Preparation and Characterization of Monodisperse Magnetic Poly(styrene butyl acrylate methacrylic acid) Microspheres in the Presence of a Polar Solvent

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ABSTRACT: Magnetic poly(styrene butyl acrylate methacrylic acid) [P(St–BA–MAA)] microspheres were prepared by emulsifier-free emulsion polymerization in the presence of a polar solvent and a ferrofluid prepared by a coprecipitation method. The effects of some polymerization parameters, such as the medium polarity, reaction temperature, initiator content, and surfactant content in the ferrofluid, on the particle diameter and particle size distribution of magnetic P(St–BA–MAA) microspheres were examined in detail. The results showed that the electrostatic repulsion in the polymerization system significantly affected the monodispersity of the resulting magnetic polymer microspheres. The proper electrostatic repulsion, achieved through changes in the medium polarity and amount of surfactant in the polymerization system, improved the monodispersity, but a higher or lower repulsion led to a decrease in the monodispersity. Although the existence of surfactant and magnetite particles reduced the monodispersity more or less, the polymerization behavior of an emulsifier-free emulsion polymerization in the presence of the ferrofluid was analogous to that of a conventional emulsifier-free emulsion polymerization. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 87: 1733–1738, 2003

Key words: emulsion polymerization; particle size distribution; surfactants

INTRODUCTION

Magnetic polymer microspheres have been tried extensively in various fields, such as cell separation, protein purification, environment and food analyses, organic and biochemical syntheses, and industrial water treatment.[1–5] The main advantage of magnetic polymer microspheres over conventional polymer microspheres is that, because of their magnetic properties, they can be rapidly separated from the mixtures by magnetic extraction. More and more techniques based on basic magnetic properties are being used, such as a rapid, sensitive, specific, and effective detection technique for identifying potential biological threat agents.[5]

A commonly used method for preparing magnetic polymer microspheres is the dispersion of magnetic powders in natural or synthetic polymers, followed by evaporation or extraction.[6] Another method is to suspend magnetic particles in the liquid phase of a polymerizable formulation and polymerize the monomer in the presence of the magnetic particles to form magnetic polymer microspheres, including suspension, emulsion, and dispersion polymerization.[7–9] Ugelstad et al.[10] also reported another method for preparing magnetic polymer microspheres, which are commercially available. As we all know, small, uniformly sized microspheres can provide monodispersity and result in less nonspecific adsorption. Unfortunately, most of these methods provide microspheres with uneven sizes and even lead to polydispersity. Okubo et al.[11] investigated the emulsifier-free emulsion polymerization of styrene (St) in an acetone/water medium, and the results showed that the addition of acetone could increase not only the rate of polymerization but also the monodispersity of polystyrene microspheres. In this study, we prepared monodisperse magnetic poly(styrene butyl acrylate methacrylic acid) [P(St–BA–MAA)] microspheres by emulsifier-free emulsion polymerization in the presence of a ferrofluid prepared by the coprecipitation method in a polar solvent (e.g., acetone, ethanol, or methanol) and water mixing medium. The effects of the solvent polarity and surfactant content in the ferrofluid on the polymerization and particle sizes of the microspheres were thoroughly studied.

EXPERIMENTAL

Materials

St (chemically pure; Dagang Yizhong Chemical Plant, Tianjin, China), butyl acrylate (BA; chemically pure;

Xinguang Chemical Plant, Beijing, China), and methacrylic acid (MAA; chemically pure; Wulian Chemical Plant, Shanghai, China) were distilled under reduced pressure before polymerization. The initiator potassium persulfate (KPS; analytical reagent; Xi'an Chemical Plant, Xi'an, China), iron trichloride hexahydrate (FeCl$_3$ · 6H$_2$O; analytical reagent; Third Chemical Plant, Tianjin, China), and ferrous sulfate heptahydrate (FeSO$_4$ · 7H$_2$O; analytical reagent; Xi'an Chemical Plant) were used without further purification. All other chemicals were analytical reagents and were used as received. All water was doubly distilled.

Preparation of the ferrofluid

A 0.5M FeCl$_3$ solution (300 mL) and a 0.5M FeSO$_4$ solution (150 mL) were placed in a 1000-mL, four-necked flask equipped with a stirrer, a condenser, a thermometer, and an N$_2$ inlet. The mixture was stirred at 55°C under an atmosphere of N$_2$, and then a 3M NaOH solution (250 mL) was added. The temperature was raised to 65°C. After 1 h, a 100-mL water solution with 0.03 mol of dissolved sodium dodecylsulfonate was added. The temperature was raised to 90°C, and the reaction was allowed to proceed for 30 min and then was cooled. After that, the resulting colloidal particles were washed with water until neutrality was achieved. Finally, the magnetite content of the ferrofluid was adjusted to 10% (w/w).

Preparation of the magnetic P(St–BA–MAA) microspheres

The ferrofluid, KPS, and a mixture of the polar solvent and water constituted the aqueous phase. St (7.5 mL), BA (2.5 mL), and MAA (0.1 mL) constituted the oil phase. The total volume of the polar solvent and water (60 mL) and the monomer composition were kept constant throughout this work. The aqueous phase was homogenized at room temperature with an ultrasound mixer for 3 min, and then the oil phase was continuously added in an aqueous phase to disperse for 5 min. The mixture was then charged in a four-necked flask equipped with a stirrer, a condenser, a thermometer, and an N$_2$ inlet and was polymerized at 70 or 80°C in a water bath under an atmosphere of N$_2$ for 10 h.

Characterization

The size and morphology of the magnetic polymeric particles were investigated with a Hitachi H-600 transmission electron microscope (Tokyo, Japan). The particle size was calculated on the basis of 100 particles. The number-average diameter (D) and the dispersion coefficient (f) were calculated according to eqs. (1) and (2), respectively, as follows:

$$D = \sum D_i / n \qquad (1)$$

$$f = (\sqrt{\sum (D_i - D)^2 / (n - 1)}) / D \qquad (2)$$

where D_i is the diameter of an individual microsphere and n is the number of calculated microspheres.

The surfactant content in the ferrofluid was determined by a direct two-phase titration procedure according to the national standard of the People's Republic of China (GB/T 5173-1995).

RESULTS AND DISCUSSION

Effect of the type of polar solvent

The effects of various polar solvents, such as acetone, ethanol, and methanol, on the particle size of the microspheres and dispersion coefficient were first investigated, as indicated in Table I. The particle sizes in methanol/water and ethanol/water systems decreased with the increase in the volume ratio of the solvent to water, whereas in the acetone/water system, there was a slight increase in the particle size.

The dielectric constants of the polar solvents methanol, ethanol, and acetone were 33.0, 25.3, and 21.0, respectively, at 20°C, all lower than the constant of water (80.1). Therefore, the addition of such a polar solvent reduced the polarity of the polymerization system; this improved the solubility of St and BA monomers in the continuous phase, and more oligomeric radicals were generated. Meanwhile, the decomposition rate of the initiator increased. More radicals were generated, and the particle size of the magnetic polymer microspheres decreased. However, the addition of the polar solvents not only reduced the hydrophilic blocks in oligomeric radical chains but also resulted in a decrease in the ionization degree of —COO$^-$ and —SO$_4^-$, which reduced the electrostatic repulsion between oligomeric radicals and particles and, therefore, made the particles bigger.

The data in Table I show the prevailing results of two roles: in the methanol/water and ethanol/water

TABLE I
Effects of Polar Solvent on Particle Size and Dispersion Coefficient

Additional polar solvent	Ratio[a] (vol.%)	Particle diameter (nm)	Dispersion coefficient (%)
Methanol	10	206	38.5
	20	188	8.4
Ethanol	10	128	16.5
	20	117	10.4
Acetone	10	119	7.3
	20	120	4.1

Reaction conditions: polymerization temperature = 70°C; ferrofluid = 5 g; KPS = 0.04 g.
[a] Solvent to water.
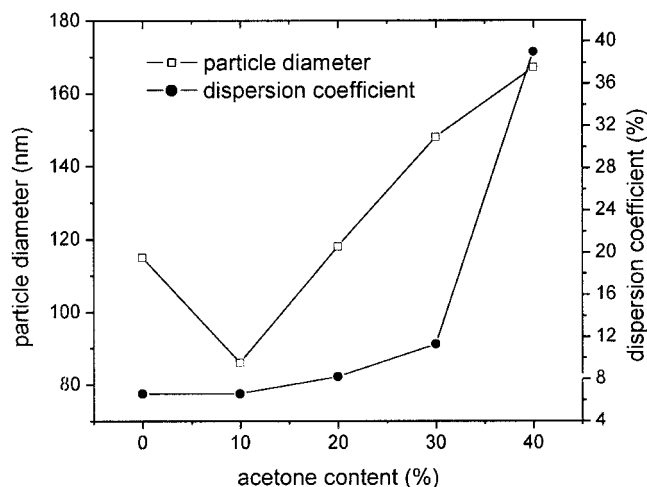
Figure 1 Effects of the acetone content on the particle diameter and dispersion coefficient at a polymerization temperature of 80°C (5 g of the ferrofluid and 0.04 g of KPS).

systems, the first role is dominant, whereas in the acetone/water system, the second role is the chief one. Consequently, in different medium systems, the variation of the particle size shows different tendencies with the variation of the medium polarity.

In Table I, the particle size distribution for a 20 vol % ratio is shown to be narrower than that for a 10 vol % ratio, no matter what solvent was used. This phenomenon may be explained by the fact that a decrease in the medium polarity effectively increased the solubility and reduced the surface charge density of oligomeric radicals, and so the growing radicals steadily coagulated into narrower particles.

These results suggest that a decrease in the medium polarity improves the monodispersity of magnetic polymer microspheres.

Effect of the acetone content

Magnetic polymer microspheres with better monodispersity were obtained in an acetone/water medium, as shown in Table I. Further experiments were performed with variations in the acetone content in the polymerization system, and the effects of the acetone content on the particle size and dispersion coefficient at 80°C are plotted in Figure 1. Figure 2 shows transmission electron microscopy (TEM) micrographs of magnetic P(St–BA–MAA) microspheres prepared with different acetone contents.

With an increase in the acetone content, the particle sizes first decreased and then increased, and the smallest microspheres were gained with a 10 vol % acetone content, as depicted in Figure 1. This phenomenon indicated the prevailing results of the two side roles previously mentioned.

Similarly, as depicted in Figure 1, with an increase in the acetone content, the dispersion coefficient

slightly decreased and then increased. When the acetone content was greater than 30 vol %, the dispersion coefficient became significantly larger, presumably because with the further decrease in the medium polarity, the stability between the radicals and particles became worse, leading to bad monodispersity. Therefore, the previous observation that a decrease in the medium polarity improves the monodispersity of magnetic polymer microspheres is finite. That is, a higher or lower electrostatic repulsion would result in a decrease in the monodispersity of the resulting microspheres.

Effect of the initiator content

With an increase in the KPS content from 0.02 g to 0.10 g, as shown in Table II, the particle size of the magnetic P(St–BA–MAA) microspheres fluctuated around 120 nm with little change; this showed that the amount of the initiator KPS in this polymerization system did not have much of an effect on the particle size. The irregular variation of the particle size may be attributed to the following two reasons. On the one hand, the increased KPS content led to a higher number of primary particles, so a smaller particle size for resulting microspheres was obtained. On the other hand, the increase in the KPS content increased the electrolyte concentration in the polymerization system; this depressed the electrical double layer of the primary particle surface, and bigger microspheres were obtained. When one of these two factors was predominant over the other one, the particles of the resulting microspheres were slightly bigger or smaller. In Table II, it can also be seen that the monodispersity of these microspheres was fairly good, and the biggest dispersion coefficient was just 7.1 at a KPS content of 0.02 g.

Effect of the reaction temperature

The effect of the reaction temperature on the polymerization was mainly on the decomposition rate of KPS, as shown in Table III. With the elevation in temperature, the particle diameters decreased. However, different acetone contents led to different decreases in the particle diameters, which could be ascribed to the different medium polarities. With the elevation in temperature, the dispersion coefficient in the 20 vol % acetone medium became bigger than that in the 10 vol % acetone medium. It is presumed that in a medium of lower polarity, the elevation of the temperature makes the stability of particles comparatively weak, and this results in an increase in the dispersion coefficient.

Effect of the surfactant content in the ferrofluid

Table IV shows the effect of the ferrofluid content on the particle diameter. An increase in the ferrofluid
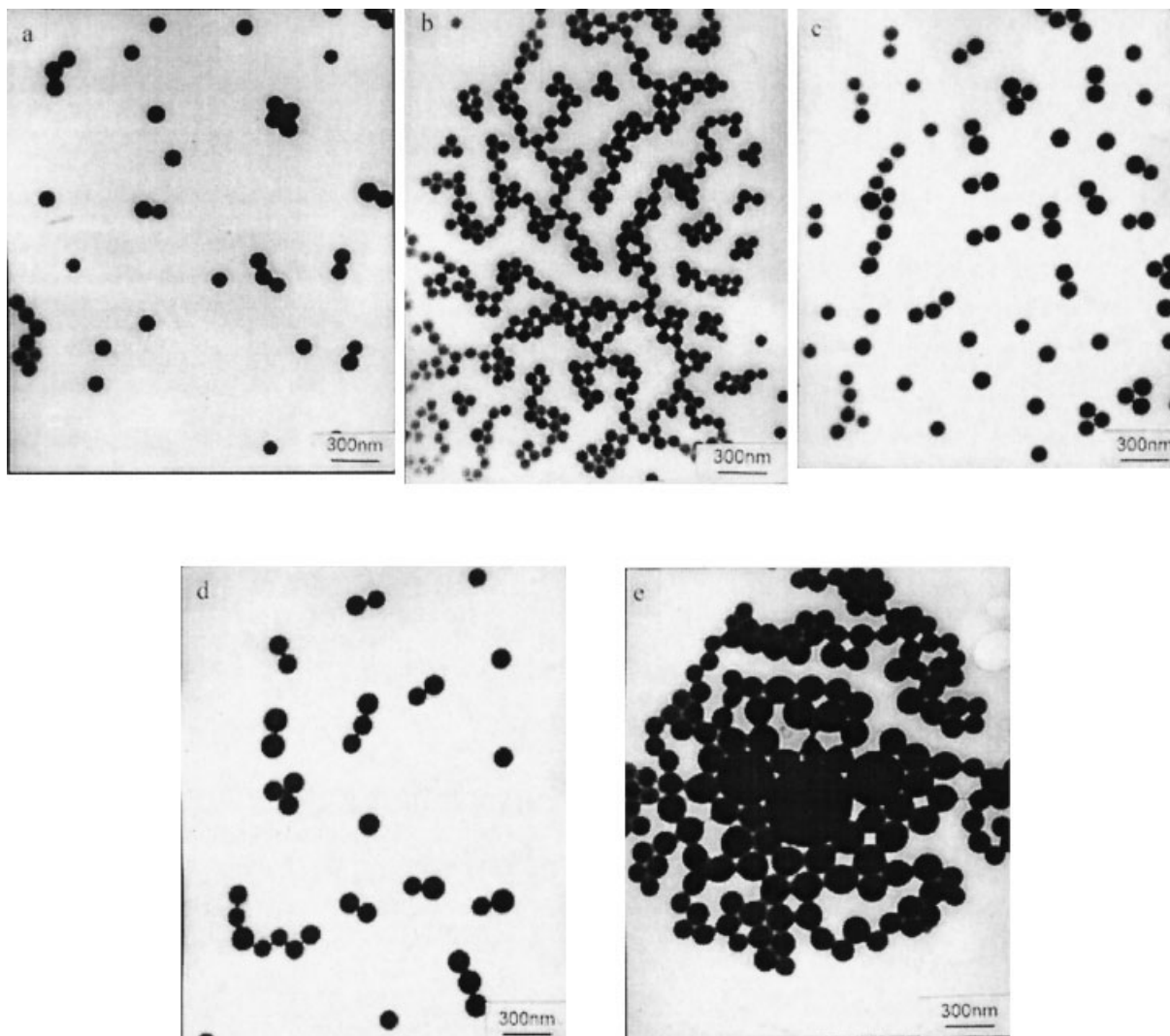
Figure 2 TEM micrographs of magnetic polymer microspheres prepared with different acetone contents: acetone/water = (a) 0, (b) 10, (c) 20, (d) 30, and (e) 40%.

content in the polymerization system reduced the particle size of the magnetic polymer microspheres, the results being similar to those reported by Kondo et al.[12] We all know that a change in ferrofluid feeding varies not only the surfactant content in the ferrofluid but also the amount of magnetite particles. Therefore,

it cannot be absolutely determined that the decrease in particle sizes derived from the increase in the surfactant.

Further experiments were performed to investigate the effects of the surfactant and magnetite particle contents, as shown in Table V. As the feeding of additional surfactant increased, the particle sizes sig-

TABLE II
Effect of KPS Content on Particle Diameter and Dispersion Coefficient

KPS content (g)	Particle diameter (nm)	Dispersion coefficient (%)
0.02	135	7.1
0.04	120	4.1
0.06	114	3.4
0.08	125	5.7
0.10	120	2.3

Reaction conditions: polymerization temperature = 70°C; ferrofluid = 5 g; acetone/water = 0.2/0.8 (v/v).

TABLE III
Effects of Reaction Temperature on Particle Diameter and Dispersion Coefficient

Temperature (°C)	Ratio[a] (vol %)	Particle diameter (nm)	Dispersion coefficient (%)
70	10	119	7.3
	20	120	4.1
80	10	86	6.6
	20	118	8.2

Reaction conditions: ferrofluid = 5 g; KPS = 0.04 g.
[a] Acetone to water.

TABLE IV
Effect of Ferrofluid Content on Particle Diameter

Ferrofluid content (g)	Particle diameter (nm)
4	120
5	101
8	79

[a] Reaction conditions: polymerization temperature = 70°C; KPS = 0.04 g; acetone/water = 0.2/0.8 (v/v).

nificantly decreased, and the dispersion coefficient increased. This phenomenon may be explained by an electrostatic repulsion analogous to that caused by the polar solvents mentioned previously. That is, the increase in the free surfactant, which adsorbed to the surfaces of the particles and radicals, increased the electrostatic repulsion between the radicals and particles, and this resulted in the decrease in the particle sizes and monodispersity of the magnetic polymer microspheres.

In practical terms, the total surfactant content of c in Table V, with maximal surfactant content, was still less than the critical micelle concentration of sodium dodecylsulfonate. This suggests that not all the polymerizations in this study followed the micellar nucleation mechanism of conventional emulsion polymerization. The effects of the surfactant on the preparation of the magnetic polymer microspheres were in common with those of conventional polymerization without a ferrofluid (see d and e, Table V). Furthermore, the effects of electrostatic repulsion resulting from the medium polarity, initiator content, and surfactant content suggest that the emulsifier-free emulsion polymerization in the presence of the ferrofluid was analogous to a conventional emulsifier-free emulsion polymerization.

Although a and d had equal surfactant contents, as depicted in Table V, the particle size of a was bigger than that of d. This reflected the fact that the free surfactant content in a was less than that in d, and this was the reason that the fractional surfactant in a was adsorbed into magnetite particles. Analogously, the fact that the particle size of d was still smaller than that of b could be explained by this reason. It seems that b should have a narrower size distribution than d

because of the smaller free surfactant content in b. However, the results show the opposite, and this was presumably due to the existence of magnetite particles reducing the system stability to some extent. With increased additional surfactant (from 0.02 to 0.04 g), the dispersion coefficient of c, 18.7, was apparently bigger than that of b, 6.7, and this was attributed not only to the increase in free surfactant but also to the existence of magnetite particles. The combed results of these two factors reduced the monodispersity of the resulting microspheres.

From analyses of the medium polarity, temperature, and initiator, the emulsifier-free emulsion polymerization in the presence of the ferrofluid was analogous to a conventional emulsifier-free emulsion polymerization. Besides, in certain samples, a bimodal distribution of particles was observed by TEM, which also revealed the similarity of these two polymerizations. Undoubtedly, the presence of the ferrofluid made the polymerization complicated. The differences between these two types of polymerizations mainly concerned the particle diameter and particle size distribution. The particle size of the magnetic P(St–BA–MAA) microspheres was significantly smaller than that of pure P(St–BA–MAA) microspheres because of the existence of the surfactant. Although magnetic P(St–BA–MAA) microspheres with narrow size distributions could be prepared by an emulsifier-free emulsion polymerization in the presence of the ferrofluid in a polar solvent/water medium, the monodispersity was still worse than that of pure P(St–BA–MAA) microspheres.

TEM observations also revealed that each microsphere contained different amounts of magnetite particles, and there were still some blank microspheres containing no magnetite particles. Moreover, the magnetite particles tended to be localized near the surfaces of the microspheres, and normally the magnetite content in the resulting magnetic composite microspheres was no more than 10% (w/w). Further research is now being underway to overcome these drawbacks.

CONCLUSIONS

Monodisperse magnetic P(St–BA–MAA) microspheres were prepared by an emulsifier-free emulsion poly-

TABLE V
Effects of Surfactant Content in Ferrofluid on Particle Diameter and Dispersion Coefficient

Sample	Ferrofluid addition (g)	Surfactant in ferrofluid (g)	Additional surfactant (g)	Particle diameter (nm)	Dispersion coefficient (%)
a	5.7	0.092	0	233	—
b	5.7	0.092	0.02	142	6.7
c	5.7	0.092	0.04	94	18.7
d	0	0	0.092	117	4.2
e	0	0	0	401	2.7

Reaction conditions: polymerization temperature = 70°C; acetone/water = 0.2/0.8 (v/v); KPS = 0.04 g.

merization in the presence of a ferrofluid in a polar solvent/water mixing medium. Studies on the particle size and dispersion coefficient of magnetic P(St–BA–MAA) microspheres revealed that electrostatic repulsion between the particles and radicals affected the monodispersity to a significant degree. Proper electrostatic repulsion improved the monodispersity, but a higher or lower repulsion led to a decrease in monodispersity. The amount of the initiator KPS had no more effect on the particle size of the resulting magnetic P(St–BA–MAA) microspheres. The polymerization behavior of an emulsifier-free emulsion polymerization in the presence of a ferrofluid was analogous to that of a conventional emulsifier-free emulsion polymerization. However, the presence of the ferrofluid reduced the monodispersity of the magnetic polymer microspheres more or less to some extent, and this was responsible for the existence of the surfactant and magnetite particles.

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