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ORIGINAL CONTRIBUTION

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Optimum conditions for preparing micron-sized PMMA beads in the dispersion polymerization using PVA

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Abstract The optimum conditions for preparing micron-sized monodisperse polymethylmethacrylate (PMMA) beads by dispersion polymerization in a methanol/water mixture were proposed. PMMA forming microspheres having an average molecular weight of 55,300 g/mol, 2.6 μm weight-average diameter, with a 5.3% coefficient of variation and 91% conversion, were successfully obtained in the presence of 15 wt.% of polyvinylalcohol (PVA), 100/50 (g/g) of MeOH/water mixtures at 70°C; the reaction lasted for 8 h. Compared to dispersion polymerization using polyvinylpirrolydone, PVA proved to be an extremely stable steric stabilizer in the dispersion polymerization of methylmethacrylate.

Keywords Dispersion polymerization · Monodispersity · Micron-size · PMMA · PVA

Introduction

The development of technologies for the preparation of controlled-size particles in particular colloidal dimensions, that is, in the size range from 0.1 to 10 μm with monodispersity in any medium, has received a great deal of attention in industry. Colloidal stability is normally achieved by the interposition of sufficient repulsive forces to overcome the inherent attractive forces of electromagnetic origin that arise when particles approach each other. Consequently, stabilization is accomplished by the use of repulsive forces generated by dispersed polymer particles—that is, by steric stabilization—but in the absence of any repulsive forces, the particles rapidly aggregate [1].

Dispersion polymerization is known to be a useful method to produce monodisperse polymer spheres less than 10 μm in size [1]. However, the number-average molecular weight (M_w) of the synthesized polymers is reported to be relatively smaller than 200,000 g/mol in dispersion polymerization [2]. Improved physical, mechanical, and thermal properties could be expected of polymers with higher M_w.

In dispersion polymerization, primary particles are generated from the precipitation of relatively large oligomeric species, and they subsequently grow to microspheres by absorbing oligomers and monomers from the medium. For the final particles to be uniform in size, a short nucleation period and uniform growth of those primary particles are necessary [2–4]. In addition, when the stabilizer content is lower than the optimal amount, which is 10–30 wt.% relative to monomers, quite polydisperse particles with insufficient stability are obtained, while particles less than 1 μm in diameter result from high stabilizer amounts [2].

In suspension polymerization, because the monomer is vigorously stirred in water to form tiny droplets, which are a sticky mixture of polymer and monomer, talc, polyvinylalcohol (PVA), or gelatin is often used to provide a protective coating for each droplet to prevent them from cohering [5]. Because PVA is too hydrophilic compared to other organic solvents used in dispersion polymerization, it is often used in suspension polymerization. Because commercial PVA is produced with a degree of hydrolysis of 80%, which is highly hydrophilic, and 20% acetyl groups intact, a weak hydrophobic nature could be attributed to the use of a steric stabilizer in dispersion polymerization in any medium. PVA is used as a protective colloid of acrylic copolymer emulsions [6] or emulsion polymerization of vinyl acetate and methylmethacrylate (MMA) [7, 8].

Recently, T. Okaya et al. reported that poly(vinylacetate) particles having less than 450 nm diameters were synthe-

sized by using PVA, as a steric stabilizer, and 2,2-azobis (*iso*butyronitrile) (AIBN), as an initiater, in an ethanol/water mixture. They discussed the particle size and the degree of polymerization in terms of the solubility parameter of the composition [9]. This is the first report to date of a successful attempt to synthesize submicron-sized particles using PVA in dispersion polymerization.

In this article, we report that we applied PVA as a steric stabilizer to polymerize MMA in dispersion polymerization using a water/methanol mixture media and surprisingly obtained monodisperse micron-sized polymethylmethacrylate (PMMA) spheres. This article reports the first experiment to successfully obtain micron-sized PMMA particles in dispersion polymerization in water/MeOH media in the presence of PVA as a steric stabilizer.

Experimental

Materials

Methyl metacrylate (Junsei Chemicals, Japan) was purchased from Aldrich, USA, and purified by using an inhibitor removal column (Aldrich) and stored at −5°C prior to use, and AIBN (Junsei) was used without purification. Polyvinylalcohol (PVA) (Kanto Chemical, Japan) was used as a stabilizer without purification; the degree of polymerization, experimentally obtained in our laboratory, was 2,080 [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 degrees of polymerization of about 500, 1,700, and 2,000, respectively. Because the degree of hydrolysis is 80.2%, the principal grades of PVA can be classified as fully hydrolyzed (97.5–99.5% degree of hydrolysis) and partially hydrolyzed (87–89% degree of hydrolysis). Thus, the calculated M_w is 109,000 g/mol. A conventional steric stabilizer, poly(*N*-vinylpyrrolidone) (PVP-40K; M_w=40,000 g/mol, Aldrich), was used for a comparison to the PVA system. Methanol (Samchun Chemical, Korea), absolute ethanol (99%; Samchun Chemical), aceton (Samchun Chemical), and double-distilled deionized water were used as polymerization media.

Polymerization

Dispersion polymerization was carried out in a 250-mL round flask with mechanical stirring at 100 rpm under a nitrogen atmosphere at several temperatures. Preweighed methanol and aqueous PVA solution were charged in the reactor and the addition of MMA was followed. After the temperature reached the desired level, AIBN dissolved in methanol was added and the polymerization was initiated. During polymerization, aliquots of the reaction mixture were taken from the reactor to examine the morphology of the products and the degree of conversion. The resultant was rinsed off repeatedly with distilled deionized water and methanol, and then centrifuged to remove the nonreacted materials.

Analysis The structure of the polymer was verified using a Varian 400-MHz high resolution nuclear magnetic resonance (^{1}H-NMR) using $CDCl_3$ containing tetramethylsilane as the solvent, and Fourier transform infrared (FTIR) spectroscopy (Bruker 48 series) was also employed. The data was obtained at 4-cm^{-1} resolution and 16 scans were accumulated in 20 s for each specimen. The molecular weights of the PMMA particles were measured using Waters gel permeation chromatography equipped with a 510-differential refractometer and a Viscotek T50 differential viscometer. Philips scanning electron microscopy (SEM) 515 was used to investigate the morphology of the synthesized PMMA particles. The fractional conversion was calculated gravimetrically. The glass transition temperature (T_g) of the sample was measured using the Perkin-Elmer differential scanning calorimeter-7 (DSC, USA). The samples were heated at a rate of 20°C/min under a nitrogen atmosphere and quench-cooled at a maximum cooling rate, and then reheated a second time. The T_g was collected at the midpoint of the transition region in the second scan.

Results and discussion

Figure 1 shows SEM photographs of the PMMA microspheres prepared using 0.1 wt.% of AIBN relative to the monomer and mixed solvents of MeOH/water (100/50 g) at 70°C using different stabilizers: 15 wt.% PVA and PVP. As seen in this figure, relatively monodisperse PMMA particles with 2.6-μm diameters were obtained with the PVA system, while polydisperse PMMA particles were obtained with PVP. This article reports the first experiment to successfully obtain micron-sized particles using PVA in dispersion polymerization.

Figure 2 represents FTIR spectra of the synthesized PMMA particles using different stabilizers: PVA and PVP. This figure verifies that methyl methacrylate is reacted with PVA or PVP. Figure 2a shows the FTIR spectra of pure PVA; the hydroxyl band (O—H) at 3,460 cm^{-1} and the CH and CH_2 stretching bands at 2,900 and 2,960 cm^{-1}, respectively, are the characteristic peaks of PVA. The medium peak at 1,728 cm^{-1} is the resonance effect of the hydroxyl band at 3,460 cm^{-1}, and the peaks observed at 1,130 and 1,180 cm^{-1} in Fig. 2a are the characteristic peaks of asymmetric and symmetric CH_3 deformation, respectively. Figure 2b shows the FTIR spectra of PMMA in the presence of PVA, and the carbonyl stretching (C=O) at 1,728 cm^{-1} and the hydrocarbon stretching at 2,900–3,000 cm^{-1} are the characteristic peaks. The intensity of the latter peaks at 2,900–3,000 cm^{-1} is bigger than that observed in Fig. 2a due to the summation

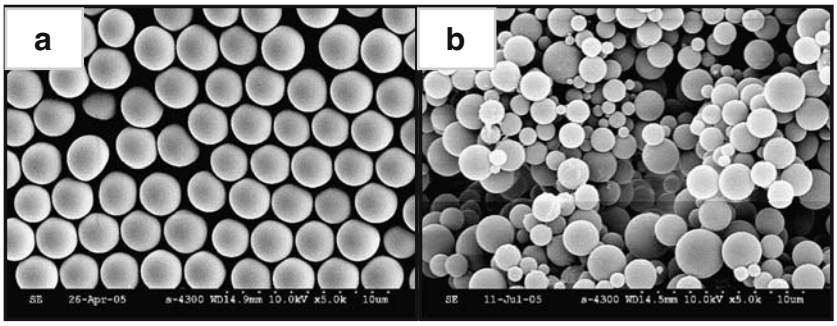

Fig. 1 SEM photographs of PMMA microspheres prepared with different stabilizers at 70°C in a water/MeOH (50/100, g/g) mixture; **a** PVA 15 wt.%, **b** PVP 15 wt.%

effect of hydrocarbon between PVA and PMMA. In addition, the hydroxyl peak at 3,460 cm^{-1} is very weak due to the disappearance of PVA. In Fig. 2c, the peaks of the primary amine, aliphatic CH and CH_2 with cyclic CH, and the carbonyl stretching in the five-membered ring of PVP are observed at 3,400, 2,900, 3,065 and 1,680 cm^{-1}, respectively. In addition, the peaks observed at 1,130 and 1,180 cm^{-1} in Fig. 2c are characteristics of asymmetric and symmetric CH_3 deformation, respectively. In Fig. 2d, due to the disappearance of PVP in the PMMA particles, the primary amine at 3,400 cm^{-1}, the cyclic CH at 3,065 cm^{-1}, and the carbonyl stretching at 1,680 cm^{-1} are all weakened or have disappeared. This is evidence showing that either PVA or PVP worked as the stabilizer. However, it seems that there are some residual peaks left between 3,400 and 3,500 cm^{-1}, as seen in Fig. 2b,d, involving PVA or PVP after completion of the reaction and followed by the cleaning. Polymeric stabilizers used in dispersion polymerization are not only physically adsorbed on the surfaces of particles, but are 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, and it has been reported that 1.1 wt.% of total added PVP was adsorbed on PMMA particles prepared by dispersion polymerization [11].

Figure 3 exhibits the SEM photographs of PMMA microspheres prepared in MeOH/water (g/g) mixtures of 120/30 (Fig. 3a), 110/40 (b), 100/50 (c), 90/60 (d), and 80/70 (e). As seen in Fig. 3a–d, the higher the MeOH content was, the bigger the average particle size obtained, but the poorer the particle size distribution. In addition, unstable particles are aggregated in Fig. 3e. Because the sizes of formed particles depend on the solubility parameter of the cosolvent used in dispersion polymerization [6], the better solvent, which has a closer solubility parameter to the monomer, would give larger particle sizes because a smaller number of nuclei are produced in the nucleation stage. It is assumed that the solubility parameter difference between hydrophilic MMA and MeOH is one of the factors affecting the particle size of PMMA. Thus, the particle size of PMMA is larger in the MeOH-rich phase than in the water-rich phase. The effect of the MeOH/water composition on the characteristics of the synthesized PMMA particles is summarized in Table 1. At 100/50 g (MeOH/water) mixture composition, monodisperse PMMA particles at 91% conversion were obtained with 2.6 μm weight-average diameter (D_w),

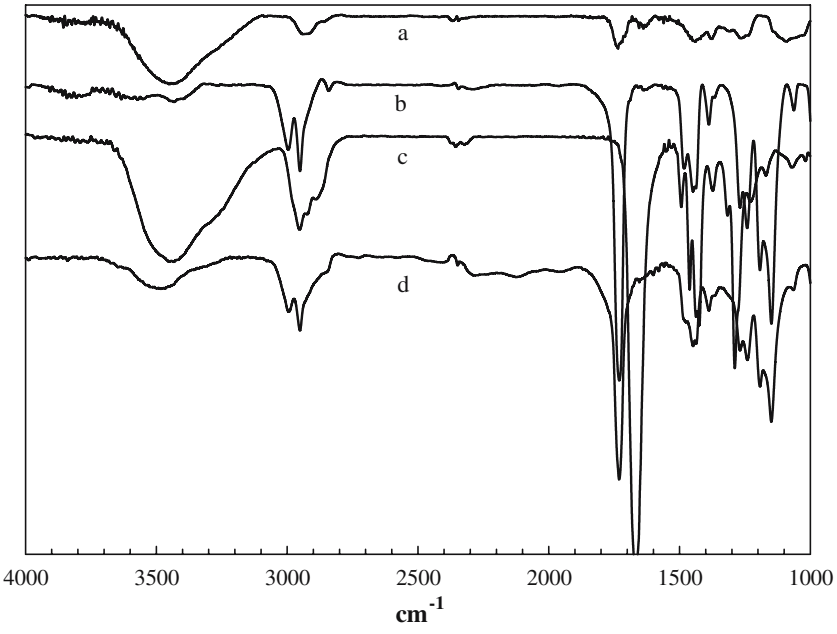

Fig. 2 Comparison of the FTIR spectra of the synthesized PMMA particles using 15 wt.% PVA and PVP. **a** pure PVA, **b** PMMA with PVA, **c** PVP, and **d** PMMA with PVP

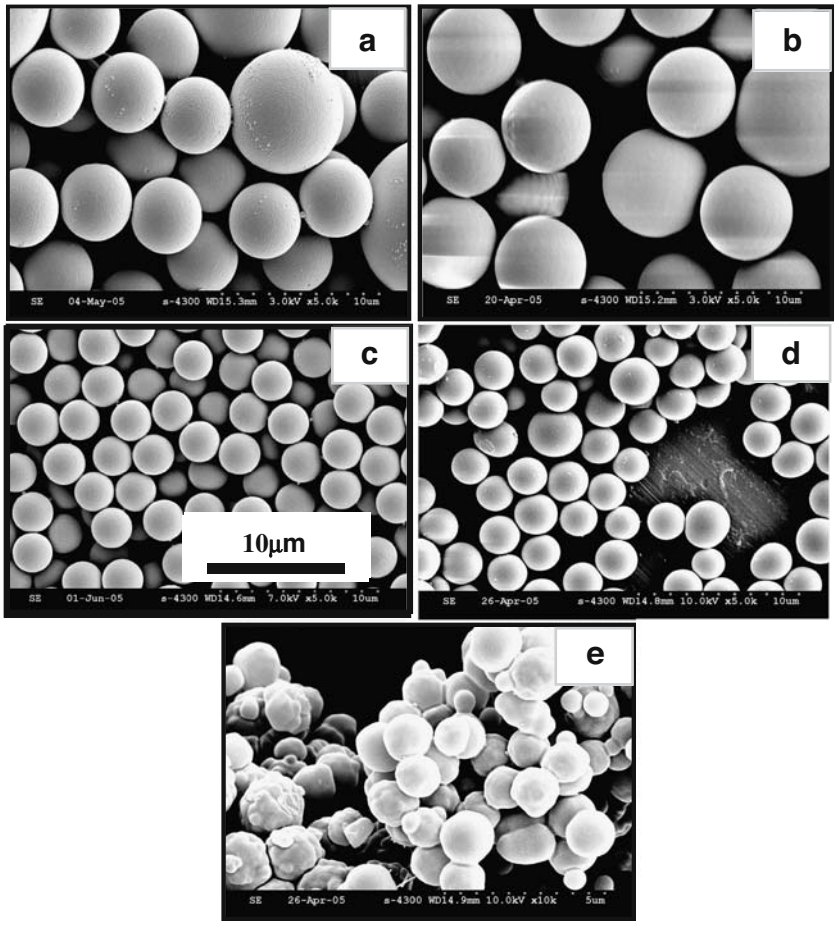

Fig. 3 SEM photographs of PMMA microspheres prepared at MeOH(g)/water(g) mixtures of 120/30 (**a**), 110/40 (**b**), 100/50 (**c**), 90/60 (**d**), and 80/70 (**e**)

5.3% coefficient of variation (C_v), an M_w of 55,340 g/mol, and 2.426 polydispersity.

Figure 4 shows the conversion and SEM photographs of PMMA particles prepared at 100/50 g (organic solvent/water) mixture and 15 wt.% of PVA at 70°C using different solvents; MeOH, EtOH, and acetone. The solubility parameters of MeOH, EtOH, and acetone are 14.7, 12.9, and 9.8 $(cal/cm^3)^{1/2}$, respectively. In the MeOH solvent system, fairly monodisperse PMMA microspheres were obtained, while polydisperse particles with partial coagulum were obtained in the EtOH solvent system. Almost no particles in the acetone system were obtained. In terms of the conversion, there is no specific difference between MeOH and EtOH, reaching up to 91% conversion at 8 h of reaction, while the conversion with acetone is 18%. Thus, MeOH was chosen as being the best solvent for the dispersion polymerization of MMA.

Table 1 Effect of MeOH/water mixture composition on conversion (%), D_w, C_v, M_w, and polydispersity index (M_w/M_n) in dispersion polymerization at 70°C for 8 h

MeOH(g)/water(g)	Conversion (%)	D_w (μm)	C_v (%)	M_w (g/mol)	M_w/M_n
120/30	45	6.4	29	14,180	5.8
110/40	71	7.0	32	28,650	5.2
100/50	91	2.6	5.3	55,340	2.4
90/60	38	2.5	13	63,000	2.3
80/70	34	Coagulation	Coagulation	140,800	5.5

Figure 5 depicts the temperature-dependent particle characteristics by studying the SEM photographs of PMMA particles prepared with 1 wt.% AIBN relative to monomer, 15 wt.% PVA (1 wt.% relative to the monomer), and 100/50 g (MeOH/water) mixture at different temperatures: 60, 70, and 80°C. As seen in Fig. 5a, a 78-nm particle size and 25% C_v with 153,920 g/mol M_w at 62% of conversion were synthesized at 60°C, while surface-stabilized micron-sized PMMA particles with 2.6 μm D_w, 5.3% C_v, 55,300 g/mol M_w, and 91% conversion were produced at 70°C. However, unstable surface morphology with polydisperse particle sizes with 80% conversion was obtained at 80°C, as seen in Fig. 5c. Thus, Table 2 summarizes the optimum condition for preparing fairly the monodisperse PMMA particles in dispersion polymerization.

The ^{1}H-NMR spectrum of PMMA prepared with 0.1 wt.% AIBN at 70°C is seen in Fig. 6; the figure shows three distinct peaks appearing at the highest field, which represent

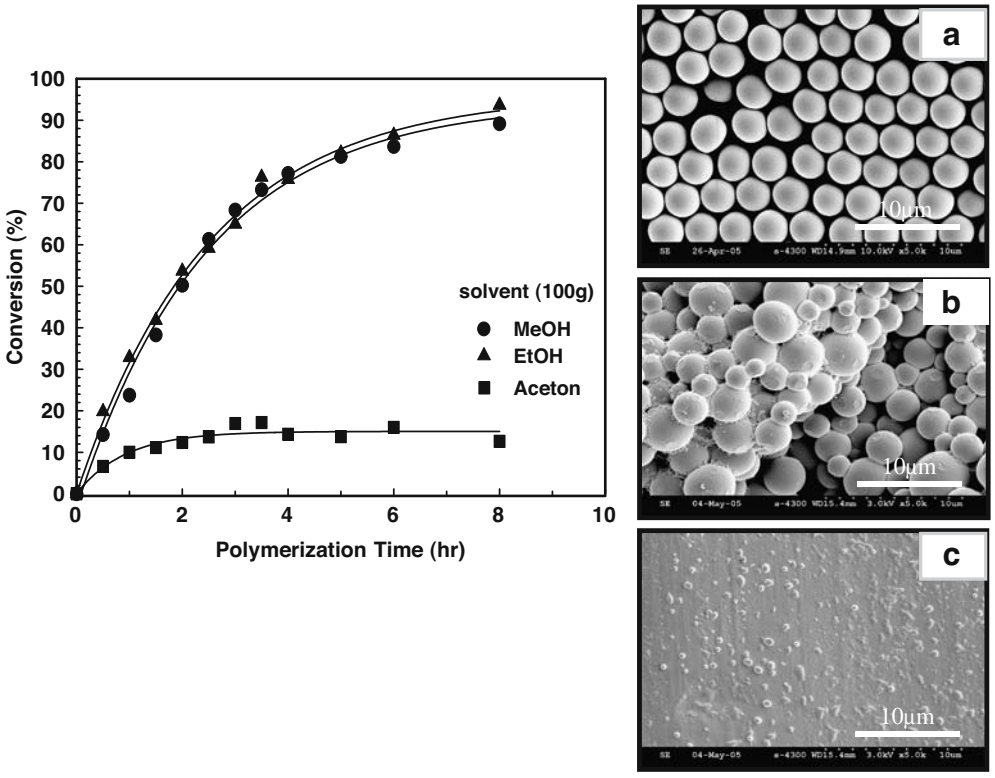

Fig. 4 Effect of solvents on conversion and particles in dispersion polymerization in a methanol/water (100/50 g) mixture at 70°C. **a** MeOH, **b** EtOH, **c** acetone

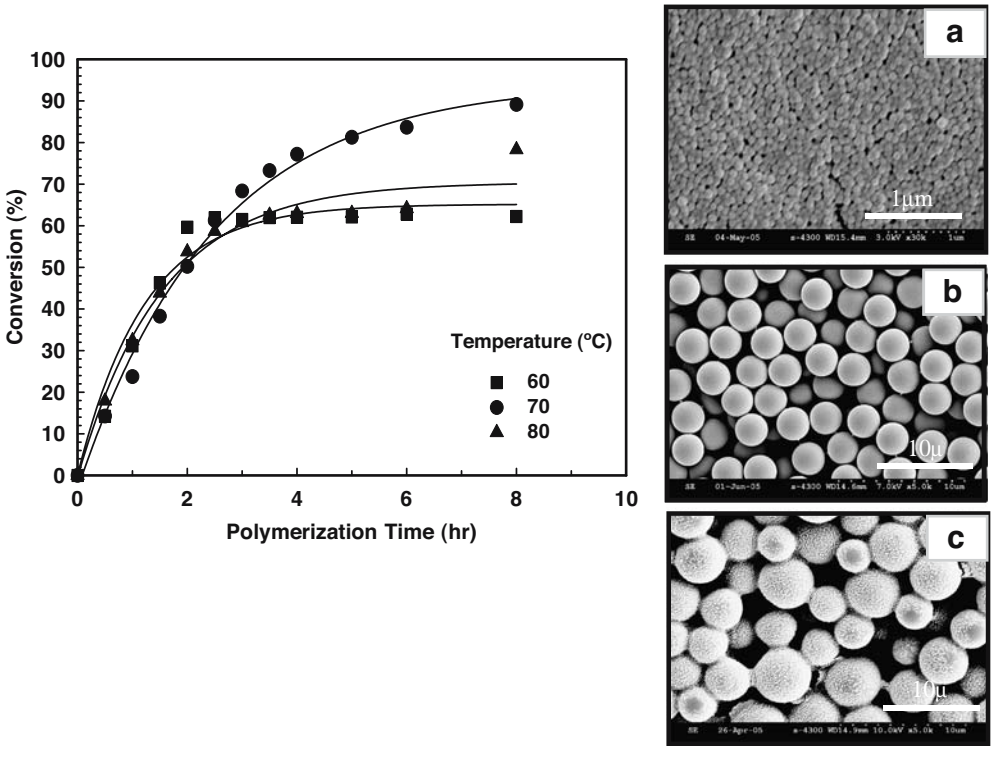

Fig. 5 Effect of temperature on conversion and particles in dispersion polymerization in a MeOH/water (100/50, g/g) mixture with 1 wt.% PVA to monomer. **a** 60°C, **b** 70°C, **c** 80°C

Table 2 Optimum conditions for obtaining micron-sized monodisperse particles in the dispersion polymerization in this study

Ingredients	Amount	Remark
Methanol	100 g	Volume of total medium was fixed at 176 ml throughout the experiments
Water	50 g	
MMA	10 g	6.7 wt.% relative to medium
AIBN	0.1 g	1 wt.% relative to monomer
PVA	1.5 g	15 wt.% relative to monomer

methacrylate methyl groups of different tacticities [12]. The bands at about 0.82, 1.02, and 1.18 ppm arise from syndiotactic (rr), atactic (mr), and isotactic (mm) methyl groups, respectively. From this figure, the ratios of the triad tacticity for syndiotacticity/atacticity/isotacticity of the PMMA particles calculated from the integrated ratios of rr, mr, and mm are 56.4/35.0/8.7, respectively. The relatively regular molecular structure of the PMMA particles is expected to affect their thermal properties or characteristics.

Figure 7a–c show the DSC thermograms of pure PVA, PMMA particles prepared with PVP as a stabilizer, and PMMA particles prepared with PVA, respectively. In this figure, we can observe that the PMMA particles prepared with PVA show not only, at 129.5°C, a higher T_g than the regular amorphous PMMA (normally, the T_g is known to be 105°C), but also a PVA melting peak near 185°C. This is evidence that the PMMA particles are physically adsorbed or chemically bounded with PVA, as discussed earlier regarding molecular weights of the PMMA particles. In addition, the T_g of the synthesized PMMA is about 129.5°C, which is fairly higher than that of commercial PMMA (T_g=105°C). The syndiotacticity of the PMMA sample prepared in this study is 56.4%, which is higher than that of a commercial PMMA,

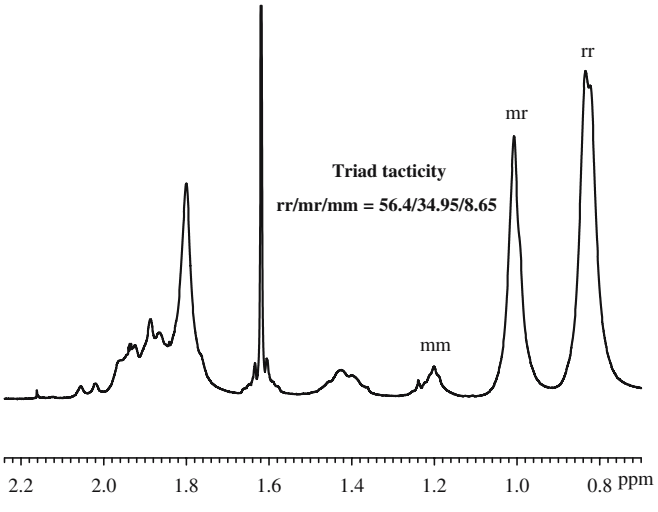

Fig. 6 ^{1}H-NMR spectrum of the obtained PMMA

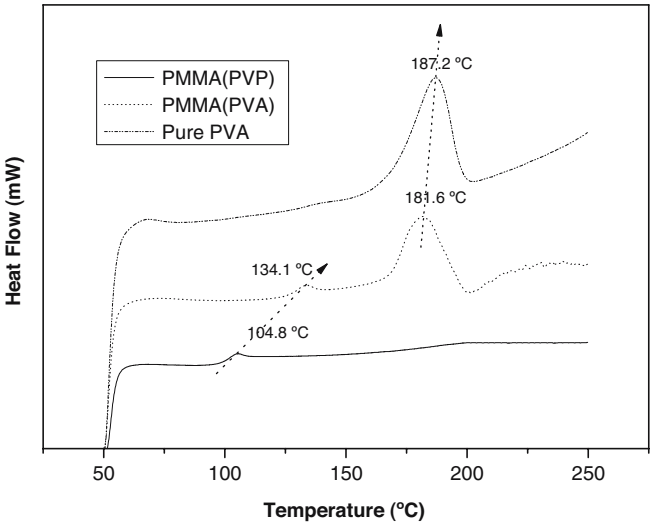

Fig. 7 DSC data with polymerization time

which bears 43% [11]. It is accepted that the T_g of PMMA is proportional to the degree of syndiotacticity and inversely proportional to the degree of isotacticity. The T_g of PMMA was reported to increase from 41.5 to 130.6°C between syndiotacticity/atacticity/isotacticity triads of 0/5/95 and 54/36/9.39. Thus, we believe that the use of PVA in the dispersion polymerization of MMA can induce different tacticities in PMMA. The high T_g of PMMA at 129.5°C is also observed in the photopolymerization of living-radical polymerization [13–16]. However, the exact mechanism for the variance in the tacticity is not yet clarified; therefore, it is under investigation.

Conclusions

To obtain monodisperse micron-sized PMMA particles, hydrophilic PVA was used in the dispersion polymerization of MMA. Thus, polymerization-parameter-dependent studies were carried out and the optimum conditions for preparing micron-sized monodisperse PMMA particles using dispersion polymerization in a MeOH/water mixture were proposed. In the MeOH/water system, fairly monodisperse PMMA microspheres were obtained. As a consequence, PMMA particles having 55,300 g/mol M_w, 2.6 μm D_w, and 5.3% C_v were successfully obtained at 91% conversion in the presence of 15 wt.% PVA and 100/50 (g/g) MeOH/water mixtures, at 70°C for 8 h of the reaction. Compared to the dispersion polymerization using PVP, PVA proved to be an extremely stable steric stabilizer.

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