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Kang-Yeol Park^a; Won-Wook Jeong^a; Kyung-Do Suh^a

^a Division of Chemical Engineering, College of Engineering, Hanyang University, Seoul, Korea

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Monodisperse Crosslinked Microsphere Polymer Particles by Dispersion Copolymerization of Glycidyl Methacrylate and Divinylbenzene

Kang-Yeol Park, Won-Wook Jeong, and Kyung-Do Suh*

Division of Chemical Engineering, College of Engineering,
Hanyang University, Seoul, Korea

ABSTRACT

Monodisperse polyglycidyl methacrylate (PGMA) microsphere particles crosslinked with divinylbenzene crosslinker were prepared by single-stage dispersion copolymerization in ethanol medium. 1 wt% of DVB was successfully incorporated due to the costabilizing effect of GMA as a surface-active monomer. This behavior may indicate that the fast formation of stable primary particle leads to monodispersity. The average particle sizes and the particle size distributions increased with the DVB crosslinker concentration. The effects of two different variables (initiator concentration, crosslinker concentration) on the rate of dispersion copolymerization have been investigated. With the initiator concentration, the polymerization procedure mainly depended on the dual natures of general dispersion polymerization, in the crosslinked state. Up to 1 wt% DVB, the particle growth was controlled by the monomer diffusion from the continuous phase into the particle phase.

Key Words: Crosslinking; Dispersion copolymerization; Medium solvency; Costabilizing effect; Polymerization rate.

*Correspondence: Kyung-Do Suh, Division of Chemical Engineering, College of Engineering, Hanyang University, Seoul 133-791, Korea; Fax: +82-2-2295-2102; E-mail: kdsuh@hanyang.ac.kr.

INTRODUCTION

In recent years, monodisperse polymer microsphere particles by dispersion polymerization have received great attention,^[1–5] which have found a wide variety of applications in coatings, inks, dry toners, instrument calibration, chromatography, biomedical treatment, biomedical analysis and microelectronics.^[6–8] However, the preparation of monodisperse crosslinked polymer microsphere particles could not readily be achieved in a single-stage dispersion polymerization, due to the instability during the dispersion polymerization.

Tseng et al.^[9] and Margel et al.^[10] first reported forming the crosslinked polymer particles by dispersion copolymerization of divinylbenzene (DVB) and styrene. In their work, coagulum or broad particle-size distribution or a dispersion of odd-shaped particles was obtained by adding the low concentration of DVB. Currently, monodisperse crosslinked polymer microsphere particles were synthesized by dispersion copolymerization.^[11–13] This stable dispersion copolymerization of crosslinked particle essentially required either high concentration of DVB or well-suited crosslinker such as urethane acrylate.

Generally, dispersion polymerization is a heterogeneous process by which polymer particles are formed in the presence of a steric stabilizer from the initially homogeneous reaction medium. The polymer chains with a molecular weight larger than the critical value precipitate and begin to form unstable primary particles. These primary particles agglomerate until the stable particles are formed. Also, it appears when all polymer particles contain a sufficient amount of surface-active groups or amphiphilic chains at the surface to provide colloidal stability.^[14] After these stable particles are formed, particles grow to reach their final size by capturing monomer or oligomeric radicals from the medium. This suggests that for the preparation of monodisperse crosslinked microparticles, essentially, the fast formation of stable primary particle is required.

In this study, in order to prepare monodisperse crosslinked polymer microsphere particles, we used glycidyl methacrylate (GMA) as a surface-active monomer. When primary particles of GMA and DVB are formed, surface-active groups in polyglycidyl methacrylate (PGMA) were expected to help the stability of the primary particles at the particle surface. The effect of DVB concentration on the particle size, the particle size distribution, and the morphology were examined. In addition, the effects of initiator concentration and crosslinker concentration on the kinetic parameters were evaluated. Finally, dispersion copolymerization mechanism for GMA and DVB in ethanol medium was proposed.

EXPERIMENTAL

Materials

The inhibitor in glycidyl methacrylate (GMA, Junsei Chemical Co.) and divinylbenzene (DVB, mixture of isomer ~50%, Fluka Chemical Co.) was removed through a removing column (Aldrich Chemical Co.). 2,2-azobis(isobutyronitrile) (AIBN, Junsei Chemical Co.) was recrystallized from methanol before use. Polyvinylpyrrolidone (PVP K-30, $M_w = 4.0 \times 10^4 \text{ g}\cdot\text{mol}^{-1}$) was purchased from Aldrich Chemical Co.

Polymerization Procedure

AIBN, PVP, GMA and DVB were weighed into 20 ml glass vials. After sealing in nitrogen atmosphere, vials were submerged in a thermostated water bath and slowly tumbled with the rotation speed of 40 rpm around its stem axis. The polymerization was carried out for 10 h at 70°C. The obtained microparticles were centrifuged for 10 min (at 6000 rpm), then supernatant was decanted and the remaining precipitate was repeatedly washed by five re-dispersions/centrifugations. The microparticles were then dried under vacuum at ambient temperature. All materials used in the standard recipe for the dispersion copolymerization of GMA and DVB in ethanol are listed in Table 1.

Characterization

The particle diameter was measured with Field-Emission Scanning Electron Microscope (FE-SEM, JSM-6330F, JEOL). Specimens were prepared by diluting the recovered particles with distilled water and placing a drop on a cover glass. The drop was dried at room temperature and then coated under vacuum with a thin layer of gold. At least 200 individual particle diameters were measured from SEM photographs and the average was taken. Polydispersity index (PDI) was obtained as following:^[15]

$$D_n = \frac{\sum_{i=1}^n d_i}{N} \quad (1)$$

$$D_w = \frac{\sum_{i=1}^n d_i^4}{\sum_{i=1}^n d_i^3} \quad (2)$$

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

Table 1. The standard recipe for the dispersion polymerization.^a

Ingredient	Weight (g)
GMA	0.990
DVB ^b	0.010
PVP K-30 ^c	0.300
AIBN ^d	0.010
Ethanol	8.690

^a 70°C; 10 h; 10 wt% of monomer concentration based on total weight.

^b Weight concentration of DVB was varied against GMA (1 wt% in this example).

^c 3 wt% of PVP K-30 ($M_w = 4.0 \times 10^4 \text{ g}\cdot\text{mol}^{-1}$) based on total weight was added.

^d 1 wt% of 2,2'-azobis(isobutyronitrile), AIBN, based on monomer weight was added.

where, D_n is the number average diameter, D_w is the weight average diameter, N is the total number counted, and d_i is the diameter of particle i .

Conversion-time curves for the set of polymerizations were calculated as:^[16]

$$\text{Conversion}(\%) = \frac{M_2 - M_1 \times (w_2 + w_3)}{M_1 \times w_1} \times 100 \quad (4)$$

where, M_1 is the weight of the sample before drying, M_2 is the weight of the sample after drying, w_1 is the weight percent of GMA and DVB in the reactor, w_2 is the weight percent of PVP in the reactor, and w_3 is the weight percent of AIBN in the reactor.

By fitting the first-order derivatives of the conversion-time curves, the polymerization rate was obtained and plotted against the fractional conversion.

RESULTS AND DISCUSSION

Morphology Observation

Crosslinked PGMA particles were synthesized with different amounts of DVB crosslinker in ethanol at 70°C for 10 h. Figure 1 shows SEM photographs at each DVB concentration based on the GMA monomer weight; (a) 0.05 wt%, (b) 1 wt%, (c) 2 wt%, (d) 3 wt%. In all DVB concentrations, stable particles were produced with sizes ranging from 1 to 2 μm without coagulum. Up to the 1 wt% DVB, morphology was remarkably not only monodisperse particle sizes but also clear particle surfaces, in the crosslinked state.

In general dispersion polymerization, it is well known that in the syntheses of crosslinked polystyrene microparticles coagulation, polydisperse, and rough surface upon addition of more than 0.5 wt% of DVB crosslinker have been observed. These results are due to the instability of primary particle formed extends during the dispersion

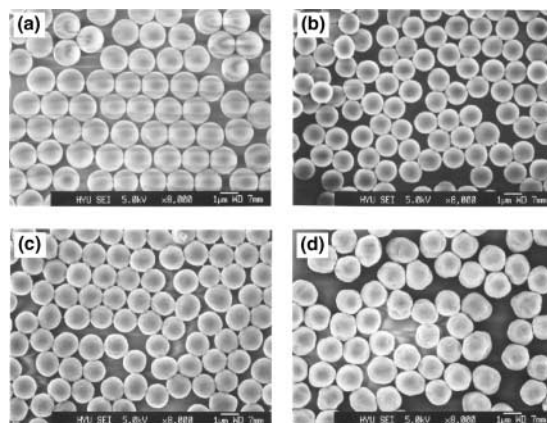


Figure 1. SEM photographs of crosslinked PGMA microparticles produced by dispersion copolymerization with the DVB concentration at 70°C for 10 h: (a) 0.05 wt%, (b) 1 wt%, (c) 2 wt%, and (d) 3 wt%.

Monodisperse Crosslinked Poly(GMA-co-DVB) Microparticles

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polymerization, that is, it isn't rapid for unstable primary particle to become stable primary particle.^[17] However, in the case of our experiment, monodisperse crosslinked PGMA particles were obtained up to the 1 wt% DVB. This behavior may indicate that costabilizing effect of surface-active groups in PGMA contributes to the stability at the surface of primary particle, and so the period of forming the stable primary particle is brief, leading to monodispersity.

The average particle sizes and the size distributions obtained with the concentration of the DVB are represented in Fig. 2. It is interesting that with increasing DVB concentration, the average particle size initially decreased to a minimum value at a DVB concentration of 1 wt% and then increased with increasing DVB concentration up to 3 wt%, as shown in Fig. 2(a). By increasing the DVB concentration, the primary particle agglomeration increased due to the extension of instability of primary particle for the polymer particles being formed during the dispersion copolymerization. These would lead to the formation of larger particles. However, increasing the DVB concentration would also increase the GMA-co-DVB segments in a PVP-g-(GMA-co-DVB) graft copolymer produced *in situ* during the polymerization, which would increase the adsorption rate of the stabilizer, favoring the formation of smaller particles. The competition between these opposing factors may explain the nonlinear change in particle size observed here.

Polymerization Kinetics for the Crosslinked PGMA Microparticles

The particle growth mechanism is rationalized by considering the dependence of polymerization kinetic on the initiator concentration. The observed crosslinked PGMA

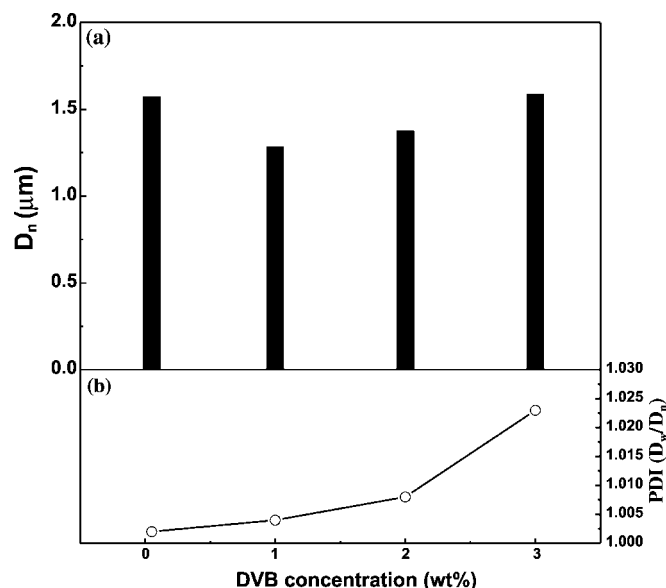


Figure 2. The effect of DVB concentration on the crosslinked PGMA microparticles: Particle size (a) and polydispersity Index (b).

conversion-curves with the AIBN concentration for each run are shown as a function of time in Fig. 3 (a), and the corresponding polymerization rate (R_p , calculated from the conversion of Fig. 3 (a)) is expressed as a function of crosslinked PGMA conversion in Fig. 3 (b). At low conversion, R_p increases with the concentration of the initiator. This result may be explained that the polymerization takes place dominantly in the solution phase. Thus, R_p is directly related to the initiator concentration. However, in the high conversion region, R_p is independent of the initiator concentration. This result implies that the polymerization dominantly proceeds through a heterogeneous mechanism in the particle phase. Such a process does not involve the formation of any new polymer chains. These suggest that there is competition between solution polymerization and heterogeneous polymerization.^[13]

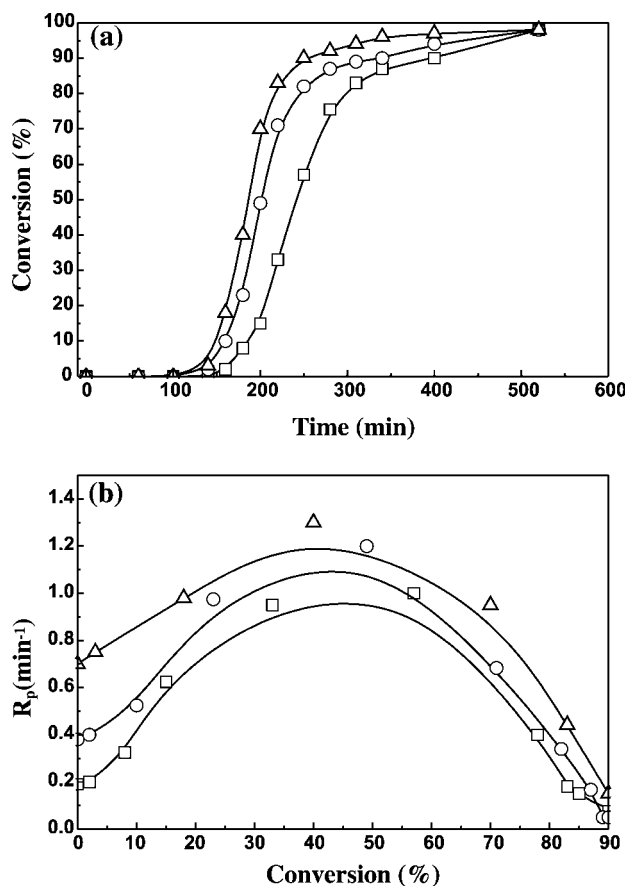


Figure 3. Conversion-time curves (a) and Polymerization rate-conversion curves (b) for PGMA microparticles crosslinked with 1 wt% DVB (based on total monomer weight) with changing the initiator concentration: 0.5 wt% (□), 1 wt% (○), and 2 wt% (Δ) at 70°C in ethanol.

Lu et al.^[18] have reported that the rate of dispersion polymerization slightly increased with the initiator concentration (the 0.1 power). This suggested that the rate of dispersion polymerization is independent of the initiator concentration in the heterogeneous polymerization process. In order to confirm the dependence of R_p on the initiator concentration, R_p in Fig. 3 (b) was plotted double-logarithmically against the initiator concentration at various fractional conversions and this plot is shown in Fig. 4. R_p was slightly increased with increasing the initiator concentration. The kinetic parameter obtained is as follow:

$$R_p = K[AIBN]^{0.14} \quad (5)$$

This result confirms that the particle growth of monodisperse crosslinked PGMA microparticle was carried out by the monomer diffusion from the continuous phase into the polymer particle phase.

In order to further understand the PGMA particle growth mechanism on the DVB crosslinker concentration, R_p was determined. The observed PGMA conversion-curves with the DVB concentration for each run are shown as a function of time in Fig. 5 (a), and the corresponding R_p (calculated from the conversion of Fig. 5 (a)) is expressed as a function of PGMA conversion in Fig. 5 (b). R_p obtained was displayed against the concentration of DVB double-logarithmically in Fig. 6.

As the concentration of DVB increased, R_p was classified into the two regions, and variations of the kinetic parameter are as follow:

$$\text{I region } R_p = K[DVB]^{0.08} \quad (6)$$

$$\text{II region } R_p = K[DVB]^{-0.99} \quad (7)$$

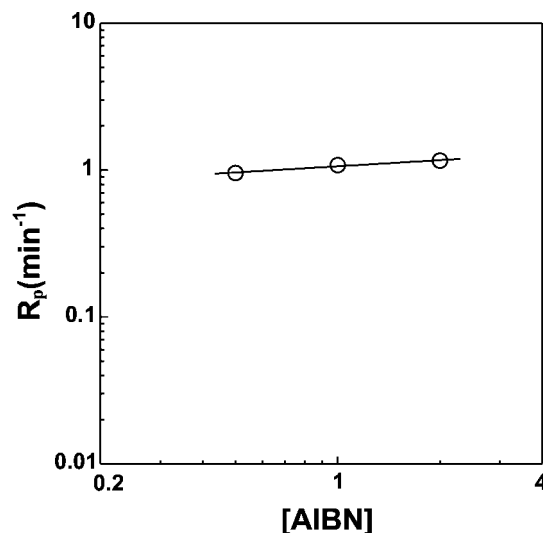


Figure 4. The polymerization rate for PGMA microparticles crosslinked with 1 wt% DVB with the initiator concentration at 70°C in ethanol. The polymerization rate was selected at 47% conversion.

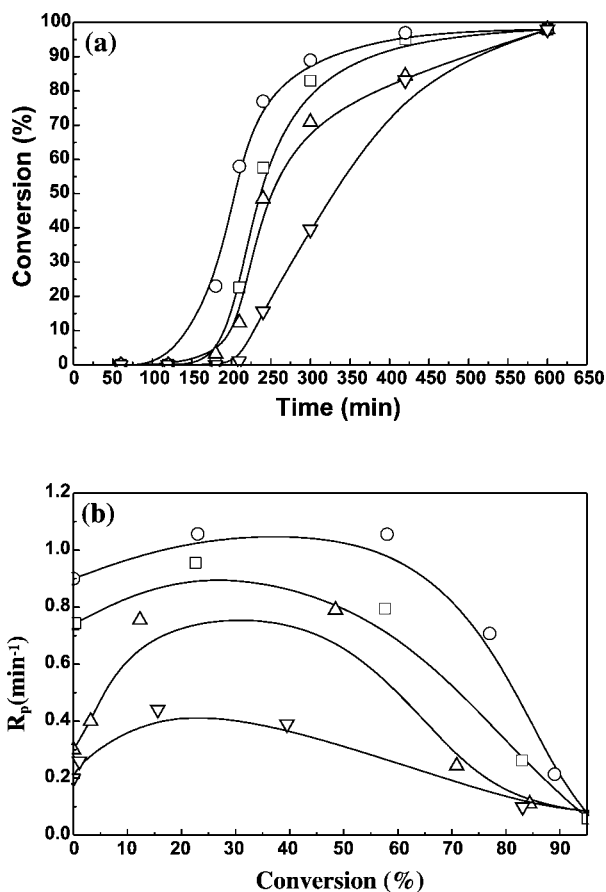


Figure 5. Conversion-time curves (a) and Polymerization rate-conversion curves (b) for PGMA microparticles with changing the DVB crosslinker concentration at 70°C in ethanol: 0.05 wt% (□), 1 wt% (○), 2 wt% (△), and 3 wt% (▽). 1 wt% initiator was added for all samples, based on total monomer weight.

These two distinct kinetic regions (i.e., positive and negative slope on the DVB concentration) were caused by different particle growth mechanisms. Increasing the DVB concentration, monomer-swelling capacity of the crosslinked polymer particles was decreased.^[11] So to speak, as the concentration of the DVB increased (more than 2 wt%), the particle growth is considered by the precipitation of growing polymer chains from the medium onto the primary particles. This result also affects polymerization kinetics, which qualitatively follow solution polymerization kinetics (decreasing polymerization rate) forming a striking contrast to an increase of polymerization rate found up to the 1 wt% DVB due to polymerization within the polymer particles. This indicates that the favor of equilibrium distribution of monomer towards the particle phase was attributed to increase of total surface area (reduction of particle size and increase of primary particle number) due to the fast formation of stable primary particle.

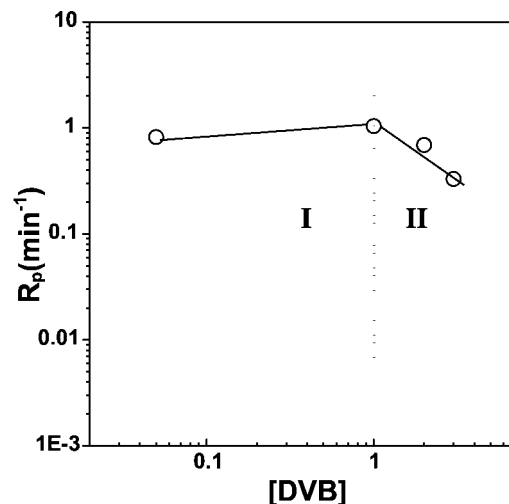


Figure 6. The polymerization rate for PGMA microparticles with the DVB crosslinker concentration at 70°C in ethanol. The polymerization rate was selected at 47% conversion.

Mechanism for the Dispersion Polymerization of the Crosslinked PGMA Particles

The mechanisms for the dispersion polymerization from unsaturated monomer^[9,11,12] have been proposed to understand the formation and growth of the polymer particles. In analogy, we suggest the mechanism shown in Fig. 7 for particle formation and growth of the crosslinked PGMA microspheres. At the start of the process, GMA, DVB, PVP, and AIBN form a homogeneous solution in the continuous phase (a). Upon heating, the initiator decomposes and the free radicals react with GMA and DVB to form oligomeric radicals (b). At a critical chain length, the oligomers precipitate to form the primary particles crosslinked with the DVB. The fast formation of stable primary particles can be generated through the adsorption of stabilizers and costabilizing effect of surface-active group (c). Once stable particles have been formed, they absorb monomer and oligomer from the continuous phase until all of the monomers are consumed (d).

In conventional dispersion polymerization of the crosslinked polymer particles, monodisperse microparticle (up to 0.3 wt% DVB) or polydisperse microparticle (more than 0.5 wt% DVB) has been obtained at moderate DVB concentration.^[9,10,11] These results were caused by the extension of instability of primary particle. The main difference of crosslinked PGMA microparticles from general ones in the mechanism is the fast formation of stable primary particle during particle formation (stage (c)). Therefore, the equilibrium distribution of monomer towards the particle phase was favorable, which leads to monodispersity (see in Fig. 1).

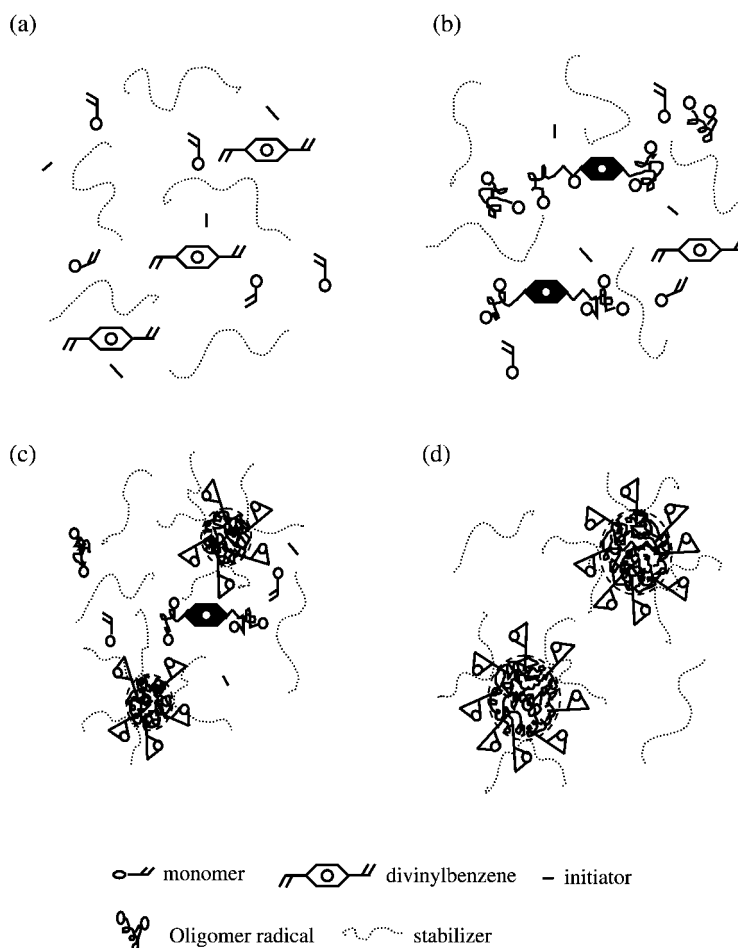


Figure 7. A schematic representation of particle formation and growth in the dispersion copolymerization of GMA and DVB in ethanol medium.

CONCLUSION

Monodisperse crosslinked PGMA microparticles were achieved by single-stage dispersion copolymerization of GMA and DVB. Monodisperse size distribution of crosslinked PGMA microparticles stemmed from the fast formation of stable primary particle. The average particle sizes and the particle size distributions of the crosslinked PGMA microparticles were changed with the stability of primary particle. The dependence of the polymerization rate on the initiator concentration followed dual nature of general dispersion polymerization, solution polymerization mechanism at low conversion region and heterogeneous polymerization mechanism at high conversion region. In addition, two distinct kinetic regions on the DVB crosslinker concentration were observed due to the difference of the particle growth mechanisms. The above-mentioned



results confirmed that the twofold DVB could be successfully incorporated due to the costabilizing effect of surface-active group.

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