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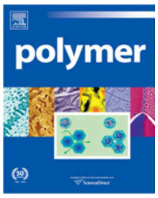

Effect of homogeneity of methanol/water/monomer mixture on the mode of polymerization of MMA: Soap-free emulsion polymerization *versus* dispersion polymerization

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ABSTRACT

The soap-free emulsion polymerization of methyl methacrylate (MMA) was carried out with varying amount of methanol in the aqueous medium. As methanol content increased, the phase of polymerization mixture (methanol/water/monomer) changed from heterogeneous to homogeneous state and the transition occurred at 30 wt% methanol. In order to identify the mechanism of the polymerization in heterogeneous and homogeneous mixture, the properties of the prepared PMMA particles were analyzed in terms of the effects of methanol content on the conversion at 1 h, initiator concentration and polymerization temperature. With the heterogeneous mixture in the range of 0–20 wt% methanol, the polymerization product and polymerization behavior resembled those typically observed in the soap-free emulsion polymerization. On the other hand, the characteristics of the polymerization products were similar to those typically obtained in the dispersion polymerization under the homogeneous mixture ranging 40–60 wt% methanol. Thus, the homogeneity in the aqueous methanol mixture can be a critical factor in determining the polymerization modes between the soap-free emulsion and dispersion polymerization.

1. Introduction

Polymer latex has a long-standing interest from both academic and industrial point of views since 1930's. The polymer latex has been traditionally used for coatings, adhesives, inks, paper, leather industry, and so forth [1,2]. Recently, the dried polymer latex into solid individual particle has received much attention since they were now used as important templates in nano- and bio-related science and technology [3–5].

Among numerous polymerization methods, suspension, dispersion, and emulsion polymerizations are the most widely implemented ways of producing polymer particles of various sizes. More sophisticated polymerization techniques have also been developed based on above methods [6]. Emulsion polymerization is a distinguished method for polymer preparing particles with size distribution between 0.1 and 1 μ, along with several advantageous characteristics such as rapid polymerization rate, high molecular weight and high conversion through environmentally-friendly process [7]. On the other hand, polymers prepared by the dispersion polymerization show the particle sizes between 1 and 10 μ with relatively slow reaction rate and low molecular weight [8]. These two methods have different polymerization mechanisms and possess disparate reaction properties: the synthesized particles show opposite size variations according to the changes in, for example, initiator concentration and temperature. It is known that the particle size decreases with the increase of initiator concentration and temperature during the emulsion polymerization, whereas such properties are opposite in the dispersion polymerization.

A typical emulsion polymerization system consists of water, monomer, initiator and surfactant (no surfactant in soap-free emulsion polymerization). In general, the monomer is sparingly soluble in water and generates a water-insoluble polymer which is swollen by monomer. The polymerization mainly proceeds in the monomer-swollen micelles/particles [9]. On the other hand, dispersion polymerization has been reported to occur in quite a complex manner in particle formation since it follows a combination of homogeneous and heterogeneous reaction mechanisms [8]. When all ingredients are reacted in reaction medium, the polymeric particles are nucleated and precipitated upon reaching the critical limit of solubility of the oligomeric species in the medium. The formed particles are normally stabilized by polymeric stabilizers [10,11].

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During the synthesis of polymer colloids, various stabilizing agents are essentially used including surfactants, dispersants, and steric stabilizers in various heterogeneous polymerizations. Although such stabilizing agents play a crucial role in the production and applications of the colloidal dispersions, they also encounter various adverse effects including foaming [12], destabilization of latex by migration in paints or films [13], and alteration of product hardness [14]. Therefore, emulsion polymerization in the absence of added surfactant has received a considerable attention as a method of producing monodisperse and clean lattices [15–17]. In such a polymerization system, polymer particles are electrostatically stabilized by decomposed initiators. A generally accepted mechanism is that water-soluble initiator molecules decompose and react with sparingly water-soluble monomers to form surface-active oligomeric radicals which, in turn, generate micelles. The polymerization mostly takes place in the micelles and monomer is supplied from large monomer droplets by diffusion through water phase [18]. Later on, Feeney et al. and Yamamoto et al. reported the detailed mechanism of the soap-free emulsion polymerization comprising homogeneous nucleation, followed by their coagulation and propagational growth to form colloidally stable latex particles [19,20].

Although the soap-free emulsion polymerization is usually conducted in a water phase, interesting results have been reported when alcohol was added to water [21–23]. For example, in a soap-free emulsion polymerization of styrene with sodium vinylbenzyl sulfonate, the presence of methanol significantly enhanced the monodispersity of the latex particles [24,25]. In most studies, however, the concentration of alcohol was limited to the amount which keeps the heterogeneous state of the medium. In addition, there was no report using same polymerization recipe using same ingredients.

In the present report, the soap-free emulsion polymerization of methyl methacrylate (MMA) by using same initiator and solvents with significantly increased methanol content to form homogeneous mixture was carried out. The polymerization mode was monitored between the soap-free emulsion and the dispersion polymerization in the system of aqueous methanol mixture. In addition, the dependence of various initiators on the modes of polymerization was also studied.

2. Experimental

2.1. Materials

Methyl methacrylate (MMA; Junsei Chemicals, Japan) was purified using an inhibitor removal column (Aldrich, USA) and was stored at −5 °C prior to use. Potassium persulfate (KPS; Junsei, Japan), ammonium persulfate (APS; Aldrich) and sodium persulfate (NaPS; Aldrich) were used as initiators without further purification. Poly(vinyl alcohol) (PVA; Kanto Chemical, Japan) was used as the stabilizer. It was noted that the degree of polymerization, weight–average molecular weight and the degree of hydrolysis of PVA were 2080, 109,000 g/mol and 80.2%, respectively. Mixtures of methanol (99%; Samchun Chemical, Korea) and double-distilled deionized water were used as polymerization media.

2.2. Polymerization

PMMA particles were prepared by the radical polymerization in various compositions of aqueous methanol media. The amount of methanol was increased from 0 to 60 wt% to water. There was no reaction occurred above 70 wt% methanol. The monomer concentration was 4 wt% of the total media. It is noted that a relatively low concentration of monomer was used to avoid the coagulation of the growing particles. The polymerization reactions were initiated using 0.75 wt% KPS (dissolved in 10 g water) with respect to the monomer. After all ingredients were charged in a 250 mL three necked round bottom flask, the polymerization was carried out with mechanical stirring at 200 rpm under nitrogen atmosphere at 60 °C for 24 h. The withdrawn polymerization products were repeatedly rinsed off with DDI water and methanol, centrifuged for removal of the unreacted materials and dried in vacuum oven at 60 °C for 24 h. Table 1 lists the recipes for the preparation of the PMMA particles in the modified soap-free emulsion polymerization in aqueous methanol media.

Table 1
Reaction recipes used in this study in various reaction conditions.

Expt. no.	Monomer contents MMA (g)	Medium content (methanol/water)	Initiator contents (g)	Rpm	Temperature (°C)
Medium ratio (expt. 1)	6	0/100	0.045	200	60
		10/90			
		20/80			
		30/70			
		40/60			
		50/50			
		60/40			
Initiator concentrations (expt. 2)	6	0/100	0.03	200	60
		10/90	0.045		
		20/80	0.06		
		30/70	0.075		
Temperature (expt. 3)	6	0/100	0.045	200	55
		10/90			60
		20/80			65
		30/70			70

2.3. Characterizations

The molecular weight of the synthesized PMMA particles was 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 were employed. The universal calibration curve was obtained with 10 PS standard samples (Polymer Laboratories, United Kingdom) with molecular weights ranging from 580 g/mol to 7500,000 g/mol. The flow rate of the PMMA solution dissolved in THF was 1.0 mL/min. A Scanning Electron Microscopy (SEM; Hitachi, S-4300, Japan) was used to investigate the morphology of the particles. SEM images were obtained using the samples sputter-coated with platinum under vacuum. The monomer conversion was calculated gravimetrically. The size of the particles and the coefficient of variation (CV) indicating the uniformity of the spherical particles were measured by the particle size analyzer (Beckman Coulter, LS230, USA) with the particles suspended in water.

3. Result and discussion

3.1. Transition phenomenon between heterogeneous and homogeneous reaction mixture

Table 1 shows the reaction recipes employed in this study; the variables were the methanol content, initiator concentration, and

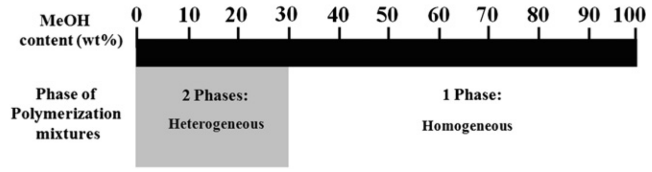

Fig. 1. Phase transition phenomenon with methanol contents in aqueous media at room temperature.

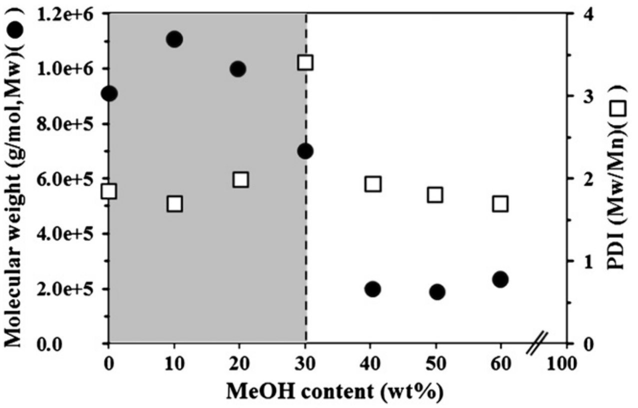

Fig. 2. The weight–average molecular weight and PDI value of the PMMA particles prepared with various methanol contents. The experimental values are the average of at least 5 measurements.

the reaction temperature in the absence of stabilizer or emulsifier. The homogeneity was verified by agitating the polymerization mixtures of monomer, methanol and water at 100 rpm. As in expt. 1, when methanol content was between 0 and 30 wt%, the polymerization mixtures were heterogeneous in which the monomer and the aqueous media remained in two different phases. As the methanol content increased from 30 to 60 wt%, the monomer and the media were mixed and showed a clear one phase due to increased solubility of the media resulting in homogeneous system at room temperature. At 30 wt% methanol, the medium was heterogeneous at room temperature, but it turned into homogeneous state at 60 °C. Thus, it seemed that 30 wt% is a transition region between homogeneous and heterogeneous phases. Thus, there were two distinctive regions around 30 wt% methanol in which media showed disparate states; one was heterogeneous region under methanol content less than 30% and another was homogeneous with methanol higher than 30 wt% as demonstrated in Fig. 1.

The weight–average molecular weight and the polydispersity index (PDI) of the synthesized final PMMA particles under varying methanol content in media were investigated as plotted in Fig. 2. Between 0 and 20 wt% methanol, the weight–average molecular weight varied between 8.5 × 105 and 1.1 × 106 g/mol and PDI varied between 1.7 and 2.0. The molecular weight of this range is a typical characteristics observed in the standard (soap-free) emulsion polymerization [6]. According to the well-established Smith–Ewart theory of emulsion polymerization [26], the polymerization kinetics follows the formula below:

$$R_P = k_P[M]_P(nN_P/N_A) \tag{1}$$

where, k_p is the propagation rate constant, $[M]_p$ the concentration of monomer in the particles, n the average number of free radicals per particle, N_A the Avogadro number, and N_p the number of latex particles per unit volume of water. Usually, high molecular weight is achieved by emulsion polymerization since the propagation takes place for a long period of time during Interval II (particle growth stage) in which the average number of free radicals per particle is about 0.5 [27].

However, between 40 and 60 wt% methanol, the weight–average molecular weight varied between 1.8 × 105 and 2.1 × 105 g/mol and the PDI was between 2.0 and 1.7, respectively, whose molecular weights were significantly lower than did in the former case. The above range of molecular weight is that typically observed in the dispersion polymerization. Like other heterogeneous polymerizations, the process of dispersion polymerization is divided into a particle nucleation stage and a particle growth stage. However, unlike other heterogeneous polymerizations, the particle nucleation stage occurs in a homogeneous phase. Once primary particles are formed by the precipitation of oligomeric free radicals, the polymerization predominantly precedes within the monomer-swollen particles. The rate of dispersion polymerization is expressed as follows [28]:

$$R_P = \alpha C_d V^{1/2} k_p (R_i/K_t)^{1/2} \tag{2}$$

where α is the monomer partition coefficient of polymer diluent, C_d the monomer concentration in diluent, V the particle volume fraction, k_p the propagation rate constant, k_t the mutual termination specific reaction rate constant, and R_i the initiation rate. The kinetics of the dispersion polymerization resembles that of bulk polymerization. Due to its relatively large particle size during dispersion polymerization, the termination reaction readily takes place since free radicals were abundantly present in the particles. As a result, low molecular weight of the resultant polymers was obtained compared to those obtained by emulsion polymerization. The noticeable decrease in the molecular weight between 20 and 40 wt% methanol was observed from 1.0 × 106 to 2.0 × 105 g/mol. Considering the homogeneity of the medium and the molecular weights of the resultant PMMA particles, it seemed that the polymerization occurred in the manner of emulsion and dispersion polymerization at 0–20 wt% and 40–60 wt% methanol, respectively. At 30% methanol, the molecular weight was 7.0 × 105 g/mol with

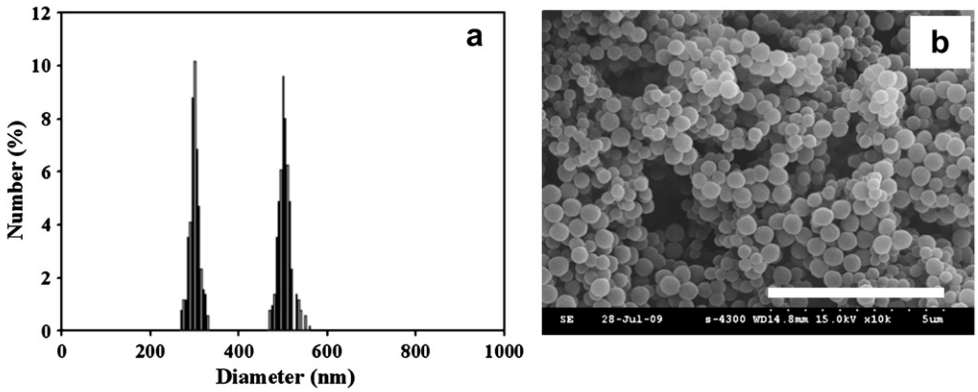

Fig. 3. (a) Size distribution of PMMA prepared with 30% methanol in reaction aqueous media and (b) SEM image of PMMA spherical particles with magnification of ×10,000 (scale bar: 5 μm).

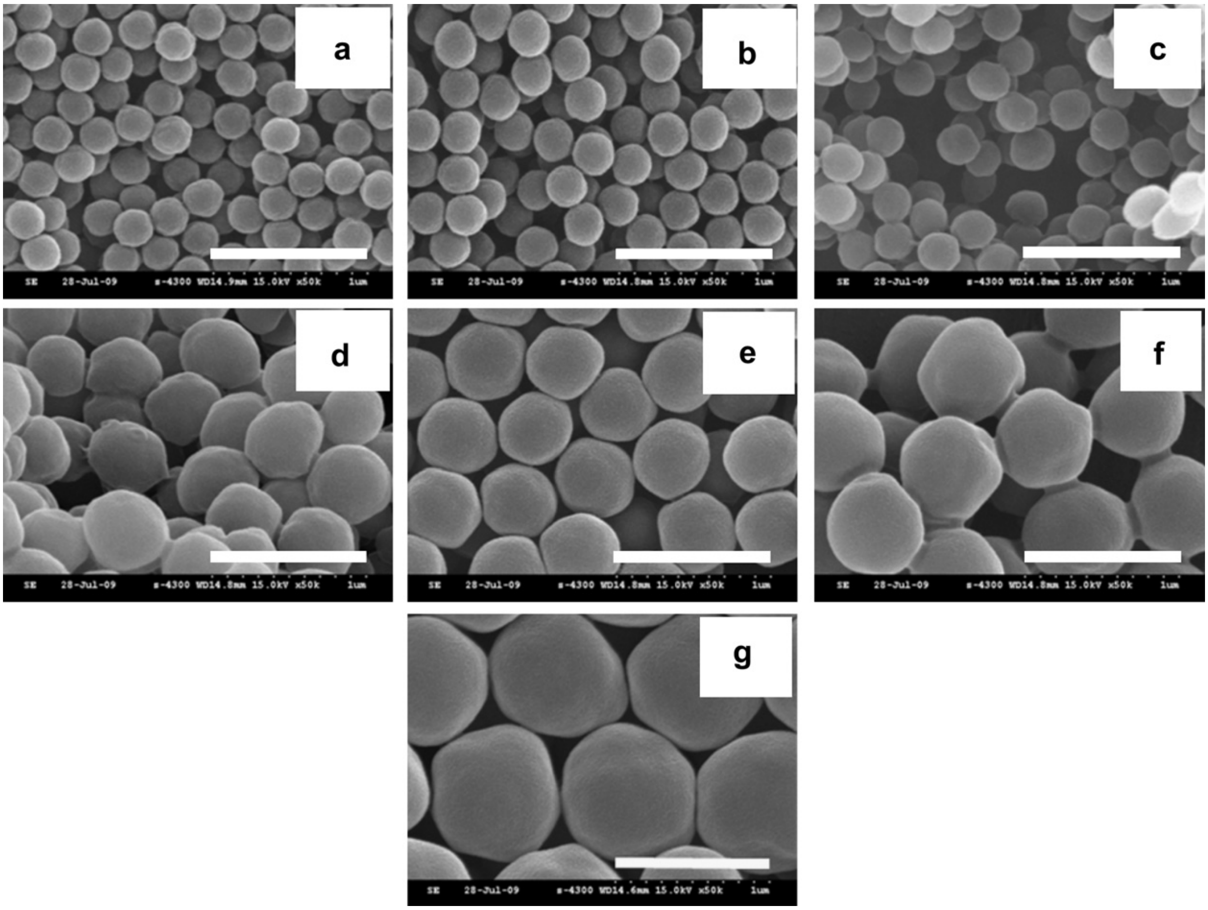

Fig. 4. SEM images of PMMA particles prepared by the soap-free emulsion polymerization with various methanol content in aqueous media: (a) 0, (b) 10 (c) 20, (d) 30, (e) 40, (f) 50, (g) 60 wt%. (scale bar: 1 μm).

the PDI of 3.5. This value of molecular weight lies between the high (at 0–20 wt% methanol) and low (at 40–60 wt% methanol) cases. In particular, the relatively high PDI values (compared to the above 1.7–2.0) might have originated from the fact that polymer molecules were obtained by both mechanisms of emulsion and dispersion polymerization. Thus, the results at 30 wt% methanol might have been caused by the bimodal distribution of particle sizes as seen in Fig. 3. Thus, the transition from emulsion to dispersion polymerization traits at 30 wt% methanol was corroborated in terms of molecular weight, molecular weight distribution and particle size.

Figs. 4 and 5 show the SEM images and the size distribution of PMMA particles obtained under varying methanol contents from 0 to 60 wt% as listed in expt. 1 in Table 1. Other conditions such as the amount of monomer, concentration of initiator, reaction temperature, and the agitation speed were maintained same throughout all experiments. According to the images obtained, the particle size increased along with the increment in methanol content. The different aspects of the variation of the particle size with respect to the content of alcohol have been reported in emulsion polymerization. Decrease in the particle size was observed in anionic emulsifier-free emulsion polymerization of styrene in methanol/water by Homola et al. [29] and in acetone/water by Okubo et al. [30] However, the increase in the particle size was also reported with the alcohol contents for anionic soap-free emulsion polymerization of styrene/sodium vinylbenzyl sulfonate in methanol/water [21] and cationic soap-free emulsion polymerization of styrene/(2-(methacryloyloxy) ethyl) trimethyl ammonium chloride in ethanol/water [31]. A complex behavior was also reported; the particle size decreased up to 9.6 wt% methanol, then increased with further increase in methanol content up to 36 wt% for cationic soap-free emulsion polymerization of styrene/butyl acrylate in methanol/water [32]. In the present study in which soap-free emulsion polymerization took place up to 20 wt% of methanol content, the particle size slightly increased with the methanol content. In soap-free emulsion polymerization, the particle size is mostly determined by nucleation rate and particle stability. It was expected that the presence of methanol would increase monomer solubility in the continuous phase. In addition, the solubility of oligomers generated in the continuous phase was estimated to increase with methanol content [29]. Upon the oligomer nucleation and adsorption, the electrostatic interactions originated from the charged groups play an important role. Evidently, an oligomer bearing more charged groups would be more rigid to nucleate or to adsorb on the likely charged particle surfaces [31]. Addition of alcohols as cosolvents normally decreases the electrostatic repulsion as confirmed by the zeta potential measurement [31]. Therefore, the addition of methanol would more likely to facilitate the oligomer nucleation and adsorption which would result in the formation of larger particles at higher methanol content. This was seen in Figs. 4(a–c) and 5(a–c) in which the soap-free emulsion polymerization was achieved.

At higher concentrations of methanol from 40 to 60 wt% where dispersion polymerization predominantly took place, the particle size also increased with the methanol content. It was noted that the resultant particles were stabilized with the aid of steric stabilizer

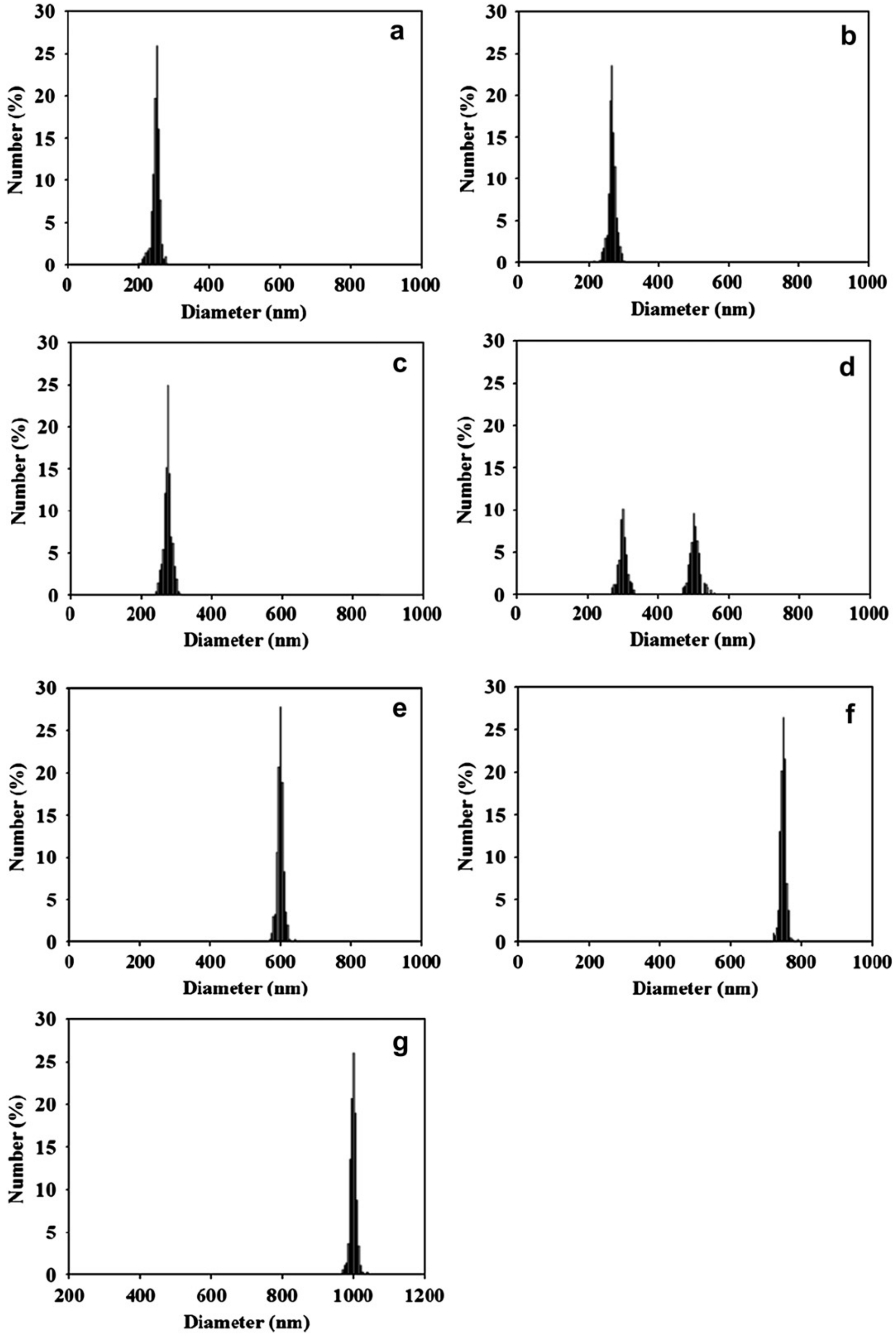

Fig. 5. Size distribution images of PMMA particles prepared by the soap-free emulsion polymerization with various methanol contents in aqueous media: (a) 0, (b) 10 (c) 20, (d) 30, (e) 40, (f) 50, (g) 60 wt%.

such as poly(vinyl pyrrolidone) [33,34], hydroxypropyl cellulose [35], poly(acrylic acid) [36] in conventional dispersion polymerization. However, the particles were electrostatically stabilized as seen in Fig. 4(e–g). In dispersion polymerization, the final particle size is determined by the initial number of nuclei which is influenced by the solvency of the polymerization media. The number of nuclei strongly depends on the solubility of the growing chains in the polymerization medium. If the medium is a good solvent for the nuclei, it dissolves most of small nuclei with low molecular weight, resulting in reduction in the number of nuclei.

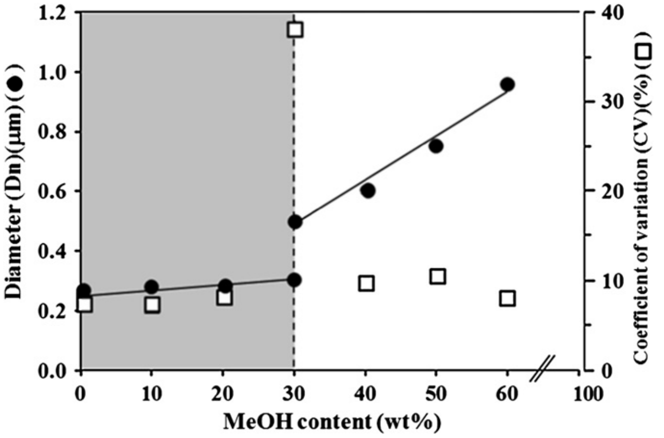

Fig. 6. The particle diameter (Dn) and the coefficient of variation (CV) of the PMMA particles prepared with various methanol contents in aqueous media.

The nuclei is once formed, monomers are swell and diffused into the nuclei and polymerized. Small number of nuclei, in the initial stage of polymerization, leads to larger particle size after completion of the polymerization [37,38]. The solubility parameters (δ) of methanol, water, and MMA are 14.5, 12.1, and 23.4 $(\mathrm{cal/cm^3})^{1/2}$, respectively [39]. When the difference in the solubility parameters of monomer and polymerization medium is small, the oligomer-solubilizing capability in medium is enhanced, in which the formation of primary particles is retarded. In turn, fairly large final particles with narrow size distribution are generated due to the presence of smaller number of primary particles which serve as the polymerization *loci* as seen in Figs. 4(e–f) and 5(e–f).

Fig. 6 represents the particle size (Dn) and its uniformity as denoted by the coefficient of variation (CV) with respect to various methanol contents. Between 0 and 20 wt% methanol in aqueous media, the particle size slightly increased from 250 to 270 nm along with relatively fair monodispersity (the CV value is less than 10). On the other hand, between 40 and 60 wt% methanol, the particle size rapidly increased from 600 nm to 1 μm. However, at 30% methanol in aqueous media, the size distribution of the particles was clearly bimodal as plotted in Fig. 5(d); 300 and 500 nm. As mentioned earlier, the solubility parameter of solvents is one of the factors affecting the particle size in dispersion polymerization, and the relationship between the solubility parameter and the particle size is known to be linear in many cases [40–42]. Importantly, Fig. 6 demonstrates that heterogeneous and homogeneous transition at 30 wt% methanol shows two different linear patterns.

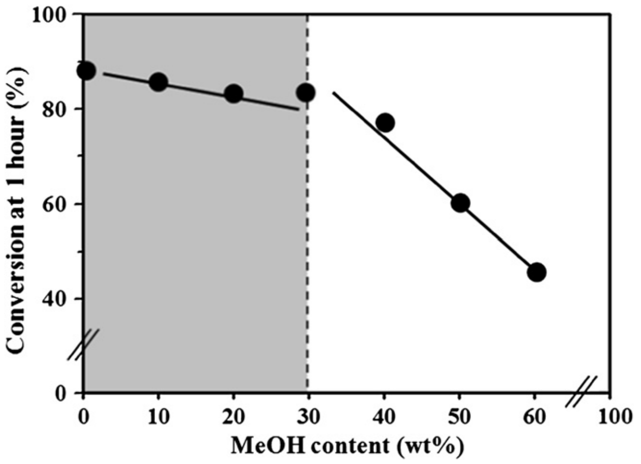

Fig. 7. The conversion at 1 h under various methanol contents.

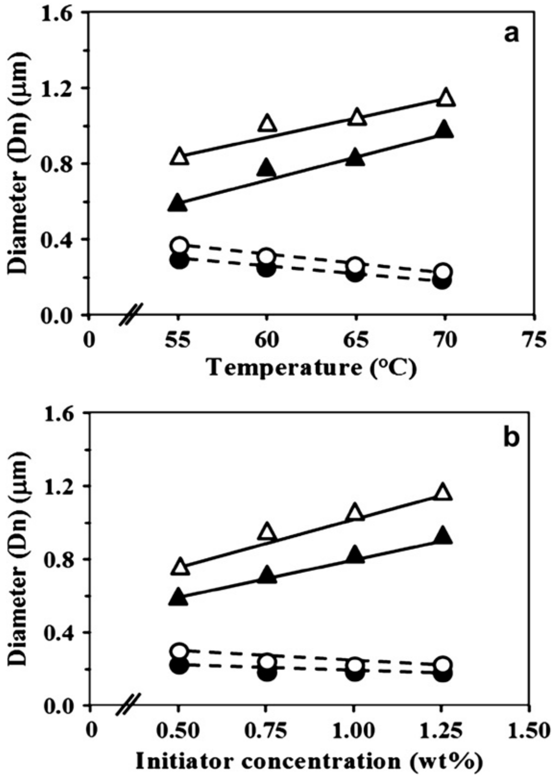

Fig. 8. The effect of temperature and initiator concentration on the size of PMMA particle prepared by soap-free emulsion polymerization in various contents of methanol: 0 (●), 10 (○), 50 (▲), and 60 wt% (△).

Fig. 7 shows the initial monomer conversion at 1 h under varying methanol contents in aqueous media. From 0 to 30 wt% methanol, the initial monomer conversion slightly decreased from 89 to 86%. In contrast, for methanol contents between 40 and 60 w%, the initial monomer conversion steeply decreased from 80 to 45%. Both in emulsion and dispersion polymerization, the number of particles in unit volume of the latex (N_p) can be calculated by the following equation:

$$N_\mathrm{p} = \frac{6WC}{\pi\rho V d^3} \qquad (3)$$

where W is the weight of monomer (g), C the monomer conversion, V the volume of dispersing medium (ml), ρ the polymer density, and d is the particle diameter (cm).

The diameter of PMMA particles formed by the emulsion polymerization is smaller than that by the dispersion polymerization, implying that the greater number of particles exists in the emulsion polymerization. Therefore, the rate of polymerization in emulsion polymerization is expected to be greater than in dispersion polymerization since the individual growing particles serve as the polymerization *loci*. The discontinuity of the conversion at 1 h in 30 wt% methanol may imply that the phase conversion in the reaction medium is occurring, thereby the transition from emulsion polymerization to dispersion polymerization.

Above results including the homogeneity of the reaction mixture, molecular weight and its distribution, particle size and its distribution, and the conversion at 1 h indicate that the shift of the reaction medium from heterogeneous to homogeneous state causes significant changes in the mechanism of polymerization and properties of the final product. Emulsion polymerization takes

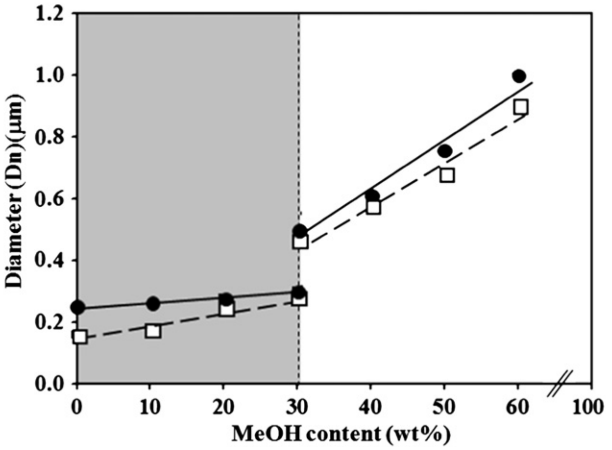

Fig. 9. The diameter (Dn) of PMMA particles in the absence of PVA (●) and presence of PVA (☐). The data for the absence of PVA are obtained from Fig. 6.

place between 0 and 20 wt% methanol, whereas the polymerization resembles dispersion polymerization between 40 and 60 wt% methanol. At 30 wt% methanol content, characteristics of both typical emulsion and dispersion polymerizations are concurrently observed. Further investigations were carried out in order to verify the characteristics and transition between two disparate polymerization processes.

3.2. *Verification of transition between emulsion and dispersion polymerization*

An important feature that demonstrates an opposite inclination in emulsion and dispersion polymerization is the particle size variation tendency examined with respect to the changes in the reaction temperature and initiator concentration. The size of particles prepared by the emulsion polymerization tends to decrease with increase in the initiator concentration and temperature [6]. In contrast, the particle size shows a proportional relationship with the initiator concentration and temperature in dispersion polymerization. In order to verify these distinctive characteristics between two polymerization processes, the particle size variation in terms of the temperature and initiator concentration under heterogeneous and homogeneous mixture was investigated.

Fig. 8 represents the effects of the polymerization temperature and initiator concentration on the size of final particles. Fig. 8(a) provides the comparison of the particle size–temperature relationship under various methanol contents. As temperature augmented from 55 °C to 70 °C, under heterogeneous systems containing 0 and 10 wt% methanol contents, the particle size linearly decreased from 310 nm to 190 nm and 380 nm to 180 nm, respectively. Whilst, under homogeneous systems consisting of 50 and 60 wt% methanol contents, the particle size increased from 550 nm to 850 nm and 950 nm to 1.2 μm, respectively. In (soap-free) emulsion polymerization, the increase in temperature leads to the decreases in the particle size. This inverse dependence between the particle size and the polymerization temperature is ascribed by the increasing decomposition rate of the initiator and monomer solubility in the aqueous phase upon raising temperature, which increases the concentration of growing chains and, thereby, reduces the particle size [43,44]. However, an inverse relationship between the polymerization temperature and the particle size was often observed in the dispersion polymerization. An increase in polymerization temperature causes an increase in the solubility of the oligomer chains and the rate constant of initiator decomposition and propagation, and reduces the viscosity of the continuous phase. These effects induce the reduced number of nuclei and aggregated primary particles, and thereby, result in larger particle size [38,45,46].

In Fig. 8(b), the effect of temperature and initiator concentration on the particle size is demonstrated. The particle size shows the opposite trends upon different methanol contents between 0–20 wt% and 40–60 wt% and this indicates the polymerization takes

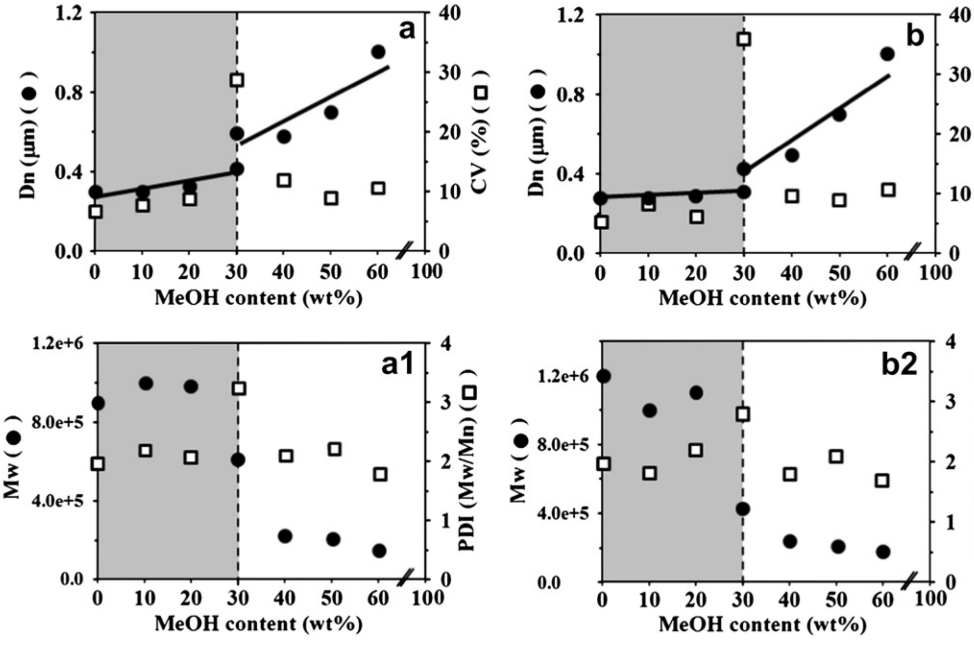

Fig. 10. The characteristics of PMMA particles prepared in various initiators with APS (a and a1) and NaPS (b and b1); (a) The variation of the number-average diameter (Dn) and (b) the coefficient of variation (CV). (a1) The corresponding changes in the weight–average molecular weight (Mw) and (b1) PDI (Mw/Mn) of PMMA particles prepared in various contents of methanol.

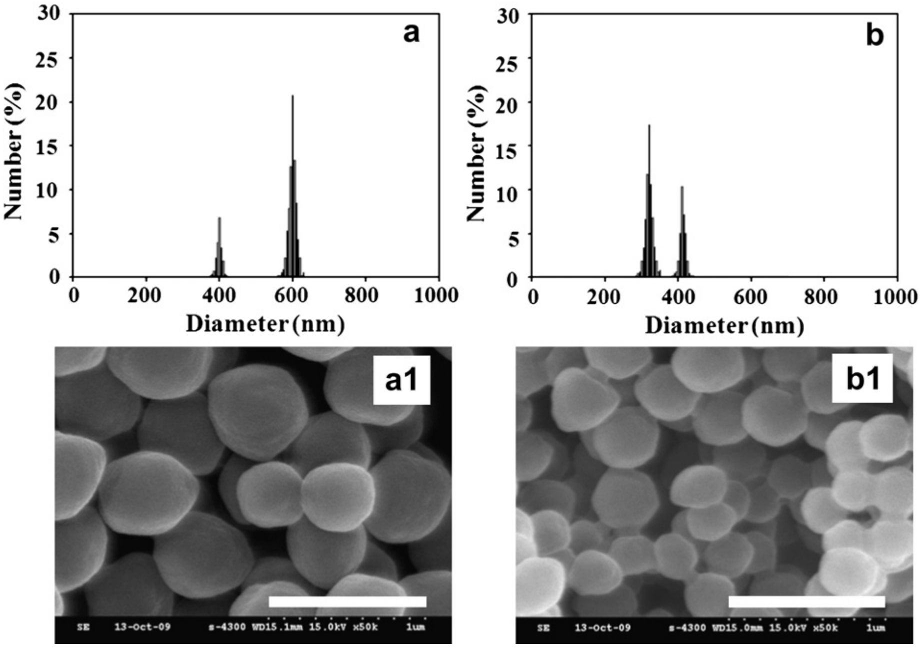

Fig. 11. Size distribution and SEM images of PMMA particles prepared with APS (a, a1) and NaPS (b, b1) as initiators at 30% methanol in aqueous media (scale bar: 1 μm).

place in different mechanisms. In soap-free emulsion polymerization, the increased initiator concentration generally leads to the decrease in the size of the particles [47,48] since the particles are generated by decomposed initiator fragments. The decomposed anionically charged persulfate groups continuously react with hydrophobic monomers such as styrene and MMA until the critical chain length is reached. With certain molecular weight of the growing oligoradicals, they become surface-active to form micelles by aggregation. This stage is called nucleation and the micelles are electrostatically stabilized. Once the nucleation is achieved, the monomer molecules diffuse into the micelles and the monomer-swollen micelles/particles serve as the main polymerization *loci*. Therefore, increasing the potassium persulfate initiator concentration increases the number of sulfate ions involved in the stabilization of the particles leading to the smaller particles. However, in dispersion polymerization, the increased initiator concentration causes the increase in the radical concentration, thereby, the increase in the concentration of shorter critical chain length of the growing oligomers due to termination or chain transfer reaction. Since most oligoradicals are still soluble in the media, the smaller number of primary particles is generated, finally resulting in larger particle size with low molecular-weight polymers [49–51].

To sum up, during the modified soap-free emulsion polymerization of MMA, the properties of typical emulsion polymerization was observed at low methanol contents of up to 20 wt%, and those of dispersion polymerization appeared with high methanol contents of 40–60 wt%. Both characteristics were simultaneously witnessed at 30 wt%, which is the transition region between emulsion and dispersion polymerization.

3.3. *Dependence of various initiators on the transition behavior*

It is likely that the phase transition of medium from heterogeneous to homogeneous state would be the main factor that influences the polymerization behaviors, and that ultimately plays a key role in determining emulsion and dispersion polymerization. In order to figure out possible other variables that affect the transition behavior, the effects of the presence of stabilizer and sorts of initiator on the transition behavior were studied.

Fig. 9 compares the size of PMMA particles prepared in the absence and presence of stabilizer, PVA. 0.2 wt% PVA with respect to total solution was added and methanol content was varied from 0 to 60 wt%. The size of PMMA particles prepared with PVA was slightly smaller than that obtained without it, since the added stabilizer induced the formation of large surface area. The size increased continuously from 160 to 220 nm as methanol content increased from 0 to 20 wt%, and showed a rapid increase from 600 to 900 nm with 40–60 wt% methanol content. In addition, at 30% methanol, the bimodal shape of distribution was observed with 300 and 580 nm in both the absence and presence of PVA, resulting in transition region

Other types of classical initiators such as APS and NaPS were tested using the same experimental conditions as did before and the results are drawn in Fig. 10. The size variation in Fig. 10(a) and (b) shows a similar pattern to the result shown in Fig. 6. The PMMA particle size increased from 210 to 300 nm with APS and 270 to 300 nm with NaPS under the methanol content of 0–20 wt%, respectively. In addition, the particle size rapidly increased from 600 nm to 1 μm with APS and 500 nm to 1 μm with NaPS under the methanol content of 40–60 wt%, respectively. The evolution of molecular weight and its distribution in Fig. 10(a1) and (b1) also changed in the same manner as shown in Fig. 2. In both cases, the high molecular weight around 106 g/mol was achieved only under the low methanol content of 0–20 wt%, and relatively lower molecular weight in the order of 105 g/mol was obtained under the methanol rich phase of 40–60 wt%. At 30 wt% methanol, the bimodal size and intermediate molecular weights upon bimodal size distribution were obtained since the polymerization took place through heterogeneous and homogeneous phases. The bimodal distributions of the particles at 30 wt% methanol are demonstrated in Fig. 11 for both cases. Again, the results followed the same pattern as those observed in Fig. 3 using KPS. Thus, the high values in CV and PDI at 30 wt% methanol in Fig. 10(a, a1) and (b, b1) would have been arise due to the bimodal distributions from different polymerization mechanisms.

In summary, the polymerizations were conducted in a wide range of methanol content from 0 to 60 wt% with water. Based on the results of particle size and its distribution, molecular weight and its distribution, the effects of polymerization temperature, the concentration of initiator and various initiators, two distinct properties were obtained; soap-free emulsion polymerization dominantly occurred in the low methanol content of 0–20w wt%, and dispersion polymerization mainly occurred in the high methanol content of 40–60 wt% where the particles were stabilized by electrostatic repulsion. Therefore, the homogeneity of the polymerization mixture was confirmed as the key factor in determining characteristics between emulsion and dispersion polymerization in aqueous methanol media.

4. Conclusion

The effect of a wide range of methanol content in the soap-free emulsion polymerization of MMA was investigated. The transition phenomenon from heterogeneous to homogeneous state appeared within medium as the methanol content was increased from 0 to 60 wt%. In order to verify the mechanism of the polymerization in heterogeneous and homogeneous mixture, the properties of the PMMA particles prepared by the same conditions and ingredients were analyzed in terms of particle size and molecular weight. In addition, the effects of methanol content, concentration of initiator, and the polymerization temperature on the conversion at 1 h were also investigated. With the heterogeneous medium in the range of 0–20 wt% methanol, the polymerization products showed the properties generally obtained in the soap-free emulsion polymerization, namely, high molecular weight in the order of 10^6 g/mol and small particle size of 200–400 nm. In this region, the effects of temperature and concentration of initiator also showed the behaviors typically observed in the soap-free emulsion polymerization.

On the other hand, within the homogeneous medium with the methanol contents of 40–60 wt%, the properties of the polymerization products showed those typically observed in the dispersion polymerization. In this region, the relatively low molecular weight in the order of 10^5 g/mol and the particle size from 400 nm to 1 μm were obtained. In this region, the effects of temperature and concentration of initiator also followed the trend observed in the dispersion polymerization.

At transition point of 30 wt% methanol, the mixed properties between the soap-free emulsion and the dispersion polymerizations were concurrently achieved with high PDI values and bimodal size distributions.

Thus, it can be concluded that the state of the homogeneity in the aqueous methanol mixture works as a critical factor in determining the polymerization modes between soap-free emulsion and dispersion polymerization.

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References

[1] Urban D, Takamura K. Polymer dispersions and their industrial applications. Weinheim: Wiley–VCH; 2002.
[2] Nomura MJ. Ind Eng Chem 2004;10:1182–216.
[3] Fudouz H, Xia Y. Adv Mater 2003;15:892–6.
[4] Ugelstad J, Stenstad P, Kilaas L, Prestvik WS, Rian A, Nustad K, et al. Macromol Symp 1996;101:491–500.
[5] Han S, Lee K, Shim SE, Choe S. Macromol Res 2007;15:403–11.
[6] Lovell PA, El-Aasser MS. Emulsion polymerization and emulsion polymers. New York: Wiley; 1997.
[7] Gilbert RG. Emulsion polymerization, a mechanistic approach. London: Academic Press; 1995.
[8] KEJ Barrett. Dispersion polymerization in organic media. New York: Wiley & Sons; 1975.
[9] Wang Q, Fu S, Yu T. Prog Polym Sci 1994;19:703–53.
[10] Tseng CM, Lu YY, El-Aasser MS, Vanderhoff JW. Ed. J Polym Sci Polym Chem 1986;24:2995–3007.
[11] Paine AJ. Macromolecules 1990;23:3104–9.
[12] Malyukova EB, Naumova SV, Gritskova IA, Bondarev AN, Zubov VP. Vysokomol Soed Ser A 1991;33:1469–75.
[13] Lam S, Hellgren AC, Sjöberg M, Holmberg K, Schoonbrood HAS, Unzué MJ, et al. J Appl Polym Sci 1997;66:187–98.
[14] Werner JB. Prog Org Coat 1992;20:235–59.
[15] Goodall AR, Wilkinson MC, Hearn J. J Polym Sci Polym Chem Ed 1977; 15:2193–218.
[16] Hearn J, Wilkinson MC, Goodall AR, Chainey M. J Polym Sci Polym Chem Ed 1985;23:1869–83.
[17] Zou D, Derlich V, Gandhi K, Park M, Sun L, Kriz D, et al. J Polym Sci Polym Chem 1990;28:1909–21. Ed.
[18] Song Z, Poehlein GW. J Colloid Interface Sci 1989;128:486–500.
[19] Feeney PJ, Napper DH, Gilbert RG. Macromolecules 1987;20:2922–30.
[20] Yamamoto TT, Kanda Y, Higashitani K. Langmuir 2004;20:4400–5.
[21] Chonde Y, Krieger IJ. Appl Polym Sci 1981;26:1819–27.
[22] Bon SAF, Beek HV, Piet P, German AL. J Appl Polym Sci 1995;58:19–29.
[23] Twigt F, Piet P, German AL. Eur Polym J 1991;27:939–45.
[24] Lü QF, Huang MR. Chem Eur J 2007;13:6009–18.
[25] Li XG, Feng H. Chem Eur J 2009;15:4573–81.
[26] Smith WV, Ewart RHJ. Chem Phys 1948;16:592–9.
[27] Chern CS. Prog Polym Sci 2006;31:443–86.
[28] Fitch RM, Kamath YK. J Colloid Interface Sci 1976;54:6–12.
[29] Homola A, Inoue M, Robertson A. J Appl Polym Sci 1975;19:3077–86.
[30] Okubo M, Yamada A, Shibao J. J Appl Polym Sci 1981;26:1675–9.
[31] Liu Z, Xiao H. Polymer 2000;41:7023–31.
[32] Zhang J, Zou Q, Li X, Cheng S. J Appl Polym Sci 2003;89:2791–7.
[33] Paine AJ. Macromolecules 1990;23:3109–17.
[34] Thomson B, Rudin A, Lajoie G. J Appl Polym Sci 1996;59:2009–28.
[35] Lok KP, Ober CK. Can J Chem 1985;63:209–16.
[36] Ober CK, Lok KP. Macromolecules 1987;20:268–73.
[37] Shen S, Sudol ED, El-Aasser MS. J Polym Sci Part A Polym Sci 1993; 31:1393–402.
[38] Shen S, Sudol ED, El-Aasser MS. J Polym Sci Part A Polym Sci 1994; 32:1087–100.
[39] Barton AFM. CRC handbook of solubility parameters and other cohesion parameters. Fla. Boca Raton: CRC Press; 1985.
[40] Cao K, Yu J, Li BG, Li BF, Pan ZR. Chem Eng J 2000;78:211–5.
[41] Yang W, Zhou H, Tao Z, Hu J, Wang C, Fu S. J Macromol Sci Pure Appl Chem 2000;A37:659–75.
[42] Horak DJ. Polym Sci Part A Polym Sci 1999;37:3785–92.
[43]. Tanrisever T, Okay O, Sönmezoğlu IÇ. J Appl Polym Sci 1996;61:485–93.
[44] Shim SE, Cha YJ, Byun JM, Choe SJ. Appl Polym Sci 1999;71:2259–69.
[45] Ober CK, Hair ML. J Polym Sci Part A Polym Chem 1987;25:1395–407.
[46] Saenz JM, Asua JM. J Polym Sci Part A Polym Chem 1996;34:1977–92.
[47] Kumar D, Butler GB. Part Sci Technol 1996;19:315–26.
[48] Madaeni SS, Ghanbarian M. Polym Int 2000;49:1356–64.
[49] Horak D, Krystufek M, Spevacek J. J Polym Sci Part A Polym Chem 2000;38:653–63.
[50] Shim SE, Jung H, Lee H, Biswas J, Choe S. Polymer 2003;44:5563–72.
[51] Tuncel A, Kahraman R, Piskin EJ. Appl Polym Sci 1993;50:303–19.