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SHORT COMMUNICATION

Emulsifier-free emulsion copolymerization of styrene and sodium 1-allyloxy- 2-hydroxypropane sulfonate

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Abstract Colloidal particles of poly(styrene-co-sodium 1-allyloxy- 2-hydroxypropane sulfonate) with diameters of 508 ~ 596 nm were synthesized by emulsifier-free emulsion copolymerization, crosslinked with divinylbenzene, and initiated by potassium persulfate/sodium bisulfite in a mixed solvent of water and acetone. The diameters of the submicrometer-sized particles were measured by dynamic light scattering (DLS) and scanning electron microscopy (SEM). The surface charge densities of the particles were determined by condutometric titration. The results showed that the highly surface charged monodispersed submicrometer-sized particles were obtained by two-stage shot growth polymerization. The particle diameters could be reduced and controlled by adding suitable amount of acetone.

Keywords Poly(styrene-co-sodium 1-allyloxy-2-hydroxypropane sulfonate) · Latex · Emulsifier-free emulsion copolymerization · Colloidal particle

Introduction

Latex polymer colloids have wide applications in many areas of technology, such as paintings and coatings, ceramics processing, microelectronics, biotechnology, and information technology. Monodispersed and highly surface charged particles are particularly interesting to chemists due to their photonic crystalline property. They can self-assemble into ordered superstructures, which have found applications in numerous scientific fields, including optical devices, filters and switches, chemical, and bio-sensors [1–5]. Usually, highly surface charged particles are synthesized by copolymerization of styrene with ionic monomers, such as sodium styrene sulfonate, unsaturated esters with end carboxyl groups, 2-hydroethyl methacrylate, acrylamide and acrylate derivatives, and quaternary cationic monomers. There have been numerous reports on the methods for preparing these kinds of particle latexes, including emulsion polymerization, seeded emulsion polymerization, emulsifier-free emulsion copolymerization, precipitation polymerization, and dispersion polymerization [6–9].

Sodium 1-allyloxy- 2-hydroxypropane sulfonate (SAHS) possesses a negative charged group and can polymerize with styrene (St) to form a stable polymer colloids. Reese et al. [10] synthesized copolymer particle latexes of poly (styrene-co-sodium 1-allyloxy-2-hydrxypropane sulfonate) with diameters of 118~365.6 nm at the present of surfactant. Tang et al. [11] studied the copolymerization of methyl methacrylate, *n*-butyl acrylate, and 1-allyloxy- 2-hydroxypropane sulfonate salt, and obtained amorphous particle latex by emulsifier-free emulsion polymerization. Our interest in this work is to investigate the behavior of emulsifier-free emulsion copolymerization of St and SAHS, as the products prepared with this method has some advantages over emulsion polymerization. The latexes prepared with emulsifier-free emulsion polymerization are easily purified and possess improved mechanical and water-resistance properties than those of prepared by surfactant-mediated emulsion polymerization. Meanwhile, larger sized particles can be gained with this method comparing to emulsion polymerization. This is desirable for the colloidal particles to be used in varied fields. We have attempted to use a batch polymerization and two-stage shot growth emulsifier-free emulsion polymerization for the preparation,

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respectively, and found that highly charged monodispersed particles are obtained by two-stage shot growth polymerization without surfactants.

Experimental

Materials SAHS was purchased from Aldrich. St, divinylbenzene(DVB), potassium persulfate(KPS), sodium bisulfite, sodium bicarbonate, and acetone were purchased from Shanghai Chemical. The St was redistillated under reduced pressure at 40 °C, and the other chemicals were used as received.

Synthesis of colloidal particle latex

A 250 ml of four neck-bottom flask was equipped with mechanical stirrer, condenser, thermometer, and nitrogen inlet. The flask was charged with 125 ml of ultrapure water, various amounts of St, sodium bicarbonate, and DVB. Nitrogen was bubbled through the water for 20 min. A mixture of SAHS and acetone was added. The flasks were immersed into an oil bath thermo-controlled at 70±1 °C. When temperature rose to 70 °C, 8 ml of aqueous solution containing KPS and sodium bisulfite was added to initiate the polymerization. The second batch of the monomers and initiator was added at varied time. The polymerization was continued at this temperature for additional 3 h.

Purification of the latex

The latex was filtrated through glass wool to remove coagulum. The filtrate was steam-stripped for removing remaining St and acetone. Subsequently, the latex was heated to 85 °C for 3 h to affect the hydrolysis of surface sulfate groups, which resulted from potassium persulfate initiator fragments. The latex was centrifuged into a pellet. The supernatant liquid was removed, and pure water was added to the pellet, which was then sonicated to disperse the individual particles. This procedure was repeated three more times. The latex was dialyzed using dialysis tubes with a cutoff molecular weight of 14,000 for at least 6 days in deionized water, which was replaced daily. The latex was passed through two columns filled with anionic and cationic exchanger resins, respectively. The positive ions on the surface of the particles were converted from sodium to hydrogen form. Finally, mixed ion exchanger resins were added to the latex for storage.

Characterization of the particles

The particle sizes were measured using dynamic light scattering (DLS, ALV-5000E, Germany) and scanning electron microscopy (SEM, JEOL, JST-300). The particle density was determined by pycnometry. The surface charge densities were determined by conductometer titration(DDS-307 Conductometer, Shanghai Analytic Instrument). It was carried out in 100 ml of diluted sample latex with 0.1 wt% solid content at room temperature. The titrations were carried out with 0.01 mol/l sodium hydroxide in a vessel equipped with a stirrer under a nitrogen atmosphere. The surface charge density, $\sigma(\mu c/cm^2)$,was calculated by the formula: $\sigma = Fn\rho r/3W$. Where F is the Faraday constant, n is the number of moles of NaOH taken up by the particles, ρ is the particle density(g/ml), r is the particle radius (nm), and W is the total solid content of latex in the titration (g) [12].

Result and discussion

Effect of SAHS content on the polymerization and particle property

To approach optimum synthetic conditions, we firstly studied the copolymerization of St and SAHS with varying molar ratio by one batch emulsifier-free emulsion polymerization. A series of copolymerizations using the recipe of Table 1 were carried out respectively. The mixture is transparent at the beginning of the polymerization but becomes milky as polymer particles are formed in the solution. It is observed in the synthesis that the time for the reacting mixture to be milky is shortened as the increase in SAHS contents in the feed, which indicates the concentra-

Table 1 Recipe for batch copolymerization of St and SAHS[a]

Sample ID	St (g)	SAHS (g)	Molar ratio St/SAHS	SEM[b]
SAHS-08	16.0	0.268	100/0.8	a
SAHS-16	16.0	0.536	100/1.6	b
SAHS-24	16.0	0.804	100/2.4	c
SAHS-32	16.0	1.072	100/3.2	d

[a] The other conditions: KPS, 0.2 g; divinylbenzene,0.45 g; sodium bicarbonate,0.08 g; water 125 ml, reacting at 70 °C for 5 h
[b] Scanning electron micrograph in Fig. 2

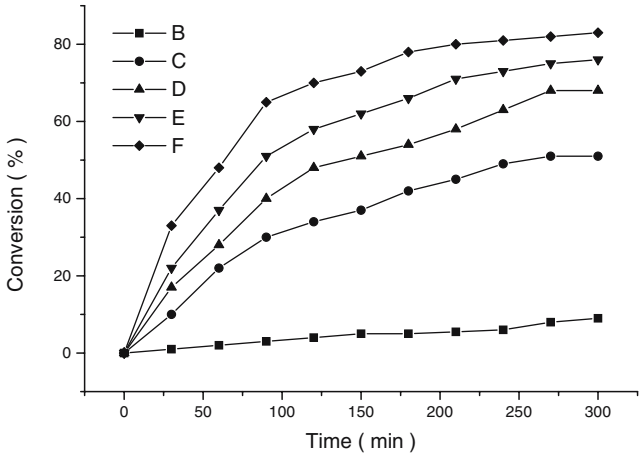

Fig. 1 Particle conversion dependence on polymerization time for St/SAHS with molar ratio: *B* 100/0; *C* 100/0.8; *D*100/1.6; *E*100/2.4, and *F* 100/3.2

tion of SAHS, affects the reaction rate significantly. Even small amount of SAHS can cause the increase in the polymerization rate a lot. The particle conversions were determined by measuring solid contents at different time. The results are showed in Fig. 1. It is seen that the conversion for homopolymerization of styrene is less than 10% after 5 h. However, the copolymerization rate and the conversion increase by the addition of SAHS comonomer. As the molar ratio of St to SAHS is 100/0.8, the conversion is 51 wt% in 5 h; as the molar ratio increases up to 100/3.2, the conversion reaches 84 wt% within 5 h. This result is explained by two reasons. On one hand, much larger number of free radicals are generated with the introduction of the functional comonomer SAHS due to its water solubility. In the classical Smith–Ewart scheme of emulsion polymerization, the rate of polymerization, R_p, is proportional to the particle number density:

$$R_p = k_p[M_p]N_p(n/N_A) \quad (1)$$

Where k_p, $[M_p]$, N_p, n, and N_A are the propagation rate constant, the monomer concentration in growing particles, the particle number density, the average radical number per particle, and the Avogadro's number, respectively. According to the equation, the polymerization rate increases with the increase in monomer SAHS concentration, as N_p is dependent on the functional monomer concentration [13]. On the other hand, the introduction of ionic comonomer SAHS will result in association between polar groups, which increases the viscosity of the system and the polymerization rate [14]. Therefore, the copolymerization rate increases, and the conversion is high within a short time.

Figure 2 shows scanning electron micrographs of the particle copolymers with varied molar ratio of St to SAHS,

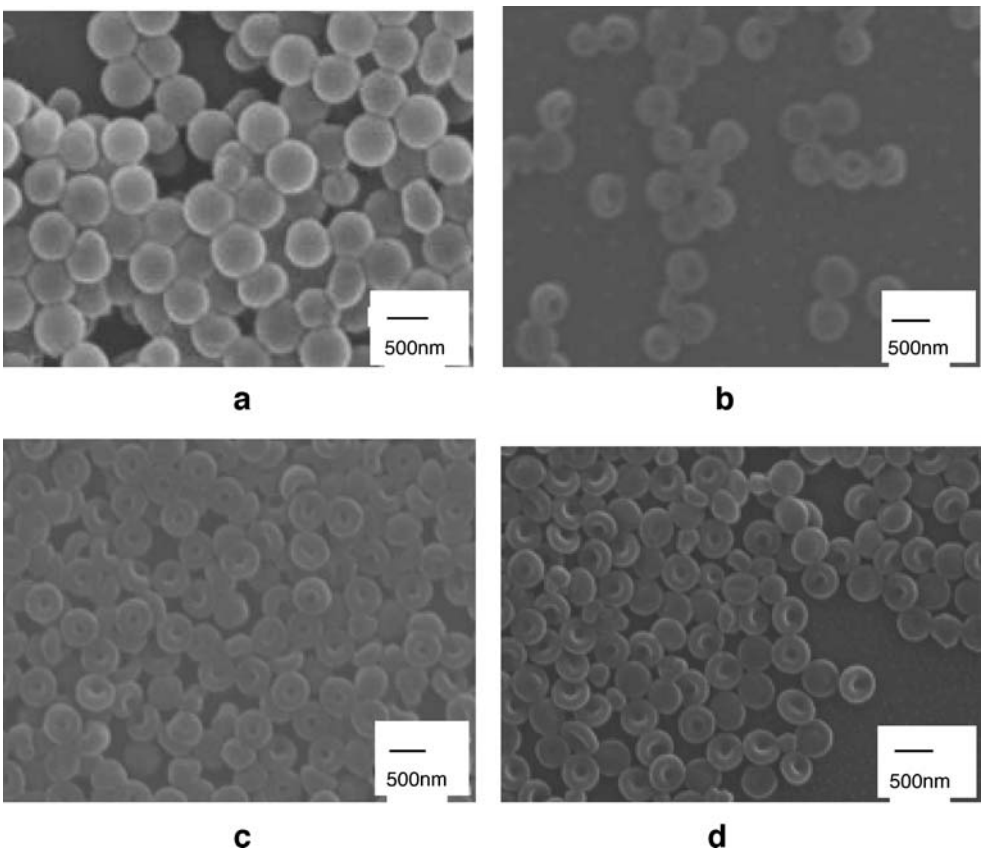

Fig. 2 SEM photographs of particle samples. **a** SAHS-08; **b** SAHS-16; **c** SAHS-24; **d** SAHS-32. The samples were synthesized with the following conditions: St, 16.0 g; SAHS, variable; DVB, 0.45 g; KPS, 0.2 g; sodium bisulfite 0.08 g; and water, 125 ml. Reacting at 70 °C for 5 h

which are identified in Table 1. As seen in the figure, normal spherical beads can be obtained at low SAHS content (Fig. 2a). But with the increase in SAHS content, the shapes of the particles are deformed (Fig. 2b–d). They are no longer spherical beads but rings with an empty hollow in a particle, and secondary particles appear. This is probably explained by the nucleation mechanism of the particle formation. The emulsifier-free emulsion polymerization of St and SAHS follows the homogenerous nucleation mechanism. At the early stage of the polymerization, monomers SAHA and St dissolved in water are initiated, and they grow into surface-active oligomeric radicals by capturing monomers until the radicals exceed their critical soluble sizes and precipitate. If the concentration of SAHS is low, the number of radicals is limited, the growing oligomeric radicals are sufficiently hydrophobic, and they are absorbed by the growing seed particles before being able to nucleate independently. This is favorable for the growth of particles as normal beads (showed in Fig. 2a). However, as the water-soluble monomer SAHS content increases, a lot of the negative charged oligomeric radicals are formed at the early stage due to the homopolymerization of SAHS with sulfonate groups. The long-chain characteristic and the electrostatic expulsive force of the negative charged oligomers may cause an empty hollow when the oligomers precipitate to form a bead. Thus, the final particles are deformed after sufficient growing. As monomer SAHS is consumed, less charged copolymer oligomeric radicals of SAHS and St in water are generated. The oligomeric radicals form coils and precipitate when their size exceeds critical length, which causes bimodal size distribution.

The formation of ring shape and deformed particles is confirmed by more experimental evidences. We have prepared particle latexes with different amount of initiator. For Fig. 3, 0.2, 0.3, 0.5, and 0.7 g of KPS are used for samples (e), (f), (g), and (h), respectively. As seen in Fig. 3, with the increase in KPS, the resultant particles are deformed and become amorphous, and the size distribution becomes polydispersed. The more the KPS is added, the more serious deformation is caused. The effect of adding more initiator is similar to increase monomer SAHS concentration. Meanwhile, the sizes of some deformed particles in the samples (g) and (h) are larger than in samples (e) and (f) (Fig. 3); this is probably because coagulation may take place between polar deformed

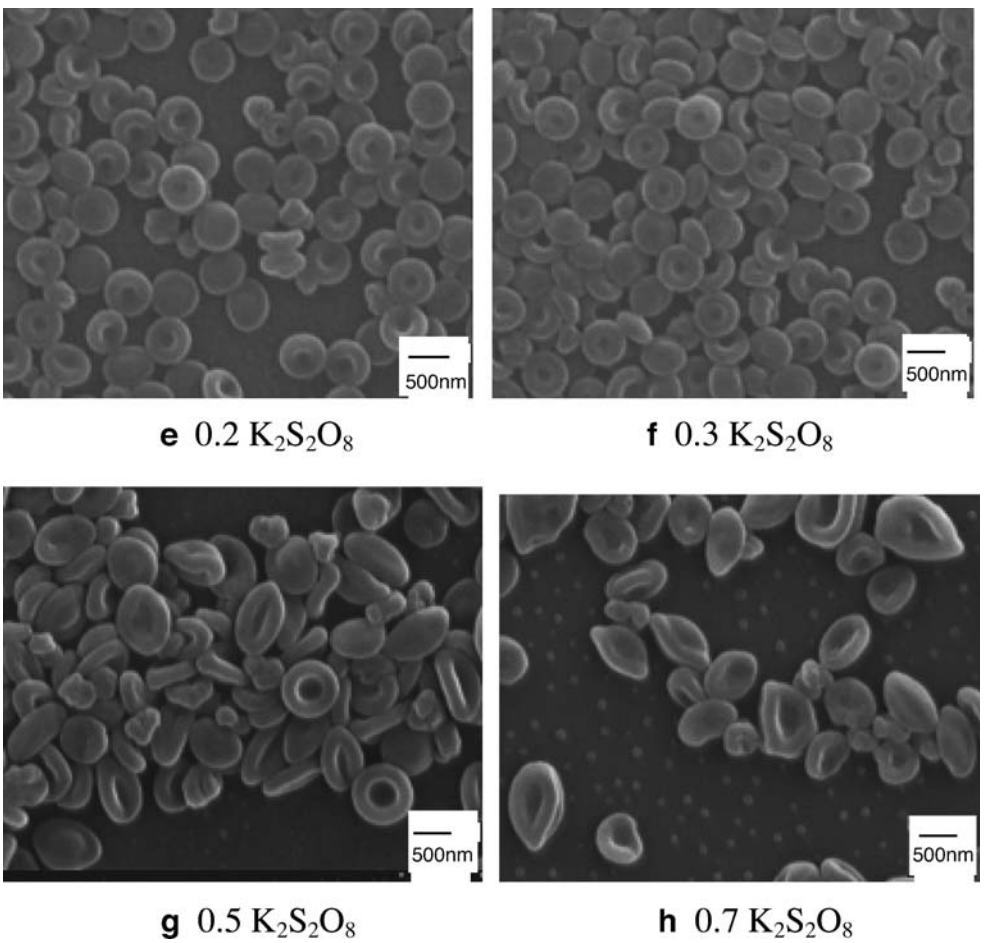

Fig. 3 SEM photographs of particle samples with different amount of KPS. **e** 0.2g; **f** 0.3g; **g** 0.5 g; **h** 0.7 g. The recipe for the preparation: St, 16.0 g; SAHS, 0.72 g; DVB, 0.45 g; SBC, 0.08 g; and water, 125 ml; reacting at 70 °C for 5 h

Table 2 The recipe of for the preparation by two-stage shot growth

Component	First shot		Second injection	
	g	mmol	g	mmol
St	16.00	153.80	3.20	30.80
SAHS	0.24	1.10	0.96	4.40
DVB	0.45	3.46	0.10	0.77
Acetone	12 (ml)	3 (ml)		
Water	125 (ml)	18 (ml)		
KPS	0.20	0.74	0.20	0.74
Sodium bisulfite	0.08	0.74	0.08	0.74
Sodium bicarbonate	0.08	0.95	0.03	0.36

particles. Comparing the images of Figs. 2 and 3, we noted that both increases in the ionic monomer and the initiator result in deformation of the particles. The mechanism for the formation of deformed particles is further being studied.

Effect of injection manner on two-stage shot polymerization

It is seen from the above study that highly charged monodispersed spherical particles of St and SAHS are difficult to be prepared by batch polymerization without surfactants. To overcome the problems and achieve high incorporations of SAHS monomer and monodispersed particles, we have employed a two-stage shot growth process for the preparation of highly charged monodispersed copolymer latexes according to the recipe indicated in Table 2. Additionally, the effect of injection manner of the second-stage batch on the formation of particles is investigated.

The technology of two-stage shot growth process was first used by Sakota and Okaya [15]. It was adapted by Chainey et al. [16] for the preparation of polystyrene/poly (alkyl acrylate) or poly(alkyl methacrylate) core-shell latex and used by Kim et al. [17], Sunkara et al. [18], and Zeng et al. [19] for preparation of poly (styrene-co-sodium styrenesulfonate) latexes. In this study, we have investigated

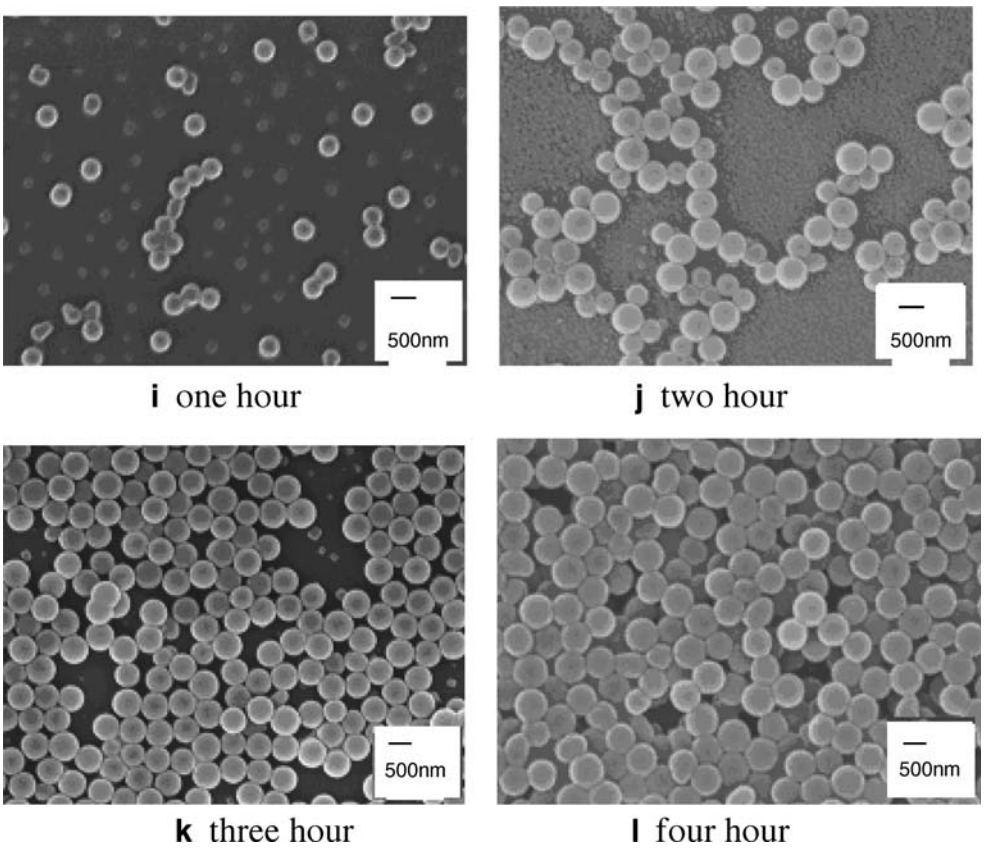

Fig. 4 SEM photographs of particle samples synthesized with the recipe indicated in Table 2, but different time intervals at which the second batch monomers are injected. The surface charge density for samples: **i** 4.25; **j** 4.92; **k** 5.01, and **l** 5.24 ($\mu c/cm^2$), respectively

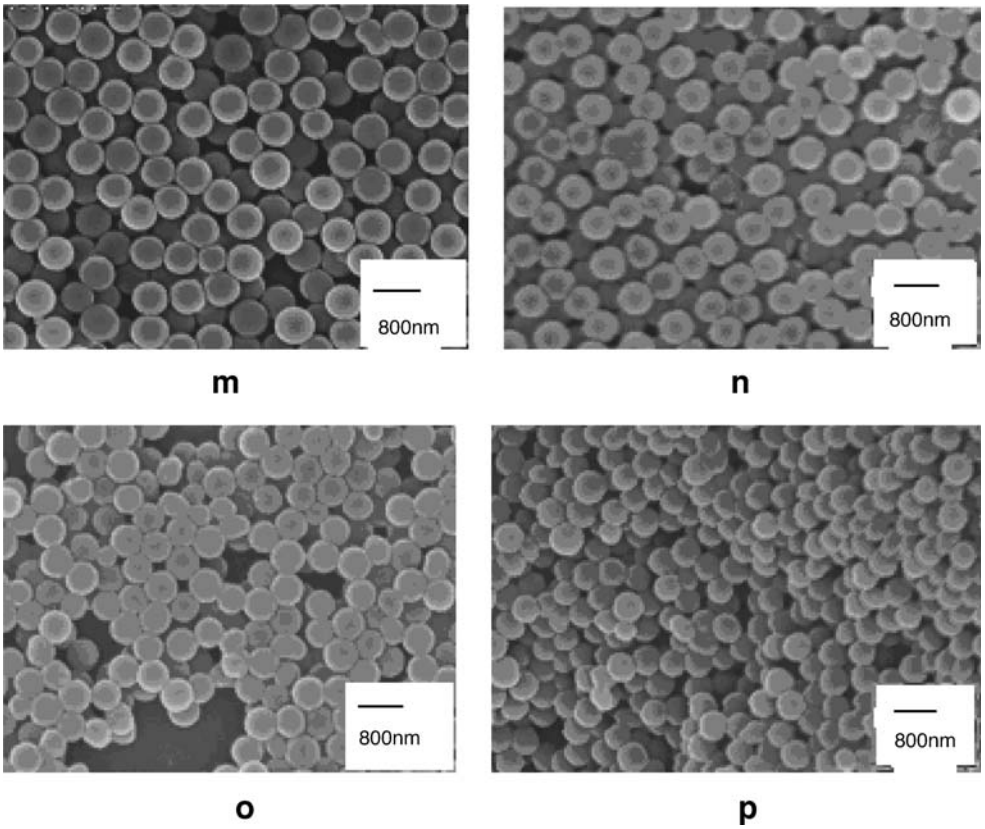

Fig. 5 SEM photographs of particle samples prepared according to the recipe indicated in Table 2 with different acetone contents: **m** 9 ml; **n** 12 ml; **o**15 ml; and **p** 18 ml, respectively

the effect of injection manner on the formation of the particles. The injection of the second batch at different time is carried out, and its effect on particle morphology and surface charge densities of the particles are investigated. It is found that as the time interval between the first batch and second batch increases, the surface charge density of the particles increases, indicating that more SAHS is incorporated into the particle surface. Furthermore, perfect monodispersed spherical particles are obtained when second batch monomers is added at high particle conversion of the first batch. This result is correspondent to the reports on the research of poly(styrene-co-sodium styrenesulfonate) [17, 19].

It can be explained according to the study on oligomeric radical diffusion of Hansen and Ugelstad [20]. To avoid secondary particles to be nucleated, the rate of radical capture by the particles, R_c, must exceed the rate of radical generation, R_i. When the second batch monomer mixture is injected at the early stage (e.g., 1 h later after the first batch injection), which is somewhat like one-shot polymerization, the monomer of SAHS homopolymerizes in aqueous phase and forms a lot of oligomers within a short time. In this case, the number density and the size of the particles generated in the first stage are not sufficient to capture all the oligomeric radicals generated in the second stage, i.e., $R_c < R_i$. Therefore, the oligomeric radical's aggregates into secondary particles as soon as their length exceed critical size. The polydispersed particle distribution will be seen in this case. If the second-stage monomers are injected at the high particle conversion time, the number and the size of the particles are enough to capture all the newly formed oligomers. Hence, monodispersed particles can be obtained. The images of the particles prepared with different injection manner are showed in Fig. 4.

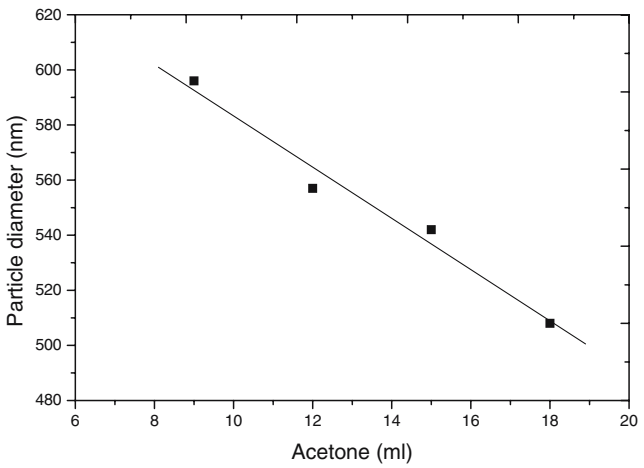

Fig. 6 Correlation between the particle diameters and the acetone content added. The recipe for the preparations is indicated in Table 2

Effect of acetone on the particle size

To adjust the particle sizes of the copolymers, we added certain amount of acetone to water as medium for the polymerization. In all of our studied cases, the monodispersed particle latexes have been obtained. The diameters of the particles are determined by DLS. It is observed that the particle diameters decrease with the increase in acetone contents within some range. For comparison, we prepared a particle sample without acetone addition. The resulting particles have average diameter of 630 nm. However, the diameters drastically decrease when prepared at the present of acetone. The measured particle diameters are 596, 557, 542, and 508 nm for samples indicated in Fig. 5 (m), (n), (o) and (p), respectively.

It is explained as follows: As the addition of acetone, the solubility of monomer styrene in the medium increases. The monomers in aqueous phase will be initiated to produce more number of radicals. The higher the monomer concentration in the polymerization phase, the more the number of radicals generated at the early stage of the polymerization. On the other hand, the mixed solvent of acetone and water is less polar than pure water. The less polar the medium is, the favorable it is for the formation of stable oligomers and primary particles. Thus, the duration for the particle formation is longer in the mixed medium than in pure water. Consequently, more particles are generated in the system, and the final particle diameters are smaller than those of prepared in pure water. This fact was observed by Zeng et al. [19] when they prepared copolymer latex of styrene and sodium styrenesulfonate. The influence of acetone content on particle diameters is showed in Fig. 6. The straight line in the figure is described by the equation $y = 676.3 - 9.3x$, where y is the particle diameter (nm) and x is the acetone added (ml). The correlation coefficient R=0.9876.

The surface charge densities were measured by conductometric titration after the particle latexes were rigorously cleaned. The surface charge densities of the particles were 4.2, 4.7, 4.8, and 4.9 ($\mu c/cm^2$) when the acetone used was 9, 12, 15, and 18 (ml), respectively. It is obvious that the surface charge density increases slowly with the increase in acetone added to the reaction system. Our explanation for the result is that as acetone increases in the reaction medium, more styrene content dissolves in the reaction medium due to its less polarity. It will result in more radical generation and cause quick consumption of styrene at the first stage. When the second batch is added, the concentration of SAHS in the system is slightly high related to that of system with less acetone. During the following propagation process, the particles capture more SAHS. Therefore, the final particles possess a higher charge density than the samples prepared with less acetone added.

Conclusion

Particle latex of poly (styrene-co-sodium 1-allyloxy- 2-hydrxypropane sulfonate) was synthesized by emulsifier-free emulsion polymerization. The highly surface charged monodispersed spherical beads could be obtained if a two-stage shot growth technology was employed for the preparation. The addition of acetone to the reaction medium caused decrease in the particle diameters. This property could be used for controlling particle size. The surface charge density slowly increased with the increase in acetone contents in the preparations.

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