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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

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Dispersion polymerization of *t*-butyl methacrylate (BMA) and a cationic comonomer, 4-(vinylbenzyl)trimethylammonium chloride (VBA) was conducted in alkaline aqueous ethanol using various aromatic poly(amic acid)s (PAA) as stabilizers. The monodisperse particles were obtained in high yield using the optimum composition of solvent mixture depending on the PAA structure. By using a cationic comonomer (VBA), PAA was quantitatively incorporated into the particles. The imidization of PAA on the particles proceeded with acetic anhydride and 4-(dimethylamino)pyridine to form PBMA-polyimide (PBMA-PI) particles. The PBMA-PI particles were maintained in spherical shape by the thermal treatment up to 280 °C.

KEY WORDS: Dispersion Polymerization / Poly(amic acid) / Polyimide / Thermal Stability / *t*-Butyl Methacrylate /

Dispersion polymerization is an attractive method for producing monodisperse polymer particles in the 0.5–10 μm size range, which 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] To disperse particles stably, a suitable steric stabilizer was used, such as polyethylene oxide,[2] polyvinylpyrrolidone,[3] poly(2-ethyl-2-oxazoline),[4] hydroxypropyl cellulose,[5] and poly(acrylic acid).[6]

Aromatic polyimides (PI) are the most useful super engineering plastics which exhibit excellent thermal, electrical, and mechanical properties, and have been used widely in aerospace, electronics, and other industries. They are generally prepared through a two-step procedure by the ring-opening polyaddition of aromatic diamines to aromatic tetracarboxylic dianhydrides giving poly(amic acid)s (PAA), followed by thermal cyclodehydration.[7,8] Since PAA has pendant carboxylic acids and is soluble in alkaline aqueous ethanol solution, it would work as a steric stabilizer for dispersion polymerization. In the previous study, we reported the dispersion polymerization of styrene (S) using various aromatic poly(amic acid)s in an aqueous ethanol medium.[9]

After the polymerization, the PAA was easily converted to polyimide to yield PS-PI particles. Thus PAA would play two important roles, *i.e.*, a steric stabilizer during polymerization, and improvement in mechanical and thermal properties of particles by means of imidization of PAA. For this purpose, PAA must be incorporated into the particles effectively. In general dispersion polymerization, most of steric stabilizers were not incorporated into the particles. To incorporate them into particles effectively, reactive stabilizers having polymerizable group[10] or radical transfer agent (mercapto group)[11] were used in the polymerization and stabilized particles even in their low concentration because they reacted with monomer and incorporated into the particles. In the previous study, a cationic comonomer, 4-vinylbenzyltrimethylammonium chloride (VBA), was employed in the dispersion polymerization of S. VBA could copolymerize with S to form cationic particles, as a result, an anionic PAA could be adsorbed onto the particles by their electrostatic attraction.[9] In this dispersion polymerization system, there were some unique features such as using of stiff PAA as a steric stabilizer and adding a cationic comonomer to incorporate the PAA. To extend the application of this polymerization method for other monomers, we attempted to use methacrylic acid esters which were studied extensively in dispersion polymerization. In this article, we describe the dispersion polymerizations of *t*-butyl methacrylate (BMA) and methyl methacrylate (MMA) stabilized by the addition of a poly(amic acid) and the preparation of poly-(methacrylic acid ester)-PI particles by dehydration of PAA on the particles. Our synthetic procedure is shown in Scheme 1.

## EXPERIMENTAL

Measurements

Diameter of polymer particle was determined by a scanning electron microscope (JEOL JSM-588 scanning microscope). Thermogravimetry (TGA) was performed with ULVAC TGD-9600 at a heating rate of 10 °C/min in argon.

Materials

MMA, BMA, and 2-diethylaminoethyl methacrylate(ME) were washed with aqueous NaOH and distilled under reduced pressure. Poly(amic acid)s (**2a-c**) were prepared by the conventional ring-opening polyaddition of aromatic tetracarboxylic dianhydrides with aromatic diamines (Scheme 2, 3).[12,13] Their inherent viscosities in *N,N*-dimethylacetamide (DMAc) at 30 °C were summarized in Table I. 4-Vinylbenzyl-trimethylammonium chloride (VBA) was synthesized by the

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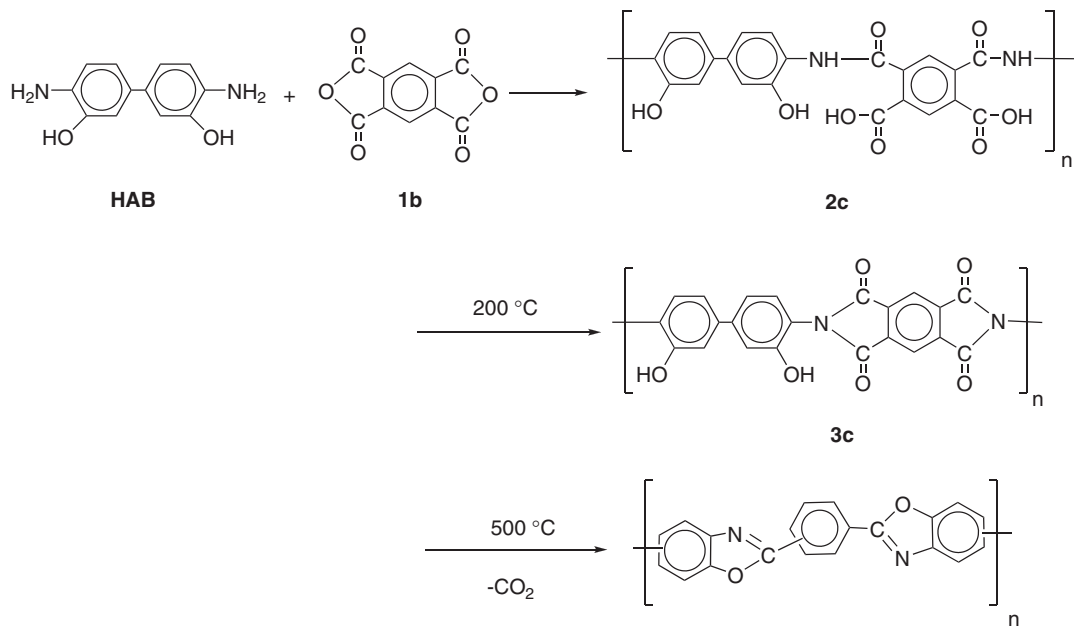*To whom correspondence should be addressed (Fax: +81-157-26-4973, E-mail: watash@mail.kitami-it.ac.jp).
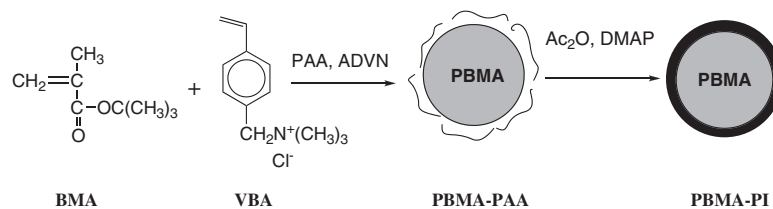
Scheme 1.
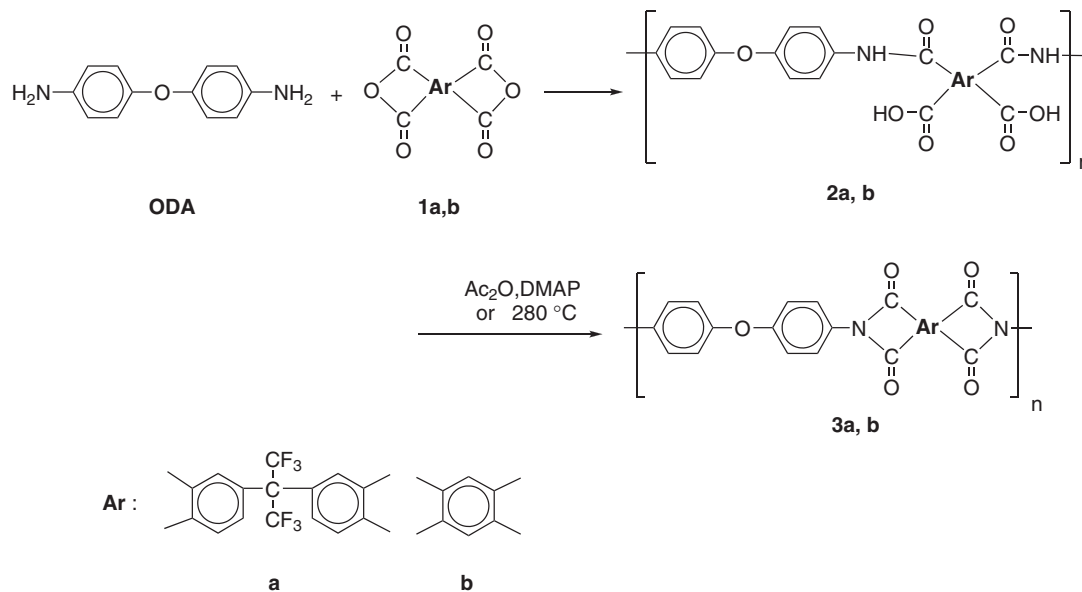
Scheme 2.

Scheme 3.

Table I. Synthesis of poly(amic acid)[a]

PAA	Viscosity[b] (dL/g)
2a	0.76
2b	0.81
2c[c]	1.63

[a]Aromatic diamines (10 mmol) and tetracarboxylic dianhydrides **1a-1b** (10 mmol) were polymerized in 25 mL of DMAc at 12 °C for 1.5 h and at room temperature for 1 h. [b]Inherent viscosity of **2a-2c** was measured in 0.5 g/dL of DMAc solution at 30 °C. [c]HAB (5.60 mmol) and **1b** (5.60 mmol) were polymerized in 100 mL of DMAc at room temperature for 10 h.

reaction of 4-vinylbenzyl chloride with trimethylamine[14] and recrystallized from a mixture of acetonitrile and acetone (v/v = 1/1). Other reagents were obtained commercially and used as received.

Dispersion Polymerization

Typical dispersion polymerization was conducted as follows. PAA **2a** (0.16 g; monomer unit: 0.25 mmol), VBA (0.106 g; 0.50 mmol), and potassium carbonate (53 mg; 0.38 mmol) were dissolved in 100 mL of ethanol-water (65/35 = v/v). Into the solution, BMA (8.0 g; 56 mmol) and 2,2′-azobis(2,4-dimethylvaleronitrile) (ADVN) (0.12 g; 0.50 mmol) were added. The mixture was purged with nitrogen and stirred at 46 °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 a mixture of ethanol and water (v/v = 65/35) for three times.

Fluorine Content of the Particles

To determine the incorporation ratio of **2a** into the particles, the fluorine content of the particles was measured by the lanthanum alizarin complexone method as described in ref. 15. Lyophilized polymer (10 mg) wrapped with filter paper (2 cm × 2 cm) was completely subjected to combustion under oxygen atmosphere in a combustion flask containing deionized water (20 mL). The evolved fluorine was absorbed into the water. Into the fluorine anion solution (1.6 mL), 1 mL of 5% aqueous alfusone® solution (DOJINDO), 0.4 mL of 1.0 M acetate buffer (pH 5.0), 2 mL of acetone, and 5 mL of deionized water were added and the solution was allowed to stand at room temperature for 1 h. The absorption of solution was measured at 610 nm.

Chemical Imidization of PAA on the Polymer Particle

Lyophilized polymer particles (1.0 g) were suspended in a solution of 2.0 g of 4-(dimethylamino) pyridine (DMAP) in 15 mL of acetic anhydride (Ac$_2$O) and stirred at room temperature for 1 d. The suspension was poured into 50 mL of water and the particles were centrifuged with a mixture of ethanol and water (v/v = 65/35) twice, and dried under reduced pressure. PBMA-PI particles were recovered quantitatively (98%).

To separate the PI shell, the resulting particles were suspended in 50 mL of ethanol and stirred at 40 °C for 24 h and centrifuged with ethanol twice.

Table II. Dispersion polymerization of MMA using poly(amic acid) **2a** as a stabilizer[a]

Run No.	PAA	Comonomer	H$_2$O/MeOH (mL/mL)	Yield (%)	Incorporated **2a**[b] (%)
1	0.50	VBA	15/60	0	—
2	0.25	VBA	15/60	0	—
3	0.25	VBA	30/70	0	—
4	0.50	ME	15/60	77	9
5	0.25	ME	15/60	86	24
6	0.50	MEA	15/60	85	15
7	0.50	MEA	30/70	68	17
8	0.25	MEA	30/70	93	8

[a]MMA: 80 mmol, ADVN: 0.50 mmol, [**2a**]/[comonomer]/[K$_2$CO$_3$] = 1/2.0/1.5 46 °C, 24 h, 120 rpm. [b]Ratio of incorporated **2a** determined by fluorine content of the particle.

RESULTS AND DISCUSSION

Dispersion Polymerization of Methyl Methacrylate (MMA)

The dispersion polymerization of methyl methacrylate was conducted using PAA **2a** as a steric stabilizer in aqueous methanol medium. In the previous study, using of a cationic comonomer (VBA) in the dispersion polymerization of styrene afforded the particles incorporated with PAA effectively by their electrostatic attraction.[9] Thus some cationic comonomers were employed in the polymerization (Table II). When VBA was used as a comonomer, all polymers were coagulated in any medium composition (run nos. 1–3). When methacrylates having tertiary-amine (ME) or quaternary ammonium chloride, [2-(methacryloyloxy)ethyl]trimethylammonium chloride (MEA) were used as a cationic comonomer, the particles were obtained in high yields. However PAA was not incorporated into the particles effectively. In the previous reports, only 18% of **2a** were incorporated into the particles obtained by the dispersion polymerization of styrene and MEA.[9] Since MEA and ME were too hydrophilic for the dispersion polymerization, they were polymerized mainly in solution, and might not be incorporated into the particles.

Dispersion Polymerization of *t*-Butyl Methacrylate (BMA)

Next *t*-butyl methacrylate (BMA) was employed in place of MMA, because BMA is more hydrophobic and PBMA has a high grass transition temperature (118 °C), which is necessary when PAA on the particles was thermally converted into polyimide to keep in spherical shape. The dispersion polymerization using VBA was performed in an aqueous ethanol medium (Table III). Particles stability was strongly affected by the solvent composition. When volume of water between 30 and 45 mL was used, monodisperse particles were yielded quantitatively (run nos. 10–13). However, the polymerization using a small amount of water (25 mL) induce the coagulation of particles (run no. 9). In case of use of styrene as a monomer, the optimum volume of water was 20 mL.[9] Since BMA was more hydrophilic than styrene, more water was necessary to get monodisperse particles. Furthermore MMA might be too hydrophilic to get the particles using **2a** and VBA (run nos. 1–3). Although particles size is generally influenced with

Table III. Dispersion polymerization of BMA using poly(amic acid) **2a** as a stabilizer[a]

Run No.	2a (mmol)	VBA (mmol)	H$_2$O (mL)	Yield (%)	D_n (μm)	D_w/D_n	Incorporated 2a[b] (%)
9	0.25	0.50	25	0[c]	—	—	—
10	0.25	0.50	30	86	0.50	1.02	97
11	0.25	0.50	35	92	0.50	1.01	92
12	0.25	0.50	40	92	0.41	1.02	92
13	0.25	0.50	45	94	0.55	1.02	94
14	0.25	0	35	87	0.52	1.02	15
15	0.25	0.13	35	87	0.53	1.01	29
16	0.25	0.25	35	96	0.51	1.01	49
17	0.25	0.38	35	95	0.55	1.01	61
18	0.25	0.75	35	0[c]	—	—	—
19	0.13	0.25	40	95	0.49	1.02	72
20	0.25	0.50	40	92	0.41	1.02	92
21	0.50	1.00	40	93	0.43	1.01	85
22	0.75	1.50	40	93	0.43	1.02	100
23	1.00	2.00	100[d]	78	0.32	1.02	92

[a]BMA: 56 mmol, ADVN: 0.50 mmol, **2a**/K$_2$CO$_3$ = 1/1.5. Solvent (H$_2$O + EtOH) = 100 mL, 46 °C, 24 h. [b]The incorporated **2a** determined by fluorine content of the particle. [c]All polymer was coagulated during polymerization. [d]EtOH (100 mL) and H$_2$O (100 mL) were used as a polymerization medium.

solvent composition, these polymerizations afforded the particles with diameters of about 0.5 μm using any solvent compositions.

The dispersion polymerization changing amount of VBA was carried out. All of the polymerization except an excess amount of VBA (run no. 18) afforded monodisperse polymer particles quantitatively. To estimate the amount of **2a** incorporated into the particles, the fluorine contents of particles were determined. The particles were completely subjected to combustion and the evolved fluorine anion was detected by the lanthanum alizarin complexone reagent.[15] In the absence of VBA at the polymerization, only 15% of **2a** was incorporated into the particles. As an amount of VBA was increased, the larger amount of **2a** was incorporated into the particles. When equimolar amount of VBA to the carboxylate of **2a** was used in the polymerization, more than 90% of **2a** were incorporated into the particles (run nos. 10–13). Cationic VBA was copolymerized with BMA to yield cationic particles and anionic **2a** was immobilized into the particles by their electrostatic attraction. Dispersion polymerizations changing the amounts of **2a** were performed. By using equimolar amount of VBA against the carboxylate, more than 70% of **2a** were incorporated into the particles. Although the polymerization using 1.00 mmol of **2a** afforded the small particles, the particle size was hardly changed by increasing **2a**. Therefore, the polymer particles containing various amounts of **2a** were obtained by the dispersion polymerization.

Based on the optimum polymerization condition using **2a**, other PAAs (**2b** and **2c**) were employed as a stabilizer (Table IV). In case of **2a**, 35 mL of water was the optimum solvent composition. However, the particles using the other PAAs tended to be coagulated during the polymerization in the same solvent composition. Especially the polymerization using **2c** resulted in the coagulation of all the polymer particles (run no. 27). As volume of water increased to 40–45 mL, the polymer particles having **2b** or **2c** were obtained in quantitative

Table IV. Dispersion polymerization of BMA in the presence of polyamic acid **2b-2c**[a]

Run No.	PAA (mmol)	H$_2$O (mL)	Yield (%)	D_n (μm)	D_w/D_n	Incorporated PAA (%)[b]
24	**2b**: 0.25	40	92	0.58	1.02	—[c]
25	**2b**: 0.50	40	89	0.70	1.02	—[c]
26	**2b**: 0.75	40	88	0.64	1.05	—[c]
27	**2c**: 0.50	35	0[d]	—[c]	—[c]	—[c]
28	**2c**: 0.50	40	92	0.70	1.03	98
29	**2c**: 0.50	45	92	0.67	1.01	95
30	**2c**: 0.75	45	91	0.53	1.02	97
31	**2c**: 1.00	45	95	0.65	1.06	96
32	**2c**: 1.25	45	0[d]	—[c]	—[c]	—[c]
33	**2c**: 0.50	50	84	0.39–12.4	—[c]	90

[a]BMA: 56 mmol, ADVN: 0.50 mmol, solvent (H$_2$O + EtOH) = 100 mL, **2b**/VBA/K$_2$CO$_3$ = 1/2/1.5, **2c**/VBA/K$_2$CO$_3$ = 1/2/3. Polymerization was conducted at 46 °C for 24 h. [b]The incorporated PAA determined by the absorbance of supernatant after centrifugation at 300 nm. [c]Not analyzed. [d]All polymer was coagulated during polymerization.

yields. Since the solubilities of **2b-c** were different from that of **2a**, the optimum solvent compositions were also changed. The amount of **2c** incorporated into the particles was measured by the absorption of supernatant after centrifugation and more than 90% of **2c** were found to be incorporated into the particles.

The imidization of PAA on the polymer particle (run no. 11) was carried out by means of Ac$_2$O and DMAP at room temperature for 1 d (Scheme 2). The fluorine content of particles was not changed after the imidization (before 173 μmol/g, after 164 μmol/g), meaning that no PI was desorbed from the particles during the imidization. To find the extent of imidization using IR spectroscopy, PBMA of the particles was removed by washing with ethanol. The IR spectra of the particles before and after treatment of ethanol are shown in Figure 1. Although characteristic absorption for PBMA at 1733, 1157 and 851 cm^{-1} remained after washing with ethanol, IR profile of the PI particles was almost identical with one of
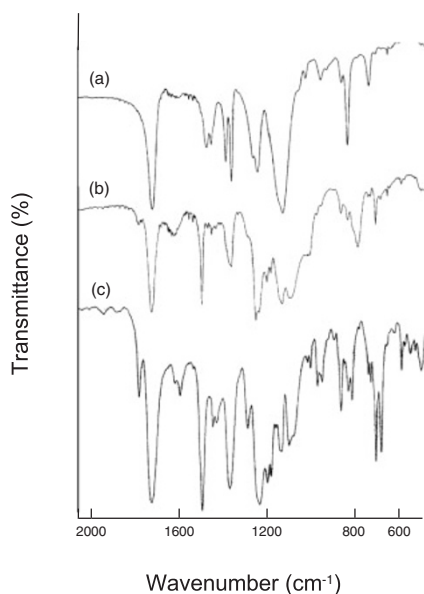
Figure 1. IR spectra of (a) PBMA-PI particles, (b) PBMA-PI particles washed with ethanol, and (c) PI film prepared with conventional thermally dehydration of **2a**.
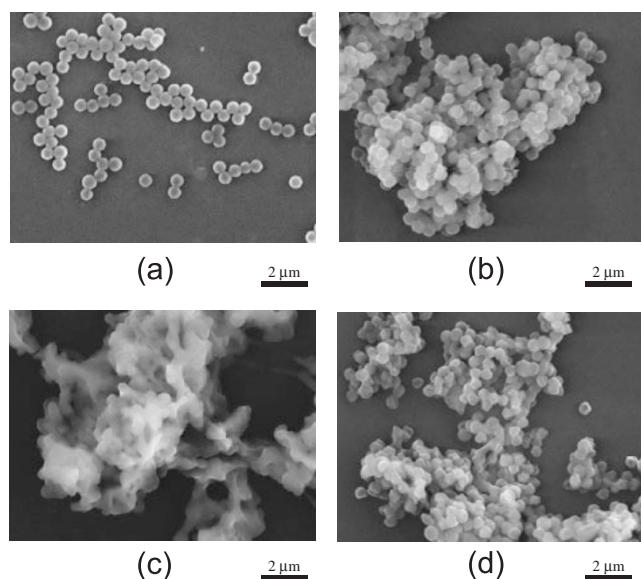

Figure 2. Scanning electron micrographs of (a) PBMA-PAA particles (run no. 11; see Table II). (b) PBMA-PI particles prepared by chemical imidization. (c) PBMA-PI particles prepared by chemical imidization after thermal treatment at 280 °C for 2 h. (d) PBMA-PAA particles after thermal treatment at 60 °C, 80 °C, 100 °C, 150 °C, 250 °C, and 280 °C for 30 min each *in vacuo*.

aromatic PI film prepared by a conventional thermal-imidization of PAA **2a**,[9] indicating the PAA was converted into PI. SEM photographs of particles were shown in Figure 2. After the chemical imidization, the particle size was not changed, however, the particles were likely to be fused together, and some gel like materials existed on the surface (Figure 2b). When the PBMA-PI particles were subjected to the thermal treatment at 280 °C for 2 h *in vacuo*, some of them were still kept in their spherical shapes (Figure 2c). The PBMA-PAA
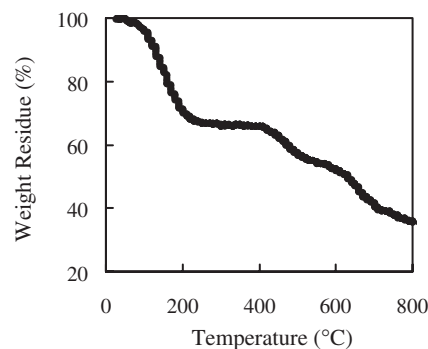

Figure 3. TGA thermogram of PAA **2c**.

particles (run no. 11) were subjected to the subsequent heating at 60 °C, 80 °C, 100 °C, 150 °C, 250 °C, and 280 °C for 30 min each *in vacuo*. PBMA particles without PAA were not kept in spherical shape, because the thermal treatment exceeded the T_g of PBMA (118 °C). On the other hand, the particles having PAA **2a** were maintained in spherical shape even after the thermal treatment and it seemed likely that they were more thermally stable than the polystyrene-poly(amic acid) particles as previously reported[9] (Figure 2d). The PBMA is changed into poly(methacrylic anhydride) by thermal treatment between 180 and 200 °C with the elimination of isobutylene and water. This anhydride might promote the cyclodehydration of PAA to yield polyimide (PI) at low temperature. Consequently, PI **3a** (T_g: 301 °C) shell protected the particles to keep in the spherical shape even at high temperature.

The poly(amic acid) having dihydroxy groups **2c** were converted to polyimide by thermal treatment at 200 °C, and that when temperature increased to 500 °C, polybenzoxazole was obtained with the elimination of carbon dioxide (Scheme 3).[13,16] The thermogravity analysis of **2c** was shown in Figure 3. The mass decrease between 100 °C and 200 °C attributed to water at formation of imide rings and solvent swelling into polymer. And that mass decrease between 400 °C and 500 °C was derived to decarboxylation, resulting in the formation of benzoxazole rings.

The SEM photographs of particles after thermal treatment at 200 °C and 500 °C in the presence of a small amount of *p*-toluene sulfonic acid were shown in Figure 4. The particles treated at 200 °C without *p*-toluene sulfonic acid did not maintain in spherical shape. Adding a small amount of *p*-toluene sulfonic acid, the particles were kept in spherical shape (Figure 4b). *p*-Toluene sulfonic acid promoted the formation of poly(methacrylic anhydride) as a acid catalyst, the anhydride converted the PAA into PI at the lower temperature. As a result, the PI shell might keep in spherical shape due to its high thermal stability. Since the isobutylene and water were eliminated from the PBMA by thermal treatment between 180 and 200 °C, the particles (diameter: 0.50 μm) became smaller than the original ones (diameter: 0.67 μm). The particles shape started to change from 250 °C. Since most of PBMA was decomposed at 500 °C, the particles were did not keep in the spherical shape.
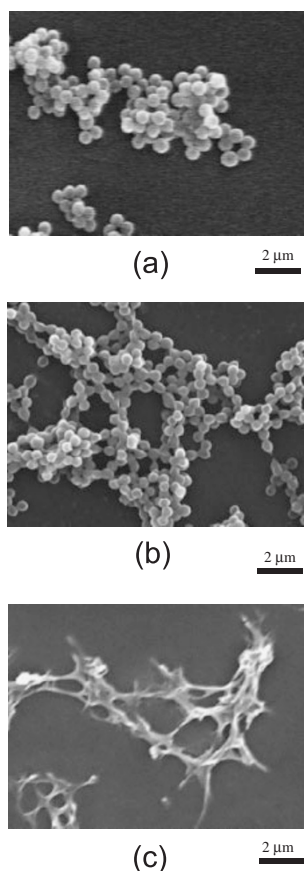
(a)   2 μm

(b)   2 μm

(c)   2 μm

Figure 4. Scanning electron micrographs of (a) PBMA-PAA particles (run no. 29; see Table IV) (b) PBMA-PAA particles after thermal treatment at 100 °C, 150 °C, and 200 °C for 30 min each *in vacuo* in the presence of *p*-toluene sulfonic acid. (c) PBMA-PAA particles after thermal treatment up to 500 °C in the presence of *p*-toluene sulfonic acid.

In conclusion, PBMA-PAA particles were prepared by the dispersion polymerization of PBMA and VBA using poly(amic acid)s as stabilizers in an aqueous ethanol. The monodisperse particles were obtained in high yield using the optimum composition of solvent mixture depending on the PAA structure. By using a cationic comonomer (VBA), PAA was incorporated quantitatively into the particles. The imidization of PAA on the particles proceeded with acetic anhydride and 4-(dimethylamino)pyridine to form PBMA-PI particles. The PBMA-PI particles were maintained in spherical shape by the thermal treatment up to 280 °C.

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