Effect of Crosslinking Agents on the Morphology of Polymer Particles Produced by One-Step Seeded Polymerization

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Abstract: One-step seeded polymerization was used to prepare 7~10 μm of crosslinked monodisperse spheres with four crosslinking agents using 4.68 μm poly(methyl methacrylate) (PMMA) seed particles in aqueous-alcoholic media in the absence of the swelling process. The crosslinking agents used were ethylene glycol dimethacrylate (EGDMA), allyl methacrylate (AMA), 1,6-hexanediol diacrylate (HDDA) and trimethylolpropane trimethacrylate (TMPTMA). The effects of the type and concentration of the crosslinking agents on the swelling, pore size, thermal property of the networks and morphology of the particles were studied. The chemical structures and concentrations of the crosslinking agents affected both the swelling ratio and the porosity of the networks. In addition, the chemistry of the reactive vinyl group and chain length of the crosslinking agents affected the stability of the monodisperse particles of the ultimate morphology.

Keywords: PMMA seed, crosslinking agent, one-step seeded polymerization.

Introduction

Monodisperse or uniform porous particles have been used in various applications including chromatographic packing materials,[1] ion exchange resins,[2] media for use in protein separation,[3] drug delivery,[4] and etc. Frechet studied the effect of polymeric porogens in the creation of macroporous beads[1] and reported that the porosity of the particles determined the efficiency of end use. These applications are associated with the remarkable morphological properties such as high degree of crosslinking density, rigid network structure in both swollen and dry state and presence of macropores that increase the accessibility into the polymeric network.

Spherical polymeric particles produced via classical suspension polymerization[5] generally possess considerable variations in size. Other techniques that can be used to produce spherical particles are emulsion[6,7] and dispersion polymerization,[8,9] which can yield monodisperse particles less than 1 and 1~10 μm, respectively. The compact or macroporous large uniform particles are also prepared by multi-step seeded polymerization techniques[10-14] despite the complex experimental procedure.

In general, the macroporous matrices are prepared by suspension polymerization using mono-vinyl and polyvinyl monomers as crosslinking agent and a porogen as diluent. In accordance with other authors,[15-18] it is shown that during the process of copolymerization, crosslinking and phase

separation occur, leading to the development of a porous structure, which depends on kind and concentration of porogen, mono-vinyl monomer and crosslinking agent,[19] temperature,[20] and agitation.

Depending on experimental conditions in suspension polymerization, expanded or heterogeneous networks could be obtained as a consequence of the phase separation process before or after gelation point.[21,22] A phase separation prior to gelation point leads to the development of networks with stable pores that do not collapse during the drying.[21,23] Besides, heterogeneities may appear in both poor and good solvents due to the polymer-solvent incompatibility and due to the increase in crosslinking density, respectively.[24] The network can be classified in three groups for the distribution of the diluent after the formation of the network structures: expanded (pre-swollen) networks, heterogeneous dry networks and heterogeneous swollen networks.[25]

Some reports were published for the influence of crosslinking on particle morphology at full conversion through an experimental approach. Until now, numerous studies of the core-shell structure have been done by using various analytical techniques, such as transmission electron microscopy (TEM),[26,27] X-ray photoelectron spectroscopy (XPS),[28] and infrared spectroscopy (IR).[29] However, the detailed phase-separated structure and the compatibility in the interphase between the core and shell, including the effects of crosslinking agents, have not been clarified well yet. It is known that the network formation in free-radical polymerization of multi-vinyl compounds depends on the primary chain length.

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In this article, we have investigated the effects of various crosslinking agents on the morphology of the polymer particles prepared by one-step seeded polymerization. The model monomer is methyl methacrylate (MMA) and the crosslinking agents are ethylene glycol dimethacrylate (EGDMA), allyl methacrylate (AMA), 1,6-hexanediol diacrylate (HDDA) and trimethylolpropane trimethacrylate (TMPTMA).

Experimental

Materials. Methyl methacrylate (MMA; Junsei Chemicals, Japan), ethylene glycol dimethacrylate (EGDMA; 98%, Aldrich, USA), allyl methacrylate (AMA; 98%, Aldrich, USA), 1,6-hexanediol diacrylate (HDDA; 80%, Aldrich, USA) and trimethylolpropane trimethacrylate (TMPTMA; Aldrich, USA) were purified using an inhibitor removal column (Aldrich) and stored at -5 °C prior to use. Analytical grade of potassium peroxodisulfate (KPS, Junsei Chemical Co. Ltd., Japan) and α,α'-azobisisobutylonitrile (AIBN; Junsei, Japan) were used as initiators without further purification. Poly(vinyl alcohol) (PVA, 80% hydrolyzed, M_w: 9,000~10,000, Aldrich Chem. Co.) was used as the stabilizer without purification. Methanol (Samchun Chemical, Korea) and double-distilled deionized water were used as polymerization media.

Preparation of Uniform PMMA Seed Particles. Uniform PMMA seed particles were prepared by modified emulsion polymerization of MMA in aqueous media of methanol (90 g) and double-distilled deionized (DDI) water (30 g). The monomer concentration was 8.3 wt% of the media and the polymerization reaction was initiated using 0.75 wt% KPS of the monomer. PVA was used 0.83 wt% with respect to the amount of the media. After all ingredients were charged in a 250 mL three neck round bottom flask, polymerization was carried out with a mechanical stirring at 100 rpm under nitrogen atmosphere at 70 °C for 12 h. The withdrawn polymerization products were rinsed off with DDI water and methanol, centrifuged repeatedly to remove the non-reacted materials and dried at room temperature for 2 days. Table I lists the standard recipe for the preparation of the seed PMMA particles used in the modified emulsion polymerization in aqueous methanol mixtures.

Preparation of Crosslinked Particles. The concentration of the PMMA seed was 8.3 wt% with respect to the total monomer content and the amount of PVA was 15.6 wt% of the total monomer. To depress the by-product of submicron-sized PMMA particles, 0.1 wt% (with respect to the media) $CuCl_2$ as a water-soluble inhibitor was dissolved in DDI water. The ratio of the seed to the total monomer including crosslinking agent was 1:8.3 (wt%). The polymerization reaction was initiated using 0.3 wt% AIBN of the total monomer concentration. After all ingredients were charged in a 250 mL three neck round bottom flask, polymerization was carried out with a mechanical stirring at 200 rpm under nitrogen atmosphere at 70 °C for 12 h. The withdrawn polymerization products were rinsed off with DDI water and methanol, centrifuged repeatedly to remove the non-reacted materials and dried in vacuum oven at 70 °C for 1 day, then used for characterization. Table II lists the recipe for the crosslinked copolymers of poly(MMA-co-EGDMA).

Characterization. The molecular weights of the synthesized PMMA particles were measured using Waters GPC (Gel Permeation Chromatography) equipped with a 510 differential refractometer and Viscotek T50 differential viscometer. The high resolution of 10^5-, 10^3-, and 10^2-Å μ-Styragel packed columns was employed. The universal calibration curve was obtained with 10 PS standard samples (Polymer Laboratories, United Kingdom) with molecular weights ranging from 7,500,000 to 580 g/mol. The flow rate of the PMMA solution dissolved in THF was 1.0 mL/min.

Hitachi SEM (Scanning Electron Microscopy) S-4300 was used to characterize the morphology of the particles. SEM images were obtained on samples coated with a thin layer of gold, to a depth of approximately 20 nm, under vacuum. The fractional conversion was calculated gravimetrically.

The glass transition temperature (T_g) and the melting temperature (T_m) of the sample were measured using the Perkin-Elmer DSC-7 (Differential Scanning Calorimeter, USA) and collected at the midpoint of the transition region in the second scan. The samples were heated at a heating rate of 20 °C/min under nitrogen atmosphere, quench cooled at a maximum cooling rate, and then reheated at the same heating rate as the first heating.

Table I. Standard Recipe for the Preparation of the Seed PMMA Particles Used in the Modified Emulsion Polymerization in Aqueous Methanol Mixtures

Ingredients	Amount	Remark
Methanol	90 g	Methanol : Water = 3 : 1
Water	30 g	
MMA	10 g	7.7 wt% to medium
KPS	0.075 g	0.75 wt% relative to monomer
PVA	1 g	0.83 wt% to medium

Table II. The Recipe for the Preparation of the Crosslinked Copolymers of Poly(MMA-co-EGDMA)

Ingredients	Amount	Remark
Seed	1.6 g	8.3 wt% to monomer
Total of Monomer	19.2 g	2.5 wt% to medium (each ratio of MMA/EGDMA)
Total of Medium	120 g	Water : Methanol = 9 : 1
$CuCl_2$	0.12 g	0.1 wt% to medium
PVA	3 g	15.6 wt% to monomer
AIBN	0.192 g	1.0 wt% to monomer

The thermal degradation temperature of the prepared spheres was measured by means of TA instrument Q50 TGA (Thermal Gravimetric Analysis) at a heating rate 20 °C/min from 0 to 800 °C under nitrogen atmosphere. The onset of the degradation temperature was determined at the transition point where the curve passed the maximum negative slope.
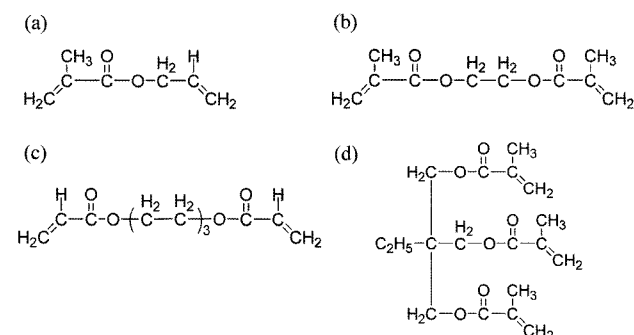
The number-average diameter (D_n) and coefficient of variation (C_v) indicating the uniformity of the particles were measured by particle size analyzer (BECKMAN COULTER, LS230, USA) with the particles suspended in water. Surface areas, pore sizes and pore volumes of the particles were determined by conventional BET analysis (nitrogen adsorption/ desorption measurements) using ASAP 2000.
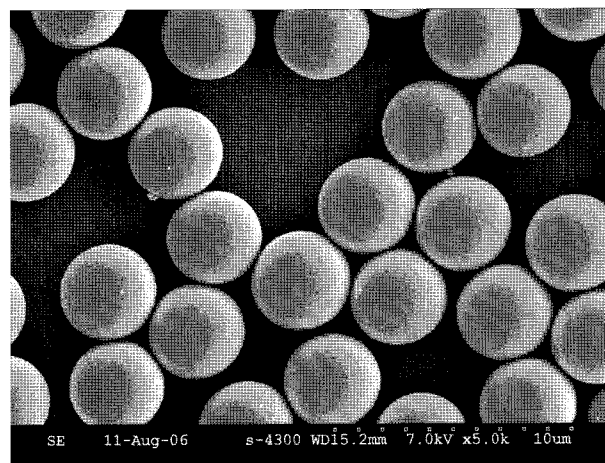
Results and Discussion

Figure 1 shows the chemical structures of the crosslinking agents. EGDMA, AMA, HDDA and TMPTMA have 2, 2, 2, and 3 functional moieties of vinyl group, respectively. In addition, it is noted that the order of the chain length between two vinyl groups in the crosslinking agent is AMA<EGDMA <HDDA and that TMPTMA has three vinyl groups.

Figure 2 shows the PMMA micropheres prepared by the modified emulsion polymerization in aqueous media at the agitation speed of 100 rpm. The characteristics of the PMMA seed latexes are the following; the conversion is 89%, the particles sizes are 4.68 μm, the coefficient of variation (C_v) is 2.57%, and the weight-average molecular weight (M_w) is 79,000 g/mol. Considering the conventional emulsion polymerization, this technique seems to be appropriate for obtaining the monodisperse PMMA microspheres due to the addition of organic solvent with a high conversion of 90%.
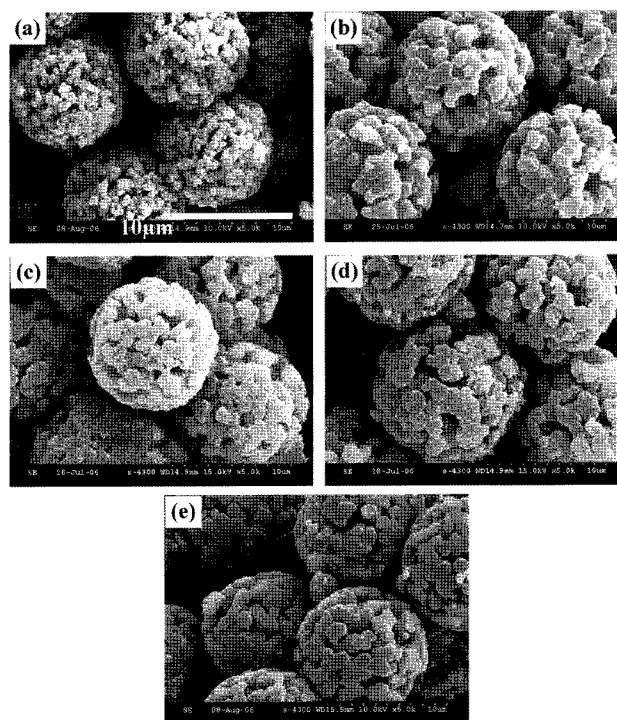
The effect of the crosslinking agents on particle formation prepared by the one-step seeded polymerization in MeOH/ water mixtures with PMMA seeds at 70 °C for 12 h was investigated. Figures 3~6 show the SEM microphotographs

Figure 2. SEM microphotographs of PMMA microspheres by modified emulsion polymerization in methanol/water (90/30 g) mixtures.

Figure 3. SEM microphotographs of poly(MMA-*co*-EGDMA) microspheres prepared by seeded polymerization in methanol/ water (10/90 g) mixtures at EGDMA concentrations (mol%) of (a) 10, (b) 25, (c) 50, (d) 75, and (e) 90 in the monomer phase.

of crosslinked microspheres prepared with various crosslinking agents such as EGDMA, AMA, HDDA, TMPTMA, respectively. In each figure, Figures (a) to (e) represent the resulting microspheres with increasing amount of crosslinking agent from 10 to 90 mol% based on methyl methacrylate, respectively. Since the order of the chain length between two vinyl groups in the crosslinking agent is AMA<EGDMA <HDDA and TMPTMA has three vinyl groups, the mor-

Figure 1. Chemical structures of the crosslinking agents used in this study; (a) Allyl methacrylate (AMA), (b) Ethylene glycol dimethacrylate (EGDMA), (c) 1,6-Hexanediol diacrylate (HDDA), and (d) Trimethylolpropane trimethacylate (TMPTMA).

phology of the crosslinked particles produced was dramatically affected by the chemistry of reactive vinyl group and chain length of crosslinking agent.

Figures 3(a)~3(e) show the PMMA/EGDMA with increasing concentrations of EGDMA form 10 to 90 mol%, the higher concentration of EGDMA affects the bigger individual pores of the particle surface. The small pores were formed locally on the particle surface at 10 mol% EGDMA [Figure 3(a)], caused by high heterogeneity between MMA and EGDMA. This seems to be an aggregation between sub-micron size particles crosslinked between MMA and EGDMA. The mechanism would be the same as described in our recent paper, of which the small particles are aggregated, showing the heterogeneous macropores by mechanical bonding.[30] As the concentration of EGDMA increases, no big difference on the surface morphology of the particles was observed. The specific surface area of porous network, which is an indicator of the number of micropores, increases with increasing content of crosslinking agent.[31] In the polymerization process, microphase separation occurred because of network formation, which causes phase heterogeneity in the polymer particle. Localized heterogeneity phenomenon causes to produce not only micro porous particles but also rough particles.

Figure 4 shows the particles with a rugged surface obtained using AMA as a crosslinking agent. The increase in the concentration of AMA leads to the lower local heterogeneity, reducing the difference between the prominence and depression. As observed in the poly(MMA-co-EGDMA) system, the crosslinked small particles are aggregated to form large particles. In addition, as the concentration of AMA increased, the copolymer particles become smaller with tighter aggregation. It is possible to obtain soother particle surface with increasing concentration of AMA as shown in Figure 4(e).

In Figure 5(a), the rugged particle surface was observed as observed in the case of AMA in Figure 4. As the HDDA concentration increased from 10 to 25 mol%, the surface of the particles turned to smoother and small grain type particles were almost disappeared on the surface. On the other hand, when the HDDA concentration increased from 50 to 90 mol%, rougher surface with small pores was dominating.

In Figure 6, the porous particle was formed from partial prominence and depression under the influence of high local concentration of double bonds below 25 mol% of TMPTMA. However, the poly(MMA-co-TMPTMA) particles at 50 mol% of TMPTMA have the smoothest surface among other concentrations [Figure 6(c)]. In addition, as the TMPTMA concentration increased from 50 to 90 mol%, the particle surface becomes rougher and the particle surface with 90 mol% TMPTMA becomes sunken surface like golf ball because of the high concentration of double bonds [Fig-
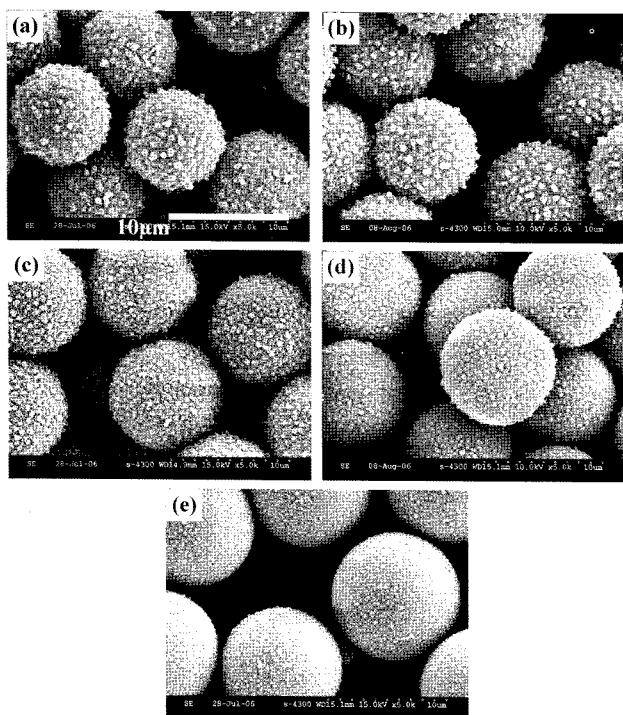
Figure 4. SEM microphotographs of poly(MMA-co-AMA) microspheres prepared by seeded polymerization in methanol/water (10/90 g) mixtures at AMA concentrations (mol%) of (a) 10, (b) 25, (c) 50, (d) 75, and (e) 90 in the monomer phase.
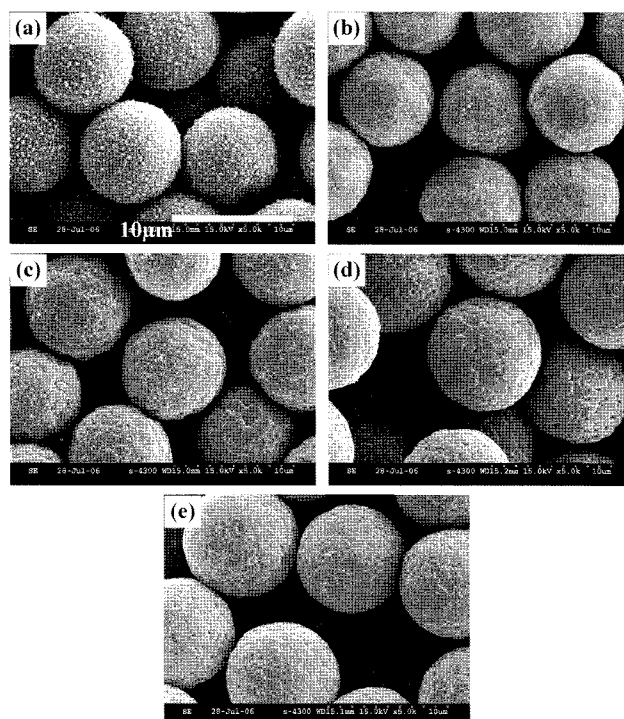

Figure 5. SEM microphotographs of poly(MMA-co-HDDA) microspheres prepared by seeded polymerization in methanol/ water (10/90 g) mixtures at HDDA concentrations (mol%) of (a) 10, (b) 25, (c) 50, (d) 75, and (e) 90 in the monomer phase.
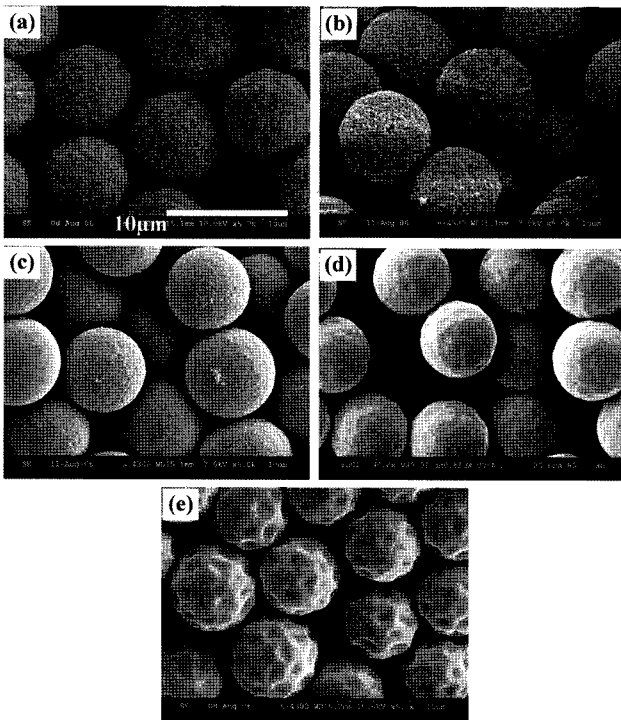
Figure 6. SEM microphotographs of poly(MMA-*co*-TMPTMA) microspheres prepared by seeded polymerization in methanol/water (10/90 g) mixtures at TMPTMA concentrations (mol%) of (a) 10, (b) 25, (c) 50, (d) 75, and (e) 90 in the monomer phase.

ure 6(e)]. Since TMPTMA molecule has a compact tetrahedral structure with double bonds at three of the four corners, the morphology is strongly influenced by the composition between MMA and TMPTMA compared to other systems containing two double bonds in crosslinking agents. If one of these three double bonds reacts to a growing polymer chain, the next two double bonds must find other molecules. When a new molecule is added to a growing chain, it is subject to steric hindrance from the two last added monomer units. In overall, since the order of the chain length between two vinyl groups in the crosslinking agent is AMA< EGDMA<HDDA, the morphology of the crosslinked particles produced was dramatically affected by the chemistry of reactive vinyl group and chain length of the crosslinking agent.

Figures 7(a)-(d) depicts the number-average particle size (D_n) and the coefficient of variation (C_v) of the particles analyzed from Figures 2~5 as a function of the concentration of various crosslinking agents. The number-average particle diameter with EGDMA, AMA and HDDA is in the range of 7~11 μm and increases with the concentration of the crosslinking agents relative to the monomer. On the other hand, the coefficient of variation (C_v) of the spherical particles is slightly reduced with the concentration of EGDMA, but no change was observed with AMA and HDDA. In the case of poly(styrene-*co*-DVB), the coefficient of variation of microspheres slightly reduced with the increasing con-
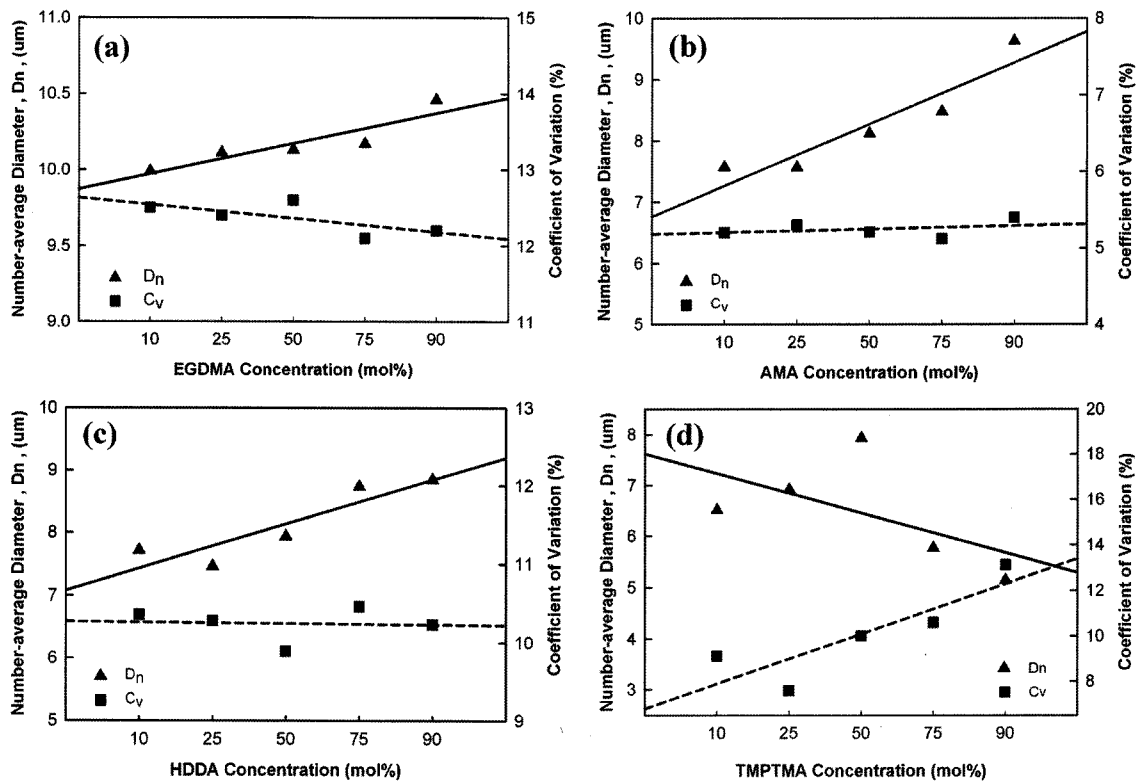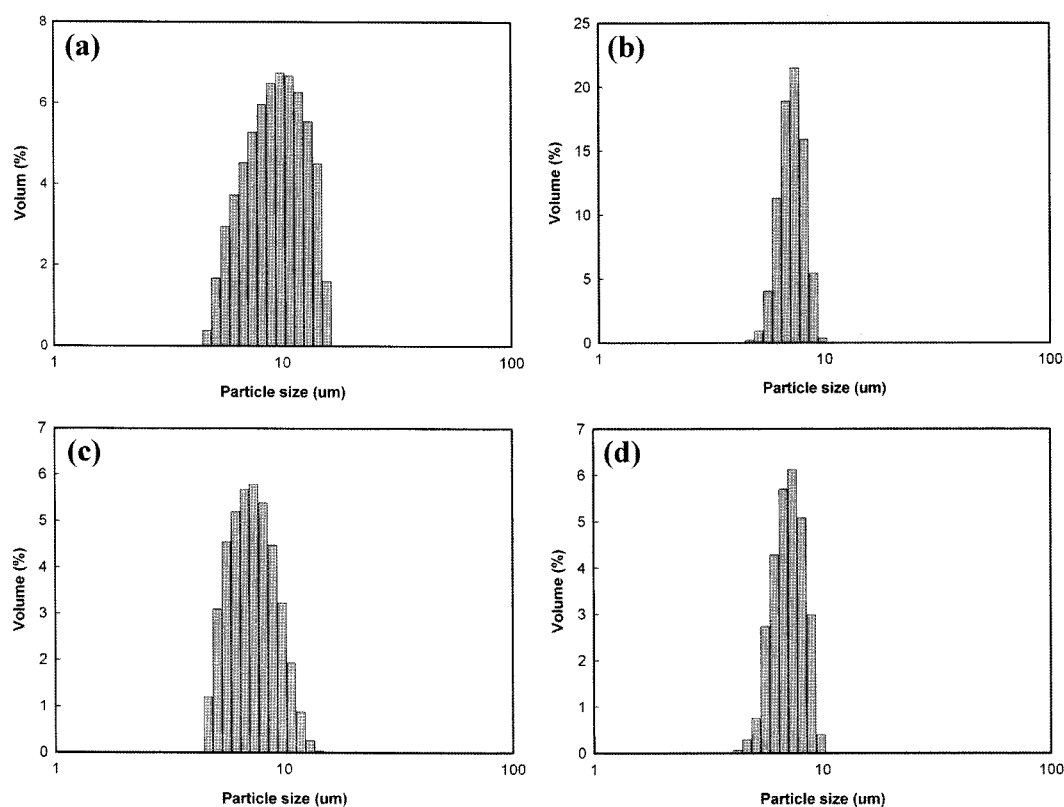

Figure 7. Effect of concentration of crosslinking agent on the average diameter (▲), and C_v (■) of final particles produced using various crosslinking agent by seeded polymerization. (a) EGDMA, (b) AMA, (c) HDDA, and (d) TMPTMA.

centration of divinylbenzene in the precipitation polymerization of styrene.[32] On the other hand, the PMMA particles with TMPTMA have a tendency to increase the number-average particle diameter up to 50 mol% and then decrease, but the behavior of the coefficient of variation shows the vise versa. Since the chemical structure of crosslinking agent plays a significant role in determining the successful formation of stable spherical shape, the bulky chemical structure and three reactive centers of TMPTMA are taken into account for explaining the unusual phenomena of the particle size and variation of the sizes. Since the steric hindrance due to the bulkiness of TMPTMA causes fast initiation and termination reaction, it is difficult to form stable particles with the concentration increment of TMPTMA. On the other hand, the average diameter of poly(S-co-EGDMA), poly(S-co-TMPTMA) and poly(S-co-PETRA) [poly(styrene-co-pentaerythritol tetraacrylate] systems, of which the chemical structures of the crosslinking agents have di-, tri-, and tertra-functional crosslinking moiety, decreased with the concentration of the crosslinking agents.[33] This may caused by the increased level of crosslinking. In addition, with poly(GMA-co-DVB) system, the average diameter and the C_v simultaneously increased with the concentration of DVB.[34]

In addition, Figures 8(a)~8(d) show the size distribution of the crosslinked PMMA particles containing 25 mol% of EGDMA, AMA, HDDA, TMPTMA, respectively. Thus, in

Figure 8, the distribution of the crosslinked PMMA particle sizes with EGDMA is broad and this is due to the bulkiest structure having two reactive centers among crosslinking agents. On the other hand, the distribution of the crosslinked PMMA particles with 25 mol% AMA is relatively narrow, showing the C_v is 5.3. TMPTMA also affords narrow size distribution although the chemical structure is bulky having tri-functional moiety.

Figure 9 compares the surface area, average-pore size and average-pore volume of the spherical particles prepared using 25 mol% various crosslinking agents. Pore formation is very complex due to the presence of multiple variables in the polymerizing system. Resenberg et al. reported that the polymerization of TMPTMA in a solvent gives a macroporous polymer with a narrow pore size distribution of small pores and broader pore size distribution of large pores, which varies with the monomer to solvent ratio.[35] The solubility of the seed polymer and second monomer may be one of the important factors in determining miscibility and phase separation. Poly(MMA-co-EGDMA) in Figure 9 showed the highest surface area, pore volume and high mean pore size. On the other hand, poly(MMA-co-HDDA) showed the lowest surface area with smooth surface containing small pore volume and mean pore size. Since the functional group of each crosslinking agent is similar, the primary chain length and bulkiness of the branch are suggested to play a crucial role

Figure 8. Effect of the type of crosslinking agent (25 mol%) on the size distribution of final particles produced using various crosslinking agent in monomer phase by seeded polymerization. (a) EGDMA, (b) AMA, (c) HDDA, and (d) TMPTMA.
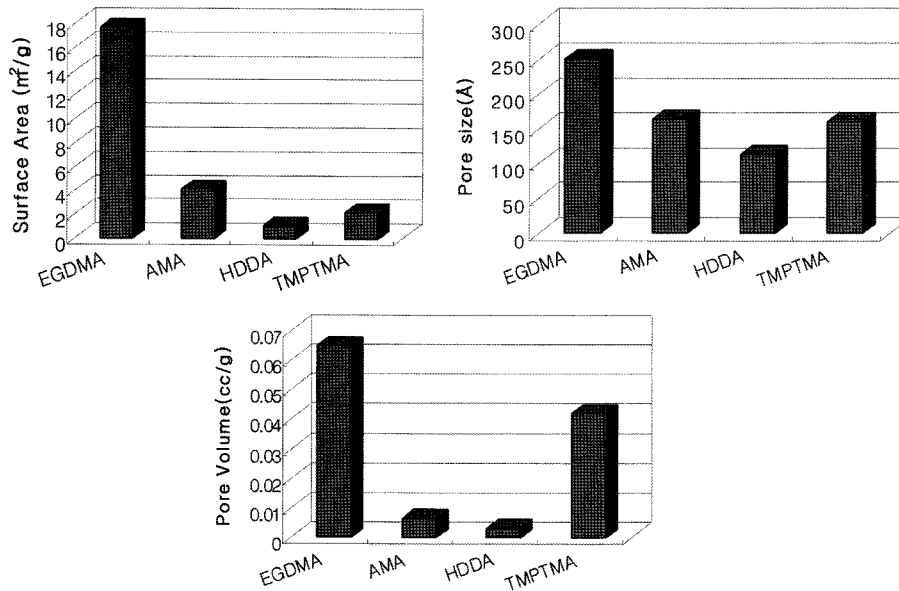
Figure 9. Effect of the type of crosslinking agent (at 25 mol%) on surface area, mean pore sizes and pore volume of final particles produced in monomer phase using one-step seeded polymerization.
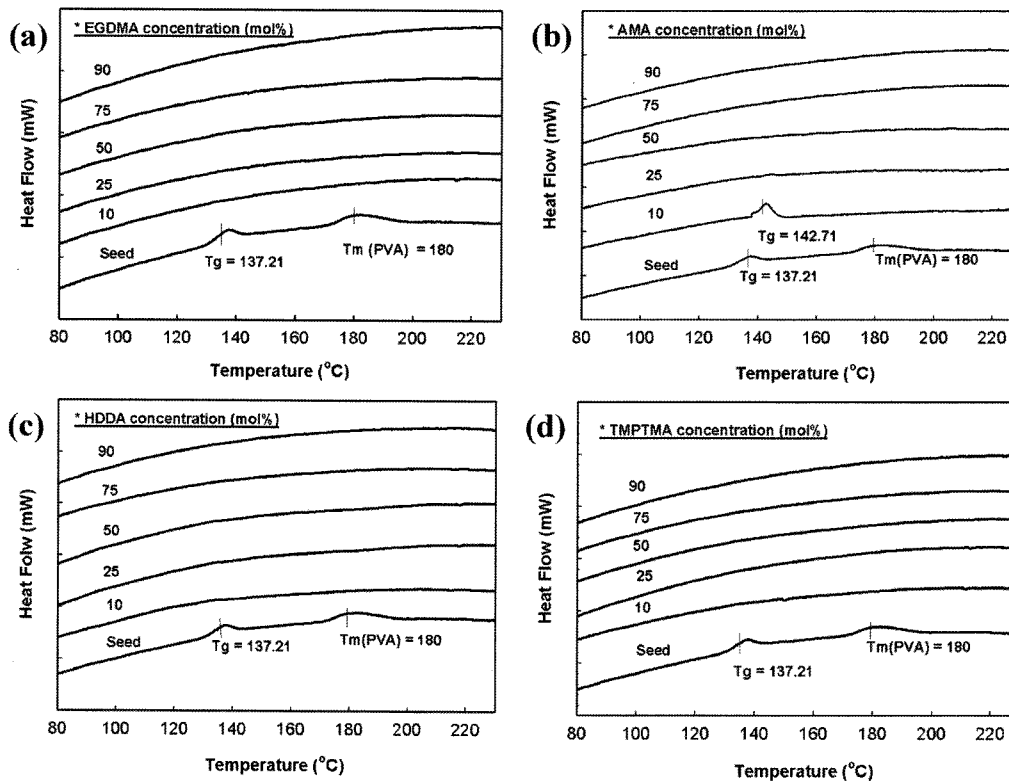
Figure 10. Effect of the concentration of crosslinking agent on thermal property of final particles produced using various crosslinking agents using one-step seeded polymerization. (a) EGDMA, (b) AMA, (c) HDDA, and (d) TMPTMA.

in phase separation resulting in the highly porous particles. Particles having high porosity were formed using EGDMA containing bulky branch and short primary chain length. Whereas, low bulkiness and long primary chain length of HDDA is responsible for inducing the smooth surface.

The thermal properties of the crosslinked particles obtained from the seeded polymerization were characterized using DSC. The observation of the glass transition temperature (T_g) of the microspheres containing various concentrations of crosslinking agents is demonstrated in Figure 10. The

glass transition temperature of the seed PMMA particles is observed at 137.2 °C, which is higher than that of the commercial PMMA (T_g=105 °C). In addition, the melting temperature (T_m) of PVA was observed at 180 °C. Polymeric stabilizers used in the polymerization are physically adsorbed not only on the particle surface, but also into the particles. The use of PVA in the dispersion polymerization of MMA can induce different tacticities of PMMA.[36] The high T_g of PMMA at 129 °C is also observed in the photopolymerization of living-radical polymerization.[37,38]

A broadening and an increase in the endothermic transition, followed by the disappearance of the glass transition temperature with the crosslinking agent content, was initially expected. However, no existence of the endothermic transition representing the glass transition temperature was observed for all examined samples except using AMA. T_g of the particles synthesized at 10 mol% AMA is observed at 142.7 °C, that is fairly higher than that of the seed polymer. AMA possesses two types of vinyl groups which are methacrylic and allylic double bonds having greatly different reactivity. The allyl group ($CH_2CH:CH_2$) is only weakly polymerizable or copolymerizable by free radical methods. This is explained simply by ready chain transfer.[39] The reactivity may vary somewhat depending on the attached groups.

Figures 11 represent the TGA onset temperature of the thermal degradation (5 wt% weight loss) of the crosslinked particles prepared with various crosslinking agents, EGDMA, AMA, HDDA, and TMPTMA, respectively. The TGA onset degradation temperature of poly(MMA-co-EGDMA) varied from 316 to 302.6 °C for 10 and 90 mol% EGDMA, respectively. The thermal stability of poly(MMA-co-AMA) is also reduced with increased concentration of AMA. Although the thermal stability of poly(MMA-co-EGDMA)
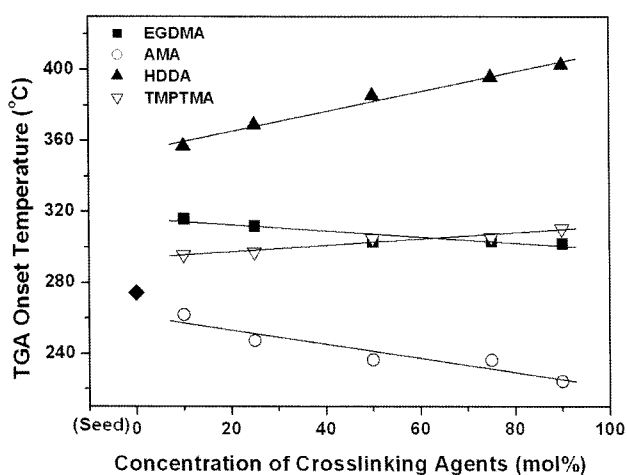
and poly(MMA-co-AMA) decreased with the concentration of EGDMA or AMA, the TGA onset degradation temperature of poly(MMA-co-AMA) is lower than that of pure PMMA seed polymer, whereas that of poly(MMA-co-EGDMA) is higher than that of the seed PMMA particles. On the other hand, the thermal degradation temperature of poly(MMA-co-TMPTMA) increased from 295 to 310 °C with the concentration of the TMPTMA from 10 to 90 mol%, respectively. In particular, the TGA degradation temperatures dramatically increased from 355 to 402 °C between 10 and 90 mol% HDDA, respectively, indicating that the enhanced thermal stability was obtained in HDDA system. Since HDDA has an aliphatic chain compared to TMPTMA having a bulky side chain with functional moiety, the molecular penetration of HDDA during crosslinking would be favorable, resulting in a higher level of crosslinking and higher thermal stability.

Overall, from the results observed from Figures 7 to 11, it is obviously seen that poly(MMA-co-HDDA) is the best for the application of crosslinked copolymer particles with uniformity, low surface area with low pore volume and significantly improved thermal stability.

Conclusions

7~10 μm of crosslinked monodisperse spheres with various crosslinking agents using 4.68 μm poly(methyl methacrylate) (PMMA) seed particles were produced in aqueous-alcoholic media by one-step seeded polymerization in the absence of the swelling process. The crosslinking agents used are ethylene glycol dimethacrylate (EGDMA), allyl methacrylate (AMA), 1,6-hexanediol diacrylate (HDDA) and trimethylolpropane trimethacrylate (TMPTMA). Particle morphology and size can be tuned by the type of crosslinking agent. In the polymerization process, microphase separation occurred because of network formation, which causes phase heterogeneity in the polymer particle. Localized heterogeneity phenomenon causes to produce not only micro porous particles but also rough particles. The chemical structures and concentration of the crosslinking agents affected both the swelling ratio and porosity of the networks. According to thermodiagram, HDDA acts as the best crosslinking agent in the comparison of thermal stability through TGA. In addition, the order of the chain length between two vinyl groups in the crosslinking agent is AMA<EGDMA<HDDA. Thus, the chemistry of reactive vinyl group and chain length of the crosslinking agents affected the stability of the monodisperse particles of the ultimate morphology.

Figure 11. Effect of the concentration of crosslinking agent on the thermal stability of the final particles produced with various crosslinking agents by one-step seeded polymerization. Symbol (♦) represents the data obtained for PMMA seed.

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