Size and Uniformity Variation of Poly(MMA-*co*-DVB) Particles upon Precipitation Polymerization

Sunhye Yang, Sang Eun Shim, Huije Lee, Gil Pyo Kim, and Soonja Choe*

Department of Chemical Engineering, Inha University, 253 Yonghyun, Nam, Incheon 402-751, Korea

Abstract: Stable poly(methyl methacrylate-*co*-divinylbenzene) (poly(MMA-*co*-DVB)) microspheres were prepared by precipitation polymerization using acetonitrile as the main medium under various polymerization conditions, including modifications of the agitation speed, monomer and initiator concentrations, DVB content in the monomer mixture, and the use of various cosolvents. Gentle agitation was required to obtain smooth spherical particles. The individually stable microspheres were obtained at monomer concentrations of up to 15 vol% in an acetonitrile medium. The number-average diameter increased linearly with respect to increases in the monomer and initiator concentrations. We found, however, that the uniformity of the microspheres was independent of the variation of the polymerization ingredients because nuclei formation was solely influenced by the crosslinking reaction of the monomers. We obtained higher yields for the polymerization at higher concentrations of monomer and initiator. The concentration of DVB in the monomer mixture composition played an important role in determining not only the size of the microspheres but also the yield of the polymerization. In addition, although we employed various cosolvents as the polymerization medium, we found that acetonitrile/2-methoxyethanol was the only system that provided spherical particles without coagulation. This finding indicates that the precipitation polymerization is strongly dependent on the solvent used as the medium.

Keywords: precipitation polymerization, poly(methyl methacrylate-*co*-divinylbenzene), microspheres.

Introduction

Polymer dispersions, also called polymer suspension and latex, are nowadays important materials in our daily living due to their versatility with respect to properties and applications including coatings, adhesives, inks, leather finishing, and construction and so on.[1] Recently, such polymer colloids have been also considered as candidate materials in advanced fields such as information technology, electric and electronic science, and biotechnology including biochemicals and bio-medicals.[2-4] In order to utilize the polymer colloids in such applications, precise control of their properties has become more important. Their size, uniformity of size, functionality of the base polymer, morphology of the polymer beads, and the degree of crosslinking etc. are main concerns in controlling properties.

General synthetic routes to prepare polymer dispersions are to use heterogeneous polymerizations such as macro-(conventional)/mini-/micro-emulsion, suspension, dispersion, and precipitation polymerizations.[5] Among them, emulsion and suspension polymerizations are characterized by the

genuine multi-phases consisting of monomer droplets in emulsion and suspension, monomer-swollen micelles in emulsion, and aqueous reaction medium. These multi-phases are generated at the innitial stage of the polymerization. In suspension polymerization, the dispersed monomer droplets stabilized by a protective colloid are converted to polymer particles. In emulsion polymerization, polymer particles are generated in the monomer-swollen micelles and the dispersed monomer droplets serve as a reservoir of monomer.

Unlike emulsion and suspension polymerizations, a single phase exists at the beginning of the reaction in dispersion and precipitation polymerizations. All polymerization ingredients are initially dissolved in the medium, and the heterogeneous phases, i.e., growing particles and medium phase, are developed in the middle of the polymerization by the precipitation of the growing oligomeric species whose molecular weight is higher than the critical limit. Consequently, the formation of polymer particles is achieved during the polymerization.[6,7]

The precipitation polymerization, the most recently invented by Stover's group,[7] provides another pathway to synthesize spherical polymer particles. The uniqueness of the precipitation polymerization lies in the absence of any stabilizing agent such as surfactants or steric stabilizers for

obtaining spherical particles. In the precipitation polymerization, the formation of stable spheres is achieved by means of a self-stabilizing mechanism via crosslinking of polymer chains. Since high level of crosslinking is developed in individual particles, the coagulation between the particles is prevented due to the hard and resilient nature of each particle.

The advantage of the precipitation polymerization would be the facile preparation of highly crosslinked micron-sized particles having monodisperse or narrow size distribution. These materials are used in high-end products such as packing materials in column chromatography or spacers in liquid crystal display due to their superior strength, thermal and chemical resistance, and anti-slip properties.[8] Since the synthesis of such microspheres is difficult, its production cost is quite high. Therefore, extensive research interest on the development of an inexpensive process to prepare fully crosslinked polymer microspheres has been always there.

Two-step swelling method has been firstly introduced by Ugelstad, in which relatively small seed polymer particles are prepared by either emulsion or dispersion polymerization. Then these are used for swelling process and a subsequent polymerization of monomer-swollen seed particles.[9-12] Obviously, a long and complicated procedure is a drawback of the swelling process. Dispersion polymerization method also produces stable micron-sized spherical particles ranging from 1 to 10 μm in organic media.[6] However, high degree of crosslinking is not achieved in the dispersion polymerization since the concentration of crosslinking agent is generally limited below 0.5 wt% based on main monomer. The addition of high amount of crosslinking agent (more than 0.5 wt%) causes a coarse surface of the final polymer particles or even popcorn-shaped particles in dispersion polymerization.[7,13,14] Precipitation polymerization as briefly mentioned earlier has found that fully crosslinked microspheres can be prepared in a simple single stage process.[15] Various monomers including methacrylate,[16] maleic anhydride,[17] and chloromethyl styrene[18] have been copolymerized to form microspheres with divinylbenzene (DVB) as the crosslinkable monomer using the precipitation polymerization.

We have also conducted the precipitation polymerization of various compositions of styrene (S) and DVB and found unexpected superior thermal properties due to the fully crosslinked microstructure of microspheres.[19,20] Furthermore, we have reported the mechanism[21] of the precipitation polymerization based on the surface properties of the microspheres, and the comparison[22] with dispersion polymerization based on the variation of the final size with respect to the polymerization ingredients.

In this article, poly(MMA-*co*-DVB) microspheres are prepared by the precipitation polymerization and characterized in terms of the polymerization parameters, including the agitation speed, monomer and initiator concentrations, DVB content in the monomer composition, and the use of various cosolvents having a wide range of solubility parameters.

Experimental

Materials. Methyl methacrylate (MMA; Samchun, Korea) and divinylbenzene (DVB; 55% mixture of isomers, Aldrich, USA) were purified using an inhibitor removal column (Aldrich) and stored at -5 °C prior to use. As an initiator, analytical grade of 2,2-azobisisobutyronitrile (AIBN; Junsei, Japan) was used without further purification. As the polymerization media, analytical grade acetonitrile (Junsei), methanol (Samchun), ethanol (Samchun), 2-methoxyethanol (Junsei), 2-propanol (Kanto, Japan), benzene (Junsei), THF (J.T. Baker, USA), toluene (Oriental Chemical, Korea) were used.

Polymerization. The polymerization ingredients simply consist of medium, various compositions of MMA and DVB comononer, and AIBN. The total amount of monomers was varied from 4 to 12 vol% of the medium. The concentration of AIBN was increased from 2 to 8 wt% with respect to the total amount of the monomers. After charging 18 mL of polymerizing mixture in a scintillation vial, it was purged with nitrogen for 15 min and sealed. Polymerization was carried out in a shaking water bath with an agitation speed in the range of 0-100 rpm at 70 °C for 24 hrs. After completion of the polymerization, the resultant particles were obtained by centrifugation and washed with methanol, repeatedly.

Characterization. Hitachi SEM (Scanning Electron Microscopy) S-4300 was used to study the morphology of poly(MMA-*co*-DVB) particles. The average diameters of the particles were obtained using Scion Image® Analyzer software by counting individual 100 particles from SEM microphotographs using the following equations.

$$D_n = \frac{\sum_{i=0}^{n} d_i}{N} \tag{1}$$

$$D_w = \frac{\sum_{i=0}^{n} d_i^3}{\sum_{i=0}^{n} d_i^2} \tag{2}$$

$$\text{Uniformity} = \frac{D_w}{D_n} \tag{3}$$

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

The circularity of the microspheres was measured by Flow Particle Image Analyzer, FPIA-2100® (Sysmex Co., Japan), by flowing approximately 5 mL of particle-suspended sheath reagent through flat sheath flow cell. The molecular weight and the polydispersity index (PDI) of the

sol separated after polymerization were measured by Waters GPC (Gel Permeation Chromatography) equipped with 510 differential refractometer and Viscotek T50 differential viscometer at a flow rate of 1.0 mL/min using THF as the eluent. 10^5, 10^3, and 10^2 Åμ-styragel packed high-resolution columns were employed. Universal calibration curve was obtained using ten PS standard samples (Polymer Laboratories, UK) with molecular weight ranging 580-7,500,000 g/mole. Once the sol part was collected by precipitating the dissolved polymer, it was dissolved in THF for GPC measurement. The yield of the polymerization was determined gravimetrically.

Results and Discussion

The Influence of Agitation on Particle Formation. Figure 1 shows the agitation effect on the formation of PMMA particles obtained by the precipitation polymerization in acetonitrile. Without agitation, the spherical particles are developed, however, partial coagulation and protrusion on the particle surface are frequently observed. The most stable and spherical particles are obtained at 20 rpm. As the agitation speed increases up to 100 rpm, severe coagulation of the particles is observed. This result implies that the formation of stable particles is quite sensitively affected by the agitation. A gentle agitation is required to achieve individually grown smooth spherical particles due to the absence of a stabilizing agent in this system. It is noted that the final conversion is not influenced by the agitation speed.

The Effect of the Concentration of Polymerization Ingredients. A drawback of precipitation polymerization lies in the fact that the solid content is substantially low compared to other heterogeneous polymerizations. Precipitation polymerization resembles dispersion polymerization in many aspects except the mechanism of the particle formation. In dispersion polymerization, a monomer concentration up to 40 vol% relative to the polymerization medium is used without resulting a coagulation.[23,24] However, a moderate monomer concentration results in the fused particles arisen from the collision of the particles since no stabilizing agent is employed in the precipitation polymerization. For example, Stöver's group, where the precipitation polymerization of crosslinkable monomer was explored, used a monomer concentration in the range 2-10 vol%.[15,18] Figure 2 represents the poly(MMA-*co*-DVB) microspheres prepared with the increasing concentration of the mixture of monomer and comonomer. It is seen that individually stable particles are generated without coagulation up to 15 vol% of monomer concentration in acetonitrile medium. However, a significant coagulation was observed above 20 vol% of monomer. The effect of the monomer concentration on the size and uniformity of the microspheres is listed in Table I. The number-average diameters linearly increase from 3.17 μm for 4 vol% of monomer to 4.55 μm for 15 vol%. However, the uniformity remains intact at nearly 1.04 with the variance in the monomer concentration. The increase in the size of the final
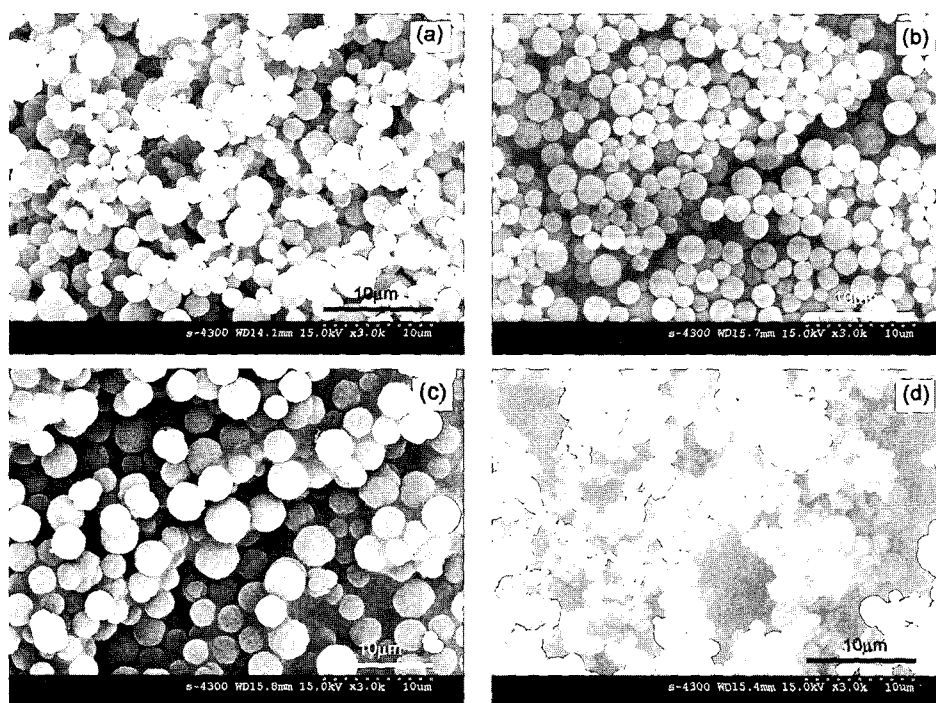

Figure 1. Effect of agitation speed on the precipitation polymerization of 50/50 mol% MMA and DVB with 2 wt% AIBN in acetonitrile at 70 °C for 24 hrs. (a) 0 rpm, (b) 20 rpm, (c) 50 rpm, and (d) 100 rpm. Total amount of monomer was 4 vol%.
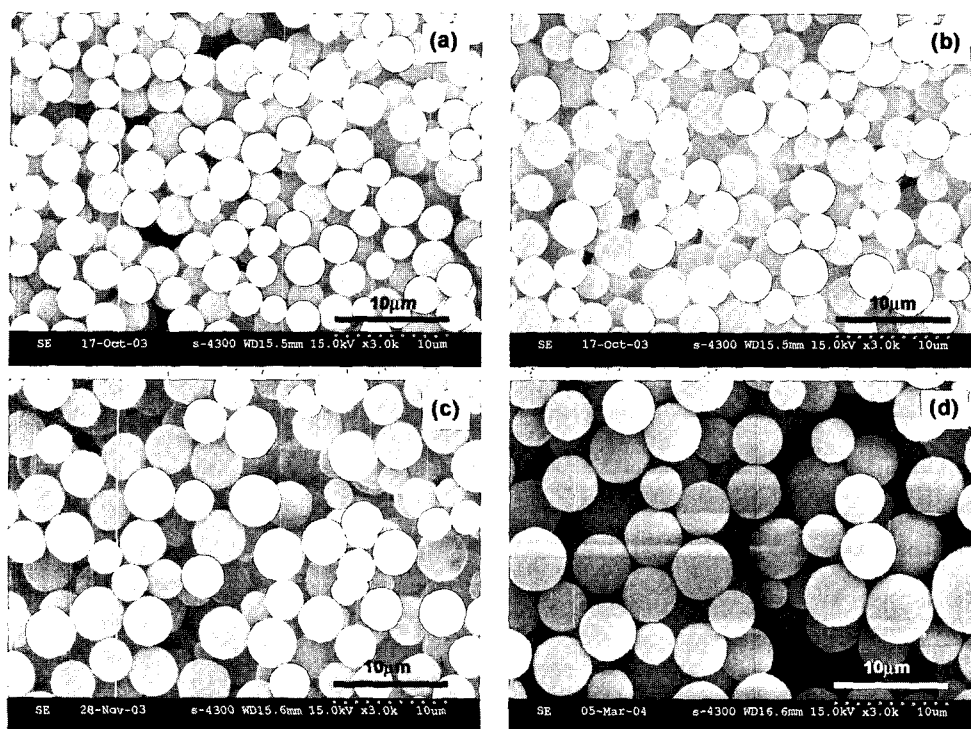
Figure 2. Effect of the total concentration of monomer (50/50 MMA/DVB) on the particle morphology with 4 wt% AIBN in acetonitrile at 70°C for 24 hrs. (a) 4 vol%, (b) 8 vol%, (c) 12 vol%, and (d) 15 vol%.

microspheres is attributed to the change of the solvency of the medium. The solubility parameters (δ) of acetonitrile, MMA, and DVB are 12.1, 9.2, and 8.5 (cal/cm^3)$^{1/2}$, respectively.[25] It is noted that the solubility parameter of DVB was calculated according to the Hansen group contribution method.[19] When the solubility parameter of the polymerization system becomes close to that of monomer, oligomeric species having a relatively high molecular weight is dissolved in the medium. Subsequently the number of primary particles formed by precipitation of the oligomeric species is reduced and finally the particle size becomes larger. When the monomer concentration is increased, the solubility parameter of the reaction system approaches to that of monomer, which results in the larger particles.

In Figure 3, the change in the circularity of the microspheres with the increasing concentration of monomer is represented. The circularity of the particles is a useful indicative of the stability of microspheres and it is defined as the ratio between the circle circumference of the equivalent area to the particle and the perimeter of the particle itself as follows:

$$\text{Circulairty} = \frac{\text{Circle circumference}}{\text{Perimeter of projected particle image}} \quad (4)$$

The more spherical particle, the closer its circularity to unity, and the more elongated particle, the lower its circularity is obtained. The particle number density (N_p) as the particle

Table I. Effects of Monomer Concentration on the Particle Size and Uniformity

Monomer Concentration (vol%)	D_n (μm)	D_w (μm)	Uniformity
4	3.17	3.29	1.04
8	3.50	3.65	1.04
12	4.17	4.28	1.03
15	4.55	4.88	1.07

number of unit quantity was calculated as follows[26]:

$$N_p = 6\frac{MY}{\pi r^3 \rho} \quad (5)$$

where, M is the monomer added, Y is the yield of the polymerization, r is the number average-radius of the microsphere, and ρ is the density of the polymer. The density (ρ) was taken to be that of amorphous PMMA (i.e. $\rho = 1.17$ g/cm^3).[27] It is natural that the particle number density correspondingly increases with the concentration of monomer since the increased particle diameter cannot compensate increased monomer concentration as seen in Figure 3. The higher particle number density in the medium leads to the higher possibility of particle collision. Therefore, the circularity of the microspheres decreases from 0.99 for 4 vol% monomer to 0.96
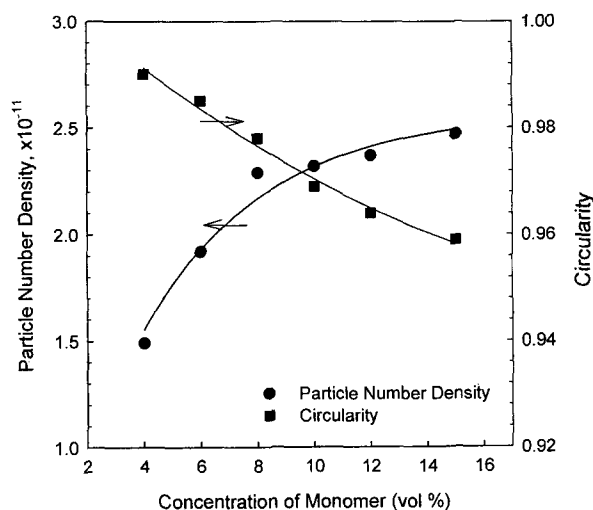
Figure 3. Circularity vs. particle number density in polymerization medium with the concentration of monomer (50/50 MMA/DVB) ranging 4 - 15 vol% and with 4 wt% AIBN in acetonitrile at 70 °C for 24 hrs.

Figure 4. Size and uniformity variation of the microspheres prepared by precipitation polymerization of 50/50 styrene and divinylbenzene with various concentration of AIBN in actonitrile at 70 °C for 24 hrs. Total amount of monomer was 4 vol%.

for 15 vol%. However, the microspheres obtained at 15 vol% of monomer concentration still remains individually stable in Figure 2.

The concentration of initiator also significantly affects the size of the microspheres as shown in Figure 4. As the AIBN concentration is increased from 2 to 8 wt%, the final diameter of the microspheres increases from 2.88 to 3.56 μm. The formation of larger microspheres at a higher initiator concentration is also attributed to the reduced number of primary particles in the early stage of the polymerization. A higher initiator concentration generates more oligomeric species, which have a low molecular weight and they prefer to stay in the medium. Consequently, a smaller amount of the oligomers are precipitated to give the reduced number of primary particles during the nucleation step.

As observed in Table I and Figure 4, the uniformity of the microspheres is found to be independent of the variation of the polymerization ingredients. This reason could be accounted from the mechanism of the particle formation. In dispersion polymerization, the increase in monomer and initiator concentration with the same concentration of other ingredients respectively gives larger particles with broadened particle size distribution.[28] The constant uniformity in precipitation polymerization would be due to the different mechanism of the particle formation. Compared to the dispersion polymerization in which polymeric stabilizer, initially dissolved in polymerization medium causes the formation of nuclei,[29] the nuclei formation in the precipitation polymerization is solely attributed to the crosslinked polymer molecules having the chain length larger than the critical limit which can not be further soluble in medium. Once the nuclei are formed, they grow to particles by continuously adsorbing the mono-
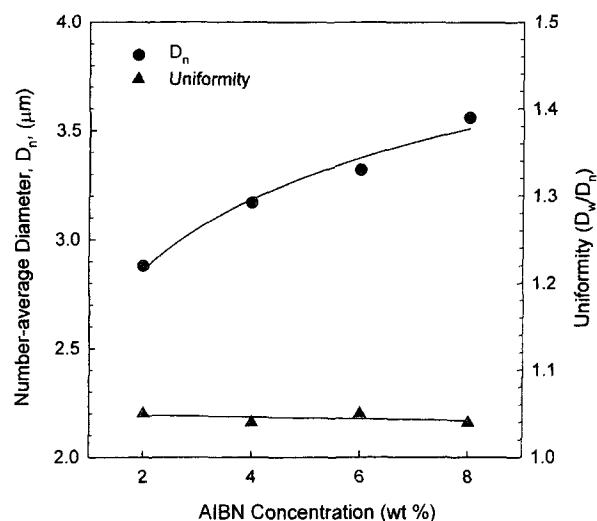
mer or oligomeric species on the particle surface. Since no giant molecule, such as polymeric stabilizer used in dispersion polymerization, exists in the polymerization medium, the low molecular weight species are readily adsorbed onto the particle surface, which minimizes the formation of secondary particles. Thus, the particle size distribution would not be much influenced by the changes in the concentration of monomer or initiator.

Figure 7 illustrates the yield of the polymerization with respect to the concentration of initiator with changing monomer content in acetonitrile. It is noted that the yield of the polymerization indicates the amount of monomer converted to microspheres. As seen in Figure 5, the yield of the polymerization increases with the concentration of initiator and the amount of monomer in the medium. This may be due to the fact that the higher initiator and monomer concentrations would lead to the formation of precipitating large oligomeric species. Therefore, the highest yield in polymerization was obtained at the lowest monomer concentration along with the highest initiator concentration.

The Effect of DVB Concentration. Table II summarizes the effect of DVB concentration on the number-average diameter, uniformity of size and yield of the polymerization. When DVB is not incorporated in the polymerization recipe, the yield of the polymerization is zero since the polymerized resultant is in a sol state, which is completely dissolved in the medium. At 10 mol% DVB, a porous resin-like coagulum instead of particles is obtained due to an insufficient stability caused by the low concentration of DVB, thus the yield of the polymerization falls zero. Stable microspheres are obtained from 20 mol% DVB. The increased DVB concentration results in the bigger size of the microspheres having
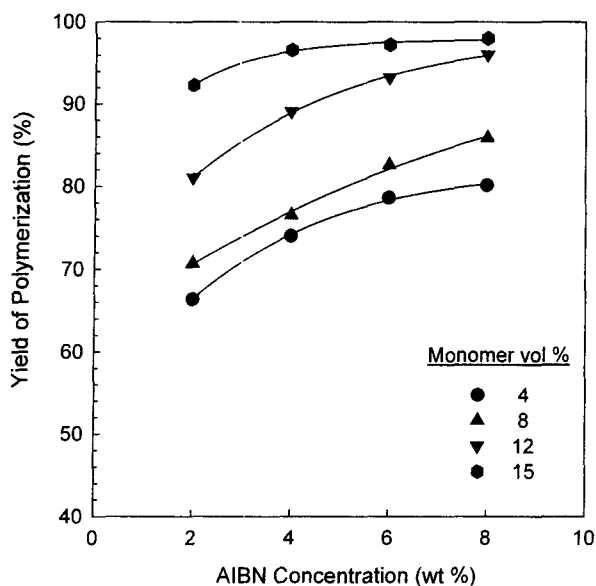
Figure 5. Yield of polymerization of 50/50 MMA/DVB with respect to the concentration of initiator for several monomer concentrations in acetonitrile at 70 °C for 24 hrs.

the improved uniformity. In addition, the yield of polymerization increases from 73.4% for 20 mol% of DVB to 98.6% for 75 mol%. In the previous study, the similar trend was also observed for poly(S-*co*-DVB) microspheres in the precipitation polymerization. It has been reported that the increased DVB concentration accelerates the polymerization rate (R_p), i.e. $R_p = $ [DVB],[0.13] however, the difference in the final conversion is negligibly marginal in dispersion polymerization.[30] However, the concentration of DVB plays an important role in determining the final yield in the precipitation polymerization. The relationship between the yield and DVB concentration could be explained by the difference in the reactivity ratios of MMA and DVB. It is reported that the reactivity ratios of r_1 and r_2 are 0.43 and 0.62 for *m*-divinylbenzene and 0.11 and 0.85 for *p*-divinylbenzene in copolymerization of MMA(1) and DVB(2).[31] The DVB used in this study consists of 55% (*meta*+*para*) isomers and the remnant is mainly ethylvinylbenzene. It is seen that the *m*-DVB has the similar reactivity ratios as MMA, but the *p*-DVB has a 7.7 times higher reactivity ratio of r_2 than r_1.

Table II. Effects of DVB Concentration on the Particle Formation and Yield of the Polymerization

DVB mol%	D_n (μm)	Uniformity	Yield (%)
10	-	-	-
20	0.72	1.35	73.4
40	1.37	1.13	95.5
50	1.48	1.16	96.7
75	2.15	1.12	98.6

This indicates that DVB is consumed much faster than MMA during the copolymerization. When the concentration of DVB is high, the formation of particles becomes easy during the entire polymerization period since the precipitating oligomers with a high molecular weight are continuously generated by crosslinking.

Figure 6 depicts the molecular weight and polydispersity of the sol separated after the polymerization. As the DVB content increases, the molecular weight and polydispersity index decrease. This phenomenon could be explained by the poor solvency of acetonitrile for the DVB-rich polymer. The similar result has been reported for the precipitation copolymerization of ethylene glycol dimethacrylate (EGDMA) and DVB.[16] In addition, the increased yield would leads to the formation of larger microspheres.

The Effect of Various Cosolvents. Various solvents having the solubility parameter (δ) from 8.9 to 14.5 (cal/cm^3)$^{1/2}$ were employed as the polymerization medium as listed in Table III. The amount of the cosolvents was fixed at 25 vol% of total volume of the medium, i.e., acetonitrile + cosolvents. It is noted that individually stable microspheres were not synthesized when each cosolvent used as the main medium. However, the spherical particles without coagulation were obtained for acetonitrile sorely and acetonitrile/2-methoxyethanol system. In addition, the particle size with acetonitrile only is smaller than in acetonitrile/2-methoxyethanol system. The reason was sought by comparing the solubility parameters. The total solubility parameter (δ) and each component (δ_d, δ_p, and δ_h) of 2-methoxyethanol are quite close to those of acetonitrile. Although ethanol and 2-propanol have similar solubility parameter, they do not serve as a good medium for particle formation. Thus, the
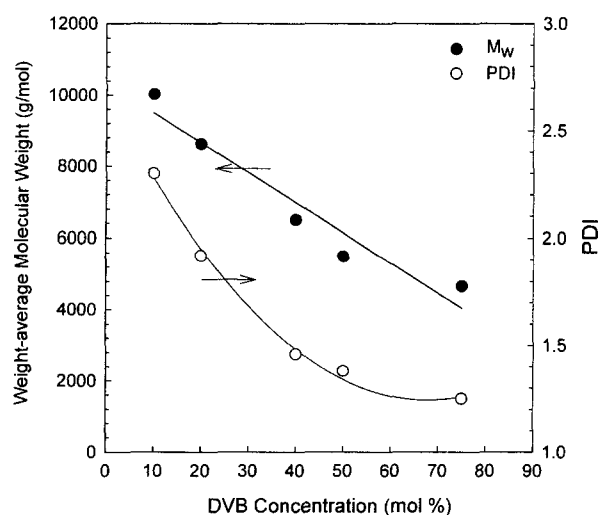

Figure 6. The molecular weight and polydispersity index of the sol with respect to DVB concentration. The polymerization was conducted for 10 vol% of monomer concentration with 2 wt% AIBN.

quite sensitive solvency-dependency is observed in the precipitation polymerization, whereas this behavior is not observed in dispersion polymerization since a variety of

cosolvents listed in Table III are successfully utilized in dispersion polymerization.[23,29,32,33] The SEM microphotographs in Figure 7 clearly show the effect of the various cosolvents

Table III. Solubility Parameters[25] of Various Solvents Used and Particle Shape of the Resulting Polymer when Used with Acetonitrile as a Main Medium

(Co) Solvent	$\delta^{\dagger}$	$\delta_d{}^*$	$\delta_p{}^*$	$\delta_h{}^*$	Particle Shape	Particle Size (μm)
Acetonitrile	12.1	5.0	5.4	9.6	spherical	1.48
Methanol	14.5	5.7	6.4	11.7	partial coagulum	-
Ethanol	12.8	6.2	5.5	9.8	partial coagulum	-
2-methoxyethanol	11.7	6.4	4.9	8.5	spherical	3.32
2-propanol	11.4	6.8	4.8	7.8	partial coagulum	-
Benzene	9.1	7.9	4.2	2.0	coagulum	-
THF	9.1	6.5	5.4	3.3	coagulum	
Toluene	8.9	8.0	3.9	0.8	coagulum	-
Methyl methacrylate	9.2	6.6	4.9	4.2	-	-
DVB[††]	8.5	-	-	-	-	-

*Dimension: (cal/cm^3)$^{1/2}$. $^{\dagger}\delta = (\delta_d{}^2 + \delta_p{}^2 + \delta_h{}^2)^{1/2}$. ††Solubility parameter of DVB: calculated by Hansen method.
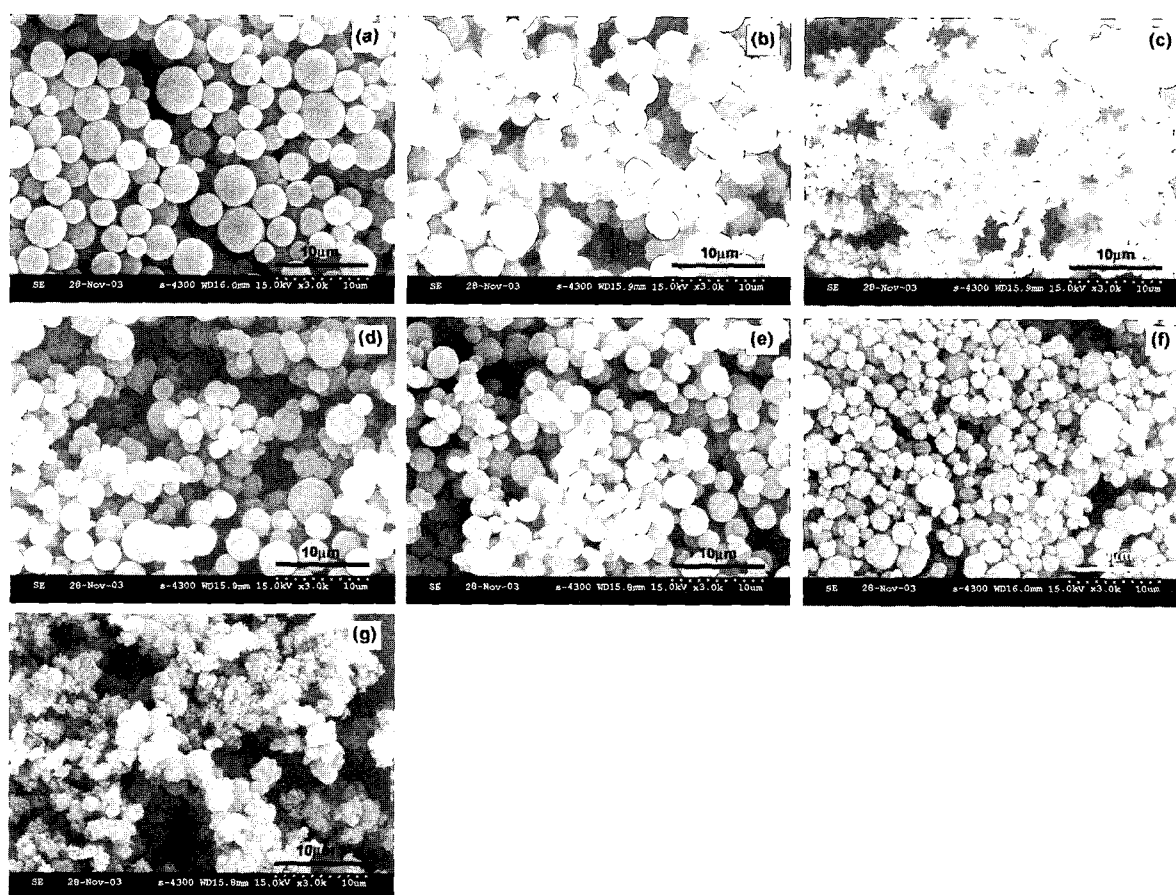

Figure 7. The effect of cosolvents on the precipitation polymerization of 50/50 MMA/DVB with 2 wt% AIBN for 2 vol% monomer in acetonitrile at 70 °C for 24 hrs with (a) 2-methoxyethanol, (b) 2-propanol, (c) benzene, (d) ethanol, (e) methanol, (f) THF, and (g) toluene. The amount of cosolvent was 25 vol% for total medium.

on the morphology of the final poly(MMA-*co*-DVB) particles.

Conclusions

Stable poly(MMA-*co*-DVB) microspheres were prepared by the precipitation polymerization under various polymerization conditions using acetonitrile as the main medium. The formation of microspheres was investigated in terms of agitation speed, monomer and initiator concentrations, DVB content in the monomer mixture, and the use of various co-solvents. Unlike other heterogeneous polymerizations, the degree of agitation sensitively affected the morphology of the resultant particles. A gentle agitation was required in order to achieve individually grown smooth spherical particles due to the absence of a stabilizing agent in the polymerizing system. The individually stable microspheres were obtained up to 15 vol% of monomer concentration in acetonitrile medium. However, a significant coagulation was observed above 20 vol% of monomer. The number-average diameter linearly increased from 3.17 μm for 4 vol% of monomer to 4.55 μm for 15 vol% since the increased monomer amount caused a reduction in the solubility parameter of the system. Furthermore, the circularity of the microspheres decreased from 0.99 for 4 vol% monomer to 0.96 for 15 vol% since the increased monomer content caused the greater probability of inter-collision among the particles. As the AIBN concentration was increased from 2 to 8 wt%, the final diameter of the microspheres correspondingly increased from 2.88 to 3.56 μm. The formation of larger microspheres at a higher initiator concentration is attributed to the reduced number of primary particles in the nucleation stage. However, the uniformity of the microspheres was found to be independent of the variation of the polymerization ingredients since the nuclei formation was solely attributed to the crosslinking reaction of monomers. The higher yield of the polymerization was obtained at a higher concentration of monomer or initiator. The concentration of DVB in the monomer mixture composition was found to play an important role in determining not only the size of microspheres but also the yield of the polymerization. In addition, various co solvents were employed as the polymerization media, however, the spherical particles without coagulation were only achieved for acetonitrile/2-methoxyethanol system. This indicates that the precipitation polymerization is strongly sensitive to the solvency of the medium.

References

(1) D. Urban and K. Takamura, *Polymer Dispersions and Their Industrial Applications*, Wiley-VCH, Weinheim, 2002.

(2) H. Fudouz and Y. Xia, *Adv. Mater.*, **15**, 892 (2003).

(3) J. Ugelstad, P. Stenstad, L. Kilaas, W. S. Prestvik, A. Rian, K. Nustad, R. Herje, and A. Berge, *Macromol. Symp.*, **101**, 491 (1996).

(4) V. L.Covolan, L. H. I. Mei, and C. L. Rossi, *Polym. Adv. Technol.*, **8**, 44 (1997).

(5) M. Antoniett and K. Tauer, *Macromol. Chem. Phys.*, **204**, 207 (2003).

(6) K. E. J. Barrett, Dispersion *Polymerization in Organic Media*, Wiley, London, 2002.

(7) K. Li and H. D. H. Stover, *J. Polym. Sci.; Part A: Polym. Chem.*, **31**, 473 (1993).

(8) M. Hattori, E. D. Sudol, and M. S. El-Aasser, *J. Polym. Sci.; Part A: Polym. Chem.*, **30**, 2027 (1993).

(9) J. Ugelstad, P. C. Mork, K. Herder Kaggerud, T. Ellingsen, and A. Berg, *Adv. Colloid Interf.*, **13**, 101 (1980).

(10) J. W. Kim and K. D. Suh, *Macromol. Chem. Phys.*, **202**, 621 (2001).

(11) M. Okubo and T. Nakagawa, *Colloid. Polym. Sci.*, **270**, 853 (1992).

(12) K. Ogino, H. Sato, K. Tsuchiya, H. Suzuki, and S. Moriguchi, *J. Chromatogr. A*, **699**, 59 (1995).

(13) M. Hattori, E. D. Sudol, and M. S. El-Aasser, *J. Polym. Sci.; Part A: Polym. Chem.*, **50**, 2027 (1993).

(14) J. Choi, S.-Y. Kwak, S. Kang, S.-S. Lee, M. Park, S. Lim, and J. Kim, C. R. Choe, and S. I. Hong, *J. Polym. Sci.; Part A: Polym. Chem.*, **40**, 4368 (2002).

(15) K. Li and H. D. H. Stover, *J. Polym. Sci.; Part A: Polym. Chem.*, **31**, 3257 (1993).

(16) W.-H. Li and H. D. H Stover, *J. Polym. Sci.; Part A: Polym. Chem.*, **37**, 2899 (1999).

(17) R. S. Frank, J. S. Downey, and H. D. H. Stover, *J. Polym. Sci.; Part A: Polym. Chem.*, **36**, 2223 (1998).

(18) W. H. Li and H. D. H. Stover, *J. Polym. Sci.; Part A: Polym. Chem.*, **37**, 2295 (1998).

(19) S. E. Shim, S. Yang, H. H. Choi, and S. Choe, *J. Polym. Sci.; Part A: Polym. Chem.*, **42**, 835 (2004).

(20) S. E. Shim, S. Yang, H. Jung, and S. Choe, *Macromol. Res.*, **12**, 233 (2004).

(21) S. E. Shim, S. Yang, and S. Choe, *J. Polym. Sci.; Part A: Polym. Chem.*, 2004 (in press).

(22) S. E. Shim, S. Yang, M.-J. Jin, Y. H. Chang, and S. Choe, *Colloid Polym. Sci.*, 2004 (in press).

(23) A. J. Paine, W. Luymes, and J. McNulty, *Macromolecules*, **23**, 3104 (1990).

(24) C. K. Ober, K. P. Lok, and M. L. Hair, *J. Polym. Sci., Polym. Lett.*, **23**, 103 (1985).

(25) A. F. M. Barton, *CRC Handbook of Solubility Parameters and Other Cohesion Parameters*, CRC Press, Boca Raton, 1985, pp 94-109.

(26) C. M. Miller, E. D. Sudol, C. A. Silebi, and M. S. El-Aasser, *J. Polym. Sci.; Part A: Polym. Chem.*, **33**, 1391 (1995).

(27) J. E. Mark, *Polymer Data Handbook*, Oxford University Press, New York, 1998, p.656.

(28) S. E. Shim, J. M. Byun, J. Jun, Y. J. Cha, and S. Choe, *Polymer(Korea)*, **24**, 287 (2000).

(29) K. P. Lok and C. K. Ober, *Can. J. Chem.*, **63**, 209 (1985).

(30) H. T. Zhang, J. X. Huang, and B. B. Jiang, *J. Appl. Polym. Sci.*, **85**, 2230 (2002).

(31) D. F. Christopher and A. Rudin, *J. Macromol. Sci. Chem.*, **A16**(7), 1275 (1981).

(32) S. Shen, E. D. Sudol, and M. S. El-Aasser, *J. Polym. Sci.; Part A: Polym. Chem.*, **31**, 1393 (1993).

(33) C. K. Ober and K. P. Lok, *Macromolecules*, **20**, 268 (1987).