

Microsphere Synthesis by Emulsion Copolymerizations of Styrene with Poly(Methacrylic Acid) Macromonomers

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ABSTRACT: The polymer microspheres were synthesized by emulsion copolymerizations of styrene with vinyl benzyl terminated poly(methacrylic acid) (PMA) macromonomers in an aqueous ethanol solution. In these copolymerization systems, the macromonomer acted not only as a comonomer but also as a stabilizer. The particle diameters obtained from the water-soluble initiator system showed smaller values than those obtained from the water-insoluble initiator system. These polymer microspheres had a very narrow particle-size distribution. The particle diameters depended strongly on the feed amount and molecular weight of PMA macromonomers, water fraction in the mixed solvent, and pH in the medium. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 85: 900–905, 2002

Key words: microsphere; macromonomer; copolymerization; stabilizer

INTRODUCTION

There have been several reports describing the preparation of monodisperse polymer microspheres. These studies were concerned with synthetic methods involving emulsion and soap-free polymerizations. In emulsion polymerization, the emulsifier stabilizes the water-insoluble monomer particles. More recently, there were several studies describing the synthesis of polymer microspheres by dispersion copolymerization using hydrophilic macromonomers such as poly(*N*-vinylpyrrolidone),^{1,2} poly(2-alkyl-2-oxazoline),^{3,4} and poly(ethylene oxide)^{2,5–7} instead of using a homopolymer as a stabilizer. The macromonomer that was used acted not only as a stabilizer but also as a comonomer.

In a previous work,⁸ we prepared polymer microspheres by dispersion copolymerization of methyl methacrylate (MMA) with vinyl benzyl terminated poly(methacrylic acid) (PMA) macromonomers in an aqueous ethanol solution. As a result, the particle size (submicrometer to micrometer range) and size distribution could be controlled by selecting the solvent composition and the feed amount and molecular weight of the PMA macromonomers.

In this article, polymer microspheres were synthesized by emulsion copolymerization of styrene with PMA macromonomers in an aqueous ethanol solution. We studied the control of particle size and particle-size distribution as functions of the initiator system, the solvent composition, the feed amount and molecular weight of PMA macromonomers, and the pH in the medium.

EXPERIMENTAL

Macromonomer Synthesis and Characterization

The well-defined vinyl benzyl terminated PMA macromonomers were derived from the hydrolysis of corresponding poly(*t*-butyl methacrylate) (PBMA) macromonomers. In short, the PBMA

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Table I Characteristics of Poly(Methacrylic Acid) Macromonomers

Code	$10^{-4} \bar{M}_n^a$	\bar{M}_w/\bar{M}_n^b	Functionality ^c
PMA1	0.75	1.02	0.95
PMA2	0.83	1.07	1.06
PMA3	2.14	1.003	0.99

^a Determined by universal calibration¹¹ ($\log[\eta]M$ versus elution volume) on gel permeation chromatography (GPC) for corresponding PBMA macromonomers.

^b Determined by GPC profiles of corresponding PBMA macromonomers.

^c Determined by ultraviolet (UV) spectra.

macromonomers were prepared by the coupling of living PBMA initiated by sodium triphenylmethane with *p*-chloromethylstyrene in tetrahydrofuran (THF) at -78°C . To obtain the PMA macromonomers, PBMA segments were hydrolyzed with formic acid.⁹ Details of the synthesis and characterization of such macromonomers have been given elsewhere.^{8,10} Table I lists the characteristics of PMA macromonomers.

Emulsion Copolymerizations

Copolymerizations were carried out at 80°C under a nitrogen atmosphere in a glass vessel. A mixture of the PMA macromonomer, styrene, and potassium persulfate ($\text{K}_2\text{S}_2\text{O}_8$) or 2,2'-azobisisobutyronitrile (AIBN) were dissolved in a mixed solvent of ethanol and water. The mixture was maintained in a thermostated bath at 80°C with shaking (150 shakes per min). After copolymerization, the resulting products were dialyzed through a cellulose tube for a period of 1 week. The polymer microspheres were then separated by centrifugation.

Measurements

The morphology and particle size of the polymer microspheres were investigated by the use of a JEOL JSM-T220 scanning electron microscope (SEM) with a tilt angle of 30° . The particle size and size distribution were determined by surveying 300 samples picked up from the photographs that were obtained.

RESULTS AND DISCUSSION

To determine the yield of polystyrene (PS) microspheres, we first examined the relationship between conversion and time. Two types of the dis-

persion/emulsion copolymerizations were carried out under the following conditions, varying the initiator systems: DP10: styrene, 0.5 mL; PMA1, 0.023 g (5 wt % based on styrene); AIBN, 9.2 mg (2 wt % based on total monomer); and ethanol/water, 7/3 (mL/mL); EP10: styrene, 0.5 mL; PMA1, 0.023 g; $\text{K}_2\text{S}_2\text{O}_8$, 9.2 mg; and ethanol/water = 7/3 (mL/mL). Figure 1 shows the time-conversion curve of the copolymerizations DP10 and EP10. In the dispersion copolymerization DP10, the polymerization rate increased during the time in which the conversion reached a plateau value ($\sim 80\%$) (i.e., after 8 h). At this time, the second addition of AIBN (9.2 mg) was performed in such a copolymerization system. As a result, the polymerization rate increased again and the conversion reached 100% after a total time of 20 h. On the other hand, in the emulsion copolymerization EP10, the polymerization rate increased gradually during the time in which the conversion reached 100% (i.e., after 24 h). Typical SEM photographs of the final polymerization products are shown in Figure 2, where photographs (a) and (b) indicate the morphological results of DP10 and EP10, respectively. All of the products obtained were spherical particles of PS.

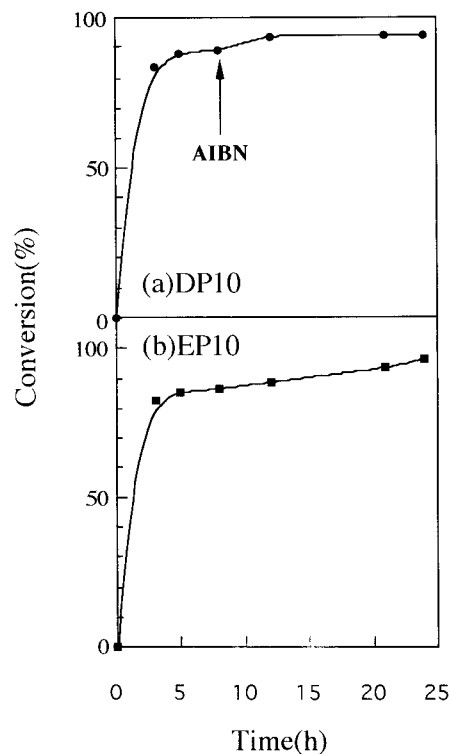


Figure 1 Time-conversion curves of dispersion/emulsion copolymerizations, varying initiator systems: (a) DP10, (b) EP10.

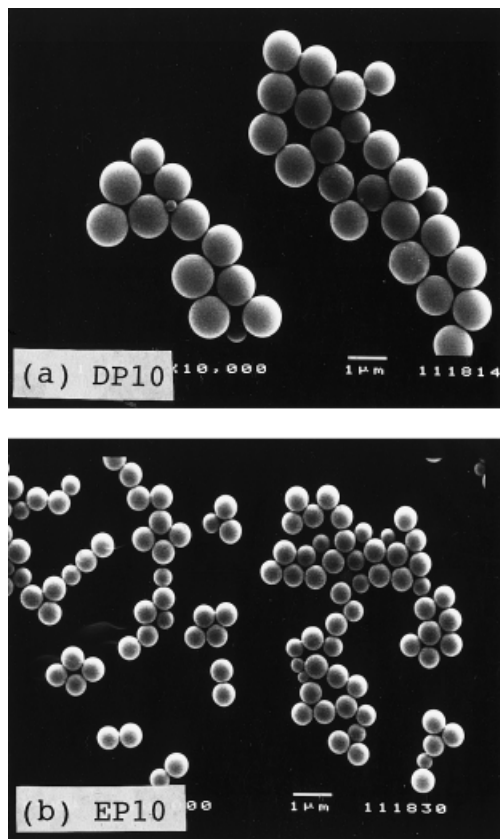


Figure 2 SEM photographs of final polymerization products: (a) DP10, (b) EP10.

It is found from these photographs that the particle size distribution of these microspheres is very narrow ($D_w/d_n = \sim 1.006$). Figure 3 shows the time dependence of particle size and size distribution for DP10 and EP10 series. The particle sizes of PS microspheres increase gradually for both copolymerization systems. It is noticed also that the particle sizes for EP10 are smaller than those for DP10.

The copolymerization mechanisms for both systems can be explained as follows (Fig. 4). The copolymerization DP10 is a heterogeneous process in which a water-insoluble styrene is dispersed in ethanol/water in the form of droplets. The droplets are stabilized with PMA macromonomers. Polymerization is initiated by means of a monomer-soluble initiator (AIBN) so that the locus of polymerization is in the individual droplets. The whole process may therefore be viewed as being made up of many separate bulk polymerizations. As polymerization proceeds, the PS particles continue to grow. The conversions are constant at some specific value. This phenomenon seems to originate from the dead-end poly-

merization mechanism of styrene monomers. That is to say, the initiator is consumed at the final stage of polymerization and polystyryl radicals are terminated with a combination process.

The copolymerization EP10 is also a heterogeneous process such as the DP10 system. Water-soluble initiator ($K_2S_2O_8$) is used so that the initial locus of polymerization is in the aqueous phase. The polymer is formed as a latex of PS particles stabilized by PMA macromonomers. Reaction of primary radicals (surface ion radical, $SO_4^{\cdot-}$) with monomer molecules present in the aqueous phases produces short-chain radicals that are captured by the emulsified monomer droplets at rates proportional to their surface areas. The propagation of polystyryl radicals proceeds with a living radical-like mechanism. As polymerization proceeds, the latex particles continue to grow. The surface areas are stabilized with not only PMA macromonomers but also with sulfate ions. Therefore, the particle sizes are smaller than those obtained in the DP10 system. We employed the EP system (polymerization time, 24 h) in the following experiments.

We then examined the effect of the solvent composition on particle sizes. These emulsion copolymerizations were carried out at 80°C for 24 h

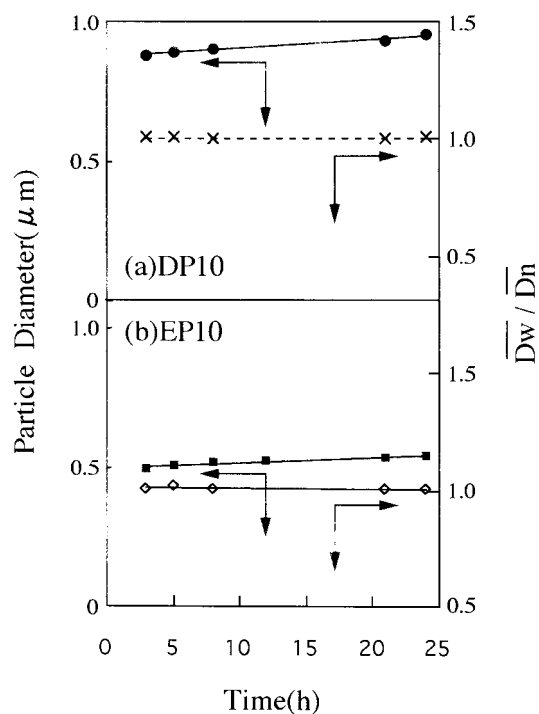
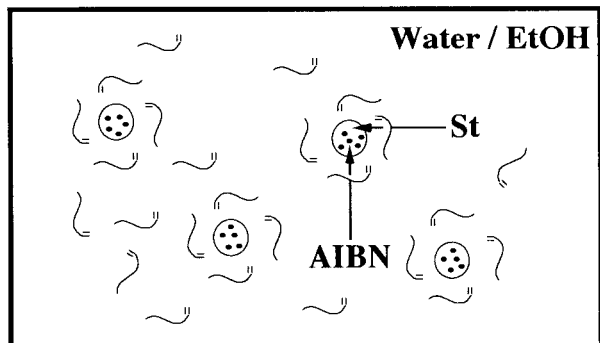


Figure 3 Time dependence on particle diameter and size distribution, varying initiator systems: (a) DP10, (b) EP10.

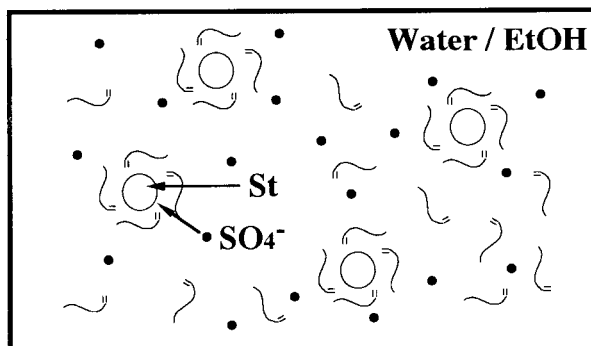
Mechanism of Polymerizations

1. DP10



Dead - End
Polymerization
Conversion (80%)

2. EP10



Living Radical
Polymerization
Conversion (100%)

Growing of Droplets

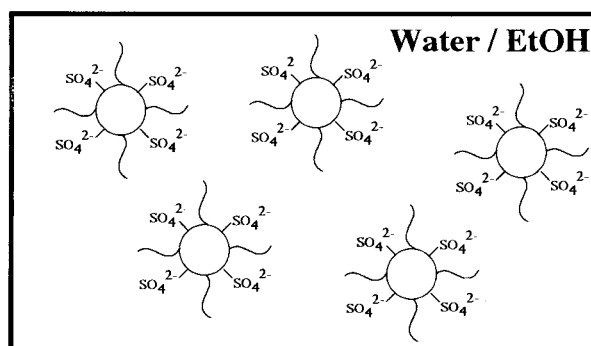
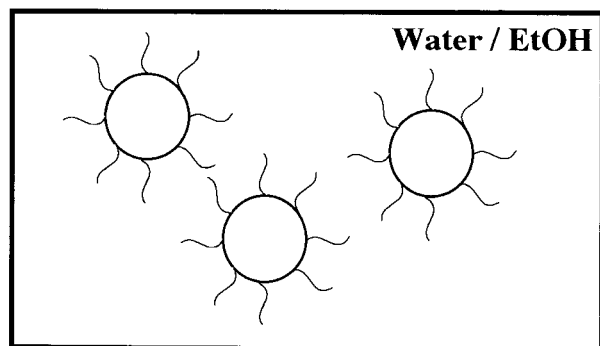


Figure 4 Schematic representation of polymerization mechanisms for DP10 and EP10.

under the following conditions: styrene, 0.5 mL; PMA1 macromonomer, 5 wt % (based on styrene); and $K_2S_2O_8$, 2 wt % (based on total monomer), while varying the solvent composition [water/ethanol = 3/7–9/1 (mL/mL)]. Figure 5 shows the effect of the solvent composition on the particle

diameter and size distribution. It is found from these plots that the particle diameters decrease with an increment of water content in the medium ($D_n = 0.55\text{--}0.16\ \mu\text{m}$). Moreover, the particle-size distribution is very narrow ($D_w/D_n = 1.003\text{--}1.02$). Thus, we observed a tendency in

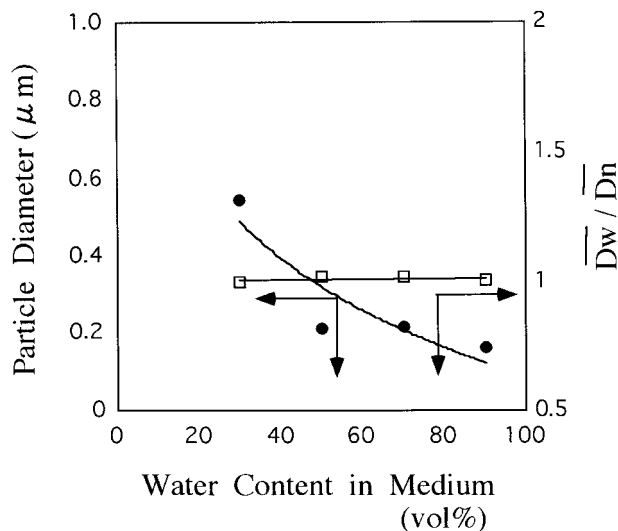


Figure 5 Effect of solvent composition on particle diameter and size distribution.

which the more hydrophilic the media became, then 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.

Figure 6 shows the effect of the concentration of macromonomer PMA1 on the particle diameter and size distribution. These copolymerization series were carried out under the following conditions: styrene, 0.5 mL; $K_2S_2O_8$, 2 wt % (based on total monomer); and water/ethanol = 3/7 (mL/mL), while varying the macromonomer PMA1

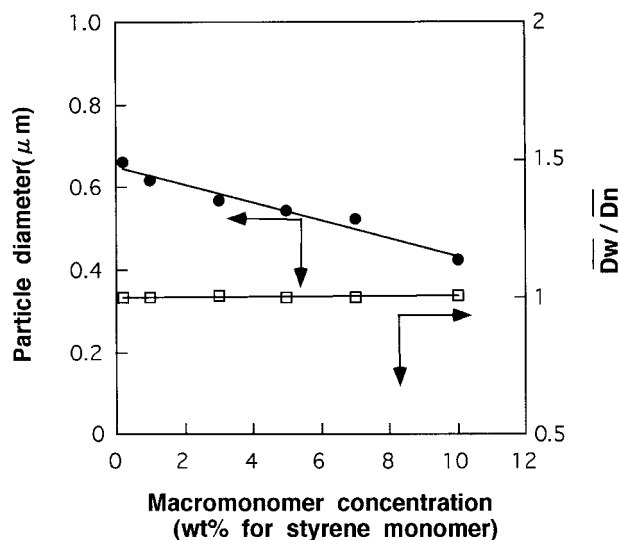


Figure 6 Effect of macromonomer concentration on particle diameter and size distribution.

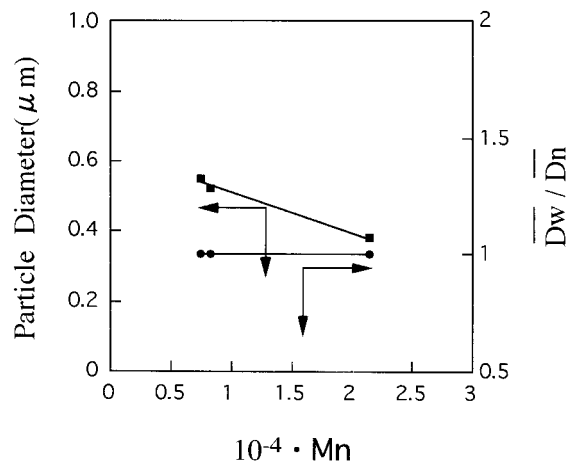


Figure 7 Effect of molecular weight of PMA macromonomers on particle diameter and size distribution.

concentration, 0.2–10.0 wt % (based on styrene). The particle diameters decrease with an increment of macromonomer concentration ($D_n = 0.66$ – $0.42 \mu\text{m}$). The submicron-sized polymer microspheres that were produced had a narrow size distribution ($D_w/D_n < 1.01$). It is remarkable that the macromonomer is able to stabilize the PS particles at even a macromonomer concentration of 0.2 wt %.

Figure 7 shows the effect of the molecular weight of macromonomers on the particle diameter and size distribution under the following conditions: styrene, 0.5 mL; PMA macromonomer, 5 wt % (based on styrene); $K_2S_2O_8$, 2 wt % (based on total monomer); and water/ethanol, 5/5 (mL/mL). The particle diameters decrease gradually with

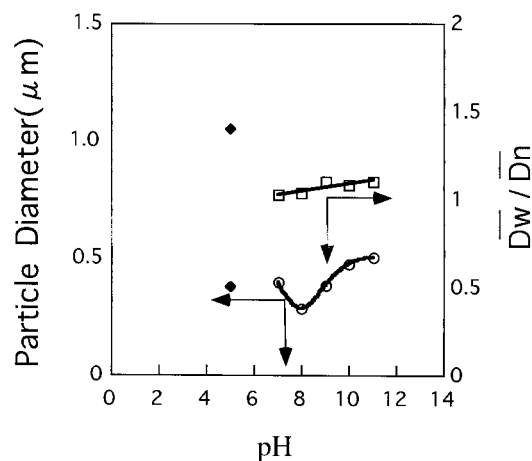


Figure 8 Effect of pH in solvent medium on particle diameter and size distribution.

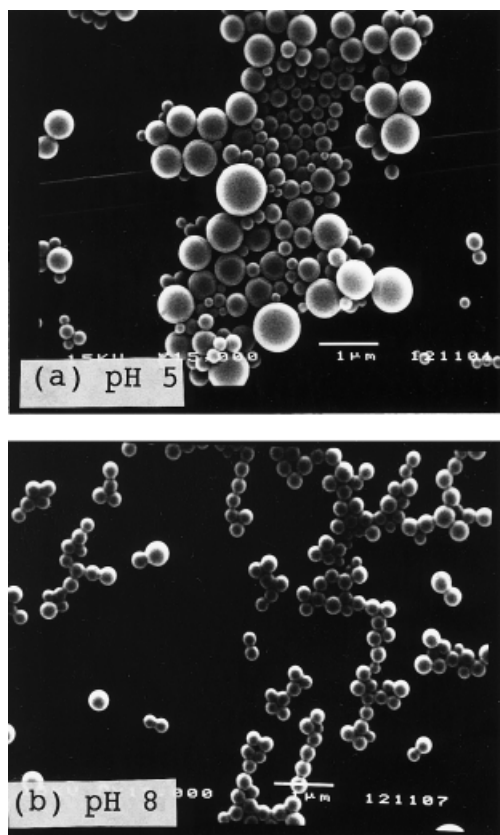


Figure 9 SEM micrographs of PS microspheres, varying pH in solvent medium: (a) pH 5, (b) pH 8.

an increment of the macromonomer molecular weight. The microspheres have a narrow size distribution ($D_w/D_n < 1.003$), regardless of any variation in molecular weight of macromonomers.

It is expected from the above results that the pH of the solvent medium drastically affects the particle size of microspheres. Figure 8 shows the effect of pH of the solvent medium on particle diameter and size distribution in water/ethanol = 5/5 (mL/mL) under the following conditions: styrene, 0.5 mL; PMA1 macromonomer, 5 wt % (based on styrene); and $K_2S_2O_8$, 2 wt % (based on total monomer). Typical SEM photographs of the PS microspheres are shown in Figure 9, where photographs (a) and (b) indicate the morphological results at pH = 5 and 8, respectively. The microspheres obtained at pH = 5 show a broad size distribution ($D_w/D_n = 0.38\text{--}1.04 \mu\text{m}$). On the other hand, the microspheres at pH = 8 have a small particle diameter ($D_n = 0.29 \mu\text{m}$) and a narrow size distribution ($D_w/D_n = 1.03$). It is

found from Figure 8 that the particle diameters decrease gradually with increasing pH until pH = ~ 8 . Beyond this pH region, inversely, the particle diameters increase with increasing pH. PMA macromonomer as an emulsifier is an anionic polyelectrolyte. In general, the hydrodynamic radius of PMA increases as the pH in an aqueous solution increases, because of the high degree of dissociation of carboxyl groups. That is to say, high expansion of macroions, such as PMA macromonomer, is favorable to the steric stability on PS particles formed by copolymerization. However, it is also well known that the viscosity of PMA aqueous solution exhibiting high neutral decreases suddenly because of an analogous effect such as thixotropy. In such a pH region, the hydrodynamic radius of PMA macromonomers seemed to decrease because of a shielding effect for the fixed charges.^{12,13} The interaction of counterions with the macroions modifies the electrostatic forces between the fixed charges. The PS particles obtained in this work are expected to possess interesting solution properties such as pH-responsive character.

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