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ORIGINAL PAPER

Preparation of monodisperse PMMA particles by dispersion polymerization of MMA using poly(styrene-co-methacrylic acid) copolymer as a steric stabilizer

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Abstract Dispersion polymerization of MMA was conducted using poly(styrene-co-methacrylic acid) copolymer as a steric stabilizer in an aqueous methanol medium. Various composition copolymers were easily prepared with a conventional radical polymerization by changing the monomer ratios of styrene to methacrylic acid, and were employed as a steric stabilizer for dispersion polymerization. The copolymers prepared with monomer ratios of 1.25–1.50 were found to be suitable steric stabilizers for dispersion polymerization. A very small amount of copolymer (0.6 wt% based on MMA) could act as a steric stabilizer effectively to obtain monodisperse PMMA particles. The particle size decreased with increasing the solvent polarity from 4 to 0.14 μm.

Keywords Dispersion polymerization · Methyl methacrylate · Poly(styrene-co-methacrylic acid) · Monodisperse particles · Steric stabilizer

Introduction

Dispersion polymerization is a versatile method for the preparation of polymer particles because monodisperse micron-sized particles are prepared in a single step. Such particles have many important applications as separation media, ion-exchange beads, toners, coatings, calibration standards, and in medical diagnostics. Especially, the polymerization of styrene and methyl methacrylate has been extensively studied in polar media [1]. Differing from emulsion or suspension polymerization, dispersion polymerization starts from a homogeneous solution

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since monomer is soluble. As the polymerization proceeds, a solution becomes turbid since a polymer was insoluble in a medium. To prevent polymer aggregation, a steric stabilizer was added into the polymerization system. Many polar homopolymers such as polyethylene oxide [2, 3], polyvinylpyrrolidone [4–8], poly(2-ethyl-2-oxazoline) [9], hydroxypropyl cellulose [10, 11], poly(acrylic acid) [12, 13], polyvinylalcohol [14], and statistical copolymer of methacrylic acid and ethyl acrylate [15] have been successfully applied as steric stabilizers in dispersion polymerizations.

In dispersion polymerization, a large amount of stabilizer (usually more than 10 wt% based on monomer) was necessary to obtain monodisperse particles. To reduce the amount of stabilizer, reactive stabilizes were employed such as polymerizable group [16–18], and chain transfer agent [19, 20]. For example, using poly(2-oxazoline) macromonomer, the dispersion polymerization of methyl methacrylate afforded monodisperse polymer particles even at a very low concentration of the stabilizer [16]. The recycling of solvent and stabilizer was also conducted after the ordinary dispersion polymerization and they were used for other polymerizations to afford monodisperse particles for three times [7]. Recently, we prepared polyimide–polystyrene [21, 22] or polyimide–poly(*t*-butyl methacrylate) particles [23] by dispersion polymerization using poly(amic acid) as a stabilizer. Poly(amic acid) was a precursor of polyimide and composed with aromatic rings and pendant carboxylic acid. Dispersion polymerization of styrene or *t*-butyl methacrylate was performed using a cationic comonomer and poly(amic acid) as a stabilizer, and then poly(amic acid) in the resulting particles was converted into polyimide. In this polymerization, poly(amic acid) was effectively incorporated into the polymer particles by using a cationic comonomer via an electrostatic attraction to afford monodisperse particles.

In this context, an anionic polymer stabilizer might be incorporated into polymer particles effectively and the amount of stabilizer might be reduced by using a cationic comonomer. As an anionic stabilizer, copolymer of styrene and methacrylic acid was employed because of structure similarity to poly(amic acid). Herein, we describe the dispersion polymerization of MMA using poly(styrene-co-methacrylic acid) copolymer as a steric stabilizer. Effects of stabilizer concentration and solvent composition on the particle size and size distribution were investigated.

Experimental

Measurements

Diameter of polymer particle was determined by a scanning electron microscope (JEOL JSM-588 scanning microscope). The molecular weight of polymer was determined by size-exclusion chromatography (SEC) measurement on a TOSOH HLC 8020 instrument equipped with a refractive index detector using tetrahydrofuran (THF) as an eluate calibrated by polystyrene standards.

Materials

Styrene and methyl methacrylate were washed with aqueous NaOH and distilled under reduced pressure. Methacrylic acid was distilled under reduced pressure. 2,2′-Azobisisobutyronitrile (AIBN) was recrystallized from methanol. Other reagents were obtained commercially and used as received.

Synthesis of steric stabilizer (SMA1.50)

Into a flask, styrene (14.8 g; 143 mmol), methacrylic acid (6.85 g; 95 mmol), AIBN (0.18 g; 1.1 mmol), and ethanol (30 mL) were added. The solution was deoxygenated by two freeze–pump–thaw cycles with N_2 and stirred at 70 °C for 24 h. The polymer solution was poured into an excess amount of water and the precipitated polymer was collected by filtration. The copolymer (SMA1.50) was obtained in 84% yield.

Methylation of stabilizer

Into a flask containing 0.50 g of stabilizer dissolved in DMSO (5 mL), pyridine (0.50 g), and *N,N*-dimethylformamide dimethyl acetal (0.82 g) in DMSO (5 mL) were added dropwise. The solution was stirred at 100 °C for 12 h and poured into methanol. The precipitated polymer was dried under reduced pressure.

Dispersion polymerization of MMA

Into the three necked flask equipped with mechanical stirrer and attached with nitrogen inlet, SMA1.50 (0.24 g; 1.0 mmol of carboxylic acid) and methanol (60 mL) were added and stirred until the stabilizer was dissolved completely. Into the solution, MMA (8.0 g; 80 mmol), 2,2′-azobis(2,4-dimethylvaleronitrile) (ADVN) (0.12 g; 0.48 mmol), 0.48 M KOHaq solution (2.1 mL; 1.0 mmol), water (18 mL), and methanol (20 mL) were added. The mixture was purged with nitrogen and stirred at 45 °C for 24 h with mechanical stirrer in nitrogen atmosphere. After removal of coagulated polymer by filtration, the resulting particles were purified with centrifugation using water for three times. The polymer particles were dispersed with water and a part of dispersion was lyophilized and weighted to determine the yield of particles.

Results and discussion

Synthesis of stabilizer

Poly(styrene-co-methacrylic acid) copolymers were obtained by a conventional free-radical polymerization of styrene and methacrylic acid in ethanol. The compositions of monomer units determined by acid–base titration were identical

Table 1 Synthesis of steric stabilizer

Stabilizer[a]	Yield (%)	St/MA[b] in polymer	Mn[c]	Mw/Mn[c]
SMA1.25	79	1.26	32,000	1.72
SMA1.50	78	1.51	32,000	1.60
SMA2.00	92	2.00	31,000	1.69

Polymerization was performed at 70 °C for 24 h. Equal mass of ethanol against of monomers was used as a solvent. [Methacrylic Acid]/[AIBN] = 95

[a] The numbers in symbol represented the feed ratio of monomer of styrene to methacrylic acid

[b] Determined by acid–base titration with 0.5 M NaOHaq solution in ethanol

[c] Measured by SEC of methylated polymer eluted with THF with polystyrene standard

with the monomer feeds of polymerization (Table 1). To determine molecular weight, the size exclusion chromatography (SEC) measurement of methyl-esterified stabilizer was conducted. From ^{1}H-NMR spectra, all carboxlic acids of stabilizers were esterified with *N,N*-dimethylformamide dimethyl acetal [24]. The methylated stabilizers were measured with SEC and their molecular weights were summarized in Table 1. The number–average molecular weights of all stabilizers were found to be about 32,000 g/mol.

Dispersion polymerization of MMA

Dispersion polymerizations of MMA were conducted using poly(styrene-co-methacrylic acid) stabilizers and equimolar amount of potassium hydroxide against the methacrylic acid unit in aqueous methanol medium (Table 2). When stoichiometric amount of [2-(methacryloyloxy)ethyl]trimethylammonium chloride (MEA) against methacrylic acid unit was used as a cationic comonomer, monodisperse particles were obtained even in a low concentration of SMA1.50. From elemental analysis of the resulting particles, most of MEA was not incorporated into the particles, i.e., the atomic ratio of nitrogen to carbon of particles was 0.42×10^{-3},which was much smaller than the calculated ratio 2.86×10^{-3} assuming that all MEA was incorporated into the particles. When dispersion polymerization in the absence of MEA was conducted in the same condition, monodisperse particles were also afforded in quantitative yield. We first expected that the SMA stabilizer was effectively adsorbed on the particles by using the cationic comonomer. However, MEA was not necessary to afford monodisperse MMA particles. Then, various compositions of SMA stabilizers were used in dispersion polymerization of MMA (Table 2). Except using SMA1.00, PMMA particles were yielded quantitatively and when SMA1.25 or 1.50 was used as a stabilizer, monodisperse particles were obtained. The polymerization using more hydrophobic SMA1.75 or 2.00 made the size distribution broader. For a comparison of SMA stabilizer, a typical conventional steric stabilizer polyvinylpyrrolidone (PVP-K30; MW = 40,000) was also used in dispersion polymerization [4–8]. When a large amount of PVP, i.e., about 10 times weight of SMA 1.50 was used, monodisperse polymer particles were obtained. However, using the same weight of

Table 2 Dispersion polymerization of MMA using various stabilizers

Stabilizer	Amount of stabilizer (g)	Yield (%)	Diameter (μm)	Cv (%)
SMA1.50[a]	0.24[b]	70	2.43	4.2
SMA1.50	0.24[b]	85	2.03	6.1
SMA1.00	0.18[b]	0[d]	–	–
SMA1.25	0.21[b]	94	2.51	8.4
SMA1.75	0.27[b]	86	1.26	13.5
SMA2.00	0.29[b]	86	1.01	11.8
PVP[c]	1.87	85	3.22	3.9
PVP[c]	0.24	0[d]	–	–

MMA: 80 mmol, ADVN: 0.48 mmol, KOH: 1.0 mmol, methanol: 80 mL H_2O: 20 mL, 45 °C, 24 h

[a] [2-(Methacryloyloxy)ethyl]trimethylammonium chloride 0.208 (1.0 mmol) was used as a cationic comonomer

[b] Stabilizers containing 1.0 mmol of MA units were used in dispersion polymerization

[c] Polyvinylpyrrolidone (PVP-K30; MW = 40,000) was used as a steric stabilizer

[d] All polymer was coagulated during polymerization

PVP against SMA1.50, all polymer was coagulated during the polymerization. In general, a large amount of steric stabilizer is necessary to obtain monodisperse particles in the dispersion polymerization. The dispersion polymerization using SMA stabilizers could obtain the particles even in their very low concentrations.

Dispersion polymerizations using SMA1.50 were performed changing amount of stabilizer and solvent composition (Table 3). All the polymerization except run nos. 9 and 12, obtained PMMA particles in quantitative yield. Kobayashi et al. reported the dispersion polymerization of MMA using polyoxazoline macromonomer as a steric stabilizer [17]. In this case, the polymerization using even a very small amount of stabilizer (0.4 wt%/MMA) could afford the particles quantitatively, since macromonomer was copolymerized with MMA and incorporated into the particles effectively. The dispersion polymerization using a very small amount of SMA1.50 (0.3 wt%/MMA) also yielded PMMA particles quantitatively. However, some small particles were contained and led the size distribution broader (run no. 1 and Fig. 1a). When 0.048 g of stabilizer was added, small particles disappeared (run no. 2 and Fig. 1b). The amount of stabilizer was still very small (0.6 wt% based on MMA), and that SMA stabilizer could be prepared by the ordinary radical polymerization of styrene with methacrylic acid. Hence, the dispersion polymerization using SMA stabilizer was versatile method to prepare micron-sized PMMA particles. The particle sizes were hardly changed in the range of 1.85–2.64 μm changing the amount of SMA1.50 (run nos. 2–8).

Solvent composition is well known to play a key role in the particle size. In general, an increase in solvent polarity leads to the formation of smaller particles because more nuclei are produced in more polar medium. In our case also, the particle size decreased with increasing the solvent polarity from 4.0 to 0.14 μm (run nos. 10–14, Fig. 1d). The polymerization using 90 mL of methanol made all

Table 3 Dispersion polymerization of MMA using SMA1.50

Run no.	Amount of stabilizer (g)	Amount of methanol (mL)	Yield (%)	Diameter (μm)	Cv (%)
1	0.024	80	75	1.8	Polydisperse
2	0.048	80	88	2.33	4.1
3	0.072	80	90	2.64	5.3
4	0.096	80	89	2.61	3.9
5	0.12	80	83	2.53	3.7
6	0.24	80	85	2.03	6.1
7	0.36	80	82	2.22	4.5
8	0.48	80	89	1.85	4.8
9	0.24	90	0[a]	–	–
10	0.24	85	88	4.0	Polydisperse
11	0.24	75	95	1.53	4.2
12	0.24	70	0[a]	–	–
13	0.24	65	95	0.59	4.2
14	0.24	60	88	0.38	5.4
15	0.24	55	94	0.24	7.0
16	0.24	50	99	0.14	9.6

MMA: 80 mmol, ADVN: 0.48 mmol, Solvent: methanol + H_2O = 100 mL, 45 °C, 24 h. Equimolar amount of KOH against MA unit of SMA1.50 was added

[a] All polymer was coagulated during polymerization

of polymer coagulated (run no. 9). Since the steric stabilizer was well-soluble in this solvent, it was not adsorbed onto PMMA particles effectively, resulting in coagulation of particles. Using 70 mL of methanol, all the polymer was also coagulated during the polymerization (run no. 12). The reason was unknown, but the particles size was significantly changed at around 70 mL of methanol, which might be related to the coagulation of the polymer. When the polymerization was performed using 85 mL of methanol, about 4 μm of particles were obtained, however, small particles were also contained leading to size distribution broader.

Although the reason for the high particle stability using SMA stabilizer was unclear, non-polar styrene segments might be adsorbed onto PMMA particles as an anchor and MA segment stabilized the particles. By copolymerizations with some molar ratios of styrene to methacrylic acid, the suitable monomer ratio for steric stabilizer must be achieved. We also tried to use poly(styrene-acrylic acid) copolymers (St: AA = 2:1, 1.5:1) as stabilizers. The dispersion polymerization of MMA using these stabilizers resulted in the coagulation of PMMA particles. Thus, the SMA might have not only the suitable monomer ratios, but also some chemical structure or some sequence of monomers for the effective steric stabilizer.

In conclusion, the dispersion polymerization of MMA was conducted using poly(styrene-co-methacrylic acid) copolymer as a steric stabilizer. A very small

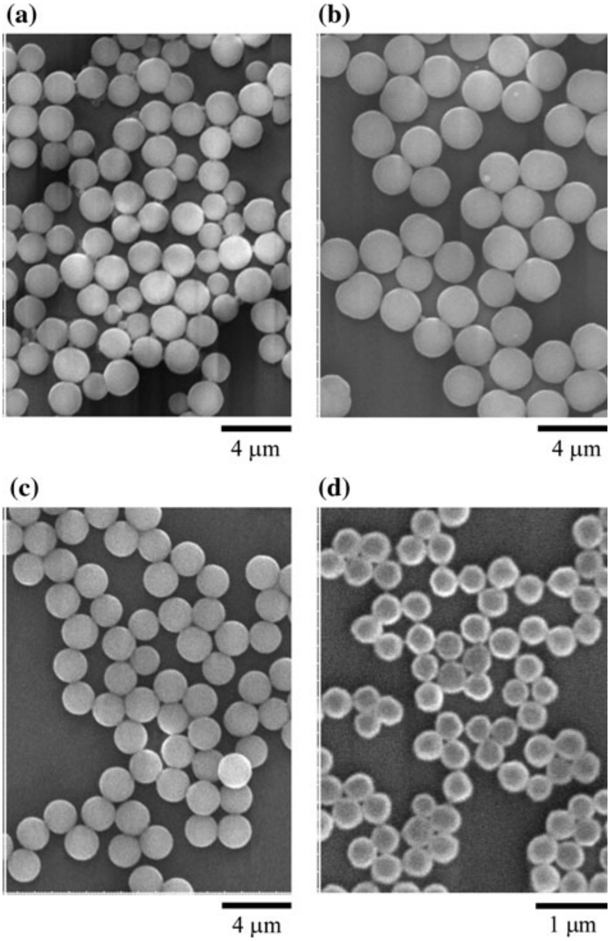

Fig. 1 Scanning Electron Micrographs of PMMA particles **a** run no. 1, **b** run no. 2, **c** run no. 8, and **d** run no. 14 (see Table 3)

amount of SMA (0.6 wt% of MMA) was necessary to obtain monodisperse PMMA particles. The particle size decreased with increasing the solvent polarity from 4 to 0.14 μm.

References

1. Narayanan K, Jayachandran N, Chatterji PR (2001) Preparation of linear and crosslinked polymer microspheres by dispersion polymerization. J Macromol Sci Polym Rev C41:79
2. Lacroix-Desmazes P, Guyot A (1996) Reactive surfactants in heterophase polymerization. 2. Maleate based poly(ethylene oxide) macromonomers as steric stabilizer precursors in the dispersion polymerization of styrene in ethanol–water media. Macromolecules 29:4508
3. Capek I, Riza M, Akashi M (1997) Dispersion copolymerization of poly(oxyethylene) macromonomers and styrene. J Polym Sci A 35:3131

4. Bamnolker H, Margel S (1996) Dispersion polymerization of styrene in polar solvents: effect of reaction parameters on microsphere surface composition and surface properties, size and size distribution, and molecular weight. J Polym Sci A 34:1857
5. Zhang C, Wei Q (2009) Influence of poly(methyl methacrylate) particles with different initial temperature rising ramps on size distribution in dispersion polymerization. J Appl Polym Sci 112:917
6. Yu DG, An JH, Bae JY, Ahn SD, Kang SY, Suh KS (2005) Negatively charged ultrafine black particles of P(MMA-co-EGDMA) by dispersion polymerization for electrophoretic displays. Macromolecules 38:7485
7. Shen S, Sudol ED, El-Aasser MS (1993) Control of particle size in dispersion polymerization of methyl methacrylate. J Polym Sci A 31:1393
8. Jiang S, Sudol ED, Dimonie VL, El-Aasser MS (2008) Dispersion polymerization of methyl methacrylate: effect of stabilizer concentration. J Appl Polym Sci 107:2453
9. Uyama H, Kobayashi S (1994) Dispersion polymerization of styrene in aqueous alcohol solution: effects of reaction parameters on the polymer particle formation. Polym Int 34:339
10. Chen Y, Yang H-W (1992) Hydroxypropyl cellulose (HPC)-stabilized dispersion polymerization of styrene in polar solvents: effect of reaction parameters. J Polym Sci A 30:2765
11. Paine AJ (1990) Dispersion polymerization of styrene in polar solvents: I. Grafting mechanism of stabilization by hydroxypropyl cellulose. J Colloid Interface Sci 138:157
12. Tuncel A, Kahraman R, Piskin E (1993) Monosize polystyrene microbeads by dispersion polymerization. J Appl Polym Sci 50:303
13. Corner T (1981) Polyelectrolyte stabilised latices part 1, preparation. Colloids Surf 3:119
14. Kim OH, Lee K, Kim K, Lee BH, Choe S (2006) Effect of PVA in dispersion polymerization of MMA. Polymer 47:1953
15. Laus M, Dinnella C, Lanzarini G, Casagrande A (1996) Core-shell functional microspheres by dispersion polymerization: 2. Synthesis and characterization. Polymer 37:343
16. Kobayashi S, Uyama H, Choi JH, Matsumoto Y (1993) Preparation of micron-size monodisperse poly(methyl methacrylate) particles using poly(2-oxazoline) macromonomer. Polym Int 30:265
17. Shay JS, English RJ, Spontak RJ, Balik CM, Khan SA (2000) Dispersion polymerization of polystyrene latex stabilized with novel grafted poly(ethylene glycol) macromers in 1-propanol/water. Macromolecules 33:6664
18. Jung H, Kim SY, Lee K, Lee BH, Shim SE, Choe S (2005) High molecular weight monodisperse polystyrene microspheres prepared by dispersion polymerization, using a novel bifunctional macromonomer. J Polym Sci A 43:3566
19. Bourgeat-Lami E, Guyot A (1997) Thiol-ended polyethylene oxide as reactive stabilizer for dispersion polymerization of styrene. Colloid Polym Sci 275:716
20. Bourgeat-Lami E, Guyot A (1995) Preparation of monodisperse polystyrene particles using thiol-ended polyethylene oxide stabilizer in dispersion polymerization. Polym Bull 35:691
21. Watanabe S, Ohmura T, Ueno K, Murata M, Masuda Y (2008) Preparation of poly(t-butyl methacrylate)-polyimide particles by dispersion polymerization of t-butyl methacrylate using poly(amic acid) as a stabilizer and subsequent imidization. Polym J 40:743
22. Watanabe S, Ueno K, Kudoh K, Murata M, Masuda Y (2000) Preparation of core-shell polystyrene-polyimide particles by dispersion polymerization of styrene using poly(amic acid) as a stabilizer. Macromol Rapid Commun 21:1323
23. Watanabe S, Ueno K, Murata M, Masuda Y (2006) Preparation of polystyrene-polyimide particles by dispersion polymerization of styrene using poly(amicacid) as a stabilizer. Polym J 38:471
24. Cohen HL (1976) Esterification of polymeric carboxylic acids. J Polym Sci Polym Chem 14:7