A Polyampholyte Triblock Copolymer Synthesized for Using as the Surfactant of Miniemulsion Polymerization and Production of Highly Uniform Microspheres

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ABSTRACT: Miniemulsions based on styrene/azobisisobutyronitrile (AIBN) in the presence of polyampholyte triblock copolymers as a surfactant and hexadecane (HD) as a cosurfactant were developed. The polyampholyte was prepared by using methyl methacrylate (MMA), methacrylic acid (MAA), and 2-(dimethylamino) ethyl methacrylate (DMAEMA) as monomers. For the sake of comparison, a miniemulsion polymerization with sodium dodecyl sulfate (SDS) was carried out using the same procedure as the above series. The monomer droplet sizes and their shelf life tests revealed that the polyampholyte could stabilize miniemulsion and lead nucleation mechanisms to droplet nucleation. Miniemulsion polymerization using SDS as the surfactant possess a higher polymerization rate than that of polyampholyte, probably due to the smaller droplet size. Production of uniform microspheres was also carried out in this work. Highly uniform microspheres prepared using polyampholyte as the surfactant in the presence of acetone could be obtained. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 87: 2230–2237, 2003

INTRODUCTION

Ugelstad et al. first studied miniemulsion polymerization in the early 1970s.[1] In miniemulsion polymerization, the particle nucleation occurs mainly in the submicron (50–500 nm) monomer droplets. These submicron monomer droplets were produced by miniemulsification processes, and stabilized with a surfactant and a cosurfactant. The surfactant such as sodium lauryl sulfate[1–6] (SLS) or sodium hexadecyl sulfate[7–10] (SHS) provides stability against coalescence. A cosurfactant such as cetyl alcohol,[3,4] hexadecane,[2,3] dodecyl mercacaptan[5] or reactive alkyl methacrylates[11–15] used in the miniemulsion polymerization retards Ostwald ripening.

Most previous workers on miniemulsion polymerization used a low-molecular-weight anionic surfactant such as SLS or SHS. The enhanced stability of the anionic surfactant system is attributed to the formation of electrostatic repulsion at the oil–water interface. Wang et al.[16] studied miniemulsion polymerization of vinyl acetate using a nonionic surfactant such as polyvinylalcohol (PVA). For the nonionic surfactant system, the enhanced stability is attributed to the formation of steric hindrance at the oil–water interface.

Landfester et al.[17] studied miniemulsion polymerization of styrene using cationic surfactants, i.e., cetyl trimethylammonium bromide, cetyl trimethylammonium tartrate, cetyl trimethylammonium terephthalate, and a nonionic surfactant, i.e., Lutensol AT50. They showed that the principle of miniemulsion polymerization could be extended to cationic and nonionic surfactants. Besides, by using group transfer polymerization,[18–20] Lim et al.[21] synthesized a well-defined hydrophilic–hydrophobic diblock copolymer with near-monodisperse molecular weight to function as an effective surfactant in a miniemulsion polymerization. This gives us a promising way to synthesize a polyampholyte triblock polymer that may also act effectively as a surfactant in a miniemulsion polymerization system. In this work, a polyampholyte triblock polymer was synthesized by using GTP, in which methyl methacrylate (MMA), methacrylic acid (MAA) and 2-(dimethylamino)ethyl methacrylate (DMAEMA) were used as monomers. At pH values 1–2 units lower than the pK of methacrylic acid (5.35), the polyampholyte could form cationic polyelectrolytes by ionizing amine groups of DMAEMA units. At pH values 1–2 units greater than the pK of the DMAEMA (8.0), the polyampholyte could form anionic polyelectrolytes by dissociation of MAA units.[22] The polyampholytes with their large graft structure also have steric hindrance properties. Thus, they could be an effective surfactant due to their electrostatic repulsion and steric hindrance properties. In fact, the
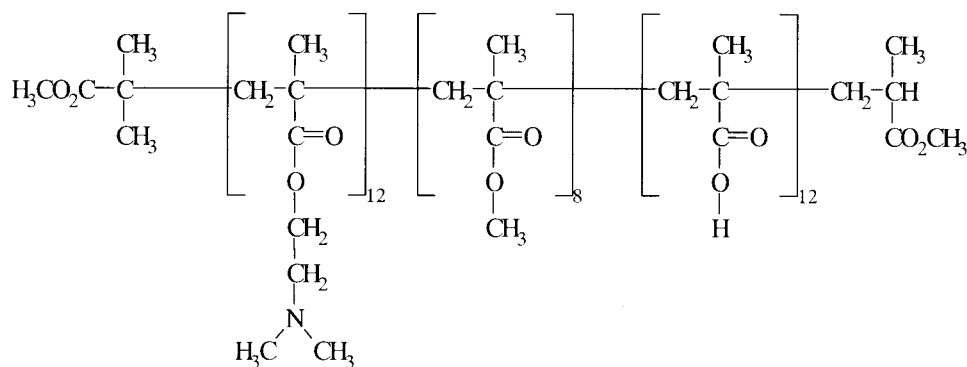
Figure 1 Structure of PDMAEMA-b-MMA-b-MAA ($B_{12}M_8A_{12}$) copolymer surfactant.

polyampholyte as a surfactant could enrich the property of microspheres in the latex since the surfaces of microspheres would be positive charge in an acid solution, negative charge in a base solution, or no charge in a neutral solution. Therefore, changing the pH value of the solution could result in changing the surface charge of the microspheres in the latex as the polyampholyte used as the surfactant. Latexes having a polyampholyte as a surfactant could have more advantages compared with those having an anionic, nonionic, or cationic surfactant. Besides, their possible applications may include tones, supports, packing materials for columns, standards, biological techniques, biological chemistry, and so on. So far as we know, the polyampholyte triblock copolymers have never been tried as the surfactant for the miniemulsion polymerization.

This work examines the feasibility of using poly(D-MAEMA-b-MMA-b-MAA) triblock copolymers as the surfactant in the miniemulsion polymerization of a styrene/azobisisobutyronitrile (AIBN) system. Data on monomer droplet sizes and shelf lives revealed that a stable miniemulsion could be achieved by using the polyampholyte triblock copolymers as the surfactant. This study also examined the parameters of surfactant concentration and how they affected the monomer droplet sizes, growth of particles, and polymerization rates. For the sake of comparison, a miniemulsion polymerization with sodium dodecyl sulfate (SDS) was carried out using the same procedure as the above series. Moreover, production of uniform microspheres was also carried out via miniemulsion polymerization using the polyampholyte triblock copolymers as the surfactant.

EXPERIMENTAL

Materials

The synthesis of the polyampholyte triblock copolymers (BMA) used in this study is described elsewhere.[18] The notation used for the monomers comprising the polyampholyte is B for DMAEMA, M for MMA, and A for

MAA. The chemical structure of polyampholyte ($B_{12}M_8A_{12}$) is shown in Figure 1. Styrene (Merck) was used after distillation under reduced pressure. SDS (Merck), azobisisobutyronitrile (AIBN; SHOWA), and hexadecane (HD; TCI), were used without further purification. The water used was distilled and deionized (DDI).

Surface tension

The surface tension (γ) measurements were carried out using the Du Nouy–Ring method. The polyampholyte were dissolved in dilute aqueous solution (pH 1). All measurements were carried out at room temperature (about 20°C), and the values obtained were adjusted according to the surface tension of the DDI water (72–73 mN m^{-1}).

Miniemulsion preparation and polymerization

Table I lists recipes for the various experiments. The desired amount of polyampholyte was dissolved in a dilute aqueous solution (pH 1). In a separate container, the AIBN and HD were dissolved in styrene. The oily and aqueous solutions were mixed (preemulsion) with a Homogenerizator (IKA T25) for 5 min at 9500 rpm. Then the system was sonicated (miniemul-

TABLE I
Recipes Used in the Miniemulsion
Polymerizations (T = 70°C)

Composition	Series		
	1	2	3
Styrene (g)	7.200	7.200	7.200
$B_{12}M_8A_{12}$ (g)	0.036[a]	0.072[b]	
SDS (g)			0.207[c]
AIBN (g)	0.180	0.180	0.180
Hexadecane (g)	0.164	0.164	0.164
DDI water (g)	72	72	72

[a] Concentration of surfactant in water phase was 1CMC.
[b] Concentration of surfactant in water phase was 2CMC.
[c] Concentration of surfactant in water phase was 1.4CMC.

sion) under agitation by a magnetic bar stirrer with a sonic dismembrator (Misonix XL2020) for 10 min at an output of 180 W. During preemulsion and miniemulsion, the vessel containing the emulsion was immersed in ice water to prevent heat-up. After sonication, the droplet size was measured by dynamic light scattering (DLS) using a Malvern 3000 apparatus. The dilution water was 0.5 critical micelle concentration (CMC) triblock copolymer solution that was saturated with styrene.

To carry out the polymerization, the miniemulsion was transferred into a 125-mL conical Erlenmeyer flask with an orbital-shaking bath preheated to 70°C. All the polymerizations were run at 70°C using a shaking speed of 150 rpm. Preparation for polymer particle measurement was the same as that of droplet size measurement.

Fourier transform infrared (FTIR) spectra were record with instrument (Bio-Rad). Samples were rinsed with DDI water for several times prior to FTIR inspection. The uniformity of resultant microspheres was measured using scanning electron microscope (SEM; Hitachi S-800).

RESULTS AND DISCUSSION

CMC of the surfactant

The CMC of the surfactant is an important parameter in miniemulsion polymerization. In this study, the polyampholyte triblock copolymers ($B_{12}M_8A_{12}$) were readily soluble in dilute aqueous HCl (pH 1). Chen et al.[22] used fluorescence spectroscopy and static and dynamic light scattering to study the micellization of
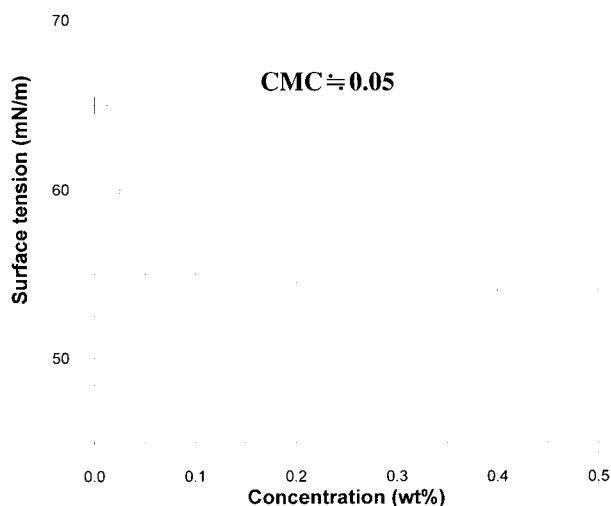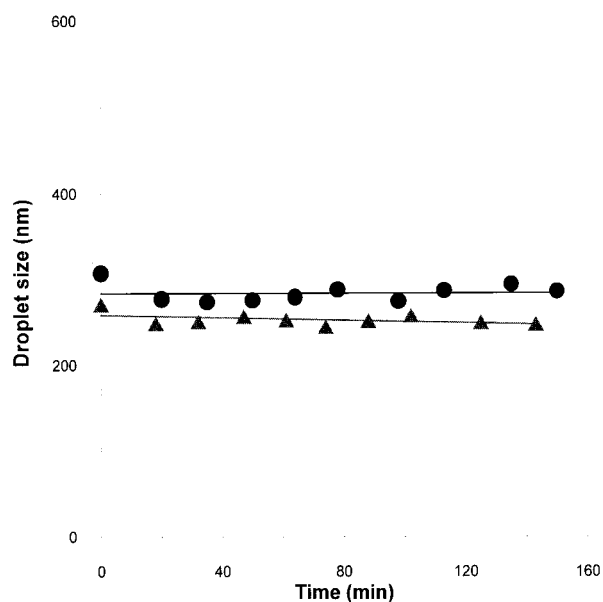
Figure 3 Time evolution of the droplet diameter for the miniemulsion using $B_{12}M_8A_{12}$ as the surfactant. Legend: (●) 1CMC and (▲) 2CMC. Reaction conditions are as shown in Table I.

PDMAEMA-b-MMA-b-MAA copolymers in dilute aqueous HCl (pH 3.7). They indicated that the CMC of the $B_{12}M_{12}A_{12}$ occurs at around 0.006–0.08 wt %. We also expected to observe a CMC for the $B_{12}M_8A_{12}$ in dilute aqueous HCl (pH 1). Figure 2 shows the relationship between the surface tension and the concentration of $B_{12}M_8A_{12}$. It indicates that the surface tension decreased rapidly with an increasing concentration of $B_{12}M_8A_{12}$ up to 0.05 wt %. Above this concentration, the surface tension remained constant at around 54 mN m^{-1}. This behavior suggests that the CMC of $B_{12}M_8A_{12}$ occurred at around 0.05 wt %.

Shelf life

Shelf life can be used to estimate the stability of the monomer droplet over time much like polymerization can. Figure 3 shows the change in the droplet diameters over time for the miniemulsion using $B_{12}M_8A_{12}$ as a surfactant. Results indicated that the initial droplet diameters were obtained in the miniemulsion size range and the time evolution of the droplet diameters obtained for both cases remained roughly constant for more than 2 h after sonication, i.e., the droplets were stable. This finding also indicated that stable miniemulsions could be prepared by using the polyampholyte $B_{12}M_8A_{12}$ as the surfactant and HD as the cosurfactant. When these stable miniemulsions were initiated, monomer droplet nucleation can be the main mechanism for polymerization (i.e., miniemulsion polymerization).
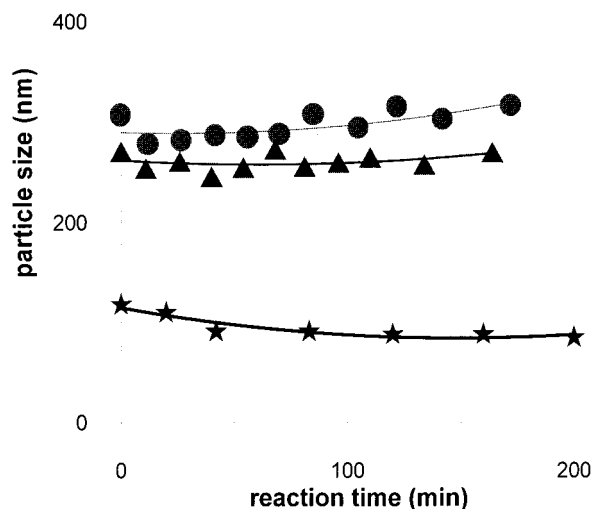
Figure 2 Variation of surface tension with triblock copolymer concentration for $B_{12}M_8A_{12}$ copolymers in water at a solution pH of 1.

Figure 4 Time evolution of the average of particle size during the miniemulsion polymerization. Legend: (●) $B_{12}M_8A_{12}$, 1CMC; (▲) $B_{12}M_8A_{12}$, 2CMC; (★) SDS,1.4CMC (10 mM). Reaction conditions are as shown in Table I.

Particle size

When $B_{12}M_8A_{12}$ or SDS is used as the surfactant, the evolution of particle growth during the miniemulsion polymerization was shown in Figure 4. It must be noted that the dynamic light scattering data only represents the average particle size of the mixture comprising the latex particles and monomer droplets. Although the average particle size was subject to slight experimental deviations, it can be clearly seen that the average particle size increased gradually, when the concentration of $B_{12}M_8A_{12}$ is 1 CMC. This gradual increase may be because of droplet coagulation or Ostwald ripening. When the concentration of $B_{12}M_8A_{12}$ increased to 2 times its CMC, the average particle size remained almost constant. This is because more $B_{12}M_8A_{12}$ was available for stabilizing the droplet surface area and avoiding droplet coagulation. Thus, the average particle size remained about constant during the polymerization. This behavior also indicated that droplet nucleation would be the main mechanism for the system using polyampholyte $B_{12}M_8A_{12}$ as the surfactant.

On the other hand, when SDS was used as the surfactant, the average particle size decreased to a minimum and then remains almost constant. The decrease in particle size is probably due to the presence of new particles. These new particles are most likely generated by aqueous (homogeneous,[11] micellar,[16] or both) nucleation. When there is no generation of new particles in the aqueous phase of polymerization, the average particle size remained about constant. This implied that miniemulsion polymerization used SDS

as surfactant would favor mainly droplet nucleation and partially aqueous nucleation. As matters stand, we believe that the polyampholyte copolymers such as $B_{12}M_8A_{12}$ could be function as an effective surfactant as SDS (an anionic surfactant).

Effect of the surfactant composition on the polymerization rate

Figure 5 shows the results of the miniemulsion polymerizations initiated with AIBN in the presence of either an anionic (SDS) or polyampholyte ($B_{12}M_8A_{12}$) surfactant. The polymerization rate of the SDS system was faster than that of the $B_{12}M_8A_{12}$ system. Leemans et al.[23] indicated that AIBN-initiated emulsion polymerization, conducted using either a polyanionic or polycationic-block-polyelectrolyte surfactant, showed no major difference between the polymerization rates of the two systems. Thus, the neutral cyanopropyl radical was unaffected by the polyelectrolyte barrier. Chern et al.[15] showed the effect of initial monomer droplet size on the polymerization rate in styrene miniemulsion polymerization using SDS as a surfactant, AIBN as an initiator, and dodecyl methacrylate as a cosurfactant. They found that the polymerization rate decreased rapidly with increasing droplet size up to 300 nm, and suggested that segregation of radicals among the discrete particles characterized a faster polymerization rate and a smaller number of radicals per particle. As mention above, the higher polymerization rate for the SDS system in this study is probably due to the smaller droplet size. The smaller the droplet
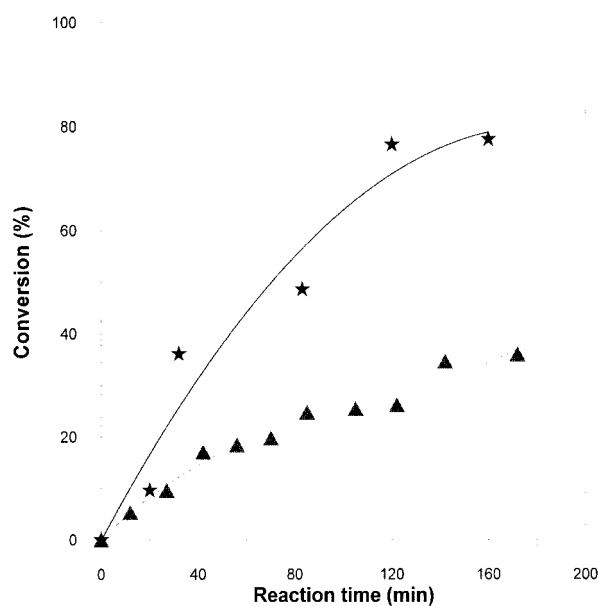

Figure 5 Time evolution of the conversion in the miniemulsion with different kinds of surfactant. Legend: (▲) $B_{12}M_8A_{12}$, 2CMC; (★) SDS, 1.4CMC (10 mM). Reaction conditions are as shown in Table I.
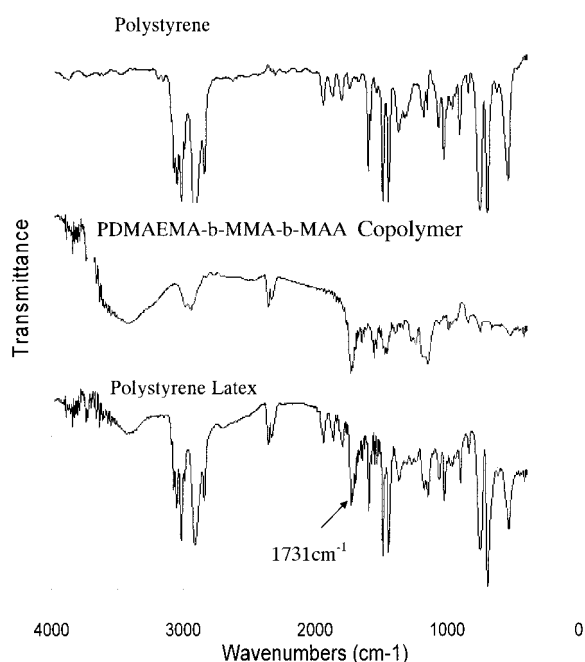
Figure 6 FTIR spectra of polystyrene, a PDMAEMA-b-MMA-b-MAA copolymer, and a polystyrene latex.

size, the larger the overall area of droplet surface. Thus, more neutral cyanopropyl radicals or oligomer radicals in the aqueous solution could be obtained by desorption of radicals from the monomer droplets or the growing polymer particles, and therefore leading to higher polymerization rate for the SDS system than that of the $B_{12}M_8A_{12}$ system. This can also be an evidence of the aqueous nucleation taken place in the SDS system.

The surface structure of the latex

Typical FTIR spectra of the polystyrene, the PDMAEMA-b-MMA-b-MAA copolymer and polystyrene latex which used the PDMAEMA-b-MMA-b-MAA copolymer as the surfactant, were shown as Figure 6. Except for two additional weak absorptions included the absorption at 1731 cm^{-1} and range about 3300–3500 cm^{-1}, the latex spectrum is essentially identical to that of polystyrene. Nevertheless, these two additional absorptions can also be seen in the spectrum of the PDMAEMA-b-MMA-b-MAA copolymer. The absorption at 1731 cm^{-1} was attributed to the carbonyl ester(s) of the surfactant[21] and therefore confirming the presence of this component. The other absorption with range about 3300–3500 cm^{-1} might be ascribed to the MAA of the surfactant since the absorption of polymethacrylic acid was located at range of 2900–3500 cm^{-1}.[24] The usual requirement for polyampholyte ($B_{12}M_8A_{12}$) block copolymer surfactant is that the hydrophobic blocks (e.g., PMMA) are preferen-

tially contained in the precipitating polymer and act as anchors for the hydrophilic blocks (e.g., PDMAEMA and PMAA),[21] which are swelled by the diluent and lead extending away from the particle surface. Since the polyampholytes with their large graft structures also have steric hindrance properties, and the external layer of the particle anchoring with both B and A blocks provides a protective barrier against coagulation. Besides, Chen et al.[22] reported that the triblock polyampholyte inherents rich solution properties, i.e., at pH values 1–2 units lower than the pK of methacrylic acid (5.35), the polyampholyte could form cationic polyelectrolytes by ionizing amine groups of DMAEMA units. At pH values 1–2 units greater than the pK of the DMAEMA (8.0), the polyampholyte could form anionic polyelectrolytes by dissociation of MAA units. Accordingly, the latex particles prepared using the $B_{12}M_8A_{12}$ polyampholyte as the surfactant would also inherent rich solution properties.

A schematic representation of a polystyrene latex particle with polyampolyte triblock copolymer as a surfactant was shown as Figure 7. Therefore, the use of polyampholyte as an effectively surfactant is
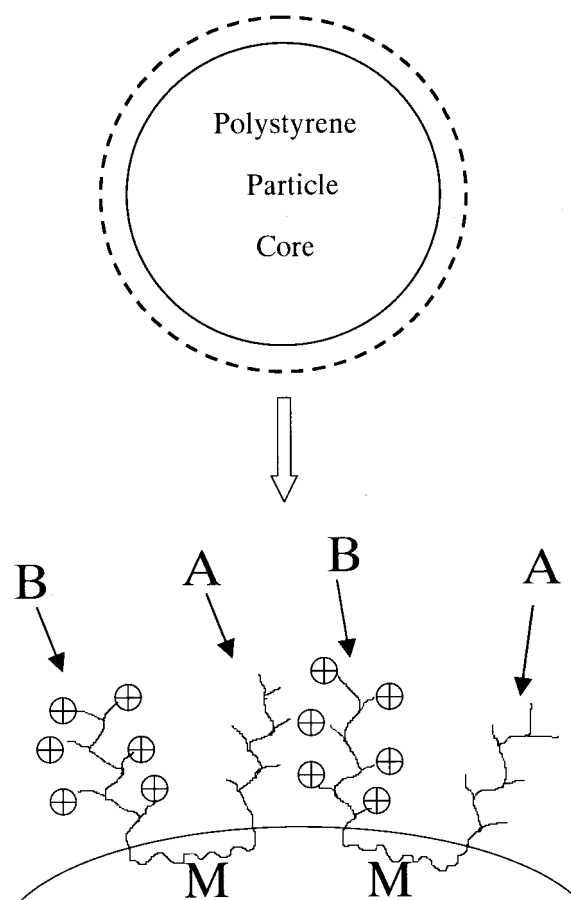

Figure 7 Schematic representation of the polystyrene latex particle with polyampolyte triblock copolymers as the surfactant.
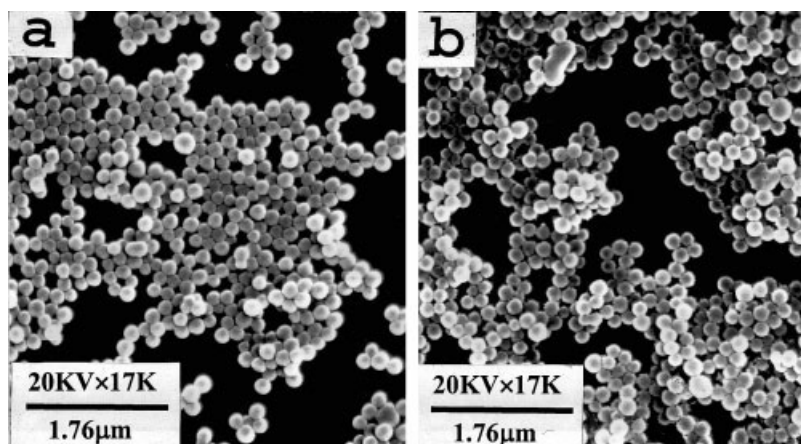
Figure 8 Scanning electron micrographs for microspheres prepared using $B_{12}M_8A_{12}$ as surfactant: (a) without cosurfactant; (b) HD used as cosurfactant. Reaction conditions are as shown in Table I.

mainly due to their electrostatic repulsion and steric hindrance as well.

Preparation of uniform microspheres

For the miniemulsion polymerization, droplet nucleation could be the main nucleation mechanism, and therefore the use of high efficiency homogenizing apparatus became one of significant important parameters for preparing monosized droplets in the early stage of polymerization, and adding a suitable amount of effective surfactant was necessary to stabilize the droplets. Monosized microspheres prepared by miniemulsion polymerization using redox initiator have been proposed by Wang et al.,[25] in which a new agitation mixer was used to homogenize the droplets and SDS was used as the surfactant. Baines et al.[20] showed that diblock copolymers synthesized using methyl methacrylate and dimethylaminoethyl methacrylate could be used as the surfactant for dispersion polymerization to prepare monosized microspheres.

As mentioned above, the polyampholytes with their large graft structure also have steric hindrance properties. Thus, they could be an effective surfactant due to their electrostatic repulsion and steric hindrance properties. This could be evidenced by studies of scanning electron micrographies as seen in Figure 8(a,b). They showed that near monodisperse microspheres, except for slight coagulation, could be prepared using $B_{12}M_8A_{12}$ (2CMC) as surfactant in the presence or absence of the cosurfactant (HD). This implied that $B_{12}M_8A_{12}$ might effectively function as the surfactant for the miniemulsion system even in the absence of the cosurfactant. Furthermore, adding a suitable amount of acetone could be taken account in reducing the difference of surface tensions between aqueous phase and droplet so as to enhance stabilizing the droplets. It therefore leads to preparation of uniform microspheres using the polyampholyte triblock copolymer as surfactant for the miniemulsion system with acetone additive. When acetone was added respectively up to 5 or 10% to the miniemulsion polymerization,
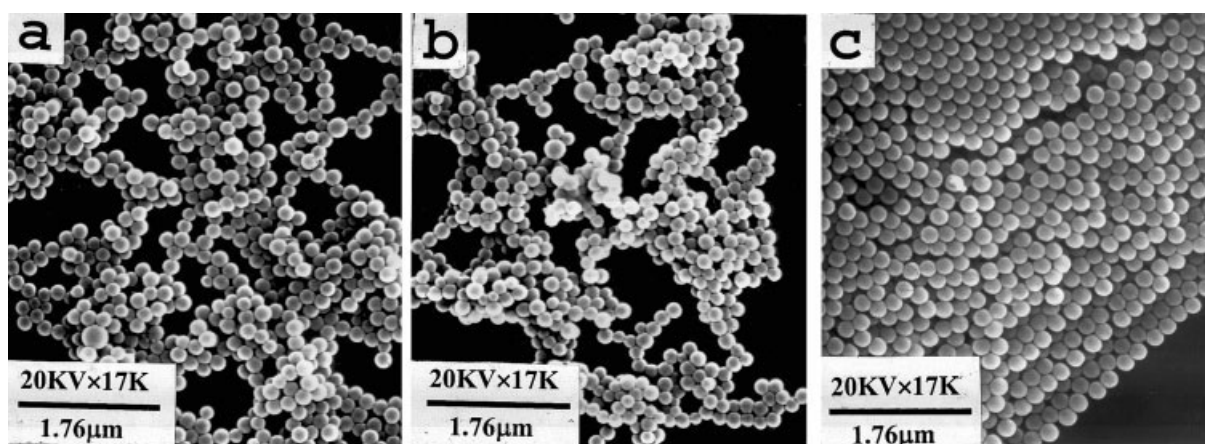

Figure 9 Scanning electron micrographs for microspheres prepared using $B_{12}M_8A_{12}$ as surfactant without using HD cosurfactant: (a) 5% acetone addition; (b) 10% acetone addition; (c) 20% acetone addition.
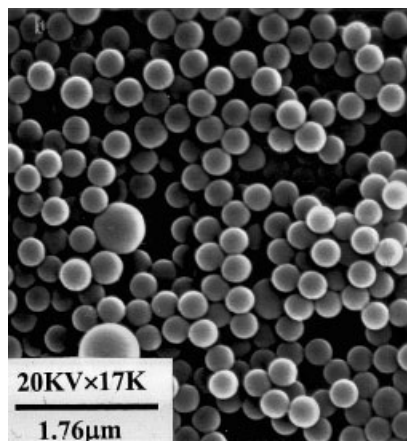
Figure 10 Scanning electron micrograph for microspheres prepared using $B_{12}M_8A_{12}$ concentration of 0.2CMC as surfactant in the presence of acetone of 20%.

scanning electron micrographies of resultant microspheres showed no evidence of difference among them as seen in Figure 8(a,b) and Figure 9(a,b). However, when the addition amount of acetone was added up to 20%, highly uniform microspheres could be obtained without using the cosurfactant shown as Figure 9(c). Besides, near monodisperse microspheres with larger particle size could also be prepared without using cosurfactant as $B_{12}M_8A_{12}$ concentration was down to 0.2CMC and an additional amount of acetone was added up to 20%, as shown in Figure 10. Due to addition of acetone in this work, we can clearly see that the miniemulsion system using $B_{12}M_8A_{12}$ as the surfactant and acetone as the solvent additive seemed to show a good approach for production of monodisperse microspheres. It gives us a promising way to prepare uniform microspheres via regulating the concentration of the polyampholyte triblock copolymer (e.g., $B_{12}M_8A_{12}$) and adding suitable amount of polar

solvent (for example, acetone) to soothe the surface tension.

On the other hand, the miniemulsion system in the presence of the cosurfactant seemed to show no promotion in the uniformity of resultant microspheres as an additional amount of acetone was added respectively up to 5 or 10%, as shown in Figure 8(b) and Figure 11(a,b). In contrast, it showed great deteriorating in the uniformity of resultant microspheres as the additional amount of acetone was added up to 20%, as shown in Figure 11(c). It was possible that acetone used to soothe the difference of surface tensions would also change the interaction between the polyampholyte triblock copolymers ($B_{12}M_8A_{12}$) and cosurfactant (HD), and therefore lead to deterioration of the uniformity of resultant microspheres. Apparently, HD cosurfactant was not necessary to a miniemulsion polymerization for production of uniform microspheres, in which $B_{12}M_8A_{12}$ was used as the surfactant and acetone as the solvent addition.

Accordingly, it was revealed that the formation of highly uniform microspheres via the miniemulsion polymerization using $B_{12}M_8A_{12}$ as the surfactant, contains three parts: (1) effectively homogenize oil phase into submicron droplets, (2) stabilize the resultant droplets, and (3) soothe the difference of surface tensions between aqueous phase and droplet.

CONCLUSION

The monomer droplet sizes and their shelf life tests revealed that $B_{12}M_8A_{12}$ could effectively function as a surfactant so as to stabilize miniemulsion system. However, the use of SDS as the surfactant for the miniemulsion system would lead to droplet nucleation mainly and aqueous nucleation partially. Different from SDS, the polyampholyte $B_{12}M_8A_{12}$ used as the surfactant favors the droplet nucleation mecha-
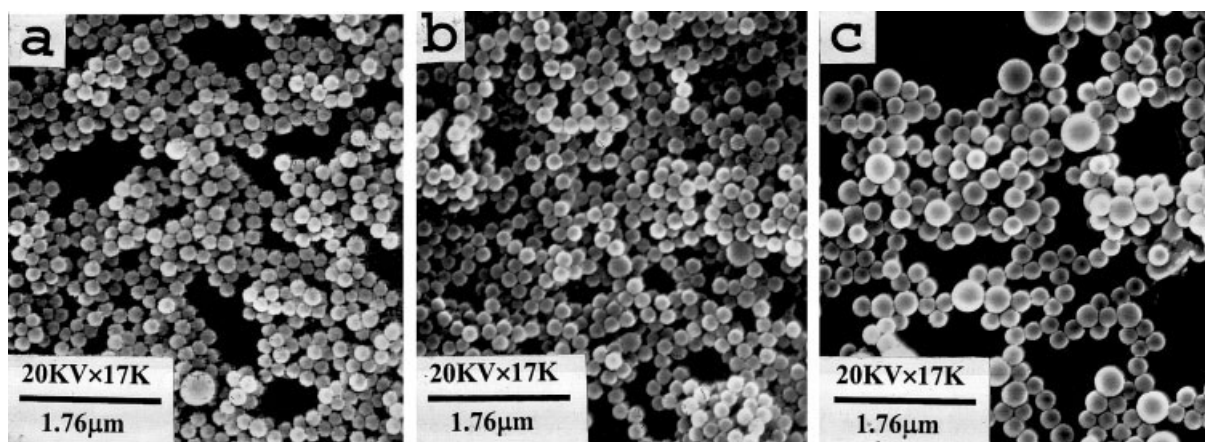

Figure 11 Scanning electron micrographs for microspheres prepared using $B_{12}M_8A_{12}$ as the surfactant and HD as the cosurfactant: (a) 5% acetone addition; (b) 10% acetone addition; (c) 20% acetone addition.

nism. On the other hand, the polymerization rate of the miniemulsion systems using SDS was higher than that using polyampholyte, probably due to the smaller droplet size. FTIR spectra revealed that the hydrophobic blocks (e.g., PMMA) are preferentially contained in the precipitating polymer and act as anchors for the hydrophilic blocks (e.g., PDMAEMA and PMAA), which are swelled by the diluent and extend from the particle surface. In the absence of cosurfactant, a miniemulsion system using $B_{12}M_8A_{12}$ (e.g., 2CMC) as surfactant in the presence of acetone up to 20% could obtain highly uniform microspheres.

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