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Microsphere synthesis by emulsion copolymerization of methyl methacrylate with poly(acrylic acid) macromonomers

Koji Ishizu*, Masao Yamashita and Ayako Ichimura
Department of Polymer Science, Tokyo Institute of Technology 2-12, Ookayama, Meguro-ku, Tokyo 152, Japan

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Vinylbenzyl-terminated poly(acrylic acid) (PAA) macromonomers were prepared by the use of a free radical polymerization technique. The polymer microspheres were synthesized by emulsion copolymerization of methyl methacrylate (MMA) with PAA macromonomers in an aqueous or aqueous ethanol solution. In this copolymerization system, the macromonomer acted not only as a comonomer but also as a stabilizer. The diameter of the polymer microspheres decreased as the water fraction in the mixed solvent, macromonomer concentration, and macromonomer molecular weight increased. It was remarkable that the diameter of the polymer microspheres depended strongly on the pH in the solvent medium. © 1997 Elsevier Science Ltd.

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INTRODUCTION

There have been several reports describing the preparation of monodisperse polymer microspheres. These studies have been almost completely concerned with synthetic methods involving emulsion and soap-free polymerizations. In emulsion polymerization, the emulsifier stabilizes the water-insoluble monomer particles. For example, micrometre-size monodisperse polystyrene particles were prepared by emulsion polymerization of styrene in the presence of poly(acrylic acid) (PAA) as a stabilizer[1].

In previous work[2], we prepared polymer microspheres by the emulsion copolymerization of methyl methacrylate (MMA) with poly(methacrylic acid) (PMA) macromonomers in aqueous ethanol solution. As a result, the particle size (submicrometre to micrometre range) and size distribution could be controlled by selecting the solvent composition, and the feed amount and molecular weight of the PMA macromonomers. However, the particle diameter did not depend strongly on the pH in the solvent medium. PAA macromonomer as an emulsifier is expected to increase the radius of gyration compared to that of PMA macromonomer, as the pH in the medium increases due to the high degree of dissociation of carboxyl groups.

Anionic living technique has already provided a well-defined PAA macromonomer[3,4]. On the other hand, poly(t-butyl methacrylate)[5] (PBM), polystyrene[6], and poly(vinyl acetate)[7] macromonomers were prepared via free radical polymerization technique as reported by the authors.

In the present article, polymer microspheres were synthesized by emulsion copolymerization of MMA with PAA macromonomers in an aqueous or aqueous ethanol solution. We studied the control of particle size and particle size distribution as a function of the solvent composition, the feed amount and molecular weight of PAA macromonomers, and the pH in the medium.

EXPERIMENTAL

Macromonomer synthesis and characterization

The synthetic method of poly(t-butyl acrylate) (PBA) macromonomer was analogous to that of the PBM macromonomer[5]. The details concerning the synthesis and characterization of macromonomers have been given in the above reference. In brief, vinylbenzyl-terminated PBA macromonomers were synthesized by the radical polymerization of t-butyl acrylate initiated by the functional initiator: 2,2′-azobis (*N*,*N*′-dimethyleneisobutyramidine) in the presence of allylmalonic acid diethylester as a degradative chain transfer agent, followed by an end-capping reaction with *p*-chloromethylstyrene (CMS). Under these reaction conditions, the polymerization of b-butyl acrylate was regarded to proceed entirely via the unimolecular termination mechanism. The allyl compound led to degradative chain transfer, because the resulting allyl radical was quite stable. The PMA prepolymer was fractionated stepwisely by the methanol–water system. Subsequently, PBA macromonomers were derived from the hydrolysis of corresponding PMA macromonomers using formic acid[8]. After the hydrolysis, a moiety of the tert-butyl groups ($\delta = 2.1$ ppm and 1360 cm^{-1}) had disappeared entirely in the ^{1}H n.m.r. and *FT*i.r. spectra, respectively. Moreover, we have confirmed the existence of the vinylbenzyl groups (characteristic absorption at 292 nm) at the terminal end of the PAA macromonomer from u.v. spectra. *Table 1* lists the

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* To whom correspondence should be addressed

Table 1 Characteristics of PAA macromonomers

Code	$10^{-4}\,\bar{M}_n{}^a$	$\bar{M}_w/\bar{M}_n{}^b$	Functionality^c (number/molecule)
PAA-M1	1.5	1.35	1.30
PAA-M2	2.5	1.48	1.86
PAA-M3	7.0	1.50	1.92

^{a} Estimated from the $\bar{M}_n$ of PBA macromonomers determined by g.p.c. (Tosoh high-speed liquid chromatograph HLC-8020 with tetrahydrofuran as eluent at 38°C, using a TSK gel GMH$_{XL}$ column and a flow rate of $1.0\,\mathrm{ml\,min^{-1}}$) using universal calibration
^{b} Determined by g.p.c. distribution functions of PBM macromonomers
^{c} Determined by u.v. spectra at 292 nm in methanol (using *p*-methylstyrene as a model compound)

characteristics of PAA macromonomers. It is noticed that the functionality of PAA macromonomers is more than unity for all samples. This result indicates that the CMS reacted not only with –NH– sites (condensation) but also with –N= sites (quaternization) of the terminal imidazoline group.

Copolymerizations of MMA with PAA macromonomers

Copolymerizations were carried out at 60°C under a nitrogen atmosphere in a glass vessel. A mixture of the PAA macromonomer, MMA, and 2,2′-azobisisobutyronitrile (AIBN) were dissolved in water or the mixed solvent of water and ethanol. The mixture was maintained in a thermostatted bath at 60°C with shaking (150 shakes $\mathrm{min^{-1}}$) for 7 h. The resulting products were dialysed through a cellulose tube for a period of a week. The polymer microspheres were then separated by centrifugation.

Measurements

The morphology and particle diameter (D_n) of the polymer microspheres were investigated by the use of a JEOL JSM-T220 SEM with a tilt angle of 30°. The particle size distribution was determined from the micrographs that were obtained.

RESULTS AND DISCUSSION

We first carried out the preliminary experiment concerning the relationship between conversion and time for emulsion copolymerizations under the following conditions: MMA = 0.5 ml, PAA-M1 = 0.023 g (5 wt% based on MMA), AIBN = 9.4 mg (2 wt% based on total monomer, and water/ethanol = 5/5 ($\mathrm{ml\,ml^{-1}}$). The polymerization rate increased during the time in which the conversion reached a plateau value (*ca.* 90%), i.e. after 6 h. Therefore, we set 7 h as the polymerization time in the following experiments.

We then examined the effect of the solvent composition on particle size. These emulsion copolymerizations (P11–P14) were carried out at 60°C for 7 h under the following conditions: MMA = 0.5 ml, macromonomer PAA-M2 = 5 wt% (based on MMA), and AIBN = 2 wt% (based on total monomer), while varying the solvent composition (water/ethanol = 3/7 ~ 10/0 (vol/vol): P11, water/ethanol = 3/7 (v/v); P12, 5/5 (v/v); P13, 7/3 (v/v); P14, 10/0 (v/v). Typical SEM micrographs of the polymerization products are shown in *Figure 1*, where micrographs (a), (b) and (c) indicate the morphological results from experiments P12, P13 and P14, respectively. All of the products obtained are spherical particles of PMMA. It is found from these micrographs that the particle size distribution of these microspheres is very narrow.

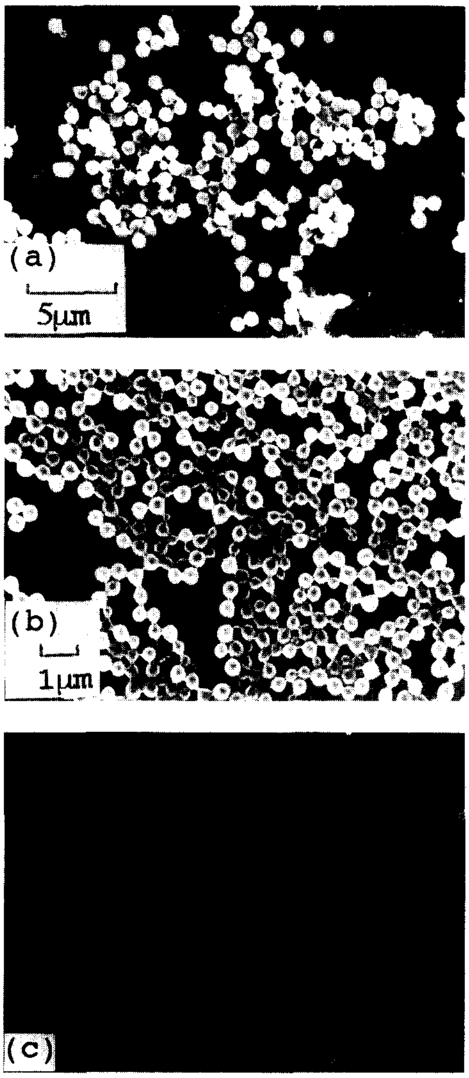

Figure 1 SEM micrographs of PMMA microspheres: (a) P12; (b) P13; (c) P14

Figure 2 shows the effects of the solvent composition on the particle average-diameters ($\bar{D}_n$) and particle size distributions ($\bar{D}_w/\bar{D}_n$). It is found from these plots that the particle diameter decreases with an increase of water content in the medium (1.62–0.17 μm). Moreover, the particle size distribution is very narrow ($\bar{D}_w/\bar{D}_n = 1.01$ for all experiments). Thus, we observed a tendency in which the more hydrophilic the media became, the smaller the particle size. This may be because the critical degree of polymerization, i.e. the level at which the oligomers form nuclei, decreases in the more hydrophilic solvent, and thus the number of nuclei increases. However, Okubo and coworkers[1] reported the different results for polystyrene microsphere formation using PAA as a stabilizer in ethanol–water medium. According to their results, the average-diameter decreased with an increase of water content, to minimum in *ca.* 30 vol%. Above the water content of 35 vol%, the distribution of particle size was broad though the size became large. In our polymerizaton systems, the macromonomer acted not only as a stabilizer but also as a comonomer. It seems that hydrophobic vinylbenzyl groups at the terminal end

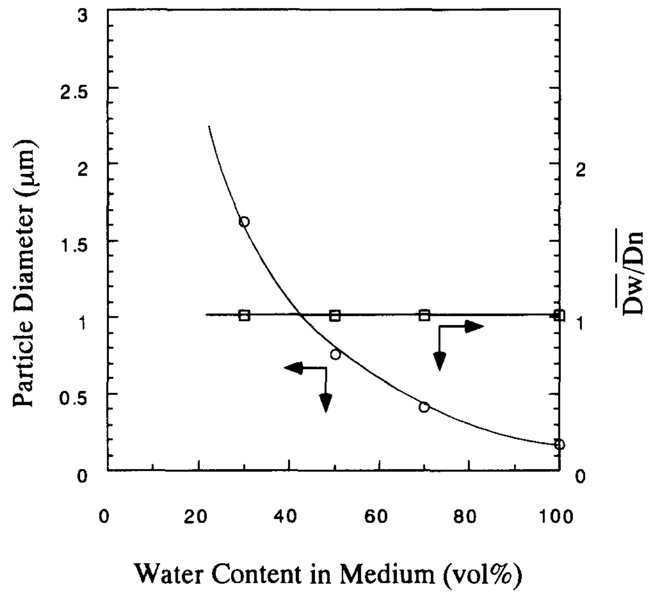

Figure 2 Effect of solvent composition on particle diameter and particle size distribution

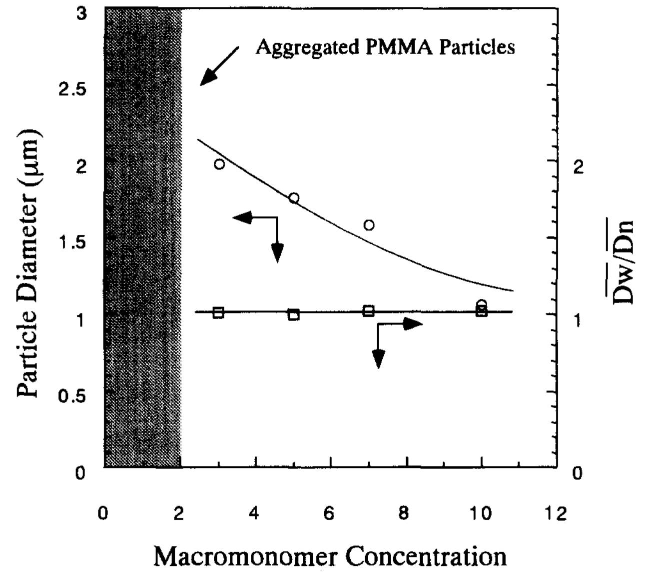

Figure 3 Effect of concentration of the macromonomer PAA-M1 on particle diameter and particle size distribution

of PAA macromonomer work effectively to form micelles in the solvent medium.

Figure 3 shows the effect of the concentration of macromonomer PAA-M1 on the particle diameter and size distribution under the following conditions: MMA = 0.5 ml, PAA-M1 = 5 wt% based on MMA, AIBN = 2 wt% based on total monomer, and water/ethanol = 5/5 (ml ml^{-1}). The micrometre-size polymer microspheres that are produced have a narrow size distribution ($\bar{D}_w/\bar{D}_n < 1.02$). The particle diameter decreases gradually with an increase of macromonomer concentration. For this solvent composition, the macromonomer PAA-M1 is able to stabilize the PMMA particles over the concentration range from 3.0 to 10 wt%. However, the polymerization product obtained from the system, macromonomer concentration = less than *ca.* 2.0 wt%, showed a morphology with aggregated PMMA particles.

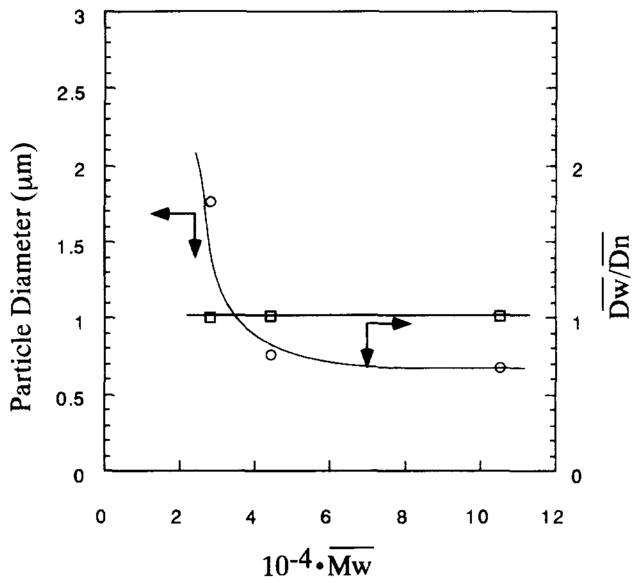

Figure 4 Effect of molecular weight of macromonomers on particle diameter and particle size distribution

Table 2 Results obtained for particle diameters, particle size distributions and grafting number of macromonomer for systems P51–P54 with varying macromonomer concentration[a]

System	Concentration of macromonomer (wt%)	$\bar{D}_n$[b] (μm)	$\bar{D}_w/\bar{D}_n$[b]	Grafting number of macromonomer (f) (number/particle)
P51	0.3	0.20	1.01	504
P52	0.5	0.16	1.01	511
P53	1.0	0.17	1.01	1227
P54	5.0	0.15	1.01	4213

[a] Polymerized in an aqueous solution at 60°C under conditions where PAA-M1 = 0.3–5.0 wt% (based on MMA) and AIBN = 2 wt% (based on total monomer)

[b] Determined from SEM

Figure 4 shows the effect of the molecular weight of macromonomers on the particle diameter and size distribution under the following conditions: MMA = 0.5 ml, PAA-M = 5 wt% based on MMA, AIBN = 2 wt% based on total monomer, and water/ethanol = 5/5 (ml ml^{-1}). The particle diameters decrease rapidly until the macromonomer molecular weight of 4 × 10^4 and are almost constant ($\bar{D}_n$ = ca. 0.7 μm) beyond the molecular weight of 6 × 10^4. The microspheres have a narrow size distribution ($\bar{D}_w/\bar{D}_n < 1.01$), regardless of any variation in molecular weight of macromonomers.

Table 2 lists the results of emulsion copolymerizations P51–P54, varying the macromonomer concentration in an aqueous solution under the following conditions: MMA = 0.5 ml, PAA-M1 = 0.1–5.0 wt% based on MMA, AIBN = 2 wt% based on total monomer. The particle diameter decreases gradually until the macromonomer concentration of 0.5 wt% and were almost constant ($\bar{D}_n$ = *ca.* 0.16 μm) beyond this macromonomer concentration. Moreoever, the microspheres have a narrow size distribution ($\bar{D}_w/\bar{D}_n = 1.01$) for all of the experimental series. It was mentioned that more than 3.0 wt% of PAA-M1 macromonomer was necessary to produce monodisperse polymer particles in an aqueous ethanol solution (see *Figure 3*). On the other hand, such polymer particles are produced using lower concentration (0.3 wt%) of PAA-M1 macromonomer in the present

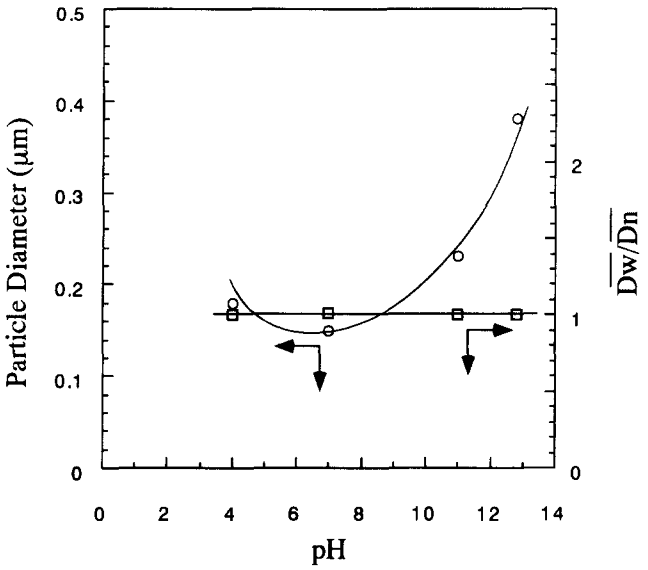

Figure 5 pH effect of the solvent medium on particle diameter and particle size distribution

system, indicating that PAA macromonomer is a very efficient stabilizer for emulsion polymerization of MMA in an aqueous solution. In these experimental series, we calculated the grafting number (f) of PAA-M1 macromonomer on a PMMA particle molecule. The total weight of PMMA particles produced is given by

$$W = W_0\theta = (4/3)\pi R^3 \rho N \qquad (1)$$

where W and W_0 are the total weight of PMMA particles and the feed weight of MMA monomer, respectively. θ is the conversion of MMA monomer. R, ρ and N are the radius, density ($1.188\,\mathrm{g\,cm^{-3}}$)[9] and the total number of PMMA particles, respectively. So, the grafting number of macromonomer (f) on a PMMA particle molecule is given by

$$f = W_M N_A/(N M_n) \qquad (2)$$

where M_n and W_M are the molecular weight and the feed weight of the macromonomer, respectively. N_A is the Avogadro number ($6.023 \times 10^{23}\,\mathrm{mol^{-1}}$). The calculated f values are also listed in *Table 2*, assuming that the conversion (θ) reaches 100% for all experimental series. Even at 0.3 wt% of macromonomer concentration, PAA-M1 macromonomers are grafted with the number of 504 on a PMMA particle molecule. Therefore, PMMA particles seem to have the structure such as crew-cut type microspheres in solution.

It is expected from the above results that the pH of the solvent medium drastically affects the particle size of microspheres. *Figure 5* shows the effect of pH of the solvent medium on particle diameter and size distribution in an aqueous solution under the following conditions: MMA = 0.5 ml, PAA-M1 = 5.0 wt% based on MMA, AIBN = 2 wt% based on total monomer. The diameter of the microspheres decreases gradually with increasing pH until pH = *ca.* 8. Beyond this pH region, inversely, the particle diameter increases with increasing pH. PAA macromonomer as an emulsifier is an anionic polyelectrolyte. In general, the radius of gyration of PAA increases as the pH in water increases due to the high degree of dissociation of carboxyl groups. That is to say, high expansion of macroions, such as PAA macromonomer is favourable to the steric satability of PMMA microspheres formed by copolymerization. However, it is also well known that the viscosity of PAA aqueous solution exhibiting high neutral decreases suddenly due to analogous effect such as thixotropy. In such pH region, the radius of gyration of PAA macromonomer decreases due to a shielding effect for the fixed charges[10,11]. The interaction of counterions with the macroion modifies the electrostatic forces between fixed charges. Therefore, PMMA microspheres obtained in this work are expected to possess interesting solution properties such as pH-responsive character.

REFERENCES

1. Okubo, M., Ikegami, K. and Yamamoto, Y., *Colloid Polym. Sci.*, 1989, **267**, 193.
2. Ishizu, K. and Tahara, N., *Polymer*, 1996, **37**, 2853.
3. Antolin, K., Lamps, J.-P., Rempp, P. and Gnanou, Y., *Polymer*, 1990, **31**, 967.
4. Varshney, S. K., Bayard, P., Jacobs, C., Jerome, R., Fayt, R. and Teyssie, P., *Macromolecules*, 1992, **25**, 5578.
5. Ishizu, K. and Mitsutani, K., *J. Polym. Sci. Polym. Lett. Edn*, 1988, **26**, 511.
6. Ishizu, K., Ono, T., Fukutomi, T. and Shiraki, K., *J. Polym. Sci. Polym. Lett. Edn*, 1987, **25**, 131.
7. Fukutomi, T., Ishizu, K. and Shiraki, K., *J. Polym. Sci. Polym. Lett. Edn*, 1987, **25**, 175.
8. Newkome, G. R., Behera, R. K., Moorefield, C. N. and Baker, G. R., *J. Org. Chem.* 1991, **56**, 7162.
9. Gall, W. G. and McCrum, N. G., *J. Polym. Sci.*, 1961, **50**, 489.
10. Huizenga, J. R., Grieger, P. F. and Wall, F. T., *J. Am. Chem. Soc.*, 1950, **72**, 2636.
11. Sakamoto, T. and Imahori, K., *Nippon Kagaku Kaishi*, 1962, **83**, 389.