

# Low Temperature Suspension Polymerization of Methyl Methacrylate for the Preparation of High Molecular Weight Poly(methyl methacrylate)/Silver Nanocomposite Microspheres

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**Abstract:** In order to prepare high molecular weight poly(methyl methacrylate) (PMMA)/silver nanocomposite microspheres, methyl methacrylate was suspension-polymerized in the presence of silver nanoparticles at low temperature with 2,2'-azobis(2,4-dimethylvaleronitrile) as an initiator. The rate of conversion was increased by increasing the initiator concentration. When silver nanoparticles were added, the rate of polymerization decreased slightly. High monomer conversion (about 85 %) was obtained in spite of low polymerization temperature of 30 °C. Under controlled conditions, PMMA/silver microspheres with various number-average degrees of polymerization (6,000-37,000) were prepared. Morphology studies revealed that except for normal suspension microspheres with a smooth surface, a golf ball-like appearance of the microspheres was observed, due to the migration and aggregation of the hydrophilic silver nanoparticles at the sublayer beneath the microsphere's surface.

**Keywords:** PMMA/silver microspheres, Nanocomposite, Suspension polymerization

## Introduction

Since Charnley's investigations in the early 1960s, self-curing poly(methyl methacrylate) (PMMA) cements have been leading to the development of new technologies for fixation of joint prostheses to bone [1]. Two-part self-curing acrylic cements are currently the only materials used for anchoring cemented arthroplasties to the contiguous bones [2]. The liquid part typically contains three basic components: acrylic monomers (97 vol.%), an inhibitor for preventing the premature polymerization of the monomer, and an accelerator of the initiator decomposition. The solid phase consists of prepolymerized PMMA beads (89 wt.%), a mineral powder such as barium sulfate or zirconium dioxide (10 wt.%) acting as radiopacifier, and a free-radical initiator such as benzoyl peroxide [3]. The resulting mechanical properties of the set cement rely on the cohesion between the initial PMMA and the polymerized monomer. The lack of adhesion between the acrylic matrix and the inorganic radiopacifying particles is sometimes responsible for a premature rupture, because the filler particles behave like voids for crack nucleation which can grow for crack propagation [4]. Therefore, it is desirable to develop a new approach that can be used to directly prepare high molecular weight (HMW) PMMA with good cohesion between polymer and inorganic radiopacifying particles.

PMMA is an important polymeric material with high light transmittancy, colorlessness, chemical resistance, and weathering corrosion resistance. Due to these superior characteristics,

PMMA has been widely used in additives, coating and polishing agents, binders, sealers, transparent neutron stoppers, optical fiber, high voltage applications, and outdoor electrical applications [5-8]. In some of these applications, the HMW PMMA is required.

Nanocomposites often exhibit physical and chemical properties that are dramatically different from conventional composites. During the past decade, a great deal of research has been conducted on the elaboration of nanocomposite systems by embedding inorganic particles into polymeric matrices [9-13]. Nanostructured polymer-inorganic composites, mixed at the molecular level or near molecular level, are much different from conventional composites with incorporation of a variety of additives in the polymer matrices. Many novel nanocomposites with improved performance properties, which may have large potential applications in the fields such as optics [14], electrical devices [15], photoconductors [16], have been reported.

Silver nanoparticles are widely used as photosensitive components [17], catalysts [18,19], and Raman spectroscopy enhancement additive [20] as well as for chemical analysis [21]. Especially, silver is known to have a wide antibacterial spectrum [22]. Additionally, due to its comparatively high safety [23], many researchers have been successful in developing antibacterial and disinfectant agents with silver loaded on various carriers. In general, the polymer-silver nanocomposites have been prepared in two steps. First, the polymer was synthesized, and then silver ions were introduced into the polymer matrix and reduced to zerovalent state by a reducing agent or by post-heating. In recent years, much effort has been devoted to the studies of the in-situ synthesis

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of metal nanoparticles in polymer matrices [24-26]. This method is based on the reduction of metal ions that are dispersed in polymer matrices. According to Zhu *et al.* [27], a completely different method was employed to produce polymer-silver nanoparticle composites, in which the reduction of silver ions and the polymerization of monomers occurred simultaneously by  $\gamma$ -irradiation. Yin *et al.* prepared polyacrylamide/silver nanocomposites by irradiating the aqueous solution of  $\text{AgNO}_3$  and acrylamide monomer with  $^{60}\text{Co}$   $\gamma$ -ray [28].

Recently, many polymer/inorganic nanocomposites were prepared by suspension polymerization. According to Duguet *et al.*, PMMA encapsulated alumina particles were prepared by suspension polymerization [29]. Huang and Brittain synthesized PMMA/layered silicate nanocomposites by in-situ suspension and emulsion polymerization [30]. According to Shim *et al.*, homogeneously zinc oxide (ZnO)-dispersed PMMA composite microspheres were produced in-situ suspension polymerization [31]. More recently, Jun and Suh synthesized poly(urethane acrylate)/clay nanocomposite particles by suspension polymerization [32]. According to Hwu *et al.* [33], polystyrene/montmorillonite nanocomposites were obtained by suspension free radical polymerization of styrene in the dispersed organophilic montmorillonite. Additionally, Yeum *et al.* reported that poly(vinyl acetate)/silver nanocomposite microspheres were formed during suspension polymerization of vinyl acetate in the presence of silver nanoparticles [34].

Recently, several researchers have been reconsidering suspension polymerization of methyl methacrylate (MMA) from an industrial viewpoint [35,36]. However, these polymerizations were conducted at polymerization temperatures of over 50 °C. In these cases, molecular weight reduction in PMMA inevitably is accelerated. In the current study, a room-temperature free-radical initiator, 2,2'-azobis(2,4-dimethylvaleronitrile) (ADMVN), which can lower the polymerization temperature to room temperature was selected for suspension polymerization of MMA with or without silver nanoparticles. The purpose of this article is to investigate the effects of silver nanoparticles on the polymerization behaviors and morphology of HMW PMMA.

## Experimental

### Materials

MMA purchased from Aldrich was washed with an aqueous solution of  $\text{NaHSO}_3$  and water and dried with anhydrous  $\text{CaCl}_2$ , followed by distillation in a nitrogen atmosphere under reduced pressure [37]. The monomer-soluble initiator, ADMVN (Wako Co.), was recrystallized twice in methanol before use. Poly(vinyl alcohol) (PVA) with number-average molecular weight of 127,000 and degree of saponification of 88 % (Aldrich Co.) was used as a suspending agent. Aqueous silver nanoparticles dispersion (AGS-WP001, 10,000 ppm) with diameters ca. 15-30 nm was purchased from Miji Tech. Co., Ltd., Korea and other extra-pure grade reagents were

**Table 1.** Suspension polymerization conditions of MMA

Type of initiator	ADMVN
Type of suspending agent	PVA
Initiator concentration	0.0001, 0.0005, 0.001 mol/mol of MMA
Suspending agent concentration	1.5, 5.0, 9.0 g/dl of water
MMA/water	0.5, 1.0 //
Rpm	500
Temperature	30 °C
Silver nanoparticles dispersion/MMA	0.2 //

used without further purification. Deionized water was used for all the experiments.

### Preparation of PMMA/Silver Nanocomposite Microspheres

To prepare HMW PMMA/silver nanocomposite microspheres, suspension polymerization of MMA in the presence of aqueous silver nanoparticles dispersion was conducted. The suspending agent was dissolved in water under a nitrogen atmosphere with constant stirring in a 250 ml reactor fitted with a condenser. After degassing, MMA monomer, aqueous silver nanoparticles dispersion, and ADMVN were added simultaneously at a fixed polymerization temperature. After predetermined times, the reaction mixture was cooled and kept for one day to separate the PMMA/silver spheres. The final PMMA/silver spheres were filtered and washed with warm water.

Conversion was calculated by measuring the weight of the PMMA/silver. In the case of calculating of conversion, the weight of silver was ignored because the weight of silver nanoparticles in the PMMA microsphere is less than 0.1 %. Conversions were averages of three determinations. The detailed polymerization conditions are listed in Table 1.

### Characterizations

The molecular weights of PMMA were calculated using equation (1) [38].

$$[\eta] = 5.5 \times 10^{-5} [M_n]^{0.76} \quad (\text{in benzene at } 25^\circ\text{C}) \quad (1)$$

where  $[\eta]$  is intrinsic viscosity. The number-average degree of polymerization ( $P_n$ ) of PMMA was calculated from  $M_n$ . To precisely obtain the  $P_n$  of PMMA, in each case, the PMMA/silver spheres were purified by reprecipitation and centrifuge (20,000 rpm) from a benzene/hexane mixture and dried in a vacuum oven at 60 °C.

The concentration of silver in the PMMA/silver microspheres was measured using Solaar AAS-S4 atomic absorption spectrometry (Thermal Elemental).

The average size and surface morphology of the PMMA/silver microspheres were examined using a Hitachi S-570 scanning electron microscope (SEM). To obtain the average size, five SEM photographs and more than 200 particles were collected by computer, and linked with the SEM, followed by statistical analysis of the data by computer.

## Results and Discussion

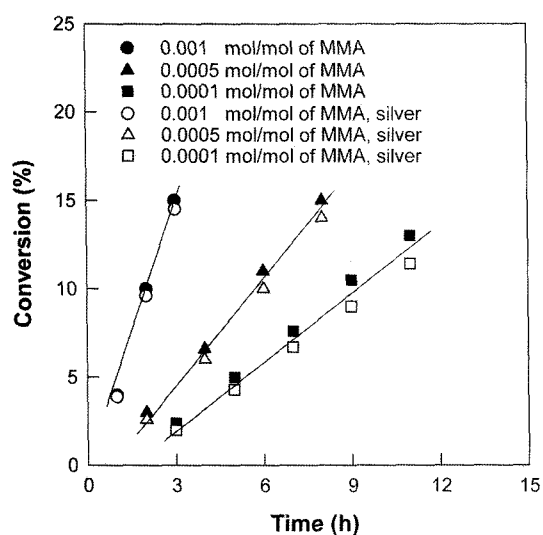
### Suspension Polymerization Behavior and Molecular Weight of PMMA/Silver Microspheres

In a free radical polymerization, the rate of polymerization ( $R_p$ ) can be expressed by equation (2) [39].

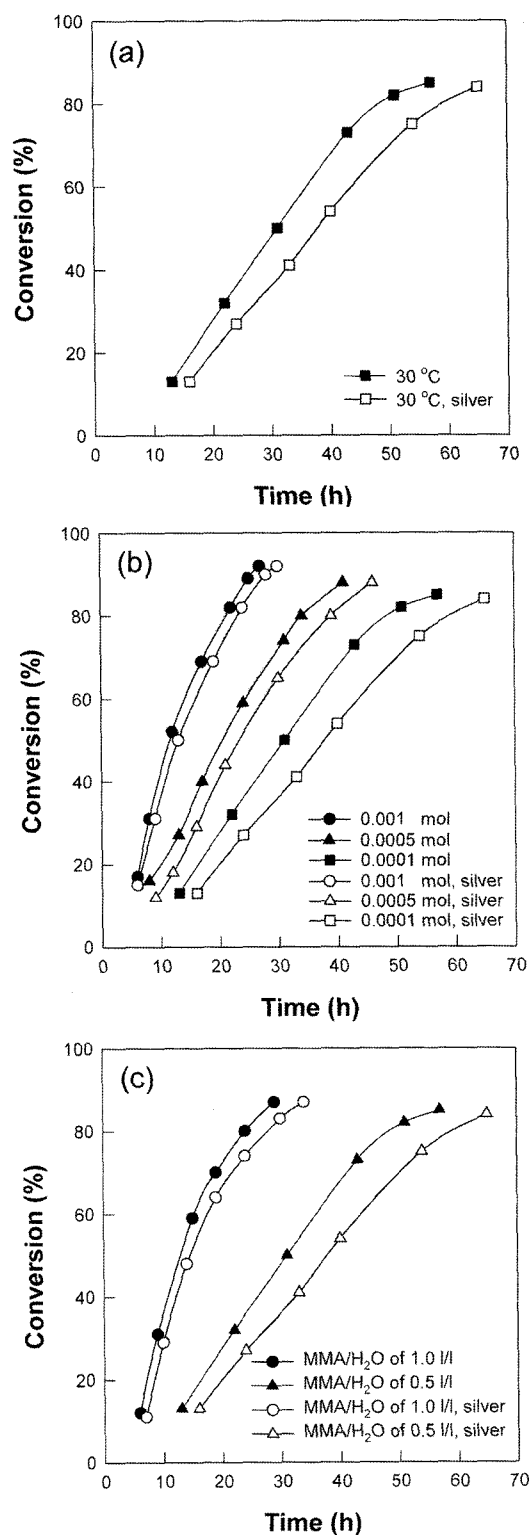
$$R_p = k_p[M][I]^{0.5}(f/k_d/k_t)^{0.5} \quad (2)$$

where  $f$  is the initiator efficiency,  $[M]$  and  $[I]$  are the concentrations of the monomer and initiator, and  $k_d$ ,  $k_p$ , and  $k_t$  are the reaction rate constants of the initiator decomposition, propagation, and termination, respectively. Accordingly, it can be predicted that the rate of polymerization will increase as the efficiency and concentration of initiator are increased. It is well known that ADMVN is an effective low temperature initiator (10 h half-life decomposition temperature of ADMVN is 51 °C) that can be used to prepare high molecular weight polymers with high yield [40-43]. In the current study, ADMVN was used to prepare PMMA/silver microspheres at room temperature. Figure 1 presents the initial conversion rate measured within 15 % conversion in the suspension polymerization of MMA with or without silver nanoparticles at 30 °C using ADMVN. As shown, the higher the initiator concentration, the higher the polymerization rate. This tendency agrees with the theoretical prediction in equation (2). Additionally, the rates of polymerization with silver nanoparticles were slightly lower than those without silver nanoparticles. It is likely that the adsorption of initiator reduces the activity of living polymer molecules.

Figure 2(a) shows the conversion as a function of reaction time at 30 °C using an initiator concentration of 0.0001 mol/mol of MMA with or without silver nanoparticles. Increase



**Figure 1.** Initial conversion of MMA into PMMA or PMMA/silver suspension-polymerized using different ADMVN concentrations at 30 °C with polymerization time (suspending agent concentration: 1.5 g/dl of water).

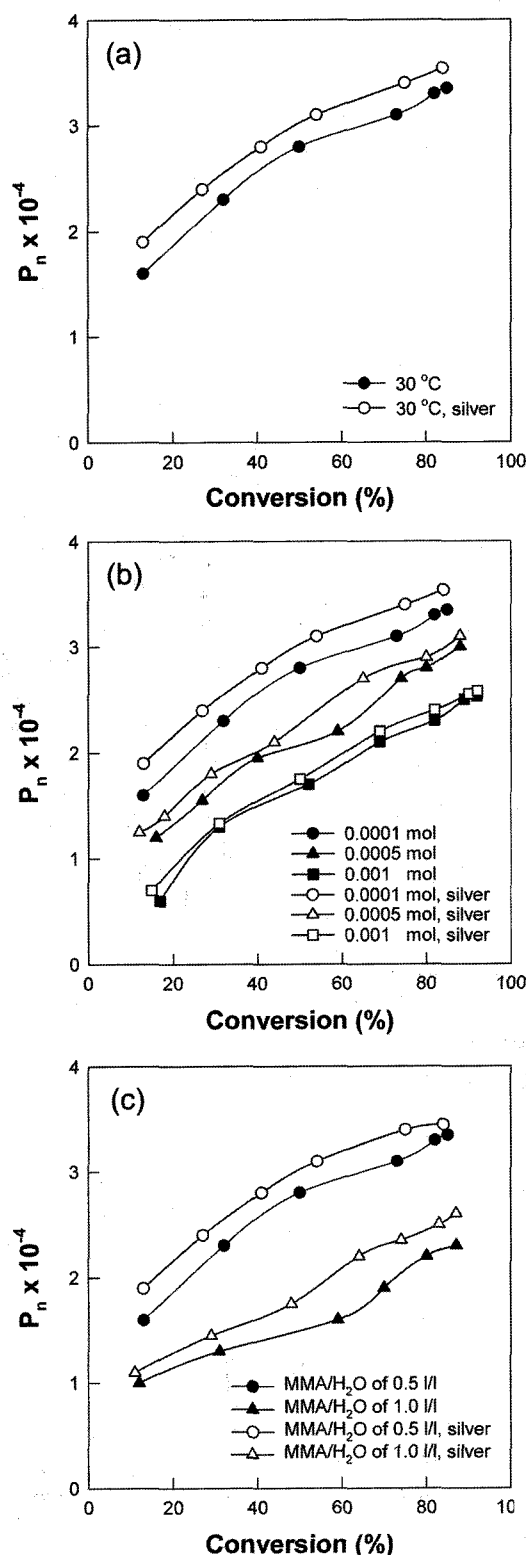


**Figure 2.** Effect of silver nanoparticles on the conversion of MMA into PMMA/silver suspension-polymerized using a polymerization temperature of 30 °C (a), different ADMVN concentrations (b), and different MMA/water contents (c) with polymerization time (suspending agent concentration: 1.5 g/dl of water).

of conversion with time was abruptly diminished during polymerization, probably due to the inefficient transfer and diffusion of heat because of the MMA formed at the early stage of polymerization. These features were clearly observed in azobisisobutyronitrile-initiated free-radical polymerization of MMA above 50 °C. Unlike conventional suspension polymerization, no auto-acceleration behavior was observed in this study. It should be noted that this polymerization was carried at a low room temperature and that the polymer propagation rate was very low. As a result, the temperature increase during the polymerization is much less significant for the system studied here than for conventional suspension polymerization at a relatively high temperature. Because of the low polymerization rate, no auto-acceleration was observed. The conversions increased up to about 85 % for the system studied in spite of the low initiator concentration of 0.0001 mol/mol of MMA. Compared with bulk polymerization, only 30-40 % conversion of MMA was obtained under same conditions [44]. In bulk polymerization, auto-acceleration is more significant than in suspension polymerization. Furthermore, the auto-acceleration behavior described above seems not to be so noticeable in the low-temperature suspension polymerization of MMA as shown in Figure 2(a). In all cases, the rates of polymerization with silver nanoparticles were slightly lower than without silver nanoparticles. There are two possible reasons for the reduction in the polymerization rate when silver particles were presented. First, the nano-silver particles may adsorb the active polymer chains so the diffusion rate of the active polymer decreases. Second, the silver particles may function as scavengers for the initiator. Further research is needed to fully understand the real mechanisms. In conclusion, the suspension polymerization of MMA in the presence of silver nanoparticles using ADMVN is an effective method to increase both yield and molecular weight of PMMA/silver microspheres at the same time.

Conversion-time plots at different initiator concentrations with or without aqueous silver nanoparticles dispersion at 30 °C are shown in Figure 2(b). The polymerization rate was increased with increasing initiator concentration, which coincided well with the theoretical predictions [33]. Figure 2(c) presents conversion-time plot at different MMA/water ratios using an initiator concentration of 0.0001 mol/mol of MMA with or without silver nanoparticles at 30 °C. In the case of a low value of MMA/water ratio, a slow polymerization rate was obtained. The polymerization rate prepared by suspension polymerization technique is controlled by the monomer/water ratio [41]. As shown in Figure 2(c), the lower the values of MMA/water ratio, the lower the polymerization rate. This might be explained by the fact that the lower chain transfer rates by water, which effectively diminishes the high exotherm of MMA generated during polymerization, decreased the polymerization rate.

The ( $P_n$ )s of PMMA and PMMA/silver prepared by suspension polymerization with conversions are shown in

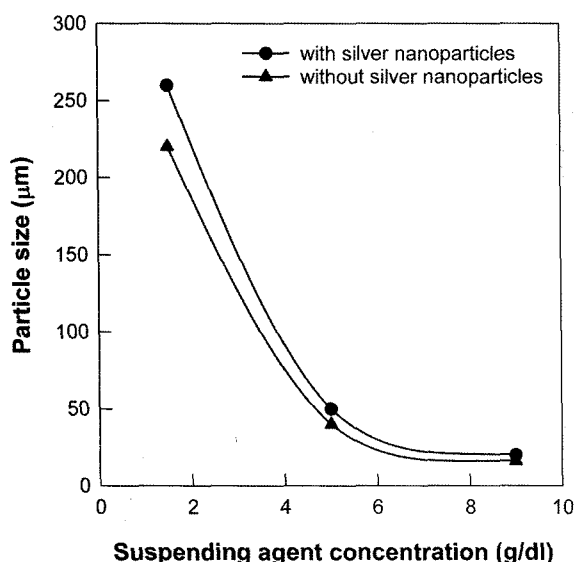


**Figure 3.** Effect of silver nanoparticles on the  $P_n$  of PMMA/silver suspension-polymerized using different polymerization temperatures (a), different ADMVN concentrations (b), and different MMA/water contents (c) with conversion (suspending agent concentration: 1.5 g/dl of water).

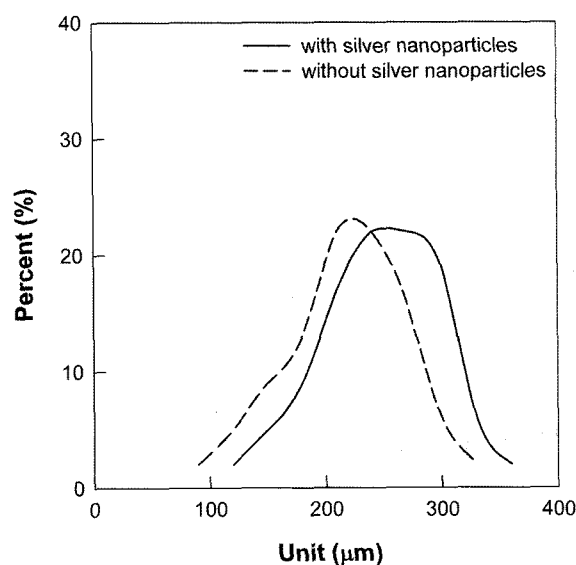
Figures 3(a) and 3(b). In accordance with theoretical prediction, ( $P_n$ )s of PMMA increased with a decrease in the initiator (ADMVN) concentration and polymerization temperature. The ( $P_n$ )s of PMMA/silver were slightly higher than those of PMMA. As mentioned above, this may be explained by the fact that polymerization rate of PMMA droplets with silver nanoparticles is slower than without silver nanoparticles. It should be noted that PMMA/silver microspheres with  $P_n$  of 6,000-36,000 could be prepared by suspension polymerization of MMA in the presence of silver nanoparticles with higher conversion. Figure 3(c) presents ( $P_n$ )s as a function of MMA/water ratio at an initiator concentration of 0.0001 mol/mol with or without aqueous silver nanoparticles dispersion at 30 °C, respectively. HMW PMMA/silver microspheres with various ( $P_n$ )s of 10,000-37,000 can be prepared by suspension polymerization of MMA in the presence of silver nanoparticles. Furthermore, in all cases, the ( $P_n$ )s of PMMA with silver nanoparticles were slightly higher than those of PMMA without silver nanoparticles.

#### Size and Morphology of PMMA/Silver Microspheres

Figure 4 shows the effect of silver nanoparticles on the average particle sizes of PMMA/silver spheres. It is well known that a high concentration of stabilizer will lead to small particles because of the decrease in interfacial tension when the stabilizer concentration is increased [45]. Our experimental results agree very well with this theoretical prediction. For the sample containing silver nanoparticles, the particle sizes increased slightly. The particle size distributions of PMMA microspheres with or without silver nanoparticles using suspending agent concentration of 1.5 g/dl of water are



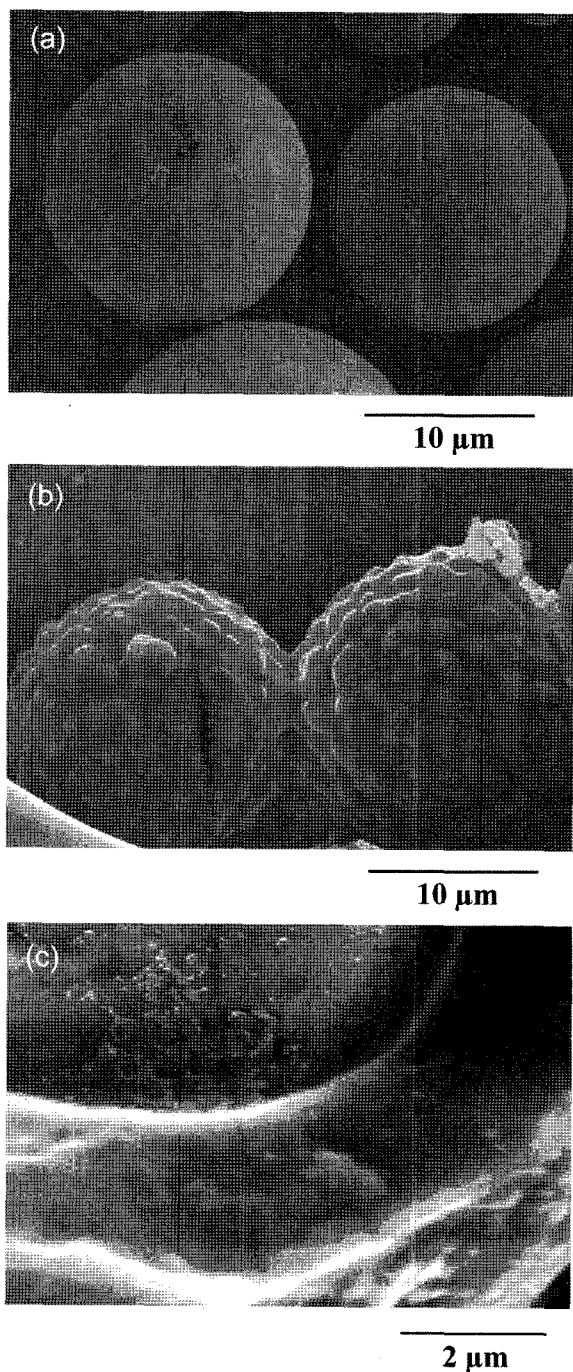
**Figure 4.** Effect of silver nanoparticles on the average particle size of HMW PMMA/silver spheres suspension-polymerized using different concentrations of suspending agent (ADMVN concentration: 0.0001 mol/mol of MMA).



**Figure 5.** Effect of silver nanoparticles on the particle size distributions of HMW PMMA spheres suspension-polymerized using a suspending agent concentration of 1.5 g/dl of water (ADMVN concentration: 0.0001 mol/mol of MMA).

presented in Figure 5. The particle size distribution of PMMA microspheres with silver nanoparticles was slightly increased. The silver nanoparticles used in this study are an aqueous suspension form and hydrophilic. Therefore, the aggregated silver nanoparticles will adsorb on the polymer matrices, resulting in irregular distribution relatively.

SEM photographs of HMW PMMA and PMMA/silver microspheres suspension-polymerized using a suspending agent concentration of 9.0 g/dl of water are presented in Figures 6(a) and 6(b), respectively. It is surprising that two different appearances of microspheres, one with a smooth surface and another with a golf ball-shaped surface, were observed for all the samples that were prepared in the presence of silver nanoparticles. Although the formation mechanism of these golf ball microspheres is not yet clear, we believe this phenomenon is related to the aggregation of silver nanoparticles during polymerization. It is noteworthy that the silver nanoparticles used in this study are in an aqueous suspension form, and that no surface modification was applied. Therefore, the silver nanoparticle surface is relatively hydrophilic and may form aggregates in the oil phase. The aggregated silver particles will adsorb on the surface of polymer microsphere, resulting in golf ball-shaped particles (The concentration of silver in the PMMA/silver microspheres detected by AAS measurement was about 1,000 ppm). The detailed mechanism, such as why only part of the microsphere (about 1/2) is golf ball-shaped, is still not clear. Further investigations in this area definitely are needed. Figure 6(c) shows the fracture surface of PMMA/silver microspheres. Silver nanoparticles were dispersed in the matrix of PMMA, although some



**Figure 6.** SEM photographs of HMW PMMA spheres (a), PMMA/silver spheres (b), and a cross section of PMMA/silver sphere (c) suspension-polymerized using a suspending agent concentration of 9.0 g/dl of water and an ADMVN concentration of 0.0001 mol/mol of MMA.

aggregates were visible from the fracture surface. As previously discussed, the silver nanoparticles are dispersed in water so the surface of the particles should be hydrophilic. For this reason, the particles may aggregate in small clusters when

they are encapsulated in the polymer phase. In order to obtain a uniformly dispersed PMMA/silver nanoparticle composite, the surface of the silver particles can be modified to hydrophobic by using a cationic surfactant. Our results in this respect will be reported separately in a subsequent article.

### Conclusions

In this work, PMMA/silver microspheres were successfully prepared by suspension polymerization of MMA in the presence of silver nanoparticles dispersion. Not only high polymerization degree (6,000-37,000), but also high conversion of the polymerization (85 %) was achieved when low temperature initiator (ADMVN) was used. The rate of polymerization was increased with increasing initiator concentration. In the case of using the silver nanoparticles, the rate of polymerization decreased slightly.

Two different surface structures were found for the PMMA/silver microspheres prepared in this study. Future work is needed to understand the formation mechanism of golf ball-shape particle formation.

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