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Effect of PVA in dispersion polymerization of MMA

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Abstract

Monodisperse poly(methylmethacrylate) microspheres having a diameter of 2.6 μm and a molecular weight of 102,277 g/mol with 5.3% of the C_v (the coefficient of variation) were synthesized by the dispersion polymerization using hydrophilic polyvinylalcohol (PVA) in methanol/water mixture media. Then, the structural verification of the synthesized materials is confirmed by using ^{1}H NMR and FT-IR spectroscopy. The effects of PVA and the polymerization parameters such as the initiator, monomer and stabilizer concentrations, and the reaction time on the characteristics of the final particles were studied. Thus, the role of PVA in the dispersion polymerization of MMA is not only a steric stabilizer by physically adsorbed in methanol phase, but also a colloid protective to give relatively monodisperse polymer particles in water phase, simultaneously.

Keywords: Dispersion polymerization; Monodispersity; Methylmethacrylate

1. Introduction

The applications of polymer colloids are dominated by chemical and/or physical properties, of which one of the most important physical properties is the size and size distribution of the final particles. Dispersion polymerization has been known as an useful method in preparing monodisperse polymer spheres ranging from 1 to 10 μm [1]. One of the disadvantages of the polymer particles prepared by dispersion polymerization is relatively low molecular weights less than 200,000 g/mole [2].

In dispersion polymerization, primary particles are generated from the precipitation of relatively large oligomeric species, and microspheres are subsequently grown by absorbing oligomers and monomers from the medium. A short nucleation period and uniform growth of the primary particles are the way to obtain uniform sized polymer particles in dispersion

Poly (vinyl alcohol) (PVA), is used industrially in various application fields, where the adhesive property to polar substances and high mechanical properties of PVA are utilized [3]. PVA is also a synthetic resin produced by polymerization of vinyl acetate (VAc) followed by hydrolysis of the poly(vinyl acetate) (PVAc). The properties depend on the degree of polymerization and the percentage of hydrolysis, both of which are controllable in processing. Water solubility increases as molecular weight decreases; strength, elongation, tear resistance, and flexibility improve with increasing molecular weight. The degree of hydrolysis (saponification) signifies the extent of conversion of PVAc to PVA [4].

Polymer emulsions using PVA as a protective colloid have several different properties compared with those using emulsifiers due to these properties of PVA [5]. On the other hand, PVA is not employed in the emulsion polymerizations of such conjugate monomers as styrene and acrylic monomers. One of the reasons is believed to be the weak capability of grafting of the monomers onto PVA. In fact, by using PVA having a reactive thiol group at one end instead of ordinary PVA [6], styrene and acrylates were successfully polymerized yielding stable emulsions, where block copolymer formation played an important role. In the presence of the large amounts of PVA, the number of new particles smaller than 80 nm continued to increase during the polymerization, while there was not much increase in the particle diameter. In the absence of PVA, the soap-free particles were formed at the very early stage and continued to grow during the polymerization. The degree of polymerization of PVA did not substantially affect the particle formation, where the particle diameter should be counted excluding the PVA shell on the particle surface.

Since, PVA has a low solubility in organic solvents and monomers, and a high hydrophilicity with 80% hydrolysis in

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water, it is not normally used as a stabilizer in dispersion polymerization. However, the weak hydrophobic nature of PVA makes it a candidate as a steric stabilizer in the dispersion polymerization in a water/alcohol mixed medium.

Recently, T. Okaya, et al. synthesized less than 450 nm sized poly(vinylacetate) particles by using PVA, as a steric stabilizer, in ethanol/water mixture and discussed on the particle size in terms of the solubility parameter [7]. This is the only report to synthesize polymer spheres using PVA in the dispersion polymerization.

The preparation of monodisperse PMMA particles are successfully obtained and the optimum conditions for preparing micron-sized monodisperse polymethylmethacrylate (PMMA) beads by the dispersion polymerization in methanol/water mixture were proposed [8].

In this article, monodisperse poly(methylmethacrylate) microspheres were successfully synthesized by the dispersion polymerization using hydrophilic polyvinylalcohol (PVA) in a methanol/water mixture media. Then, the effects of PVA and the polymerization parameters such as the initiator, monomer and stabilizer concentrations, and the reaction time on the characteristics of the final particles were studied. This is the first report to disclose the preparation of the micron-sized monodisperse polymer particles in the dispersion polymerization using PVA.

2. Experimental

2.1. Materials

Methyl metacrylate (Junsei Chemicals, Japan) was purified using an inhibitor removal column (Aldrich) and stored at −5 °C prior to use. Polyvinyl alcohol (PVA), Kanto Chemical, Japan, was used as a stabilizer without purification; the degree of polymerization, experimentally obtained in this laboratory, was 2080 (based on the viscosity in centipoise (cp) of a 4% aqueous solution of PVA at 20 °C). The major PVA product is a low-viscosity group of approximately 5 cp, a medium viscosity group of 20–30 cp, and a high viscosity group of 40–50 cp, which correspond to the degree of polymerization of about 500, 1700, and 2000, respectively. Since, the degree of hydrolysis is 80.2%, the principal grades of PVA can be classified as fully hydrolyzed (97.5–99.55% degree of hydrolysis) and partially hydrolyzed (87–89% degree of hydrolysis). Thus, the calculated weight-average molecular weight is 109,000 g/mol. Poly(N-vinylpyrrolidone) (PVP-40 K; weight-average molecular weight = 40,000, Aldrich, USA), was used for a comparison to PVA. 2,2′-Azobisisobutyronitrile (AIBN; Junsei) was used as an initiator without purification, and methanol (Samchun Chemical, Korea) and double-distilled deionized water were used as the polymerization media.

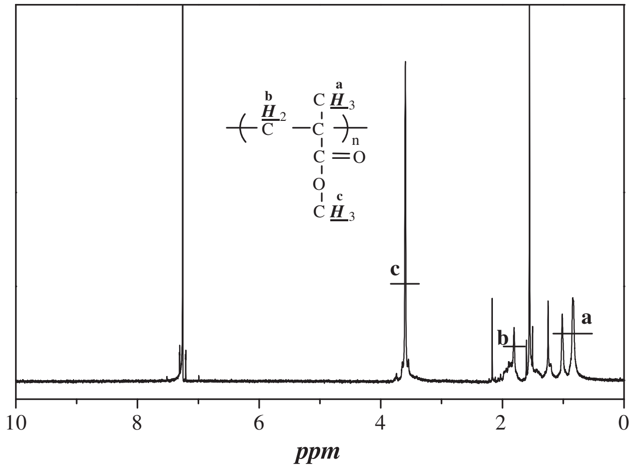

Fig. 1. ^{1}H NMR spectra of the polymerized PMMA particles using PVA.

2.2. Polymerization

Dispersion polymerization was carried out in a 250 mL round flask with a mechanical stirring at 100 rpm under nitrogen atmosphere at 70 °C. Pre-weighed methanol and aqueous PVA solution were charged in the reactor and followed the addition of MMA. Then, the AIBN dissolved in methanol was added and the polymerization was initiated. During the polymerization, aliquots of the reaction mixture were withdrawn from the reactor to examine the conversion upon reaction time and the characteristics of the particles. The withdrawn polymerization products were rinsed off with DDI water and methanol, centrifuged repeatedly to remove the non-reacted materials and dried in vacuum oven at 60 °C for 2 days, then used for characterization. The detailed polymerization method and the optimum conditions for the preparation of monodisperse polymer particles are described in the elsewhere [8].

2.3. Chericterizations

The structure of the polymer upon reaction time was verified using the Fourier transform infrared (FTIR) spectroscopy (Bruker 48 series) and a Varian 400 MHz ^{1}H NMR using $CDCl_3$ containing TMS (tetramethylsilane) as the solvent. The FT-IR data was obtained at 4 cm^{-1} resolution and 16 scans were accumulated in 20 s for each specimen. The molecular weights of the synthesized PMMA particles were measured using Waters GPC (Gel Permeation Chromatography) equipped with 510 differential refractometer and Viscotek T50 differential viscometer. 10^5, 10^3, and 10^2 Å μ-Styragel packed high-resolution columns were employed. A universal calibration curve was obtained based on ten PMMA standard samples (Polymer Laboratories, UK) with molecular weights ranging 1,944,000–1020 g/mol. In order to prepare the GPC sample, an aliquot of the sample taken from the reaction vessel was washed with excess methanol and centrifuged at 9000 rpm, repeatedly. The final obtained PMMA dissolved in THF as the mobile phase was injected at a flow rate of 1.0 mL/min. Philips SEM (scanning electron microscopy) 515 was used to characterize the morphology of the PMMA particles. The fractional conversion was calculated gravimetrically.

Table 1
Recipe Used in Dispersion polymerization

	Methanol (g)	Water (g)	MMA (g)	AIBN (g)	PVA (g)
Monomer Concentration	100	50	3.3	0.1	1.5
	100	50	6.6	0.1	1.5
	100	50	10	0.1	1.5
	100	50	13	0.1	1.5
Initiator Concentration	100	50	10	0.05	1.5
	100	50	10	0.1	1.5
	100	50	10	0.2	1.5
	100	50	10	0.4	1.5
PVA Concentration	100	50	10	0.1	1.0
	100	50	10	0.1	1.5
	100	50	10	0.1	2.0
	100	50	10	0.1	2.5

3. Results and discussion

3.1. Structural verification of PMMA.

The reaction recipe for preparing micron-sized monodisperse PMMA particles is listed in Table 1.

The structural verification [9] was examined using ^{1}H NMR as seen in Fig. 1. The representative confirmation of PMMA is shown in Fig. 1 and the peak assignment is the following. The strong signal at 3.6 ppm (c) characterizes methyl protons (–CH_2–) of PMMA, whereas the methyl protons (–O–CH_3) of the methacrylate group of PMMA are observed at 1.8 ppm (b). The methyl protons (–CH_3) of PMMA are detected at 1.0 and 0.8 ppm (a) and the signal at 7.2 and 1.6 ppm are characteristic peaks of the $CDCl_3$. No other characteristic peaks were detected from the ^{1}H NMR spectrum of PMMA in Fig. 1.

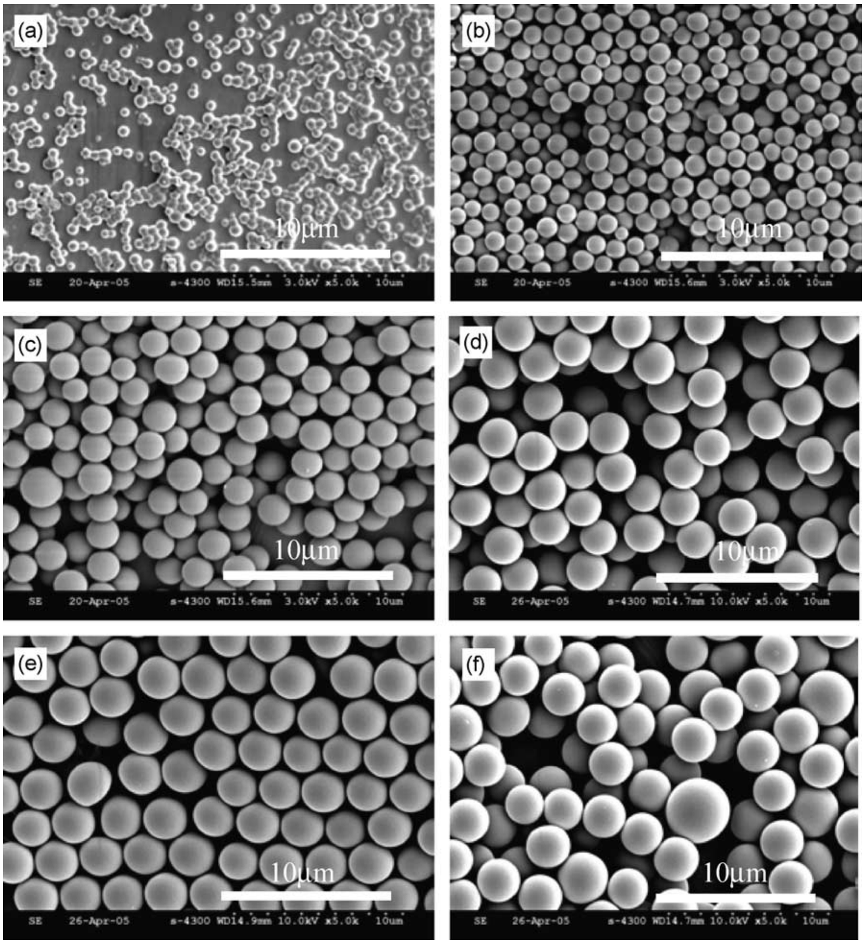

Fig. 2. SEM micrographs of PMMA microspheres prepared by dispersion polymerization in methanol (100 g)/water (50 g) mixtures at 70 °C for (a) 0.5 h, (b) 1 h, (c) 2 h, (d) 4 h, (e) 6 h, (f) 8 h.

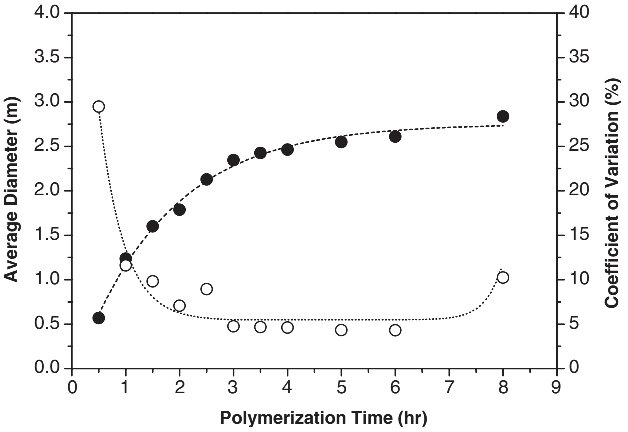

Fig. 3. Effect of polymerization time with average diameter (solid symbol) and Cv (open symbol) in the dispersion polymerization in methanol (100 g)/water (50 g) mixtures with 15 wt% PVA and 1 wt% AIBN at 70 °C.

Therefore, one can conclude that PVA can serve a stabilizer and PMMA is successfully synthesized in this dispersion polymerization.

3.2. *Effects of the polymerization parameters*

Fig. 2(a)–(f) show the SEM microphotographs of PMMA particles prepared by the dispersion polymerization using PVA in MeOH (100 g)/water (50 g) mixture at 70 °C for various reaction time, from 0.5 to 8 h, respectively. In the beginning of the reaction, for example at 0.5 h as shown in Fig. 2(a), the part of the particles are not perfectly sphere form and some are partially coagulated, thus 0.5 h is not sufficient to form spherical particles as well as the stabilization is not effective at this time scale. However, at 1 h, the spherical particles are formed without coagulation. As the further reaction proceeds, the particle size increases with narrow particle size distribution up to 6 h of the reaction time, but the particles size distribution becomes poor at 8 h.

Fig. 3 lists the weight-average particle size and the coefficient of variation (Cv) of PMMA prepared in MeOH/water (100/50) mixture media with 15 wt% PVA and 1 wt% AIBN at 70 °C upon polymerization time. The average particle size increased from 1.2 to 2.6 μm from 1 to 6 h reaction, respectively, while the Cv varied from 29 to 5.3% in the same time which means the particle size distribution enhances (i.e. Cv decreases) with time except at 8 h. Thus, 6-h reaction is enough to prepare PMMA particles using this technique.

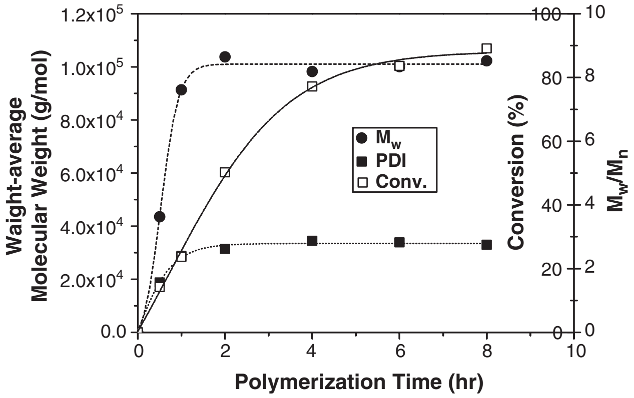

Fig. 4. Effect of polymerization time on the molecular weight (–●–), conversion (–□–), and PDI [M_w/M_n(–■–)] using MeOH/water (100/50 g) mixture with 15 wt% PVA and 1 wt% AIBN at 70 °C.

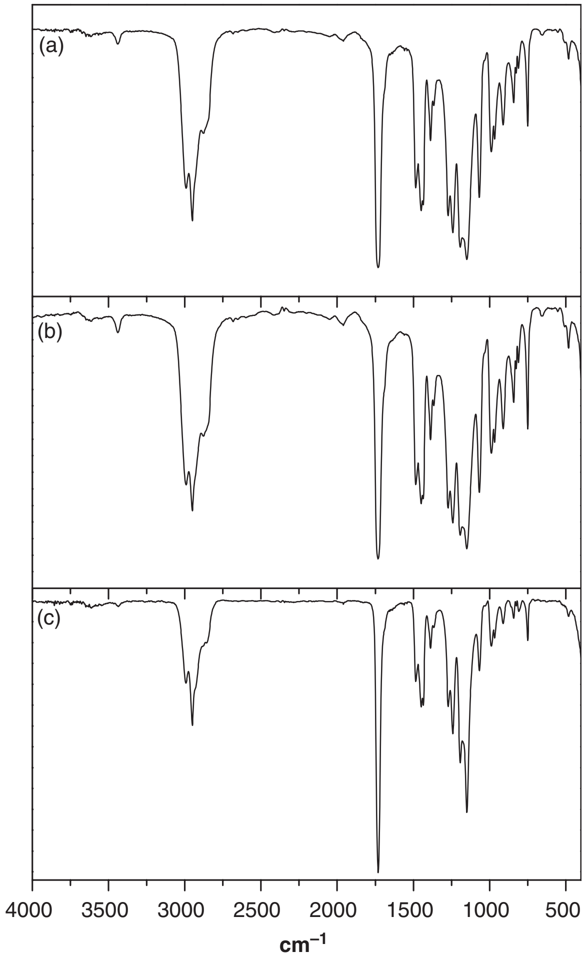

Fig. 5. Comparison of the FT-IR spectra of the synthesized PMMA particles by (a) soap-free emulsion polymerization, and dispersion polymerization using (b) PVP and (c) PVA.

In addition, Fig. 4 represents the reaction time dependent conversion and weight-average molecular weight of the PMMA particles prepared using MeOH/water (100/50 g) mixture with 15 wt% PVA and 1 wt% AIBN at 70 °C. As the reaction time increases, the conversion increases up to 91% for 8 h of the reaction and the weight-average molecular weight increases up to 2 h and saturated. The weight-average molecular weight is about 100,000 g/mol and the polydispersity index (PDI) gradually increases from 1.6 to 2.4 for 8 h reaction. The behavior in conversion and molecular weight profile typically follow the manner observed in free-radical polymerization.

In order to investigate the role of PVA in PMMA particles (whether PVA is physically adsorbed on the surface of the PMMA particles or chemically bound by forming a covalent bond with PMMA), the structural verification upon various

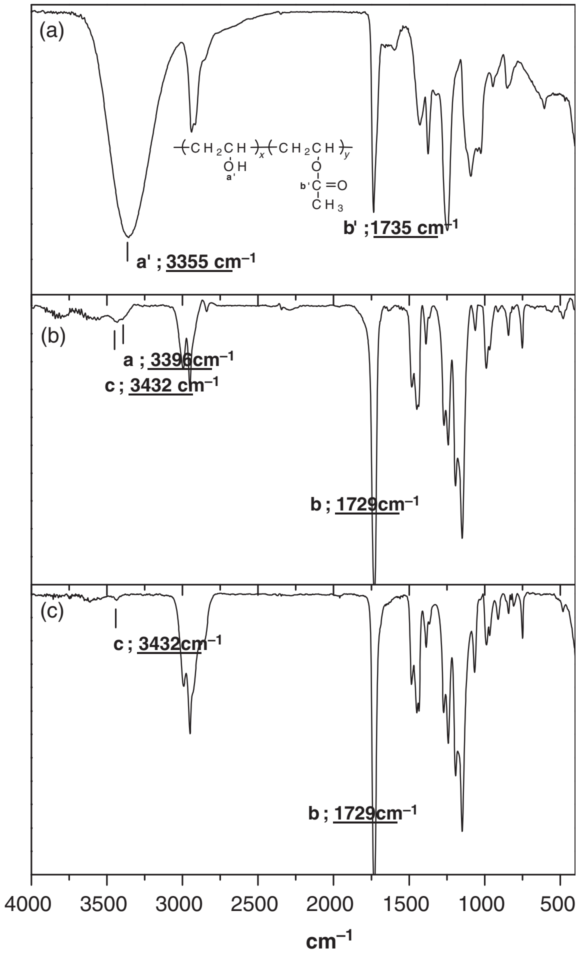

Fig. 6. Comparison of the FT-IR spectra of (a) pure PVA, (b) PMMA particles prepared using PVA, and (c) filtered PMMA (synthesized using PVA) solution after dissolved in THF.

polymerization methods using FT-IR spectroscopy was carried out using the synthetic recipe listed in Table 1. The FTIR spectra of the synthesized PMMA particles by the soap-free emulsion polymerization, dispersion polymerization using PVP and PVA as a steric stabilizer are represented in Fig. 5(a)–(c), respectively. No difference in the FTIR spectra of three figures is observed as seen in Fig. 5, thus, PVA is confirmed to work as a steric stabilizer as well as PVP.

In addition, the FTIR spectra of the pure PVA, PMMA particles prepared using PVA without any modification, and filtered PMMA (after synthesized using PVA) solution dissolved in THF are drawn in Fig. 6(a)–(c), respectively. The strong peaks observed at 3355 and 1735 cm^{-1} in Fig. 6(a) are the characteristics of the hydroxyl group (–OH) of PVA and carbonyl group (C=O) of PVAc (polyvinylacetate), respectively. Since PVA is prepared from PVAc, it is verified that 19.8% of PVAc is left in PVA. In Fig. 6(b), the peak at 1729 cm^{-1} is the characteristic peak of the carbonyl group (C=O) of PMMA. The small peak of the hydroxyl group (–OH) at 3396 cm^{-1} is originated from PVA as seen in Fig. 6(a), which means that PVA is left in the PMMA particles. On the other hand, the FTIR spectrum of the filtered PMMA solution in Fig. 6(c) shows the characteristic peak of the carbonyl group (C=O) of PMMA at 1729 cm^{-1} as seen in Fig. 6(b) and nothing related to hydroxyl group (–OH) of PVA near 3400 cm^{-1} is observed. From the above observation, one can suggest that the existence of PVA molecules on the PMMA particles (Fig. 6(b)) and absence of that in the filtered PMMA solution (Fig. 6(c)) are the result that the hydroxyl group of PVA is physically adsorbed on the PMMA particles. Therefore, PVA is working as a steric stabilizer in our present system. Polymeric stabilizers used in dispersion polymerization are often reported not only physically adsorbed on the surface of

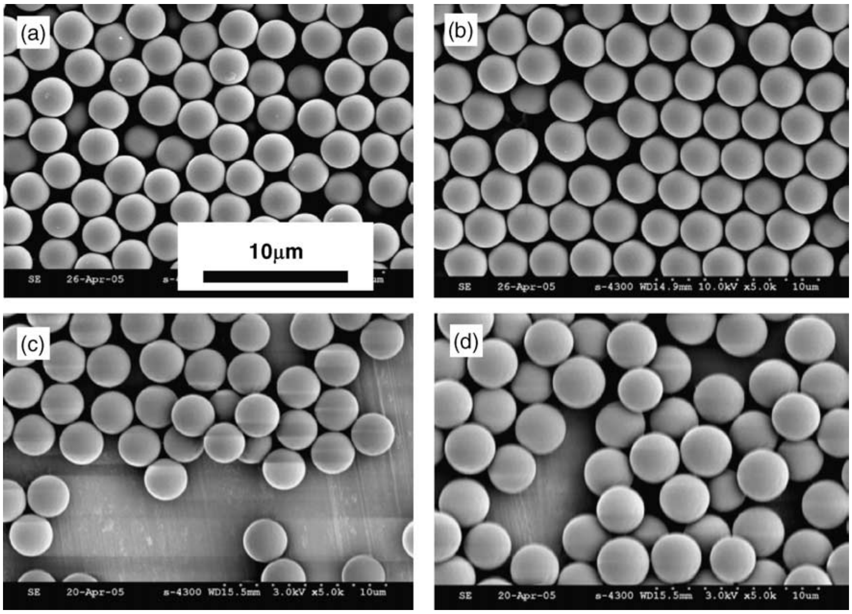

Fig. 7. SEM photographs of PMMA microspheres prepared at initiator concentrations of (a) 0.5% w/w, (b) 1% w/w, (c) 2% w/w, and (d) 4% w/w relative to monomer.

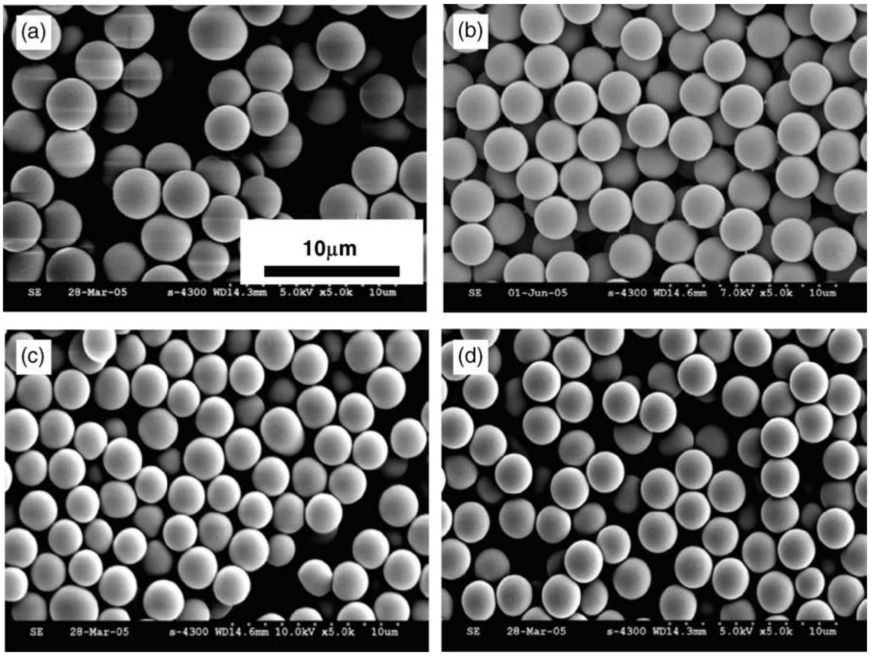

Fig. 8. SEM photographs of PMMA microspheres prepared at PVA concentrations as stabilizer of (a) 10% w/w, (b) 15% w/w, (c) 20% w/w, and (d) 25% w/w relative to monomer.

particles but also chemically bound by forming a covalent bond with polymer molecules [10]. The existence of PVP molecules on the resulting polymer particles has been verified [11], and it has been reported that 1.1 wt % of total added PVP was adsorbed on PMMA particles prepared by dispersion polymerization [11].

The final diameter of the microspheres with respect to the initiator concentration from 0.5, 1, 2, and 4 (w/w) % relative to monomer is investigated and the SEM microphotographs are shown in Fig. 7. The corresponding increase in the size of the microspheres from 2.4 to 2.8 μm with the initiator concentration from 0.5 to 4 wt% resembles that of the dispersion polymerization using AIBN [12,13]. The initiator concentration dependent Dw, Cv, Mw and polydispersity index are studied, the Cv remains between 5.3 and 8.4%, while the weight-average molecular weight decreases from 128,100 to 79,300 g/mol, respectively. The formation of larger microspheres at a higher initiator concentration is also attributed to

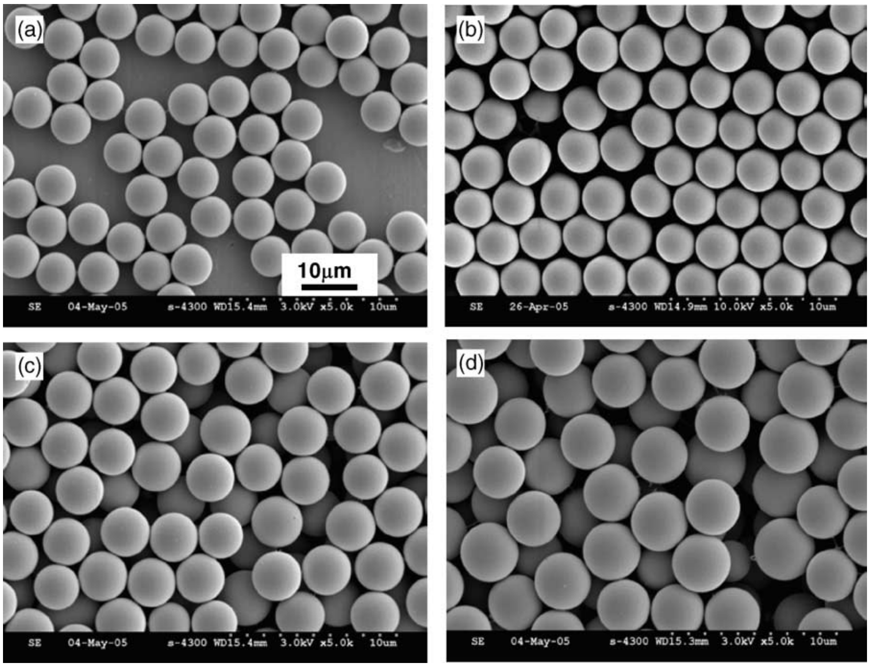

Fig. 9. SEM photographs of PMMA microspheres prepared at monomer concentrations of 3.3% w/w (a), 6.6% w/w (b), 10% w/w (c), and 13% w/w (d) relative to medium.

the reduced number of primary particles in the early stage of the polymerization. A higher initiator concentration generates large amount of oligomeric species, which result a low molecular weight and prefer to stay in the medium. Consequently, a smaller amount of oligomers are precipitated to give the reduced number of primary particles during the nucleation step.

Fig. 8(a)–(d) represent the SEM photographs of PMMA microspheres prepared with 15 wt% PVA and 1 wt% AIBN at 70 °C with different monomer concentration from 3.3, 6.7, 10, and 13 wt% relative to medium, respectively. The conversion reaches between 87 and 93.5% upon monomer concentration. The average-diameter increases from 2.4, 2.6, 2.8, to 3.4 μm, the Cv varies from 5.8, 5.3, 9.4, and 9.2%, the average-molecular weight increases from 51,300, 100,200, 117,600 to 121,200 g/mol, and the polydispersity varies from 1.95, 2.43, 3.40 to 1.91, respectively. The similar trend is also observed in the dispersion polymerization of styrene due to the change in the solvency of the medium by increased amount of monomer. In dispersion polymerization, the increase in monomer and initiator concentration with same concentration of other ingredients, respectively, gives larger particles with broadened particle size distribution [14].

Fig. 9 shows the SEM photographs of PMMA microspheres depending on the PVA concentration with 6.7 wt% monomer and 1 wt% of AIBN at 70 °C. As seen in this figure, the average-particle size decreases from 2.9, 2.6, 2.3 to 2.2 μm, while the Cv varies from 7.2, 5.3, 6.2 to 5.9% with the PVA concentration from 10 to 25%. In addition, the molecular weight varied from 129,500 to 75,100 g/mol, of which the molecular weight decreases with the particle size. In dispersion polymerization, polymeric stabilizer initially dissolved in polymerization medium causes the formation of nuclei [15].

From Figs. 7–9, the PMMA particles are fairly monodisperse what so ever experimental methods employed. We believed that one of the reasons will be the following. Since, PVA is used in methanol/water mixture in the dispersion polymerization, it is a steric stabilizer in methanol phase, while it is a colloid protective in water phase, followed by a formation of relatively monodisperse polymer particles.

4. Conclusions

Monodisperse poly(methylmethacrylate) microspheres were synthesized using hydrophilic PVA in water/methanol mixture media by the dispersion polymerization. Then, the effects of the polymerization parameters such as initiator, monomer, and stabilizer concentration, and the reaction time on the characteristics of the final particles were studied. The final particle sizes are affected by the concentration of the polymerization ingredients: the higher the monomer and initiator concentration, the larger the microspheres are obtained. In addition, the particle size decreases with the PVA concentration. The best conditions for the micron-sized monodisperse PMMA particles are obtained with 1 wt% of AIBN and 15 wt% PVA using 6.7 wt% MMA in the water/MeOH mixture media at 70 °C and the final particles are 2.6 μm and 102,277 g/mol of molecular weight with 5.3% of Cv. It is verified a possibility of preparing micron-sized stable PMMA particles and the precise control of the polymerization parameters is, therefore, essential for obtaining individually stable spherical particles. The use of PVA in the dispersion polymerization of MMA is working not only as a stable steric stabilizer by physically adsorbed in methanol phase, but also a colloid protective to give relatively monodisperse polymer particles in water phase, simultaneously.

Acknowledgements

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