

Preparation of Ultra Fine Poly(methyl methacrylate) Microspheres in Methanol-enriched Aqueous Medium

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Abstract: Monodisperse PMMA microspheres are prepared by means of a simple soap-free emulsion polymerization in methanol-enriched aqueous medium in a single step process. The size and uniformity of the microspheres are dependent on the polymerization temperature. In a stable system, the uniformity is improved with the polymerization time. The most uniform and stable microspheres are obtained under mild agitation speed of 100 rpm at 70°C. The monodisperse PMMA microspheres in the size range of 1.4-2.0 μm having less than 5% size variation are successfully achieved with varying concentrations of monomer and initiator. As the monomer and initiator concentrations increase, the larger microspheres with enhanced uniformity are obtained. However, the decreased amount of water induces the polydisperse PMMA particles due to the generation of secondary particles.

Keywords: monodisperse microspheres, poly(methyl methacrylate), soap-free emulsion polymerization.

Introduction

Since the seminal concept of the photonic band-gap (PBG) crystals was proposed by Yablonovich¹ and John,² explosive researches have been flushed in the fabrication methods and synthesis of the potential material for PBG crystals due to their attractive features in controlling and confining light.³⁻⁵ The unique features of this new functional materials are of importance because they lead to a fabrication of more efficient light-based detectors, modulators, data storages, and circuits.⁶ These materials are generally constructed by spatially periodic self-assembly of monodisperse spherical organic or inorganic colloids.^{7,8} Among them, nano/micron-sized polymer colloids provide a facile and inexpensive route in the fabrication of PBG crystals.^{9,10} Therefore, the preparation method of extremely monodisperse polymer colloids having a desired size is still in great interests. In manufacturing PBG crystals, polystyrene¹¹⁻¹³ and poly(methyl methacrylate)¹⁴⁻¹⁸ nanospheres with a diameter of less than 1 micrometer are the representative examples of the most frequently used polymer colloids.

In most cases, polymer latex used in PBG crystals are produced by (soap-free) emulsion polymerization^{19,20} in order to ensure the size uniformity within 5% of deviation. However, the final particle size has a limitation of maximal 1 μm due to its micellar mechanism. Recently, photonic crystals using

micron-sized polymer colloids have been exploited and found that they allow to shift the stop-band in NIR and IR region.²¹

In the synthesis of micron-sized polymer colloids via emulsion polymerization, several attempts have been made. Homola *et al.* prepared polystyrene spheres up to 1.6 μm with the help of an electrolyte by means of soap-free emulsion polymerization in methanol/water mixture as the medium.²² Gu *et al.* have reported that polystyrene spheres in the size range of 2-2.5 μm with 20-30% deviation could be produced by addition of cationic surfactant such as cetyltrimethylammonium bromide at the very early stage of emulsion polymerization.^{23,24} Zhang *et al.* were able to produce 1.65 μm sized polystyrene colloids employing seeded growth technique in various alcohols/water medium (It is noted that the deviation of uniformity was not given for micron-sized spheres in their report).²⁵ Our group has developed a modified soap-free emulsion polymerization technique to prepare polystyrene microspheres having a diameter of approximately 2 μm ,²⁶ and now this method has been adopted for the synthesis of template colloids in the fabrication of PBG crystals.²⁷ However, this polymerization technique requires a long polymerization time due to the successive monomer feeding although a swelling step is omitted.

Since soap-free emulsion polymerization in alcohol/water mixture has not been much studied to date, the number of reports in the open literature is still limited.²⁸⁻³¹ Furthermore, these studies are limited to polystyrene. In this article, we propose a simple route to prepare PMMA microspheres up to the diameter of 2 μm within 5% of size variation in a rel-

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atively short polymerization time in alcohol-rich aqueous media without any additional ingredient other than monomer, medium, and initiator, which would be useful for fabricating PBG crystals.

Experimental

The inhibitor was removed from methyl methacrylate (MMA; Junsei, Japan) by use of an inhibitor removal column (Aldrich, USA). Potassium persulfate (KPS; Junsei, special grade) was used as received. Methanol (Samchun Chemical, Korea) and double-distilled deionized water were used as polymerization media.

Polymerization was carried out in a 250 mL round flask with a mechanical stirring at 100 rpm under nitrogen atmosphere at several temperatures. Pre-weighed methanol and water were charged in the reactor and the addition of MMA was followed. After the temperature reached a desired level, the aqueous KPS solution (10 mL) was then added and the polymerization was initiated. During the polymerization, aliquots of the reaction mixture were withdrawn from the reactor to examine the morphology of the particles and the conversion. The conversion was measured gravimetrically. The particle size and the coefficient of variation were obtained by counting 100 particles using Scion Image Analyzer[®] from the micrographs taken by Hitachi SEM (Scan-

ning Electron Microscopy) S-4300.

Results and Discussion

Figure 1 shows the formation and growth of the PMMA microspheres prepared by soap-free emulsion polymerization (standard recipe in Table I) at the mild agitation speed of 100 rpm. It is worthy to note that the agitation speed was varied at 100, 200, and 300 rpm. Although the conversion of the polymerization, and the size of intermediate and final particles were marginally affected by the agitation speed, the coefficient of variation (C_v) was significantly influenced. For the microspheres collected at the end of the polymerization, the C_v value decreases upon the agitation speed: 8.88, 6.48, and 3.66% at 300, 200, and 100 rpm, respectively.

Table I. Standard Recipe Used in Soap-free Emulsion Polymerization in Methanol/Water Mixture

Ingredients	Amount	Remark
Methanol*	100 g	*Volume of total medium was fixed at 176 mL
Water*	50 g	throughout the experiments
MMA	5 g	3.3 wt% relative to medium
KPS	0.0375 g	0.75 wt% relative to monomer

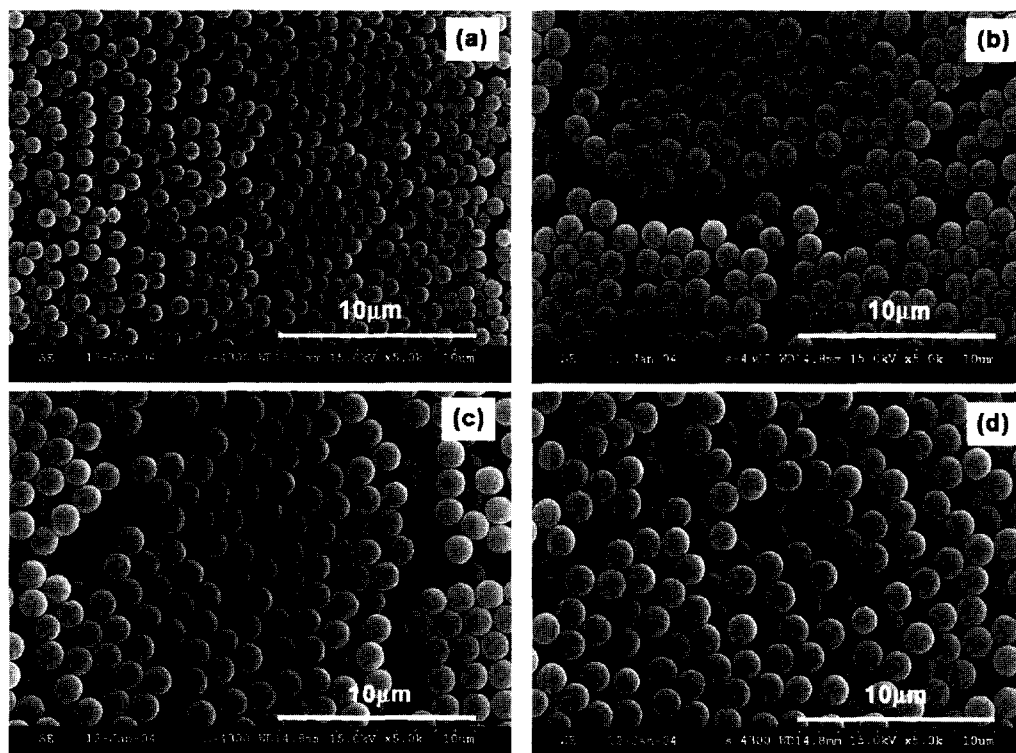


Figure 1. SEM micrographs of monodisperse PMMA microspheres prepared by soap-free emulsion polymerization in methanol (100 g)/water (50 g) mixture at different times at 70°C. (a) 1 hr, (b) 4 hr, (c) 10 hr, and (d) 24 hr.

Therefore, the 100 rpm was chosen in order to obtain the best uniformity. In Figure 1, the monodisperse particles are formed at the very early stage of the polymerization and they progressively grow in size until the completion of polymerization.

Figure 2 depicts the effects of the polymerization temperature on conversion, number-average diameter and C_v of the PMMA particles prepared in the mixture of methanol (100 g) and water (50 g). In Figure 2(a), the conversion shows interesting phenomena with respect to the temperature. At 60°C, the conversion continuously increases almost in linear fashion up to the end of the polymerization. At 70 and 80°C, the conversions are much faster than in 60°C, however, they appear to reach a maximal point at a certain time (96.7% for 12 hrs at 70°C, and 92.2% for 8 hrs at 80°C, respectively), and then decrease substantially. The apparent decrease of the conversion is due to the coagulation of particles and the coagulated particles precipitate to the bottom of the reactor. During the polymerization, the particles grow with time and the sizes are dependent on the temperature as seen in Figure 2 (b). It is noted that the collection of the sample for measuring the size and uniformity was made for uncoagulated suspended particles during the polymerization. The final sizes are 1.53, 1.62, and 2.06 μm for 60, 70, and 80°C, respectively. In Figure 2(c), the uniformity measured in terms of the coefficient of variation is displayed. In stable systems of 60 and 70°C, the C_v decreases as the particles grow with time and remarkably uniform PMMA microspheres having the C_v of 4.1% at 60°C and 3.7% at 70°C. However, the C_v increases to 7.6% at 80°C. In addition, the more uniform particles are obtained especially at the beginning of the polymerization at higher temperatures. However, the uniformity deteriorates after 4 hrs at 80°C due to exceedingly uncontrolled growth of the particles. Accordingly, the polymerization temperature of 70°C seems to be appropriate for obtaining the monodisperse PMMA microspheres with a high conversion in a relatively short period of polymerization.

In Figure 3, the effects of the amounts of monomer on the size and uniformity are shown, where the amount of MMA was solely varied while the other ingredients were kept at the same level. Increased monomer concentration results in the larger particle size with improved uniformity. The C_v values are controlled quite low in the range of 2-4%. The similar results on the increase in particle size with the monomer concentration in alcohol/water medium are reported elsewhere.^{22,25} It has been suggested that the amounts of initiator should correspondingly increase in order to maintain the uniformity when the monomer content is augmented.²⁵ However, as shown in Figure 3, excellent uniformity was achieved at the fixed initiator concentration probably due to the low monomer concentration (3.3 wt%) in the medium.

The final particle size and uniformity of the microspheres obtained with increasing concentration of initiator at fixed

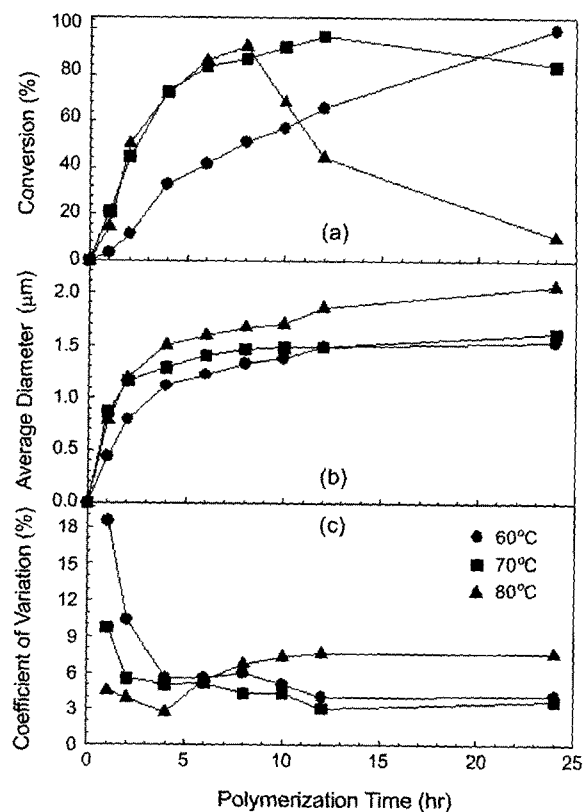


Figure 2. Effect of polymerization temperature on (a) conversion, (b) average diameter of microspheres, and (c) coefficient of variation in the soap-free emulsion polymerization in methanol (100 g)/water (50 g) mixture.

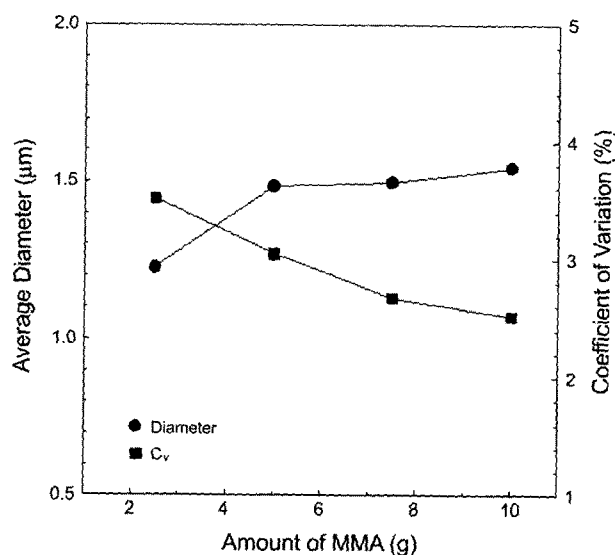


Figure 3. Effect of the amount of monomer, MMA, on the size and uniformity of PMMA microspheres prepared by soap-free emulsion polymerization in methanol (100 g)/water (50 g) mixture at 70°C.

monomer and methanol/water ratio are shown in Figure 4. In conventional (soap-free) emulsion polymerization, an inverse relationship between the particle size and concentration of initiator is often observed since the increased initiator causes a greater number of micelles which subsequently grow to particles.³² Contrary to this classical concept, the particle size increases with the initiator concentration as shown in Figure 4. This phenomenon is often observed in the dispersion polymerization where all ingredients are dissolved in medium such as methanol or ethanol.^{33,34} In the early stage of the dispersion polymerization, oligomers generated in homogeneous phase (i.e., solution polymerization occurs at this stage), grow until the critical chain length which cannot remain dissolved in the medium, and then precipitate to form primary particles. When the solvency of the medium is better, a smaller number of primary particles is generated since most oligomers exist in the medium, resulting in larger final particles. In this soap-free emulsion polymerization, all the ingredients are soluble in the methanol/water mixture, hence, initial reaction starts in solution phase to give surface active oligomeric species originated from the decomposition of KPS. It is thought that the oligomers with a lower average molecular weight would be formed with increasing initiator concentration, and that the oligomers would prefer to stay in the methanol/water medium. Hence, the number of micelles, which is formed by the precipitation of the oligomers from the medium, would decrease to give a larger particle size.

This phenomenon is truly seen in Figure 4. In addition, the C_v tends to decrease with the amount of initiator within 0.4–2%.

The amount of water was decreased in order to investigate the possibility to enlarge the particle size. In Figure 5, SEM

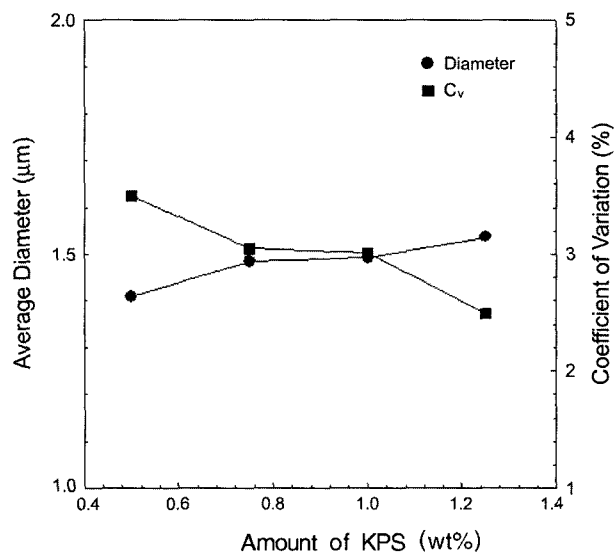


Figure 4. Effect of the amount of initiator, KPS, on the size and uniformity of PMMA microspheres prepared by soap-free emulsion polymerization in methanol (100 g)/water (50 g) mixture at 70°C.

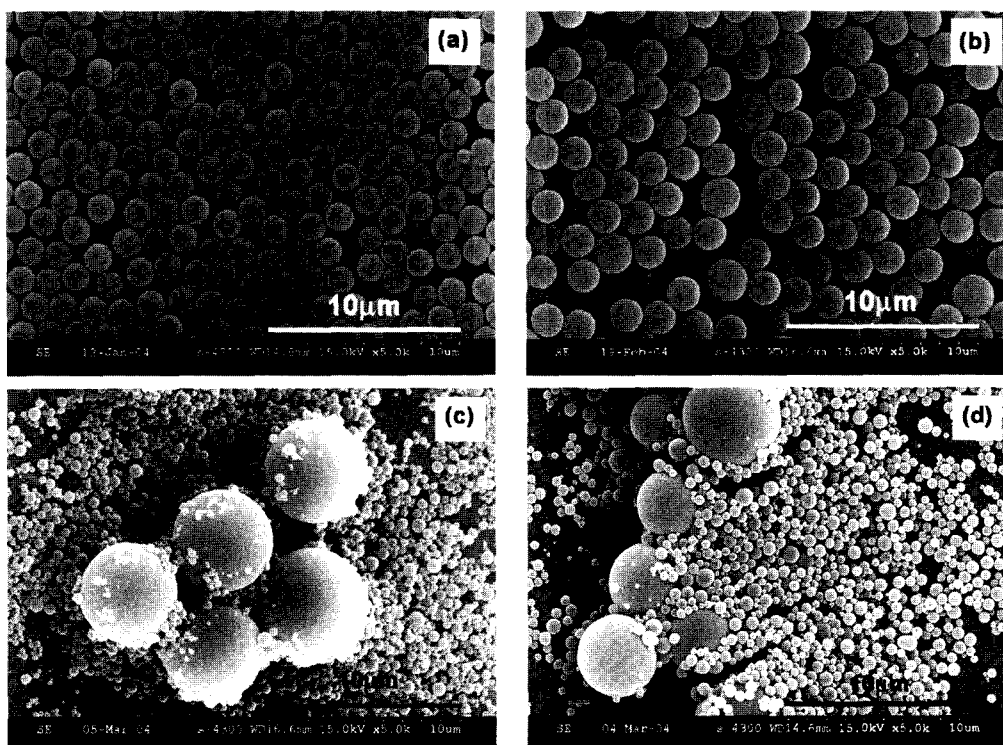


Figure 5. Effect of the increased water amount on the formation of PMMA microspheres prepared by soap-free emulsion polymerization for 12 hrs in various ratios of methanol:water mixture at 70°C. (a) 100 (g) methanol : 50 (g) water, (b) 100 : 40, (c) 100 : 35, and (d) 100 : 20.

images of the PMMA microspheres obtained with 5 g MMA and 0.0375 g KPS for 12 hrs. Initially, it was expected that reduced water content would result in a larger particle size. When the water content was reduced from 100 (g) methanol : 50 (g) water to 100 : 40, the particle size tends to increase from 1.49 to 1.80 μm , however, the uniformity becomes poor with the C_v change from 3.05 to 9.52%. When the water content was further reduced to 100 : 35, a bimodal distribution consisting of 5.5 μm and submicron-sized particles was obtained as shown in Figure 5(c). It is noted that the secondary small particles are generated at the 4 hrs of polymerization time. The primary and secondary particles competitively grow during the polymerization, which leads to the bimodal distribution. When a ratio of 100 (g) methanol : 20 (g) water was used, the similar bimodal distribution is obtained with non-uniform microspheres and polydisperse submicrospheres having the diameter less than 1 μm . Apparently, the reduction of water content shows an adverse effect in controlling the particle size. In addition, it is noted that no particles are obtained using acetone and ethanol instead of methanol at the same recipe as given in Table I.

Conclusions

In this study, we propose a simple synthetic route to prepare PMMA microspheres in a short polymerization time in methanol-enriched aqueous media without any additional ingredient other than monomer and initiator, which would be useful for fabricating PBG crystals. The size and uniformity of the microspheres are dependent on the polymerization temperature. The higher the polymerization temperature, the larger the particle size was obtained. In the stable system at 60 and 70 °C, the uniformity is improved with the polymerization time; thereby the most uniform and stable microspheres are obtained under mild agitation speed of 100 rpm at 70 °C. The monodisperse PMMA microspheres in the range of 1.4–2.0 μm having less than 5% C_v are successfully achieved with varying concentration of monomer and initiator via soap-free emulsion polymerization in a single step. As the monomer and initiator concentrations increase, the larger microspheres with enhanced uniformity are obtained. When the water content in the medium was reduced from 100 (g) methanol : 50 (g) water to 100 : 20, the particle size tends to grow, however, the uniformity of size becomes poor and a bimodal distribution is obtained due to the generation of secondary particles.

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