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ORIGINAL CONTRIBUTION

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Synthesis of high molecular weight poly(methyl methacrylate) microspheres by suspension polymerization in the presence of silver nanoparticles

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Abstract To prepare high molecular weight (HMW) poly(methyl methacrylate) (PMMA)/silver microspheres, methyl methacrylate was suspension-polymerized in the presence of silver nanoparticles using a low-temperature initiator at different conditions. The rate of conversion was increased with increasing initiator concentration. In the case of adding silver nanoparticles, the rate of polymerization decreased slightly. High monomer conversion (about 95%) was obtained in spite of low polymerization temperature of 30 °C. Under controlled conditions, PMMA/silver microspheres with various viscosity-average degree of polymerization (6,000–37,000) were prepared.

Keywords PMMA/silver microspheres · High yield · Suspension polymerization

Introduction

Poly(methyl methacrylate) (PMMA) is an important polymeric material with high light transmittancy, colorlessness, chemical resistance, and weathering corrosion resistance. Due to these superior characteristics, PMMA was widely used as additives, coating and polishing agents, binder, sealer, transparent neutron stopper, optical fiber, high-voltage application, and outdoor electrical application [1, 2]. In some of these applications, the high molecular weight PMMA is required.

Since the work by Charnley in the early 1960s, self-curing PMMA cements have been leading to the development of new technologies for fixation of joint prostheses to bone [3]. Two-part self-curing acrylic cements are currently the only materials used for anchoring cemented arthroplasties to the contiguous bones [4]. The liquid part contains typically 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 (BPO) [5, 6]. The resulting mechanical properties of the set cement rely on the cohesion between the initial PMMA and the polymerized monomer.

Nanocomposites often exhibit physical and chemical properties that are dramatically different from conventional composites. During the past 10 years, a lot of works were conducted on the elaboration of nanocomposite systems by embedding of inorganic particles into polymeric matrices [7–11]. Nanostructured polymer/inorganic composites, mixed at the molecular level or near molecular level, are much different from the 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 [12], electrical devices [13], photoconductors [14] were reported.

Silver nanoparticles are widely used as photosensitive components [15], catalysts [16, 17], Raman spectroscopy enhancement additive [18] as well as chemical analysis [19]. Especially, silver is known to have a wide antibacterial spectrum [20]. Also, due to its comparatively high safety [21], many researchers were successful in developing antibacterial and disinfectant agents with silver loaded on various carriers. In general, the polymer/silver nanocomposites were prepared in two steps. Firstly, the polymer was synthesized, and then the silver ions introduced into the polymer matrix were reduced to zerovalent state by a reducing agent or by post-heating. In recent years, much effort was devoted to the studies on the in situ synthesis of metal nanoparticles in polymer matrices [22–24]. This method is based on the reduction of metal ions that are dispersed in polymer matrices. According to Zhu et al. [25], 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 γ-irradiation. Yin et al. [26] prepared polyacrylamide/silver nanocomposites by irradiating the aqueous solution of $AgNO_3$ and acrylamide monomer with ^{60}Co γ-ray.

Recently, many polymer/inorganic nanocomposites were prepared by suspension polymerization. According to Duguet et al. [27] PMMA encapsulated alumina particles were prepared by suspension polymerization. Huang and Brittain [28] synthesized PMMA/layered silicate nanocomposites by in situ suspension and emulsion polymerization. According to Shim et al. [29] homogeneously zinc oxide (ZnO)-dispersed PMMA composite microspheres were produced in situ suspension polymerization. More recently, Jun and Suh [30] synthesized poly(urethane acrylate)/clay nanocomposite particles by suspension polymerization. According to Hwu et al. [31], polystyrene (PS)/montmorillonite nanocomposites were obtained by suspension free radical polymerization of styrene in the dispersed organophilic montmorillonite.

Recently, several researchers were reconsidering suspension polymerization of MMA with an industrial viewpoint [32, 33]. These polymerization, however, were conducted at polymerization temperature of over 50 °C. In these cases, molecular weight reduction in PMMA is accelerated inevitably. In this 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 in 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 PMMA/silver particles.

Experimental

Materials

Methyl methacrylate (MMA) purchased from Aldrich was washed with an aqueous solution of $NaHSO_3$ and water and dried with anhydrous $CaCl_2$, followed by distillation in nitrogen atmosphere under a reduced pressure.

The monomer-soluble initiator, ADMVN (Wako Co., 10 h half-life at 51 °C), 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 dispersant. Aqueous silver nanoparticle dispersion (AGS-WP001, 10,000 ppm) with diameter ca. 15–30 nm was purchased from Miji Tech. Co., Ltd., Korea. Deionized water was used for all the experiments.

Preparation of PMMA/silver microspheres

To prepare HMW PMMA/silver microspheres, suspension polymerization of MMA in the presence of aqueous silver nanoparticles dispersion was conducted. Dispersant 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 at once at a fixed polymerization temperature. After predetermined times, the reaction mixture was cooled and kept for 1 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, 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.

Table 1 Suspension polymerization conditions of MMA

Type of initiator	ADMVN
Type of dispersant	PVA
Initiator concentration	0.0001, 0.0005, 0.001 mol/mol of MMA
Dispersant concentration	1.5, 5.0, 9.0 g/dL of water
MMA/water	0.5, 1.0 L/L
Rpm	500, 1,000
Temperature	30, 40, 50 °C
Silver nanoparticles dispersion/MMA	0.2 L/L

Characterizations

The molecular weights of PMMA were calculated using Eq. 1 [34].

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

where $[\eta]$ is intrinsic viscosity. Viscosity-average degree of polymerization (P_v) of PMMA was calculated from M_v. To precisely obtain P_v 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, size distribution and surface morphology of PMMA/silver microspheres were examined using a Hitachi S-570 scanning electron microscope (SEM). To obtain the average size and size distribution, five SEM photographs and more than 200 particles were collected by computer, which linked with the SEM, followed by statistical analysis of 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) may be expressed by Eq. 2 [35].

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

where f is the initiator efficiency, $[M]$ and $[I]$ are the concentrations of monomer and initiator, and k_d, k_p, and k_t are reaction rate constants of initiator decomposition, propagation and termination, respectively. This expression predicts that the rate of polymerization is increased as the efficiency and concentration of initiator are increased. It was known that ADMVN is an effective low-temperature initiator (10 h half-life of ADMVN is 51 °C) that can be used to prepare high molecular weight polymer with high yield [36–39]. Because of the low reaction temperature, the low initiation rate was expected. It is interesting that not only high molecular weight, but also high conversion was achieved for the system studied here. This can be contributed to the low termination rate of living polymer at low temperature. Figure 1a shows the conversion as a function of reaction time at different polymerization temperatures using initiator concentration of 0.0001 mol/mol of MMA with or without silver nanoparticles. Irrespective of usage of silver nanoparticles, the rate of conversion

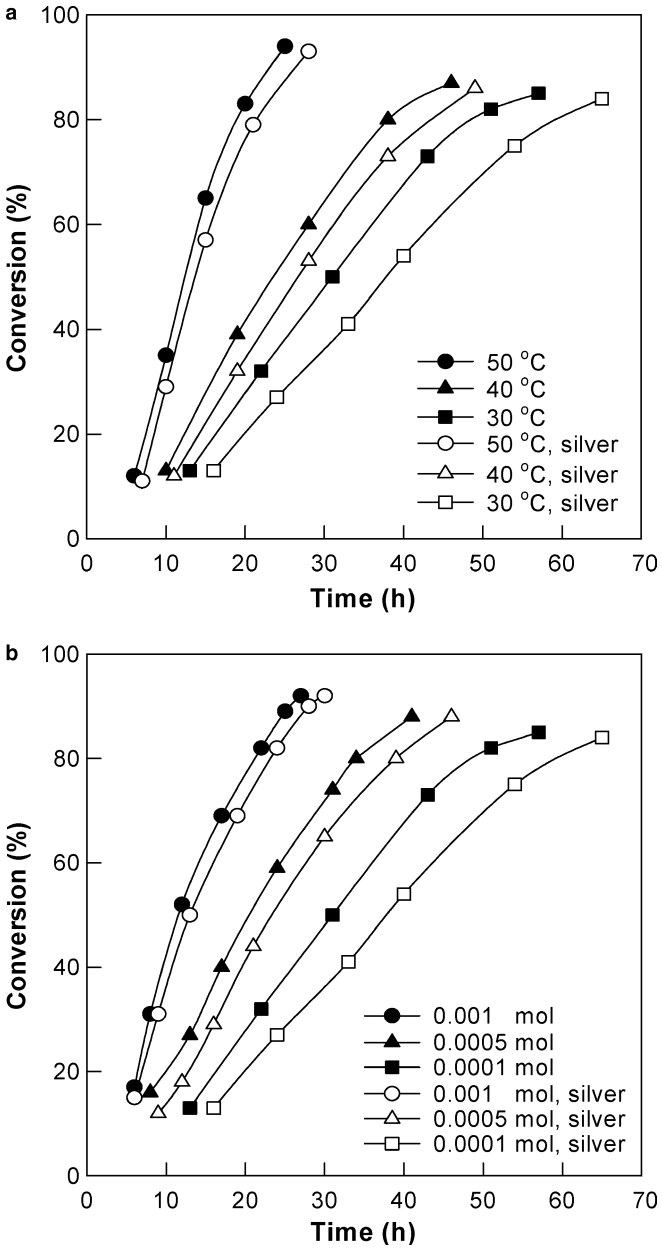

Fig. 1 Effect of silver nanoparticles on the conversion of MMA into PMMA/silver suspension-polymerized using different polymerization temperatures (**a**) and different ADMVN concentrations (**b**) with polymerization time. (Dispersant concentration 1.5 g/dL of water)

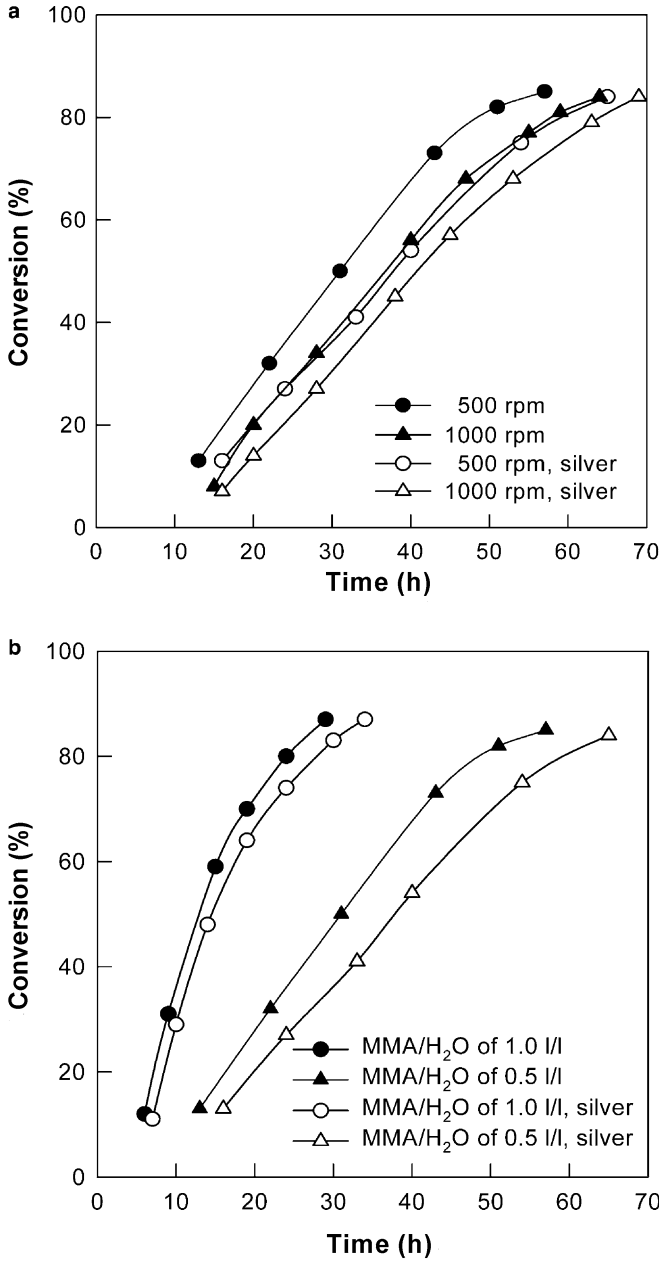

Fig. 2 Effect of silver nanoparticles on the conversion of MMA into PMMA/silver suspension-polymerized using different agitation speeds (**a**) and different MMA/water contents (**b**) with polymerization time. (Dispersant concentration 1.5 g/dL of water)

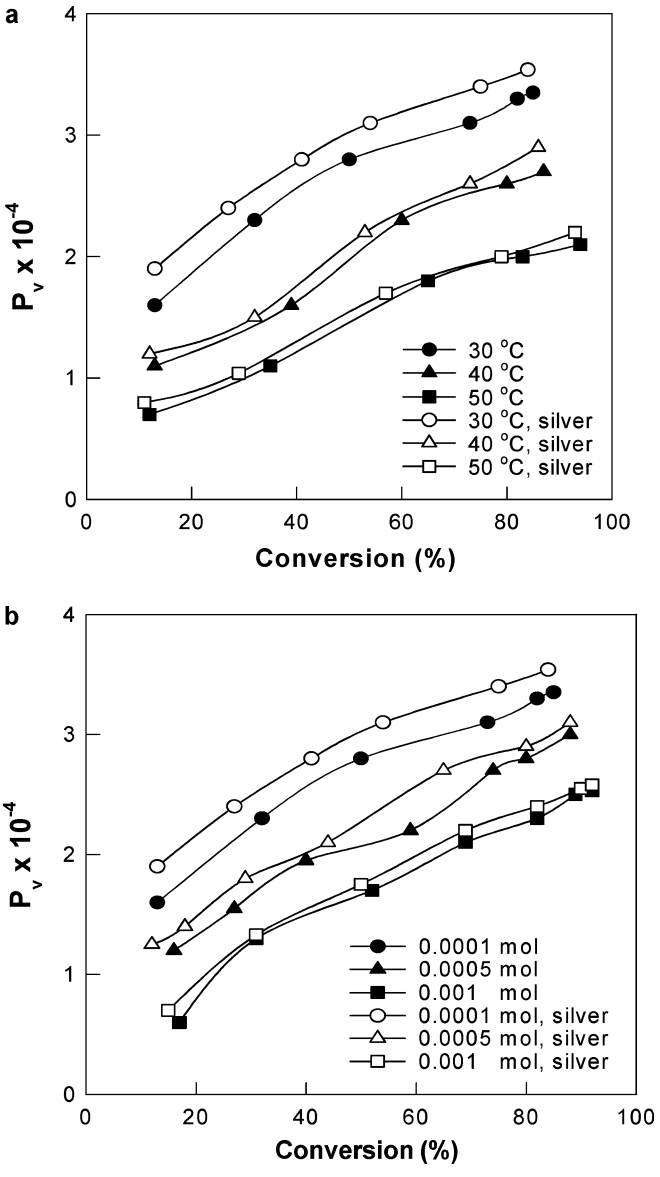

Fig. 3 Effect of silver nanoparticles on the P_v of PMMA/silver suspension-polymerized using different polymerization temperatures (**a**) and different ADMVN concentrations (**b**) with conversion. (Dispersant concentration 1.5 g/dL of water)

was increased with increasing polymerization temperature. Increase 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 a conventional suspension polymerization, the auto-acceleration behavior was not observed in this study. It should be noted that this polymerization was carried at low room temperature and the polymer propagation rate is very low. As a result, the temperature increase during the polymerization is insignificant for the system studied here than a conventional suspension polymerization at relatively high temperature. Because of the low polymerization rate and good heat dissipation, no auto-acceleration was observed. It can be seen that the conversions increased up to about 85–95% for the system studied in spite of low initiator concentration of 0.0001 mol/mol of MMA. Compared with bulk polymerization, only 30–40%

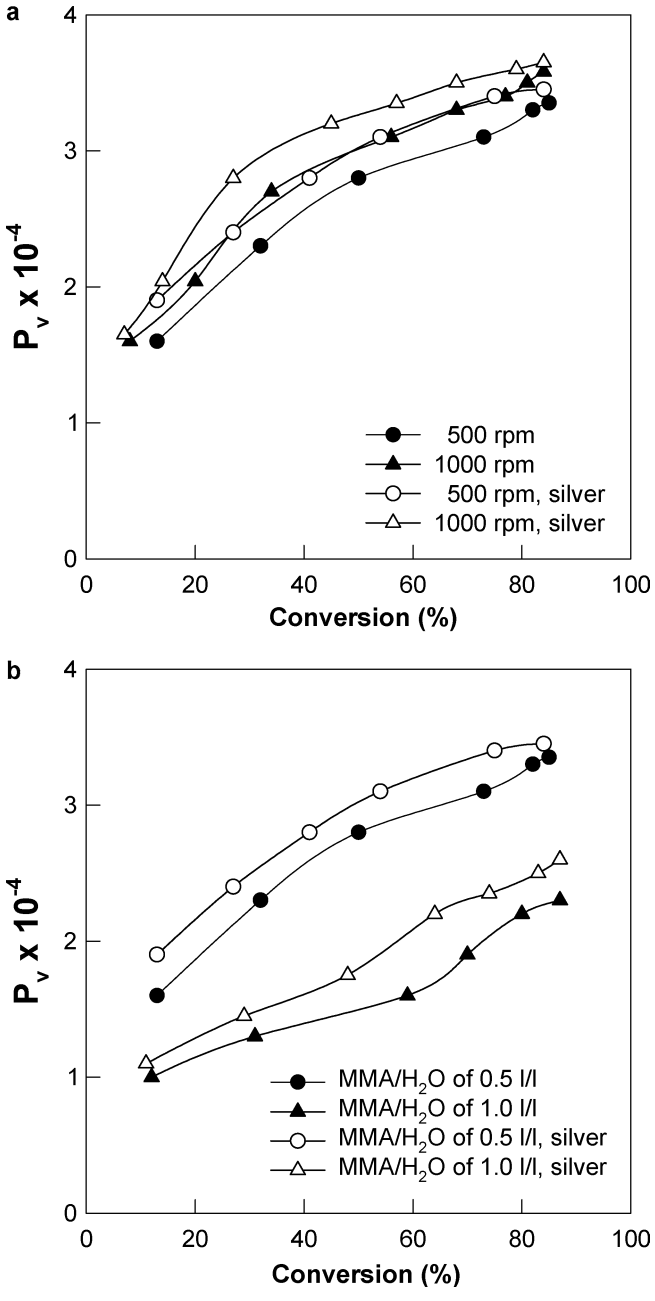

Fig. 4 Effect of silver nanoparticles on the P_v of PMMA/silver suspension-polymerized using different agitation speeds (**a**) and different MMA/water contents (**b**) with conversion. (Dispersant concentration 1.5 g/dL of water)

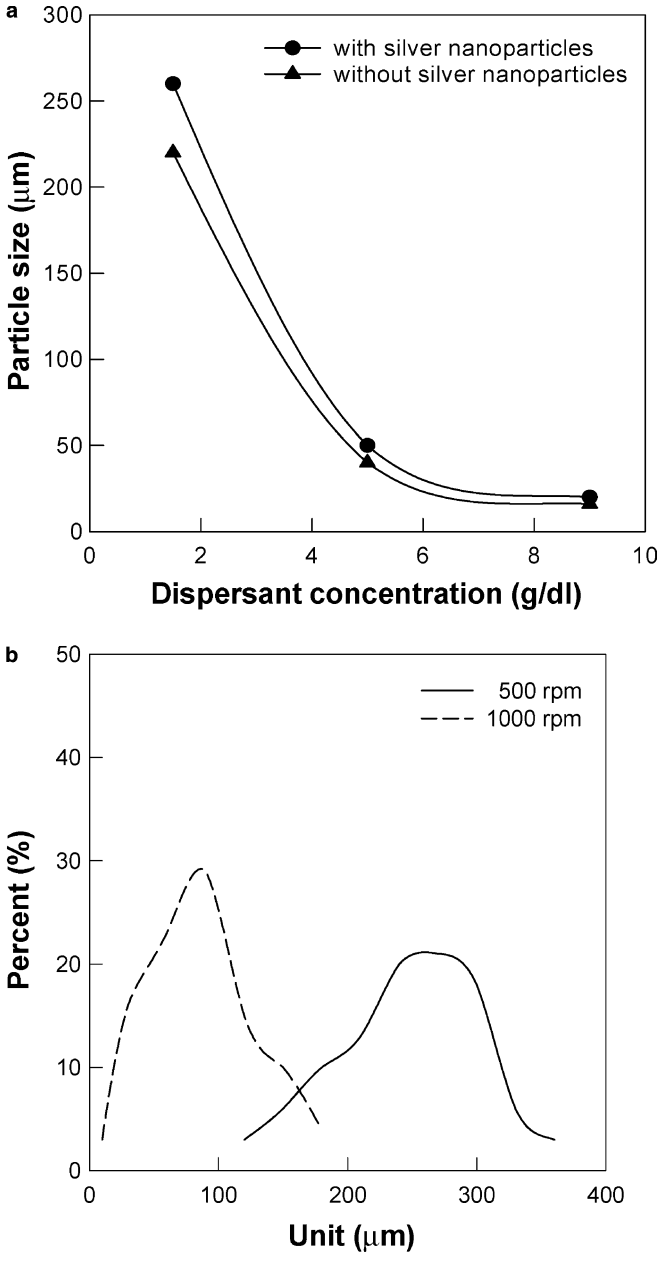

Fig. 5 Effect of silver nanoparticles on the average particle size of HMW PMMA/silver spheres suspension-polymerized using different concentrations of dispersant (**a**) and different agitation speeds (**b**). (ADMVN concentration 0.0001 mol/mol of MMA)

conversion of MMA was obtained under same condition [40]. In bulk polymerization, auto-acceleration is more significant than that in suspension polymerization; so the low conversion rate is usually obtained. However, auto-acceleration behavior described above seems not to be so noticeable in the low-temperature suspension polymerization of MMA as shown in Fig. 1a. In all cases, the rates of polymerization with silver nanoparticles were slightly lower than those without silver nanoparticles. There are two possible reasons for the reduction in the polymerization rate when silver particle was presented. First, the nano-silver particles may adsorb the living polymer molecules so the diffusion rate of the living polymer decreases. Second, the silver particles may function as a scavenger for the initiator. The further research is needed to fully understand the real mecha-

nisms. 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 concentration with or without aqueous silver nanoparticles dispersion at 30 °C are shown in Fig. 1b. The conversion rate was increased with increasing initiator concentration, which coincided well with the theoretical predictions [31]. Figure 2a, b present conversion–time plots at different agitation speeds (a) and different MMA/water ratios (b) using initiator concentration of 0.0001 mol/mol of MMA with or without silver nanoparticles at 30 °C, respectively. In the cases of high agitation speed and low value of MMA/water ratio, the slow rate of polymerization was obtained. The polymerization rate in suspension polymerization is also affected by the agitation speed and the monomer/water ratio. As shown in Fig. 2a, b, the higher the agitation rate, the lower the polymerization rate. It was also found that the lower ratio of MMA/water, the lower polymerization rate. The similar phenomenon was also reported in the literature [37]. These might be explained by the fact that the high agitation rate resulted in better heat dissipation, therefore, the reaction temperature of the system was lower at high agitation condition then at low agitation condition. As a result, the polymerization rate at high agitation condition is slightly lower than that at low agitation condition. For the similar reason, it is expected that the high monomer/water ratio will produce more exothermal energy during the polymerization causing the fastness of the polymerization rate. In all cases, the rates of polymerization with silver nanoparticles were lower than those without silver nanoparticles.

The (P_v)s of PMMA and PMMA/silver prepared by suspension polymerization with conversions are shown in Fig. 3a, b. In accordance with theoretical prediction, (P_v)s of PMMA were increased with decrease in the initiator (ADMVN) concentration and polymerization temperature. (P_v)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 that without silver nanoparticles. It should be noted that PMMA/silver microspheres with P_v of 6,000–36,000 could be prepared by suspension polymerization of MMA in the presence of silver nanoparticles with higher conversion. Figure 4a, b present (P_v)s as a function of agitation speed (a) and MMA/water ratio (b) at the 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_v)s of 10,000–37,000 could be prepared by suspension polymerization of MMA in the presence of

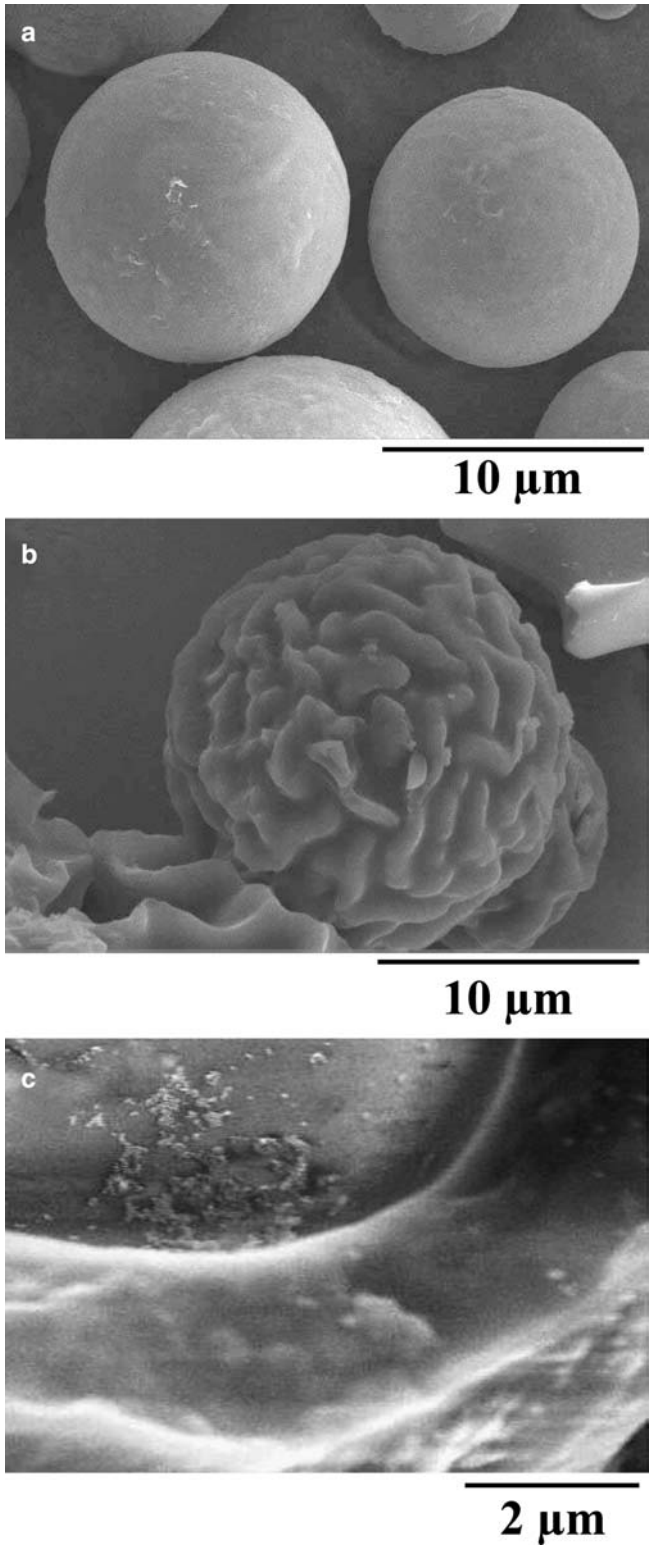

Fig. 6 SEM photographs **a** pure PMMA spheres, **b** PMMA/silver spheres, **c** cross section of PMMA/silver sphere. Dispersant 9.0 g/L of water; ADMVN: 0.0001 mol/mol of MMA

silver nanoparticles. Furthermore, in all cases, the (P_v)s of PMMA with silver nanoparticles were slightly higher than those of PMMA without silver nanoparticles.

Size and morphology of PMMA/silver microspheres

Figure 5a shows the effect of silver nanoparticles on the average particle sizes of PMMA/silver spheres. It is well known that high concentration of stabilizer will lead to small particles because of the decrease in interfacial tension when stabilizer concentration is increased [41]. Our experimental results agree very well with this theoretical prediction. For the sample containing silver nanoparticles, the particle sizes increased slightly. Particle size distributions of PMMA/silver microspheres using a concentration of dispersant of 1.5 g/dL with different agitation speeds are shown in Fig. 5b. Particle size distribution of PMMA/silver microspheres decreased with an increase in the agitation speed.

The SEM photographs of HMW PMMA and PMMA/silver microspheres suspension-polymerized using dispersant concentration of 9.0 g/dL of water is presented in Fig. 6a, b, respectively. It is surprising that two different appearances of microspheres, one with smooth surface and another with golf ball-shape 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 clear, we believe this phenomenon must relate to the aggregation of silver nanoparticles during the polymerization. It should be noted that the silver nanoparticles used in this study is in an aqueous suspension form, and no surface modification was applied. Therefore, the silver nanoparticle surface is relatively hydrophilic and may form aggregates in oil phase. The aggregated silver particles will adsorb on the surface of polymer microsphere, resulting in golf ball-shape particles (The concentration of silver in the PMMA/silver microspheres detected by Solaar AAS-S4 atomic absorption spectrometry measurement was about 1,000 ppm). The detail mechanism, such as why only part of microsphere (about 1/4) is in golf ball shape, is not clear. Further work in this area definitely is needed. Figure 6c shows the fracture surface of PMMA/silver microspheres. Silver nanoparticles were dispersed in the matrix of PMMA although some aggregates are visible from the fracture surface. As discussed before, the silver nanoparticles are dispersed in water so the surface of the particles should be hydrophilic. For this reason, the particles may aggregate to small clusters when they are encapsulated in 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 cationic surfactant. This work will be reported separately later.

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 (90–95%) was achieved when low temperature initiator (ADMVN) was used. The rate of conversion 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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