EGDMA and added to the reaction at the second step, wrinkle of the particle surface was observed due to phase separation occurred. If 2 wt% EGDMA was added to the reaction at first step, the cross-link density of particle surface further increases, the second aliquot of infiltration of EGDMA was strained causing deformation of the particle. Due to highly cross-link density on the particle surface when 3 wt% EGDMA added to the reaction at the first step, the remaining monomer exists in the polymerization media is insufficient to infiltrate MMA. The coagulation and secondary small particles were observed due to increase of cross-link density on the particle surface when 5 wt% of EGDMA added to the reaction at the second step. Consequently, 1 \rightarrow 5 wt% EGDMA, monodisperse, smooth surface particle was prepared, and thereby 1 wt% of EGDMA at first step is the most suitable. The case of the seeded batch dispersion polymerization, monodisperse, smooth surface particles with 5 wt% of DVB were obtained. On the other hand, this method can be made at 6 wt% EGDMA. Therefore, multi-addition of cross-linker is suitable at second stage.

Three-Times Addition in Seeded Multi-batch Process.

Also, we tried to apply the three-times addition method of EGDMA to produce monodisperse particle with higher

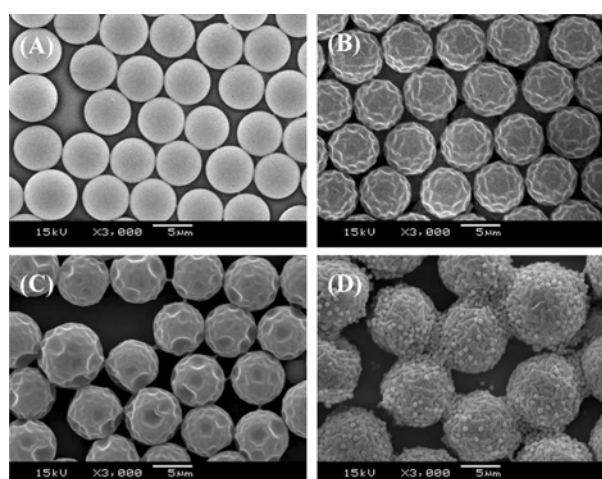


Figure 9. Scanning electron micrographs of cross-linked PMMA particles prepared at two-times addition in multi-batch process ((A) 1 \rightarrow 5 wt%, (B) 1 \rightarrow 6 wt%, (C) 2 \rightarrow 5 wt%, (D) 3 \rightarrow 5 wt% of EGDMA).

cross-linker concentration without particle deformation due to the formation of more uniform cross-link structure.

Figure 10 is schematic diagram of preparation of cross-linked PMMA particle by three-times addition of EGDMA in seeded multi-batch process. The first aliquot of 1-2 wt% EGDMA was added to the reaction at a temperature of 70°C, and then after 3 h, the second aliquot of EGDMA (1-2 wt%) was added, and then the last aliquot of EGDMA (4-5 wt%) was added after 6 h. The reaction was continued for 19 h. Table VIII and Figure 11 show the particle size, size distribution, and morphology prepared by three times-addition method. In case of 1 \rightarrow 1 \rightarrow 5 wt% of EGDMA, monodisperse and smooth particle were obtained (Figure 11(A)). However, when 1 \rightarrow 2 \rightarrow 5 wt% of EGDMA was added, the partial deformation on the particle surface was observed (Figure 11(B)). In the case of 2 \rightarrow 1 \rightarrow 4 wt% of EGDMA, the lava surface and secondary small particle were observed (Figure 11(C)).

If cross-linker of more than 2 wt% was added to the reaction at the first or second step, the infiltration of MMA was refrained due to the highly cross-link density on the particle surface, and when added in the third step, the particle deformation and secondary small particle were observed. This is

Table VII. Two-Times Addition in Seeded Multi-batch Process*

	EGDMA (wt%) ^a	\overline{D}_n (μm)	PDI	Particle Shape
A	1 \rightarrow 5	6.3	1.09	Monodisperse & smooth surface particle
B	1 \rightarrow 6	6.5	1.12	Wrinkled particle
C	2 \rightarrow 5	6.8	1.09	Slightly dimpled particle
D	3 \rightarrow 5	Broad		Heavily wrinkled surface & coagulum & secondary nucleated small particle

*70°C, 24 h, 120 rpm. ^aBased on total amount of seed and monomer.

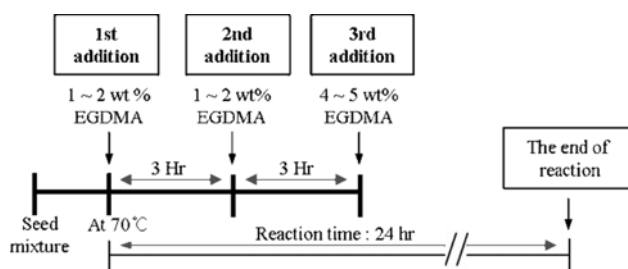


Figure 10. Schematic diagram of three time addition in seeded multi-batch process.

due to phase separation caused by the increase of cross-link density on the particle surface and the remaining monomer in the polymerization media. According to this phenomenon, it revealed that although the cross-link formation occurred due to the addition of 1 wt% of EGDMA at first or second step, the monodisperse, smooth surface particle can still be obtained because of easy infiltration of MMA. As a result, we were able to obtain spherical particles with a narrow size distribution at 7 wt% of EGDMA in three times-

addition process.

Alternative Addition in Seeded Multi-batch Process.

We tried to make more highly cross-linked and spherical particles by dividing and alternate addition of MMA and EGDMA into the reaction. Figure 12 is a schematic diagram of preparation of cross-linked PMMA particle by alternative addition of MMA and EGDMA in seeded multi-batch process. At the second stage of reaction, 1 wt% of MMA was added to the reaction and polymerized for 2 h as for first step, and then 1 wt% of EGDMA was added again and polymerized for 1 h at second step, this process was repeated until all MMA and EGDMA was consumed. To minimize the generation of remain monomer, the reaction time extended for 48 h, and the initiator was mixed with each MMA and EGDMA and was added into reaction. Most of the polymerizations carried out in this study showed greater than 95 wt% conversion.

Figure 13 shows SEM micrographs of the cross-linked PMMA particle prepared by alternative addition process. The more uniform cross-link density of particle was achieved by the alternative addition process as shown in Figure

Table VIII. Three-Times Addition in Seeded Multi-batch Process*

	EGDMA (%) ^a	\overline{D}_n (μm)	PDI	Particle Shape
A	1 → 1 → 5	6.5	1.08	Monodisperse & smooth surface particle
B	1 → 2 → 5	6.5	1.2	Slightly dented particle & secondary nucleated small particle
C	2 → 1 → 4	6.5	1.2	Lava surface particle & secondary nucleated small particle

*70°C, 25 h, 120 rpm. ^aBased on total amount of seed and monomer.

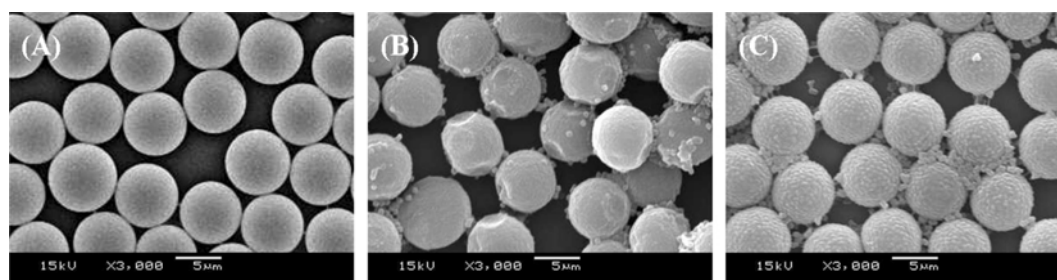


Figure 11. Scanning electron micrographs of cross-linked PMMA particles prepared at three time-addition in multi-batch process ((A) 1 → 1 → 5 wt%, (B) 1 → 2 → 5 wt%, (C) 2 → 1 → 4 wt% of EGDMA).

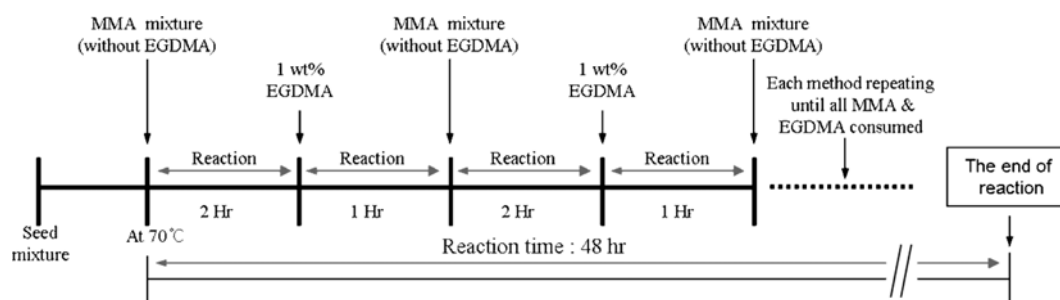


Figure 12. Schematic diagram of alternative addition in seeded multi-batch process.

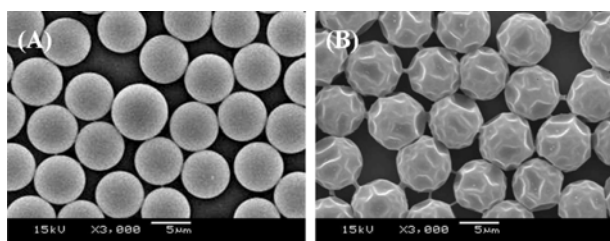


Figure 13. Scanning electron micrographs of cross-linked PMMA particles prepared at alternative addition in multi-batch process ((A) 8 wt%, (B) 9 wt% of EGDMA).

13(A). The particles are monodisperse and smooth surfaces with 8 wt% of EGDMA. However at higher EGDMA concentration (9 wt%), the dispersed particles wrinkle (Figure 13(B)).

Conclusions

The nucleation stage of dispersion polymerization is very sensitive because the particle deformation and coagulation could be caused by even very small amount of cross-linker. Different processes were employed for the preparation of highly cross-linked and monodisperse particles by adding in the first 5 μm diameter seed particles taken from the initial stage of polymerization. The monodisperse and spherical particles containing 3 wt% of DVB could be prepared by seeded batch dispersion polymerization at the second stage. With further modification of polymerization media, it was found that the MeOH/water ratio of 70/30 resulted in smooth surface particles due to active infiltration of MMA and DVB inside the particle. Furthermore by decreasing the polymerization temperature less than 60°C, uniformly cross-linked particles could be formed with smooth surface particles containing up to 7 wt% of DVB. Spherical particles could also be prepared by using seed/monomer ratio of 100/0 with DVB up to 7 wt%, beyond this concentration, wrinkling of the particles observed.

Based on the results, the cross-link density of particle inside can affect the particle morphology. When the cross-link density of the particle surface increases, the particle deformation and secondary small particle were observed due to the refrainment of infiltration of MMA and occurrence of phase separation. On the other hand, when the uniform cross-link density in the particle inside achieved, the smooth surface particle was obtained due to easily infiltration of MMA. It is important that the preparation of particle without deformation is the easily infiltration of cross-linker into the particle and the occurrence of uniform cross-link density of particle inside.

Furthermore, the spherical particle without deformation and higher cross-link concentration can be executed with multi-addition of cross-linker process. The smooth surface

particle containing up to 7 wt% of EGDMA could be prepared by three times-addition during the polymerization reaction. To get maximum uniform cross-link density inside the particle, alternative addition of MMA and EGDMA was done. By this method, the monodisperse, smooth surface particle containing up to 8 wt% of EGDMA could be obtained.

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