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Emulsion polymerization of methyl methacrylate using the reverse iodine transfer polymerization (RITP) technique

Hong Choul Shin, Hyung Geun Oh, Kangseok Lee, Byung H. Lee, Soonja Choe*

Department of Chemical Engineering, Inha University, Yonghyundong 253, Namgu, Incheon 402-751, Republic of Korea

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ABSTRACT

The targeted molecular weight poly (methyl methacrylate) [PMMA] latex was successfully prepared in the presence of 4,4-azobis(4-cyanopentanoic acid) (ACPA) and various surfactants using the reversible iodine transfer polymerization (RITP)-emulsion polymerization at 85 °C for 7 h in the absence of light. The properties of PMMA particles upon the various ratios of ACPA to iodine within the concentration ranges of ACPA (1.0–2.0 mmol) and iodine (0.1–1.0 mmol) with various surfactants were investigated by means of GPC, SEM and particle analyzer. The weight-average molecular weight and the conversion increased with the ratio of [ACPA]/[I_2], but no correlation between the particle size and the [ACPA]/[I_2] ratio was obtained. The initiator, ACPA, was important in the formation of PMMA spherical particles, while molecular iodine dominated in controlling the molecular weight, inhibition period and the conversion. In overall, the appropriate concentration of ACPA, iodine and anionic or anionic with non-ionic surfactants controls the targeted molecular weight less than 100,000 g/mol and the enhanced conversion higher than 90% along with particle stability.

1. Introduction

In the polymer industry, radical polymerization provides numerous industrially diversified products [1]. The emulsion polymerization is the primary polymerization technique in the radical polymerization which has some advantages and disadvantages [2,3]. The advantages are good heat transfer, low viscosity, high monomer conversion, direct application, and high surface area. However, it also has some drawbacks including the contamination of product with additives and no easy control in the case of hydrophilic monomers and polymer structures (composition, shape, topology, and functionality) [4–6]. In order to overcome those disadvantages, the living/controlled radical polymerization (L/CRP) was developed [7,8]. Unlike the conventional radical polymerization which includes initiation–termination process, a steady state of growing radicals was established through the activation–deactivation process rather than initiation–termination. These techniques make it possible to design copolymers with unusual chain microstructures, copolymers of complex architectures that were only accessible by other specific methods such as living ionic polymerization [9,10]. Among CRP, the most widespread methods were nitroxide-mediated polymerization (NMP) [11], atom transfer radical polymerization (ATRP) [12], iodine transfer polymerization (ITP) [13], reversible addition–fragmentation chain transfer polymerization (RAFT) [14], and reverse iodine transfer polymerization (RITP) [15].

Iodine was studied as an inhibitor in the free radical polymerization of vinyl acetate and styrene [16], and as a chain transfer agent in the thermal polymerization of MMA [17]. RITP of MMA initiated by AIBN in the dispersion polymerization was studied to elucidate the mechanism and to investigate the inhibition and polymerization periods [18]. In ab initio emulsion polymerization of butyl acrylate (BuA) by RITP, the side reactions between iodine and water were responsible for an upward deviation of the molecular weight [19]. The polymerization of styrene was initiated by bis(4-*tert*-butylcyclohexyl) peroxydicarbonate at 60 °C with dodecylsulfate sodium salt (SDS) as surfactant and hexadecane as hydrophobe, yielding a stable and uncolored latex [20]. In the RITP polymerization, the monomer conversion was lower than that of conventional radical polymerization due to the inhibition period. The inhibition period was able to control by reaction conditions such as temperature or molar ratio of initiator to iodine. In addition, since the conversion in RITP was higher than that in RAFT with maintaining properties of living/controlled radical polymerization, the RITP was favorable in industrial field.

The first results on RITP of *n*-butyl acrylate in water based emulsion showed that the molar mass of the polymer could be tuned, indicating that the RITP process should be applicable to heterogeneous processes, which were of major industrial importance

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* Corresponding author.
E-mail address: sjchoe@inha.ac.kr (S. Choe).

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[21,22]. The overall time of polymerization was effectively shortened by controlling the inhibition period, while keeping a good control of the final molar mass of the polymer. Since the iodine was hydrolyzed in water phase, two methods preventing the hydrolysis were reported; one was to use the initiator (hydrogen peroxide) and another was to use initiator (potassium persulfate) [23]. To overcome the hydrolytic disproportionation of iodine in emulsion polymerization, persulfate was used as both initiator and oxidant and the mechanism of RITP in solution was introduced [24].

In general, emulsion polymerization of acrylate based monomers produced high molecular weight (M_w) polymers higher than a few hundreds of thousands g/mol. However, the control of the molecular weight less than 100,000 g/mol with high conversion using an environmentally-friendly emulsion process is of great importance in the industrial point of view.

Our previous efforts focused on the synthesis of PMMA in the RITP-emulsion polymerization using persulfate related initiators such as KPS, APS, and NaPS were not successful. In this article, the PMMA latexes ranging the weight-average molecular weight less than 100,000 g/mol with high conversion was successfully synthesized in the presence of 4,4-azobis(4-cyanopentanoic acid) (ACPA) with various surfactants using the RITP-emulsion polymerization at 85 °C for 7 h. The surfactants used were dodecylsulfate sodium salt (SDS), dodecyl benzenesulfonic acid sodium salt (SDBS) hexadecyltrimethylammonium bromide (CTAB), poly(ethylene glycol) ethyl ether methacrylate (PEG-EEM) and Tween80 (Uniqema).

2. Experimental

2.1. Materials

Methyl methacrylate (Junsei Chemicals, Japan) was purified using an inhibitor removal column (Aldrich) and stored at −5 °C

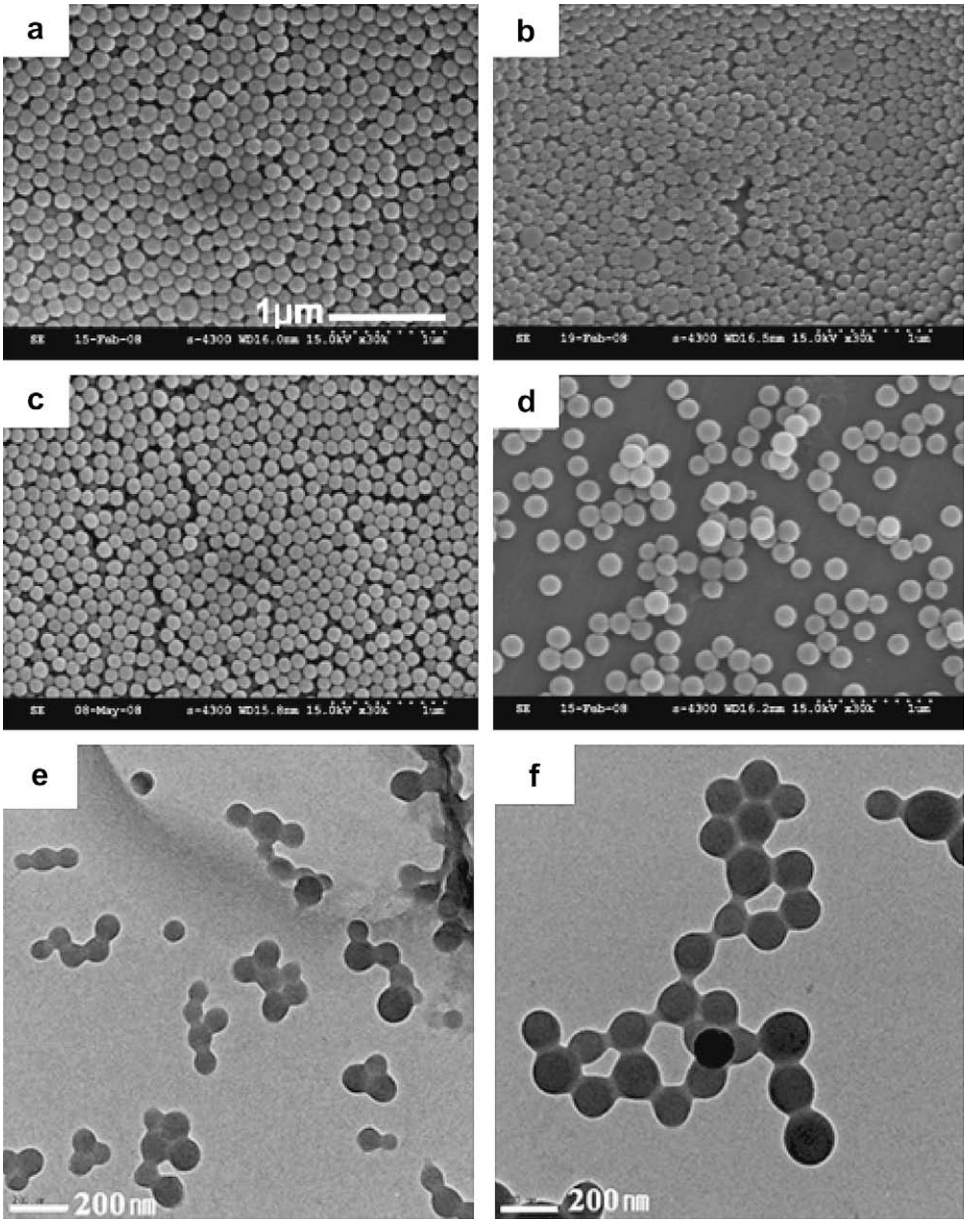

Fig. 1. The representative SEM photographs of the synthesized PMMA particles by the various concentrations of [ACPA] with $[I_2] = 0.5$ mmol; [ACPA] (a) 1.0, (b) 1.5, (c) 1.75, (d) 2.0 mmol. TEM photographs (e) and (f) represent the same sample shown as the above SEM pictures (b) and (c), respectively.

prior to use. 4,4′-Azobis(4-cyanopentanoic acid) (ACPA, Aldrich, USA) was used as an initiator without further purification. Iodine (99.9%, Aldrich, USA) was used for RITP technique and stored at −5 °C prior to use. The surfactants such as dodecylsulfate sodium salt (SDS, Junsei Chemical Co. Ltd., Japan), dodecyl benzenesulfonic acid sodium salt (SDBS, Junsei Chemical Co. Ltd., Japan), hexadecyltrimethylammonium bromide (CTAB, Aldrich, USA), poly (ethylene glycol) ethyl ether methacrylate (PEG-EEM, Aldrich, USA) and Tween80 (Uniqema, UK) were used as received. Suitable amount of sodium hydroxide (98%, Samchun Chemicals, Korea) was used as neutralizer ACPA into its sodium salt. The double-distilled deionized water was used as the polymerization media.

2.2. Polymerization of PMMA

The PMMA spherical particles were prepared by the emulsion polymerization of MMA using RITP technique in double-distilled deionized water. The monomer concentration was 7.94 wt% of the media. The polymerization reaction was initiated using ACPA at 3.5 wt% of the monomer. All surfactants were used at the critical micelle concentration (CMC) of them. After all ingredients were charged in a 250 mL three neck round bottom flask, the polymerization was carried out with a mechanical stirring at 250 rpm under argon (Ar) atmosphere at 85 °C for 7 h in the absence of light. The resulting polymerization products were rinsed off with DDI water and methanol, and centrifuged repeatedly to remove the non-reacted materials. Then, they were dried at room temperature for 2 days and used for characterization.

2.3. Characterization

The molecular weights of the synthesized PMMA particles were measured using Waters GPC (Gel Permeation Chromatography, USA) equipped with 510 differential refractometer and Viscotek T50 differential viscometer (Viscotek, USA). The PDI was calculated as the ratio of the weight-average and number-average of molecular weight (M_w/M_n). Hitachi SEM (Scanning Electron Microscopy, Japan) S-4300 was used to study the morphology of PMMA particles. The number-average diameter (D_n) and coefficient of variation were measured by particle size analyzer (BECKMAN COULTER, LS230, USA) with the particles suspended in water. The conversion was measured by gravimetrically.

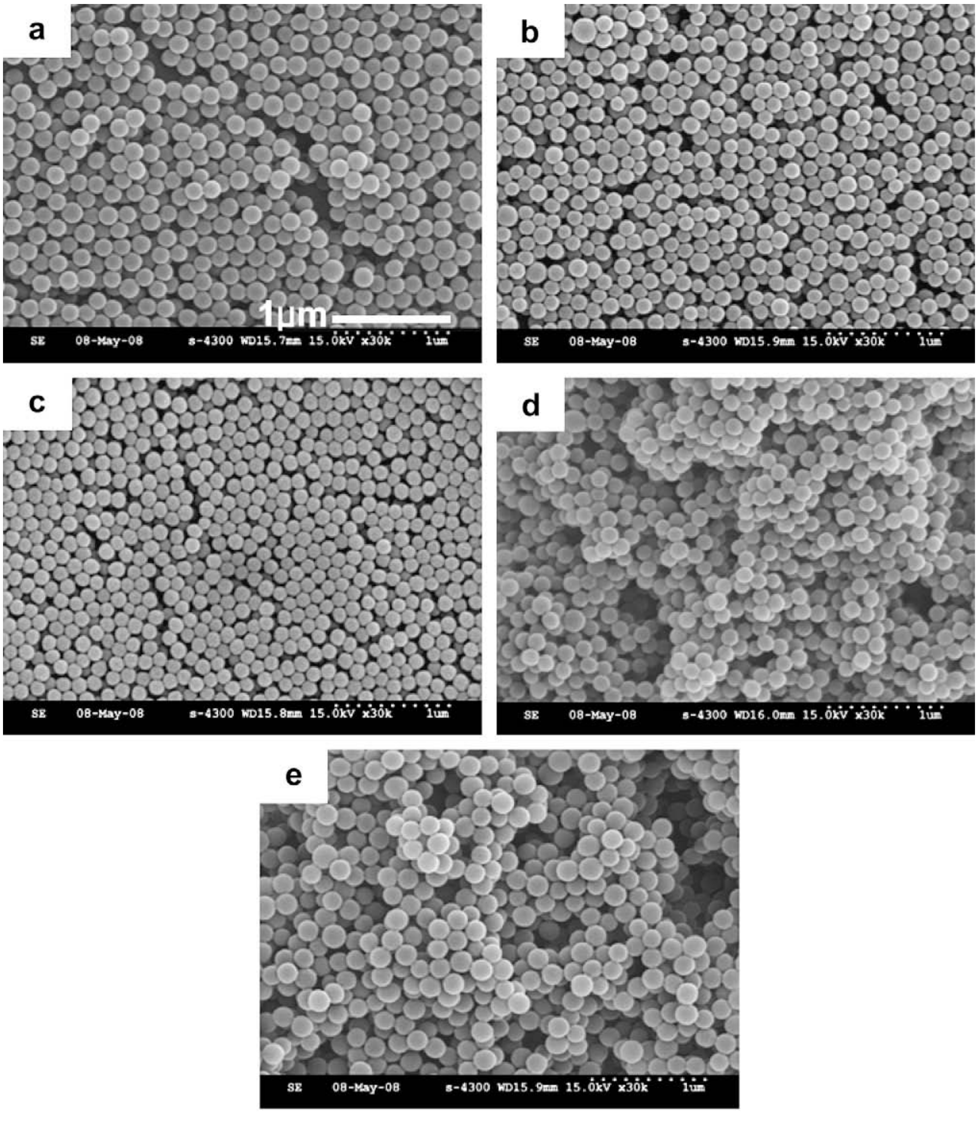

Fig. 2. The representative SEM photographs of the synthesized PMMA particles by the various ratios of [ACPA]/[I_2] with [ACPA] = 1.75 mmol; [ACPA]/[I_2] (a) 17.5, (b) 7, (c) 3.5 (this picture is the duplicate of Fig. 1(c) and (d)) 2.3, (e) 1.75.

3. Result and discussion

3.1. *Effects of the initiator and iodine concentrations*

Fig. 1 shows the representative SEM photographs of PMMA particles prepared in the presence of SDS by changing the ACPA concentrations using RITP-emulsion polymerization at 85 °C for 7 h. In addition, Fig. 1(e) and (f) represents the TEM photographs of the same samples used for Fig. 1(b) and (c), respectively. All figures showed spherical particles that ACPA, which was a water soluble azo compound, came out to be a proper initiator to prepare PMMA spherical particles using RITP-emulsion polymerization technique. Thus, ACPA was verified to replace the persulfate related initiators such as KPS, APS, and NaPS, in forming spherical PMMA particles using the RITP-emulsion polymerization.

Fig. 2 shows the representative SEM photographs of PMMA particles prepared by emulsion polymerization in the presence of SDS with various ratios of [ACPA]/[I_2] at 1.75 mmol [ACPA] by RITP at 85 °C for 7 h. All spherical particles were apparently stable and the ratios of [ACPA]/[I_2] did not affect the particle size and its stability.

Fig. 3 shows the evolution of the monomer conversion vs time for the RIPT-emulsion polymerization of MMA in the presence of SDS with various concentrations of ACPA and iodine at 85 °C for 7 h. The iodine concentrations varied from 0.1 to 0.75 mmol and the ACPA concentrations varied between 1.0 and 2.0 mmol. The conversion slightly increased with the concentration of ACPA, but was rather strongly influenced by the iodine concentration. In addition, the higher the iodine concentration, the longer the inhibition period was observed. In particular, the inhibition period at [I_2] = 0.75 mmol was almost half (4 h) of the reaction period (7 h). Thus, it was verified that the use of molecular iodine strongly controls the inhibition period and the molecular weight due to the effect of hydrolysis of iodine in water [16], while ACPA and SDS affect the formation of spherical PMMA particles.

Fig. 4 summarizes the weight-average molecular weight (M_w) and the monomer conversion variation of PMMA particles prepared with various ratios of [ACPA]/[I_2] at different concentrations of ACPA and I_2. As the ratio of [ACPA]/[I_2] increased, the molecular weight of PMMA particles increased in linear shape and the conversion increased as well. In addition, the increment of ACPA concentration under the fixed ratio of [ACPA]/[I_2] resulted in the decrease in the molecular weight of PMMA due to the augmented number of polymer chains. When the fixed monomer concentration was dissolved in the reaction media, more reactive radicals from the increased initiator reacted with the monomers. In addition, the higher the iodine concentration, the lower the molecular weight of PMMA was observed. Thus, it was confirmed that the iodine strongly influences the molecular weight and the conversion of PMMA.

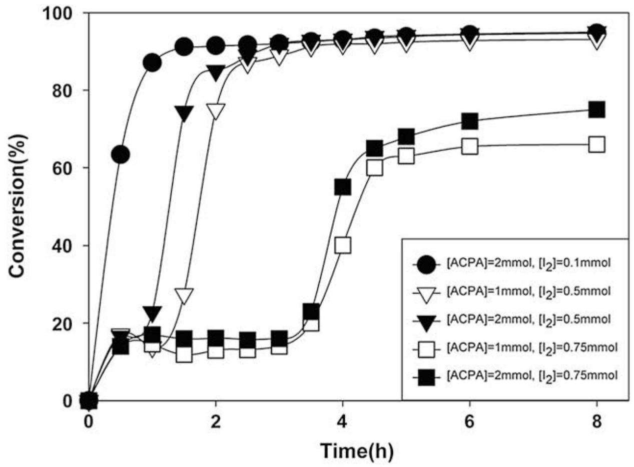

Fig. 3. Evolution of monomer conversion as a function of time for the RITP-emulsion polymerization of MMA at various concentrations of ACPA and iodine at 85 °C for 7 h. ●: [ACPA] = 2.0, [I_2] = 0.1 mmol, ▽: [ACPA] = 1.0, [I_2] = 0.5 mmol, ▼: [ACPA] = 2.0, [I_2] = 0.5 mmol, □: [ACPA] = 1.0 mmol, [I_2] = 0.75 mmol, ■: [ACPA] = 1.0 mmol, [I_2] = 0.75 mmol.

In RITP, the controlled molecular weight of polymers can be obtained by the reaction between radicals induced from initiator and I_2. As seen in Figs. 3 and 4, the molecular weight of PMMA and the conversion were more influenced by the amount of I_2 as a chain transfer agent than ACPA as an initiator. Thus, I_2 dominates the polymerization kinetics. This makes the different mechanism from that of the general emulsion polymerization. This was also discussed in various researchers [15,18,19,21,22].

Since we were interested in preparing PMMA particles with the molecular weights (M_w) less than 100,000 g/mol with conversion higher than 90%, 3.0 and 3.5 of [ACPA]/[I_2] with 1.5 and 1.75 mmol of [ACPA], respectively, were intensively studied as the following.

3.2. *Effect of the surfactants in the RITP-emulsion polymerization*

Surfactant was one of the important factors which affect the properties of PMMA particles prepared by the RITP-emulsion polymerization. Thus, various surfactants including anionic, cationic, non-ionic and reactive surfactant, and co-surfactants between anionic and non-ionic one were used for the synthesis of PMMA using the above recipe. As described before, two different conditions were 1.5 mmol [ACPA] with 3.0 of [ACPA]/[I_2] and 1. 75 mmol [ACPA]

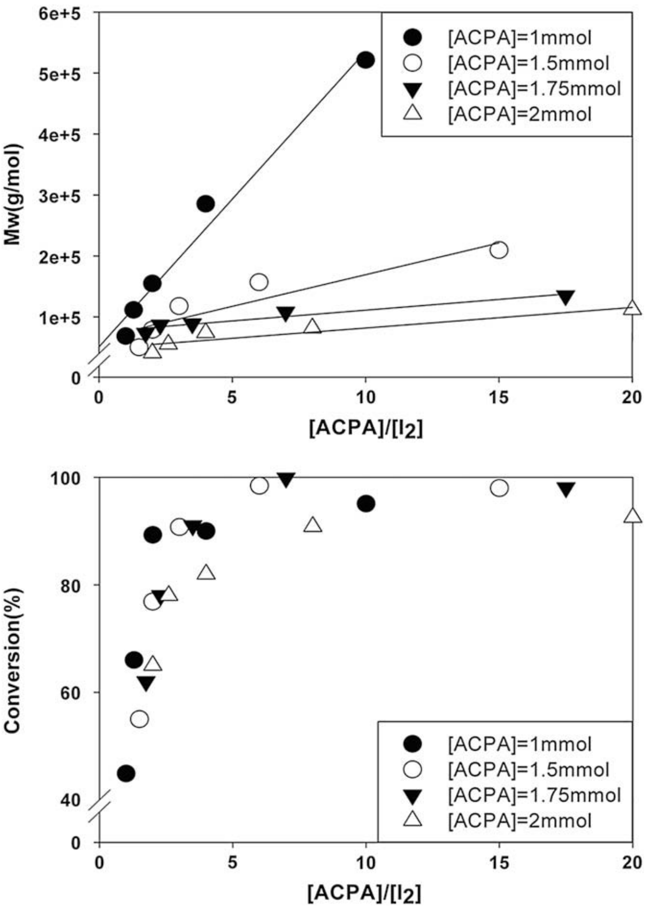

Fig. 4. The weight-average molecular weights (g/mol) and conversion (%) of PMMA prepared by the various concentrations of ACPA and iodine. ●: [ACPA] = 1.0 mmol, ○: [ACPA] = 1.5 mmol, ▼: [ACPA] = 1.75 mmol, △: [ACPA] = 2.0 mmol.

with 3.5 of [ACPA]/[I_2] ratio. Fig. 5 shows the SEM photographs of PMMA particles prepared with various surfactants (SDS, SDBS, CTAB, PEG-EEM, SDS + Tween80, SDBS + Tween80, and Tween80) at 3.0 of [ACPA]/[I_2] and 1.5 mmol [ACPA]. The PMMA particles prepared with CTAB, SDS + Tween80 and Tween80 were unstable, whereas those prepared with SDS, SDBS, PEG-EEM and SDBS + Tween80 were stable with large particle surface. Although the spherical particle shape was stable with PEG-EEM, the conversion was too low (28%). Thus, SDS, SDBS and SDBS + Tween80 were proper surfactants and the M_w varied between 100,320 and 117,730 g/mol, and the conversion varied between 91 and 96%, respectively.

In addition, the SEM photographs of PMMA particles prepared with the above surfactants at 3.5 of [ACPA]/[I_2] and 1.75 mmol [ACPA] are drawn in Fig. 6. The PMMA particles prepared with SDS, SDBS, SDS + Tween80 and SDBS + Tween80 were stable with large particle surface, but those prepared with CTAB, PEG-EEM and

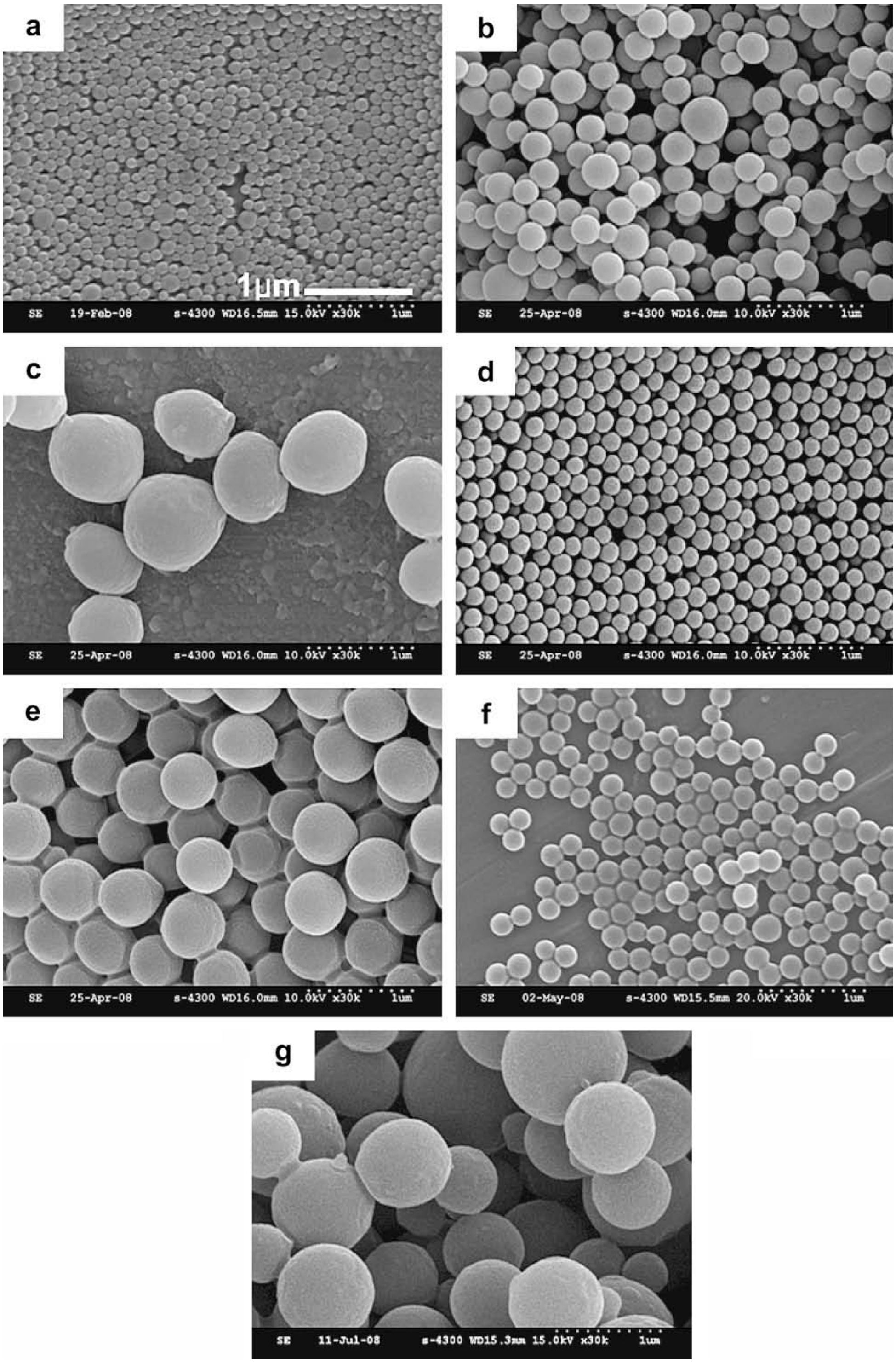

Fig. 5. SEM photographs of the synthesized PMMA with [ACPA]/[Iodine] = 3.0 at [ACPA] = 1.5 mmol with various surfactants; (a) SDS, (b) SDBS, (c) CTAB, (d) PEG-EEM,(e) SDS + Tween80 (50/50 mol%), (f) SDBS + Tween80 (50/50 mol%), (g) Tween80.

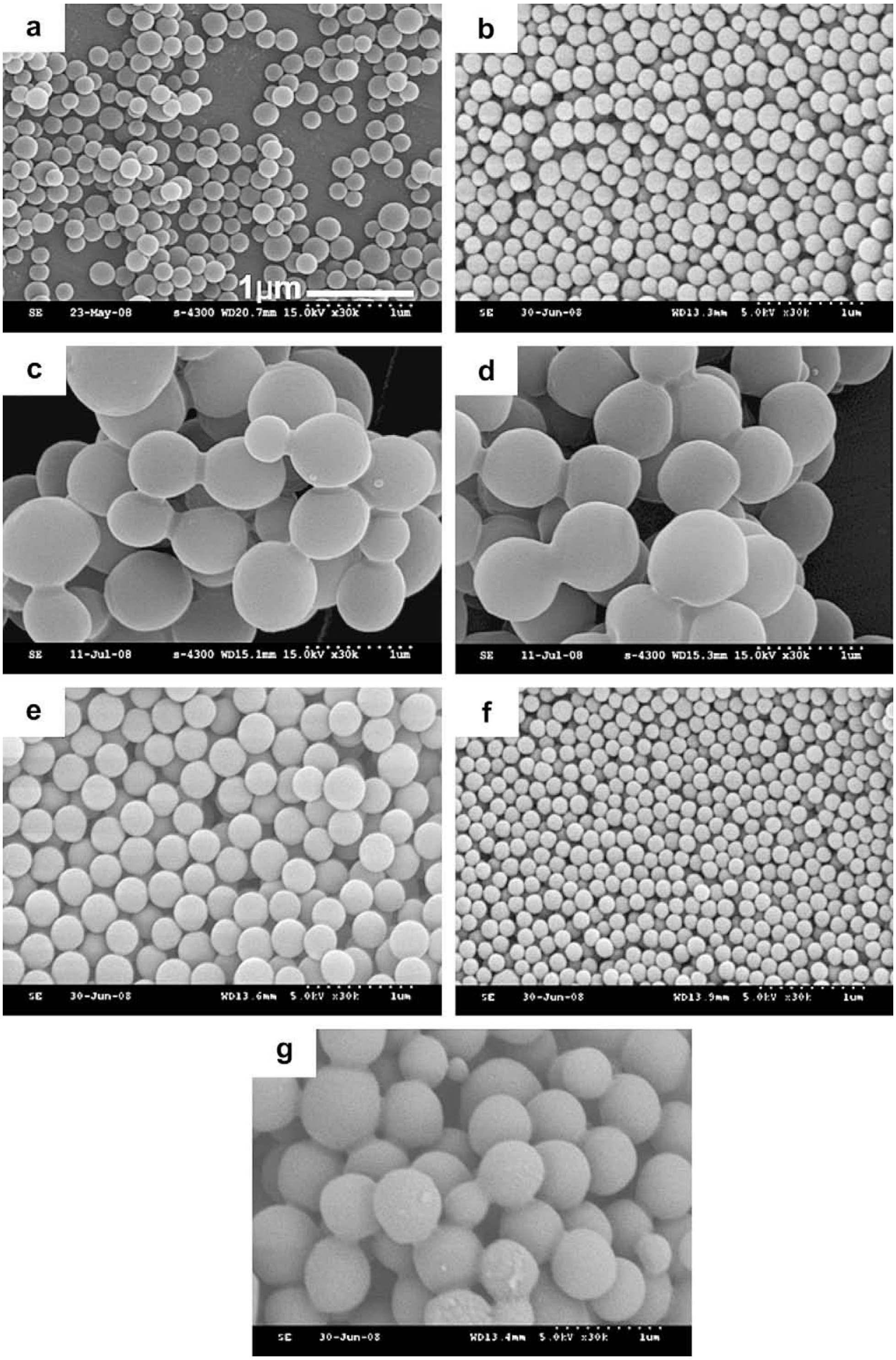

Fig. 6. The weight-average molecular weight, conversion, and PDI of PMMA particles at [ACPA]/[I_2] = 3, 3.5, 4 by changing [ACPA] between 1.5 and 2.0 mmol at [I_2] = 0.5 mmol using SDS (open symbol) and SDBS (solid symbol). (M_w: circle (○, ●), conversion; triangle (△, ▲), PDI; square (□, ■)).

Tween80 were unstable. The characteristics of the PMMA particles using various surfactants with 3.0 and 3.5 of [ACPA]/[I_2] are listed in Table 1. The particles with unstable morphology resulted in low conversion due to the insufficient capability to stabilize particles. Among these, the proper surfactants effective for the formation of targeted specifications (the M_w is less than 100,000 g/mol and the conversion is higher than 90% with particle stability) were SDS, SDBS and co-surfactant, Tween80, into SDS and SDBS at 3.5 of [ACPA]/[I_2] with 1.75 mmol [ACPA]. At this condition, the M_w of PMMA particles varied between 72,860 and 88,800 g/mol and the conversion varied between 91 and 92%. In overall, the anionic SDBS and its co-surfactant with non-ionic Tween80 seem to be better system by providing higher conversion with reasonable molecular weights ranges. The sulfonate group in SDBS is more stable due to the stronger bonding energy than that of SDS at lower pH, whereas the sulfate group in SDS can be hydrolyzed at acidic pH [25]. A one-

Table 1
The characteristics of PMMA particles with various surfactants.

No	Surfactant				M_n (g/mol)	M_w (g/mol)	PDI	D_n (nm)	Conv.(%)	Stability
	Type	Name	CMC							
A	Anionic	SDS	0.2 mM/L	a*	55,410	117,730	2.12	120	91	Yes
				b*	43,950	88,800	2.01	185	91	Yes
B	Anionic	SDBS	0.17 mM/L	a*	54,250	100,320	1.90	224	96	Yes
				b*	44,250	80,190	1.81	190	93	Yes
C	Cationic	CTAB	1.00 mM/L	a*	57,170	160,540	2.82	700	82	No
				b*	41,100	109,840	2.67	800	71	No
D	Reactive	PEG-EEM	1 g	a*	18,490	73,530	3.94	166	28	Yes
				b*	18,490	108,950	5.89	700	26	No
E[a]	Anionic + non-ionic	SDS + Tween80	0.1 mM/L + 0.0075 mM/L	a*	47,570	99,390	2.01	463	92	No
				b*	49,550	85,220	1.96	220	91	Yes
F[a]	Anionic + non-ionic	SDBS + Tween80	0.058 mM/L + 0.0075 mM/L	a*	53,730	112,680	2.05	178	91	Yes
				b*	36,950	72,860	1.97	125	97	Yes
G	Non-ionic	Tween80	0.015 mM/L	a*	37,890	148,620	3.92	780	78	No
				b*	24,600	98,271	3.99	600	80	No

a*: The ratio of [ACPA]/[Iodine] = 3.0 and [ACPA] = 1.5 mmol.
b*: The ratio of [ACPA]/[Iodine] = 3.5 and [ACPA] = 1.75 mmol.
[a] For E and F, the ratio of SDS to Tween80 and SDBS and Tween80 was 50 to 50.

step ab initio emulsion polymerization of *n*-butyl acrylate in the presence of molecular iodine has been successfully performed using sodium 1-hexadecanesulfonate as a surfactant with potassium persulfate playing the dual role of radical initiator and oxidant [22].

In order to confirm the optimum condition for the targeted molecular weight and conversion with particle stability using anionic surfactants, SDS and SDBS, the polymerization at various ratios of [ACPA]/[I_2] at 3.0, 3.5 and 4.0 by changing the concentration of ACPA between 1.5 and 2.0 mmol at fixed [I_2] at 0.5 mmol was carried out and the characteristics were studied. All PMMA particles were apparently stable. The M_w, conversion and the PDI of the PMMA particles are plotted in Fig. 7. The M_w of PMMA prepared by SDS varied between 117,730 and 54,530 g/mol and that of PMMA prepared by SDBS varied between 100,320 and 74,280 g/mol at the ratio of [ACPA]/[I_2] between 3.0 and 4.0, respectively. This above behavior followed by the general observation in emulsion polymerization; the higher the initiator concentration, the more the radical chains and the lower the molecular weight were obtained. The PDI of PMMA particles with SDS varied from 2.01 to 2.42 and that with SDBS varied from 1.81 to 1.96 as well. In addition, the monomer conversion with SDBS was slightly higher than that with SDS. In particular, SDBS was more effective in controlling the molecular weight, molecular weight distribution and the conversion due to less hydrolysis of iodine in water phase than SDS. Thus, the optimum conditions for the synthesis of stable PMMA particles with the targeted molecular weight and the conversion were at [ACPA]/[I_2] = 3.5 and [ACPA] = 1.75 mmol using SDBS.

3.3. *Effect of the non-ionic surfactant with anionic one*

Since the mixed surfactants (50:50 molar ratio) between SDS and Tween80, and between SDBS and Tween80 showed higher conversion with narrow molecular weight distribution in Fig. 7, the PMMA particles were synthesized by varying the compositions of SDS or SDBS with Tween80. Fig. 8 shows the SEM photographs of PMMA particle prepared by two surfactants systems (SDS/Tween80 and SDBS/Tween80) at [ACPA]/[I_2] = 3.5 with [ACPA] = 1.75 mmol. The mole fractions were calculated based on the CMC of each surfactant as listed in Table 1. Although the PMMA particles prepared with Tween80 were unstable seen in Fig. 8(e), those with SDS and SDBS showed different behaviors. As a result, the PMMA particles prepared with various ratios of SDS/Tween80 and SDBS/Tween80 as seen in Fig. 8(b)–(e) and (b′)–(d′) were fairly stable. This might come from the balance between anionic and non-ionic surfactants. It was also reported that small amount of anionic surfactant in the co-surfactant system could stabilize particles in the aqueous phase [26].

Fig. 9 represents the weight-average molecular weight, PDI, and the conversion of PMMA prepared by various mole fractions of anionic (SDS and SDBS) to non-ionic (Tween80) at [ACPA]/[I_2] = 3.5 mmol with [ACPA] = 1.75 mmol and [I_2] = 0.5 mmol. The concentration of SDS, SDBS and Tween80 was the CMC of each surfactant. For the co-surfactant system of Tween80 with SDS, the M_w varied from 75,130 to 98,170 g/mol depending on the mole fraction of the SDS and the monomer conversion varied between 80 and 96%. For Tween80 with SDBS, the M_w varied from 67,180 to 96,700 g/mol and the conversion varied between 80 and 94%. In the conventional emulsion polymerization, the conversion increased with the efficiency of thermal transfer and followed by the increased molecular weight as well due to the large surface area. In addition, the primary role of a surfactant is stabilization of the polymerizing particles, and ideally it does not further affect the course of polymerization. However, in some cases, anionic surfactant influenced the polymerization rate and simultaneously the conversion rate [25]. In our system, the mixture of anionic and non-ionic surfactant affected the molecular weight and the conversion possibly due to I_2 as an inhibitor and chain transfer agent.

From the above observations in Figs. 8 and 9, the followings were observed; (a) the molecular weights of PMMA particles with co-surfactant was lower than those with the constituent in both systems, SDS + Tween80 and SDBS + Tween80. (b) The molecular weight of

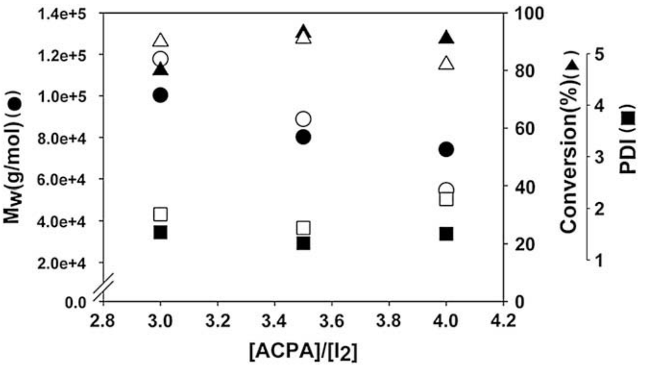

Fig. 7. The weight-average molecular weight, conversion, and PDI of PMMA particles at [ACPA]/[I_2] = 3, 3.5, 4 at [I_2] = 0.5 mol using SDS (open symbol) and SDBS (solid symbol). (M_w: circle (○, ●), conversion; triangle (△, ▲), PDI; square (□, ■)).

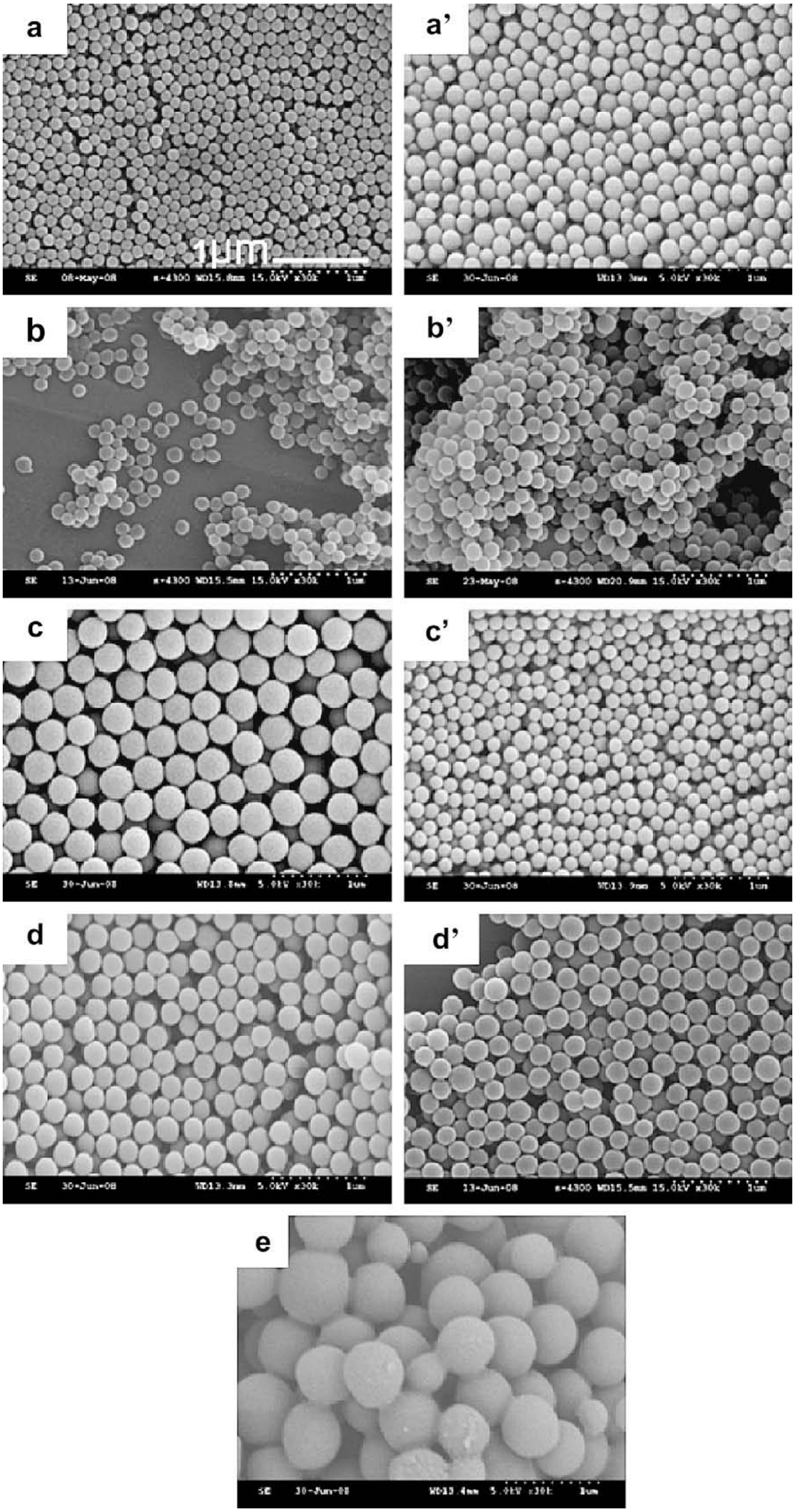

Fig. 8. SEM photographs of the synthesized PMMA prepared by various mole fractions of [SDS]:[Tween80] and [SDBS]:[Tween80] at [ACPA]/[I_2] = 3.5 mmol and [ACPA] = 1.75 mmol; [SDS] to [Tween80] are (a) 1.0:0.0, (b) 0.8:0.2, (c) 0.5:0.5, (d) 0.2:0.8, (e) 0.0:1.0 (this picture is the duplicate of Fig. 6(g)), and [SDBS] to [Tween80] are (a′) 1.0:0.0, (b′) 0.8:0.2, (c′) 0.5:0.5, (d′) 0.2:0.8, respectively.

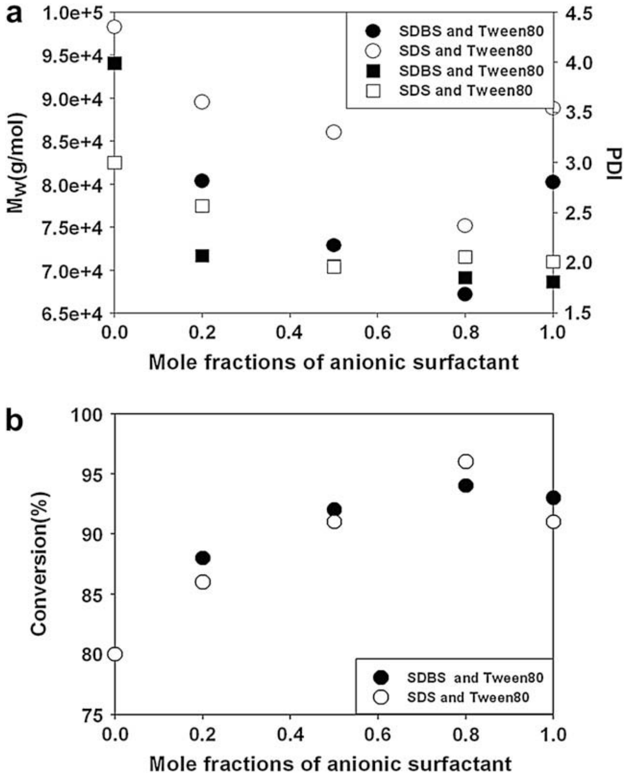

Fig. 9. (a) The weight-average molecular weight (circle) and PDI (square), and (b) conversion of PMMA prepared by various mole fractions of anionic (SDS and SDBS) to non-ionic (Tween80) at $[ACPA]/[I_2] = 3.5$ mmol with $[ACPA] = 1.75$ mmol and $[I_2] = 0.5$ mmol; (open symbol: SDS and Tween80, solid symbol: SDBS and Tween80). The concentration of each surfactant was the CMC.

PMMA with SDBS + Tween80 was slightly lower than that with SDS + Tween80, while the monomer conversions of two different systems were similar. (c) For two co-surfactant systems, more than 50 mol% of SDS and SDBS was able to control the molecular weight and molecular weight distribution along with high conversion. The number-average molecular weights (M_n) with SDS/Tween80 and SDBS/Tween80 ranging 80/20–20/80 were 34,740–43,950 g/mol and 39,280–46,660 g/mol, respectively. In addition, the PDI for SDS and SDBS system varied 1.96–2.57 and 1.85–2.07, respectively. (d) The particle stability with SDBS + Tween80 was much better than with SDS + Tween80. The measured PDI and number-average molecular weight (M_n) were comparable with the RITP-emulsion polymerization of methyl acrylate [27], whereas 1.89–1.98 and 10,700–21,200 g/mol, respectively.

In overall, anionic surfactant SDBS was more effective than SDS for the synthesis of the stable PMMA particles having the weight-average molecular weights less than 100,000 g/mol and the conversion higher than 90% using the RIPT-emulsion polymerization. In addition, the use of non-ionic co-surfactant, Tween80, with SDBS was more effective for reducing the molecular weights down to 67,180–72,860 g/mol and enhancing the conversion. It is not cleared yet why SDBS was more effective anionic surfactant on the molecular weight than SDS and why non-ionic surfactant Tween80 affects the molecular weight and the conversion as well. This is still under investigation and will be disclosed shortly.

4. Conclusions

The submicron-sized poly (methyl methacrylate) latex was prepared using ACPA and various surfactants by the RITP-emulsion polymerization in the absence of light at 85 °C for 7 h. This method leaded to molecular weight of PMMA lower than 100,000 g/mol with high conversion (>90%), which was comparable with the general emulsion process inducing more than a few hundreds of thousands of molecular weights. The weight-average molecular weight and the conversion increased with the ratio of $[ACPA]/[I_2]$, but no correlation between the particle sizes and the ratios of $[ACPA]/[I_2]$ was observed. The optimum conditions for the preparation of PMMA to the targeted molecular weight less than 100,000 g/mol and the conversion higher than 90% were the followings: at $[ACPA]/[I_2] = 3.5$ with 1.75 mmol of ACPA and SDBS. Furthermore, anionic surfactant such as SDBS influences on the formation of spherical PMMA particles and the addition of non-ionic surfactant (Tween80) into anionic one also expanded the molecular weight window and the conversion along with particle stability. In overall, the initiator, ACPA, was important for forming PMMA particles, while molecular iodine, I_2, dominates in controlling molecular weight, inhibition period and the conversion rather than ACPA. Thus, the environmentally-friendly emulsion polymerization process using the RITP technique was worth while in preparing the PMMA particles with the targeted molecular weight and the high conversion.

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