

Study on the influence factors of the stability during preparation of high-solid content P(MMA/BA/AA) latex. Part I: re-nucleation and percent coagulum

Rui Deng · Chen Cheng · Zhi Ying Wang ·
Zhao Quan Ai · Hong Tao Zhang

Received: 24 April 2010 / Revised: 31 July 2010 / Accepted: 18 August 2010 /
Published online: 30 August 2010
© Springer-Verlag 2010

Abstract Using large-sized and mono-dispersed seeded latex as medium plus a semi-continuous monomer-feeding technology was an effective method for preparing high-solid content (HSC) latex. A series of runs indicated that the influence of key factors, such as surfactant, monomer composition, seed particle size, reaction temperature, and feeding rate were the most sensitive issues in maintaining the stability during preparation of HSC Poly (methyl methacrylate/*n*-butyl acrylate/acrylic acid) [P(MMA/BA/AA)] latex. It was also shown that the effect of these factors on the coagulum content played an important role in preparation process. In addition, the amount of gel content was more related to re-nucleation and particle size distribution (PSD) control. And the results seemed to be more different from that of produced in a low disperse phase system by conventional semi-continuous emulsion polymerization.

Keywords High-solid content · Latex · Re-nucleation · Coagulum

Introduction

High-solid content (HSC) latexes refer to the aqueous polymer dispersion, the solid content of which is more than 60% [1]. In contrast to the conventional latexes (the solid content of which is 30–50%), HSC latexes have attracted considerable attention due to the following advantages: high-specific productivity, short film-forming time, and low storing and transporting cost [2]. As a result, HSC latexes have a wide range of potential application in adhesives, coatings, textile manufacturing, paper paints, floor polish, and makeup.

R. Deng · C. Cheng · Z. Y. Wang · Z. Q. Ai (✉) · H. T. Zhang
Ministry of Education Key Laboratory for Preparation and Application of Functional materials,
Faculty of Material Science and Engineering, Hubei University, Wuhan 430062, China
e-mail: aiz-q@sohu.com

High-solid content and low-viscosity (HSC/LV) latexes have attracted considerable attention due to their unique characteristics. Recently, a number of researches are devoted to improve preparation strategies. In particular, semi-continuous emulsion polymerization has drawn much attention because of its ability to provide large size and sharp distribution [3]. During the last decades, many scholars like Chu [4–6], Schneider [7–9], Salima Boutti [10], Sajjadi and Brooks [11–13], as well as our group, have been engaged in producing HSC latex in semi-continuous emulsion polymerization. The way they have used could be mainly divided into three categories [4]: adding additional surfactant, adding pre-formed seed emulsion, and adding surfactant + seed. In a word, the semi-continuous emulsion polymerization has remarkable advantages in controlling particle size and their PSD.

Nevertheless, as the volumetric concentration of the dispersed phase increases to more than about 60%, particle–particle interactions have a strong responsibility for the stability of colloid system because of the particles' deformable and the potential changes of double electrode layer [14]. Thus, the stability of colloidal system begins to become more sensitive with the increase of their solid content. Therefore, controlling the coagulum content is of great significance for preparation reproducibility, especially depended on re-nucleation and process conditions. It was reported that homogeneous nucleation might occur when water-soluble monomers such as methacrylic acid (MAA), acrylic acid (AA), vinyl acetate (VAc), and methyl methacrylate (MMA) were used [8]. The influence of the monomer composition had a significant impact on PSD, it was found that the increasing of MMA strongly reduced the gel content because of the decreasing the risk of chain transfer to polymer in copolymerization reaction [15]. And the gel content of the final copolymer increased with the increasing of initiator concentration and decreasing of reaction temperature [16]. Compared to conventional semi-continuous emulsion polymerization, the influence of process conditions were more sensitive to coagulum percent when it was under a higher concentrate suspension. It was reported by our group that more than 70 wt% solid content P(BA/MMA/AA) [17] and P(BA/MMA/AA)/P(St/AA) [18] composited HSC could be obtained. In addition, in order to optimize the technology of emulsion polymerization and obtain higher solid content, the random-designed experiments were then applied to regression analysis with the known statistical analysis system (SAS) by Zhao et al. [19], and the results remarked that the square value of solid content, the interaction between the initiator concentration and functional monomer concentration, the square value of emulsifier content, the interaction between monomer concentration and reaction temperature, all greatly affected the particle size.

As we know, the process of re-nucleation has a great influence on stability, many preparation methods have been reported in several publications, but no suggestions about re-nucleation and coagulum percent. This work is an attempt to have a systematical study about the influence of different preparation factors on the percent coagulum when prepared HSC latex with the technology of using seeded latex as medium plus a semi-continuous monomer-adding stage. The chosen monomer system is MMA, BA, and AA due to its typical role in the theoretical and industrial study of emulsion polymerization, and the designed solid content is 72.5 wt%. It is

expected that this research is of great value for HSC latex preparation of other monomer systems. We also hope that this study can enrich our knowledge in understanding and controlling of the stability during preparation of bi or tri-modal latex.

Experiments

Materials

The monomers used in this study were butyl acrylate (BA), methyl methacrylate (MMA), and acrylic acid (AA) (Beijing DONGFANG Chemical Company, Beijing, China). All of the monomers were filtered through inhibitor removal columns before it was used. The initiators used in the experiments were ammonium persulfate (APS) and sodium bicarbonate (SBC, Sinopharm Chemical Reagent Co., Ltd, China) was used as buffering agent, the non-ionic surfactant was polyoxyethylene (15) lauryl ether (OS-15) and the anionic surfactant sodium dodecyl sulfonate (SDS) (Sinopharm Chemical Reagent Co., Ltd, China), were all used as received. The water was deionized.

Emulsion polymerization

Large-size seeded latex

Large-size seeded latex was prepared with seeded semi-continuous emulsion polymerization, which were performed in a 1000-ml four-neck flask equipped with a reflux condenser, nitrogen gas inlet tube, polytetrafluoroethylene (PTFE) stirrer, a feeding tube for monomers or pre-emulsified monomers, and a thermometer. Pre-emulsified monomer was prepared in a mono-neck flask by the addition of water, surfactant, buffer, and monomers successively under vigorous stirring at room temperature. And the whole reactive devices were carried out in heated water bath for temperature control. The typical recipes and properties were listed in Table 1.

Table 1 Recipe and characteristics of seeded latex

Emulsion	BA (g)	MMA (g)	AA (g)	H ₂ O (g)	OS-15 (g)	SDS (g)	APS (g)	SBC (g)	T (°C)	Time (min)	D_p (nm)	SC (%)
SE												
IC	24	16	–	360	1.4	0.02	0.72	0.24	75	50	487	50
EM	269	179	12.4	128	10	0.12	0.72	–	75	300		

Where IC is initial charge, EM is pre-emulsified monomers, CR is coagulum rate, D_p was the average diameter of particles, SC is solid content, and Time represents the reaction and feeding time, respectively. T is the reaction temperature during the initial and feeding period, respectively, which will be finally risen to 80 °C after the addition for another 30 min to finish the reaction

HSC *P*(MMA/BA/AA) latex

Using the large-sized and mono-dispersed seeded latex as medium plus a semi-continuous monomer-feeding technology is an effective method for preparing HSC latex. Compared with the reactor within preparing lager seed, 250 ml four-neck flask was chosen to accomplish the polymerization. Such seed latexes, SDS, APS, and SBC were mixed in the reactor for about 20 min, followed by raising the temperature to 80 °C and beginning the reaction. The remained monomer was fed in about 1 h. After the addition of monomers, the polymerization was conducted for another more 40 min to complete the reaction. The typical recipe was tabulated in Table 2. And the experimental procedure was detailed in ref. [19].

Samples were occasionally withdrawn through a valve in the bottom of the reactor for analysis. In order to facilitate the discussion, the difference recipes used would be detailed during the discussion of the results.

Characterization

Samples were withdrawn during the process, and the polymerization was stopped with hydroquinone. The overall conversion was determined gravimetrically. Solid content (SC) was measured with thermogravimetry. The particle size and distribution of seeded latex were characterized with an Autosizer Loc-FC-963 apparatus (Malvern Instruments, Malvern, UK) and checked with transmission electron microscopy (TEM, JEM-100SX, Tokyo, Japan). The rheological properties of the latexes were estimated with a rotation viscometer (NXS-11, Chengdu Instruments Co. Chengdu, China) at room temperature. The stability during polymerization was evaluated with coagulum ratio (CR), which was determined as follows. The latexes were filtered through a 120-mesh filter at ambient temperature. Then, the coagulum in the filter and that on the stirrer and the wall of reactor was collected carefully. The coagulum was rinsed with deionized water and dried in an oven at 105 °C for 24 h. CR was calculated as follows:

$$\text{CR}(\%) = G_2 / (G_1 - G_0) \times 100$$

where G_1 was the mass of the latex, G_2 was the mass of the dried coagulum, and G_0 was the mass of the volatile materials in the latex.

TEM pictures (Fig. 1) show that the seed latex we had obtained was mono-dispersed with the particle size at about 487 nm, and the PSD of HSC latex was bimodal with the large and small particle size at about 500 and 90 nm, respectively.

Table 2 Recipe and characteristics of HSC latex

SE (g)	SDS (g)	APS (g)	SBC (g)	AD Mon (g)	FT (Min)	SR (r/min)	CR (%)
125	2	0.23	0.23	100	60	250	0.8

Where SE is the seeded emulsion prepared with recipes in Table 1, AD Mon is addition quantities of mixed monomer, the constituent of which is BA:MMA:AA = 60:40:3. FT is feeding time of the monomer, SR is the stir rate, and CR is the coagulum ratio. The temperature during the feeding period is 80 °C, which will be finally risen to 85 °C for the other 15 min to finish the reaction

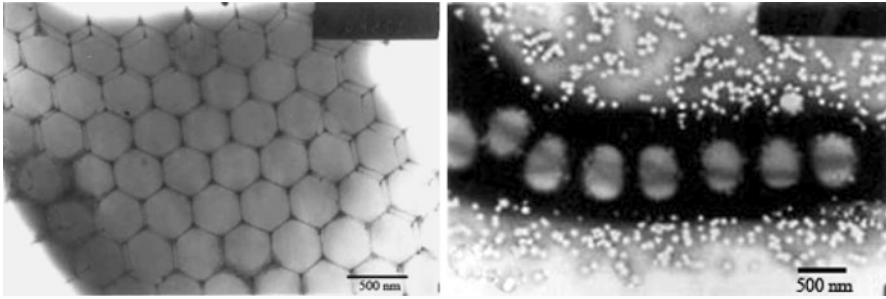


Fig. 1 Transmission electron micrographs (JEM-100SX) of SE (*left*) and HSC (*right*) prepared with recipes in Table 1. Phosphotungstic acid was used as a marker to allow us to detect the small particles in the film for HSC (Observed at room temperature)

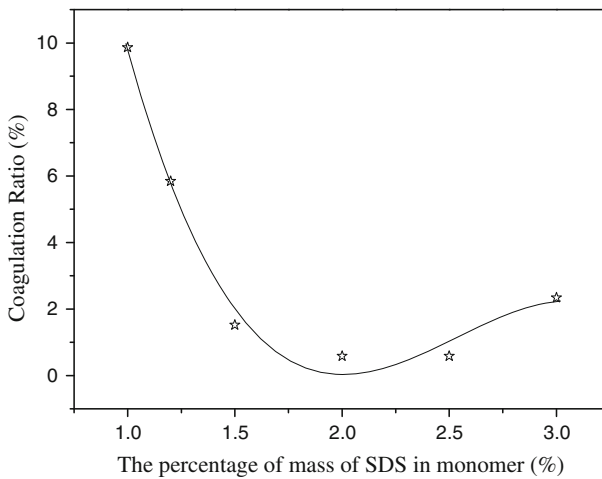


Fig. 2 Influence of SDS content on the coagulation ratio of HSC Latex. Where $m(\text{SE}, 487 \text{ nm}) = 125 \text{ g}$, $m(\text{APS}) = 0.23 \text{ g}$, $m(\text{SBC}) = 0.23 \text{ g}$, $m(\text{Mon}) = 100 \text{ g}$, stir rate was 250 r/min. Since the temperature reached 80 °C, mixed monomer began to be added by dropwise and the fending time was 60 min

Results and discussion

Effect of dosage of emulsifier

Based on recipe in Table 2, the random copolymers of poly(MMA-*co*-BA) with different dosage of surfactant were prepared by free radical semi-continuous emulsion polymerization. Anionic surfactant sodium dodecyl sulfonate (SDS) was used as the only surfactant to help to arouse secondary nucleation. The results in Fig. 2 show that coagulum percent decrease with the increase of SDS content. However, when surfactant content is more than 2.5 wt%, the coagulation content begins to increase slightly. For a proper interpretation of the distinctive increase, it was necessary to understand that the surfactant not only helped to stabilize the colloids, but also worked on nucleation in our experiments.

In Fig. 3a, TEM photograph shows the original morphology of particles when the percentage of SDS in monomer was 3 wt%. It was found that the nucleated particles flocculate onto others and/or on larger particles, and the small particles seemed to be rod-like. Obviously, this was a universal phenomenon existing in the final latex. That might be attributed to linear fused aggregates of two or more small spherical particles. Figure 3b also clearly shows that the larger particles were enveloped by lots of small particles, and the surface of these colloids seemed more roughness. We believed that ionic strength might be the main reason to be responsible for this instability. Excess addition of ionic surfactant not only generated more new particles, but also increased the ionic strength of the aqueous phase, thus the stability of the dispersion was greatly influenced by surface potential density of each particle, which finally led to particles' deformation and aggregation. In addition, excess foams caused by much surfactant in aqueous suspensions would also rebound adversely on forming micelle structure.

Effect of type and ratio of surfactant

One of the major difficulties of in situ nucleation is lack of reproducibility of the processes. It was reported that addition of compound surfactant (anionic and nonionic) was a useful route to increase the stability during semi-continuous emulsion polymerization [10]. Anionic surfactant favors to provoke a strong nucleation, but has no ability to stabilize the particles sufficiently especially when it is at the later period of polymerization. Therefore, effect of type and ratio of surfactant were investigated in the following experiments. As shown in Table 3, coagulum content decreased with a bit addition of nonionic surfactant, nucleation and stability both improved greatly as well. In our experiment, anionic surfactant SDS and nonionic surfactant OS-15 was used as a compound system. Particle size and their distribution with different ratio of surfactants were investigated during the preparation.

The PSD results of re-nucleation process are also given in Table 3. The size of large and small particles both increased with the increasing of OS-15 content. Meanwhile, it was found that SDS had a great influence on the population of new

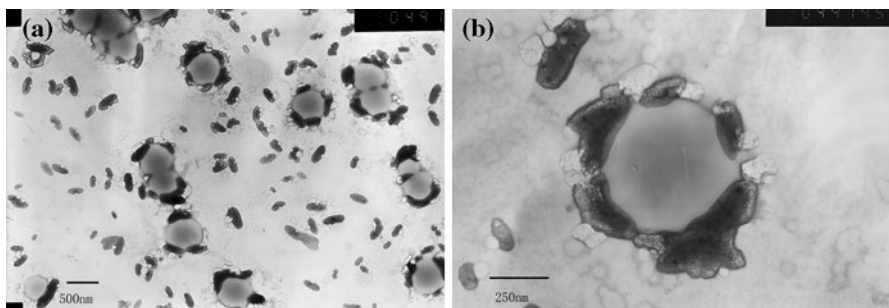


Fig. 3 Transmission electron micrographs (TEM) photograph of particle morphology when the percentage of SDS mass in monomer was 3 wt%, observed at room temperature

Table 3 Recipe for HSC latex in the seeded semi-continuous emulsion polymerization of BA/MMA/AA at 80 °C

Run	Seed (nm)	SDS (g)	SDS/OS-15 (g)	Large population			Small population			CR (%)
				d_p (nm)	%V	Δd_p	d_p (nm)	%V	Δd_p	
1201	487	2	–	515	75.4	28	95	24.6	95	0.99
1202	487	–	2(3/1)	550	81.6	63	103	18.4	103	0.54
1203	487	–	2(1/1)	734	90.1	247	141	9.9	141	1.54

Δd_p is the increment of growing particle's diameter (at the beginning, large particle of initial stage was 487 nm and small ones was 0 nm)

small particles. Interestingly, coagulation content decreased firstly and then increased with the increasing of OS-15. When SDS/OS-15 = 3/1, the results revealed that the created particles' sizes and PSD were in accordance with rheological parameters of HSC latexes [20]. From Figs. 4 and 5 for the growth of particles versus reaction time, we can see that the amount of small particles and the corresponding monomer consumed for their growth have increased with the increasing amount of second polymer particles. Small particles were likely to grow more quickly than larger ones, but the absolute increment was limited. It was considered that the particle precursors formed from re-nucleation were easily stabilized by anionic surfactants, which also allowed the fine tuning of the nucleation process, and that of the PSD. In addition, particle sizes of the large and small particle increased with the increase of relative proportion of non-ionic surfactant. That might be attributed to its higher molecular weight, which led to a slow diffuseness to the growing interfacial of particles. Consequently, with the increasing of non-ionic surfactant, the population of new small particles was likely less and the particle size seemed larger. It was necessary to note that non-ionic surfactant could not stabilize the newly formed particles quickly, nevertheless, once adsorbed, they would provide excellent salt and freeze–thaw stability.

Effect of particle size of seed

In order to reach a polymer content more than 60%, the seed particle diameter should be at least 450–550 nm (if the diameter is much lower than this, the viscosity will be too high and a large number of coagulum will emerge). The preparation procedure of mono-dispersed seed from 250 to 980 nm was similar with the recipe in Table 2. A initial seed of 10% solid content latex was firstly synthesized, then solid contents were raised to 50% by addition of pre-emulsified monomer prepared by OS-15. The sizes of mono-dispersed colloids could be controlled by the amount of OS-15 or compound surfactant (if using compound surfactant, OS-15 should be more than 98%, a small raise of SDS was available). As shown in Fig. 6, coagulation ratio decrease with the increasing of seed size, especially when the diameter of seeds reach about 500, coagulum percent keeps a lower level, less than 1 wt%. The obtained results were in good agreement with experimental data from

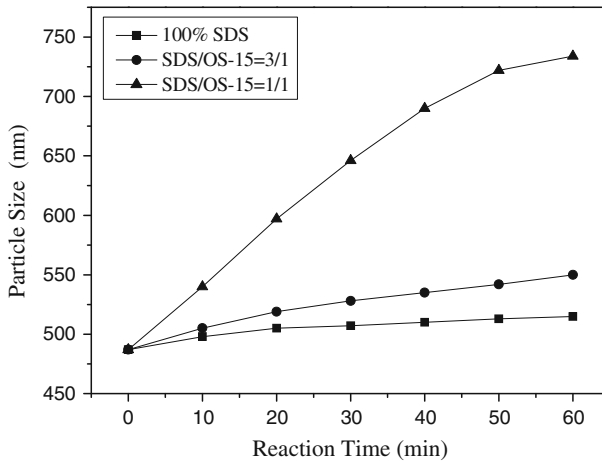


Fig. 4 The growth of large particles with the increasing of reaction time. Where $m(\text{SE}, 487 \text{ nm}) = 125 \text{ g}$, $m(\text{APS}) = 0.23 \text{ g}$, $m(\text{SBC}) = 0.23 \text{ g}$, $m(\text{Mon}) = 100 \text{ g}$, stir rate was 250 r/min. Since the temperature reached 80 °C, mixed monomer began to be added by dropwise and the fending time was 60 min

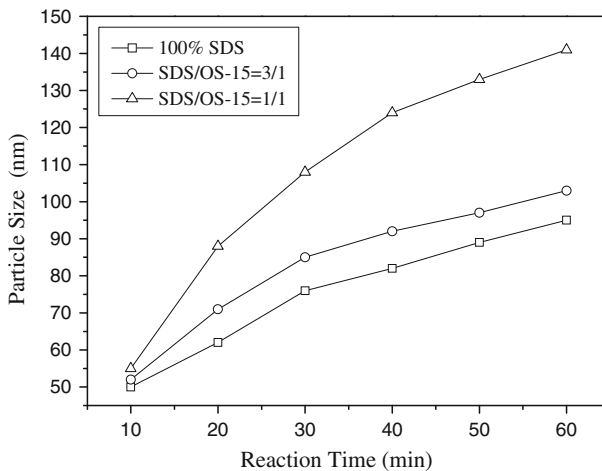


Fig. 5 The growth of small particles with the increasing of reaction time. Where $m(\text{SE}, 487 \text{ nm}) = 125 \text{ g}$, $m(\text{APS}) = 0.23 \text{ g}$, $m(\text{SBC}) = 0.23 \text{ g}$, $m(\text{Mon}) = 100 \text{ g}$, stir rate was 250 r/min. Since the temperature reached 80 °C, mixed monomer began to be added by dropwise and the fending time was 60 min

Chu et al. [21], those who had attempted to study rheological regulars of HSC latexes by means of mixing with mono-dispersed latexes in different particle sizes.

Actually, for conventional emulsion polymerization, the stability of emulsion products would decrease with the growth of particles due to the non-equilibrium thermodynamics. However, for high-concentrated bimodal suspension, the result was likely to be something different. As shown in Fig. 7, original photographs from

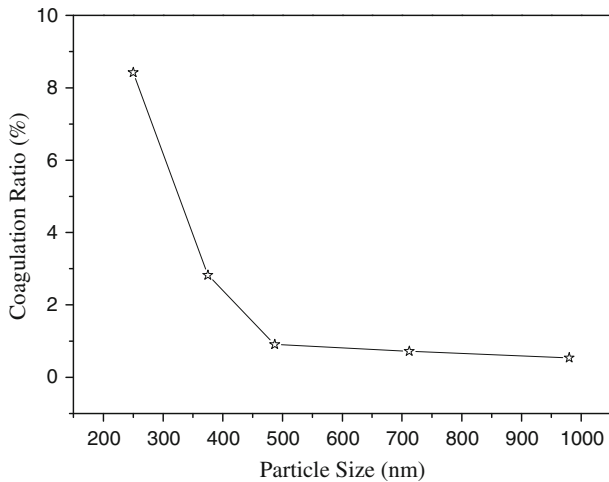


Fig. 6 Influence of the particle size on the coagulation ratio of HSC Latex. Where $m(\text{SE}) = 125 \text{ g}$, $m(\text{SDS})/m(\text{OS-15}) = 1.5/0.5$, $m(\text{APS}) = 0.23 \text{ g}$, $m(\text{SBC}) = 0.23 \text{ g}$, $m(\text{Mon}) = 100 \text{ g}$, stir rate was 250 r/min . Since the temperature reached $80 \text{ }^\circ\text{C}$, mixed monomer began to be added by dropwise and the feeding time was 60 min

Malvern Instrument indicate that large seeded particles help to generate more small particles, and the size and population of small particles also increase with the increase of seeded size. Obviously, this result was related to the re-nucleation processes, it seemed that large particles were able to provide more room and/or interstice to accomplish re-nucleation. Therefore, in a certain sense, particle–particle interactions (such as collision and extrusion between particles) played an important role in colloidal stability especially at a higher polymer concentration, i.e. in a certain solid content, particles with larger size obviously had a smaller population, which directly decreased the risk of colloidal collision. Thus, latex product produced by lager seed would have lower particle–particle interaction and less coagulum. It is worth mentioning that the storage stability of colloidal particles are prone to reduce sharply when the size of the particles reach more than 800 nm [3], what is harmful to the application of final product.

Effect of MMA content in monomer

Based on recipes in Table 2, mono-dispersed seed with an average particle size of 487 nm was adopted in this section. As shown in Fig. 8, it is observed that the addition of increasing MMA lead to a sharp decrease of the coagulum content, the higher the amount of MMA, the lower the gel content it has. However, when the weight fraction of MMA was more than $40 \text{ wt}\%$, coagulum percent seemed to have a slight rise. There are two reasons that may be account for this gel phenomenon, one is attributed to intermolecular network crosslinking by termination of MMA and/or BA unit chains. The other was colloidal agglomeration and coagulation caused by particle arrangement when undergoing re-nucleation in a

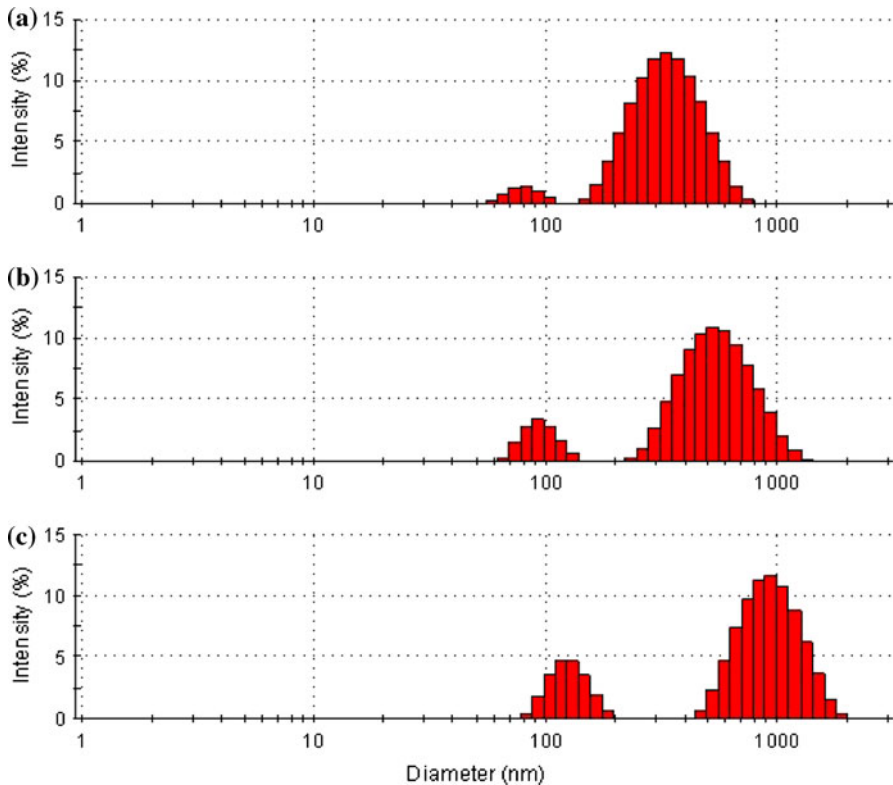


Fig. 7 Final particle size and distribution of latex prepared from different seeds. **a** seed of 487 nm, **b** seed of 712 nm, and **c** seed of 980 nm

high concentration suspension. On a whole, the results were similar with the results obtained by Inigo Gonzalez et al. with a semi-continuous emulsion copolymerization at a designed polymer content not more than 50% [15].

For the gel formation, the lower reactivity of the MMA radicals reduced the instantaneous conversion because of the lower propagation rate coefficient of the MMA as compared to that of BA. And the level of branches also correspondingly decreased with the increase of MMA, which directly reduced the probability of network crosslinking of the intermolecular (see ref. [15]). On the other hand, copolymerization reaction with too much water-soluble monomer MMA drove up the proportion of homogeneous nucleation to some extent, especially when the weight fraction of MMA was more than 40 wt%, Fig. 9 shows the morphology of particle produced by different MMA content. The size of large particles in Fig. 9a (when composed of 20 wt% MMA) seemed larger than those in Fig. 9b and c. It was evident that small particles became irregular when MMA reached to 60 wt%. Therefore, a violent uncontrolled re-nucleation resulted by homogeneous nucleation led to an irregular particle arrangement as reflected in Fig. 9c. This inevitably provoked a strong interaction among particles in the later period of polymerization

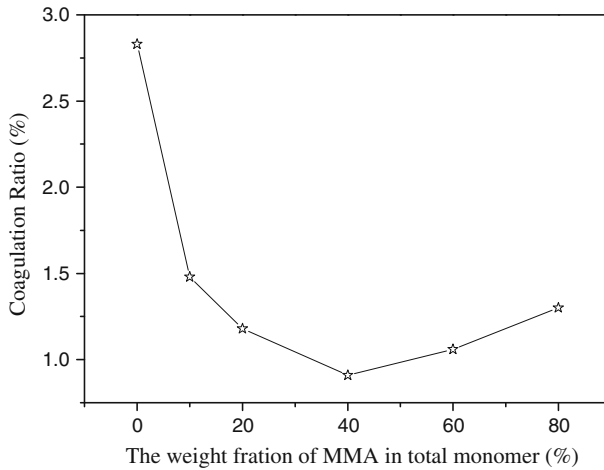


Fig. 8 Influence of the weight fraction of MMA on the coagulation ratio of HSC Latex. Where $m(\text{SE}, 487 \text{ nm}) = 125 \text{ g}$, $m(\text{SDS})/m(\text{OS-15}) = 1.5/0.5$, $m(\text{APS}) = 0.23 \text{ g}$, $m(\text{SBC}) = 0.23 \text{ g}$, $m(\text{Mon}) = 100 \text{ g}$, stir rate was 250 r/min. Since the temperature reached 80 °C, mixed monomer began to be added by dropwise and the feeding time was 60 min

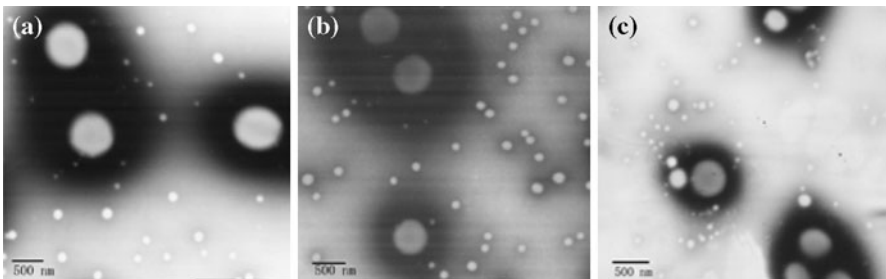


Fig. 9 Transmission electron micrographs (TEM) photograph of particle morphology when comprised of different MMA. **a** 20 wt% MMA; **b** 40 wt% MMA; **c** 60 wt% MMA. Phosphotungstic acid was used as a marker to allow us to detect the small particles in the film for HSC latex, observed at room temperature

reaction. Furthermore, the strong interactions increased the risk of particles' deformation and aggregation. Finally, the rough PSD aroused amount of coagulum content. As a result, it was difficult to control the size and number of small particles when homogeneous nucleation occurs. Therefore, experimental results showed that a mixture of monomer composed of 40 wt% MMA could avoid uncontrollable homogeneous nucleation, and meanwhile assured the stabilization of copolymerization reaction. Undoubtedly, the temperature of glass transition (T_g) of particles also tend to rise with the increase of MMA. It is worth pointing out that relationships between gel formation and intermolecular termination need further study.

Effect of AA content in monomer

Mixture monomer, MMA, and BA with a certain amount of functional monomer acrylic acid AA, were chosen to accomplish polymerization in this work. As can be seen in Fig. 10, the system seems to be more unstable without AA.

As previously mentioned, AA was one of the highly water-soluble monomers. When the AA content ranged from 1 to 5 wt% of total monomers, the latex kept a low level of coagulation ratio. Possible reason might be attributed to the following two: copolymerization with AA composed of $-\text{COOH}$ unit greatly increased colloidal electrostatic stabilization, and negatively charged radicals provided more surface potential density. Thus, the colloidal hydration and double electrode layer would be enhanced. On the other hand, a small number of AA was possible to help to generate a second crop of small particles during nucleation reaction, correspondingly, the coagulum percent also kept lower than 1.2 wt%. It is important to note that, for this strategy, the role that monomer played on the generation of new particles could not be disassociated from its role on the particle stabilization [22]. However, when AA was more than 7 wt%, there would be a dramatic increase in coagulum content, which was similar to the result obtained by conventional emulsion polymerization. Strong interactions caused by hydrogen bonding were the possible reason being responsible for uncontrolled colloidal agglomeration. In other word, too much AA might have a profound impact on colloidal interaction as it was beyond the tuning of the buffer SBC in our experiments, and the formation of the hydrogen bonding carried by carboxyl groups caused neighboring colloidal coalescence. Furthermore, the existence of experimental system with high volume fraction disperse phase (more than 64%) inevitably accelerated to generate gel.

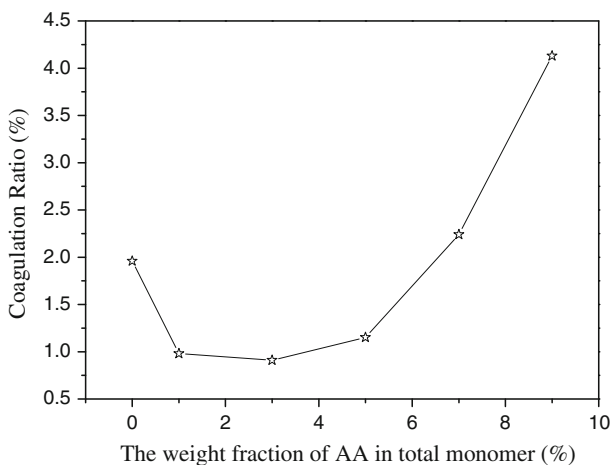


Fig. 10 Influence of the weight fraction of AA on the coagulation ratio of HSC Latex. Where $m(\text{SE}, 487 \text{ nm}) = 125 \text{ g}$, $m(\text{SDS})/m(\text{OS-15}) = 1.5/0.5$, $m(\text{APS}) = 0.23 \text{ g}$, $m(\text{SBC}) = 0.23 \text{ g}$, $m(\text{Mon}) = 100 \text{ g}$, stir rate was 250 r/min. Since the temperature reached 80 °C, mixed monomer began to be added by dropwise and the fending time was 60 min

Effect of reaction temperature

Reaction temperature was one of the sensitive influence factors, and the re-nucleation under higher temperature was likely easier to create new small particles. The higher the reaction temperature was, the more the population of small particles would be created. As compared to 80 °C, the mixed monomer initiated at 75 °C was far more likely to be consumed for the growth of seeded particles rather than generate new particles, which finally broke the balance of the optimum PSD (in order to get such similar rheological behavior, it was necessary to have very similar PSD). Therefore, the corresponding seed particles grew more quickly, their size seemed much larger when nucleation at a lower temperature. In addition, the coagulum content seemed lower than that of initiated at a higher temperature. For a proper interpretation of increasing coagulum when initial polymerization at 85 °C, it was necessary to note that higher temperature would provoke a strong and uncontrolled re-nucleation, which certainly changed the particle–particle interaction. Newly created small particles were detected by laser light scattering (LLS). However, the PSD results in Table 4 could not represent a real interaction among particles.

The latex viscosity, which depended on the population of new created small particle, was possible to account for the strong particle–particle interaction at a higher temperature. In other word, particle size and their distribution can be reflected in the viscosity curves (Fig. 11), for a similar polymer content, similar viscosity value was observed, and the shear thinning behavior could be seen for all three runs. Obviously, viscosity value obtained at 75 °C were higher than that of at 80 and 85 °C, and the differences in 80 and 85 °C were not significant. Increasing temperature only increased the risk of non-reproducible nucleation because the polymerization and nucleation rates are both enhanced. Thus, the irregular PSD provoked by strong and uncontrolled re-nucleation had important impacts on the coagulum content. In addition, it was found that the HSC latex was pseudo-plastic fluid.

Effect of feeding rate

It is interesting that the longer the feeding time, the lower coagulum it has. In Fig. 12, when feeding time is 40 min (feeding rate is 2.5 g/min), it has much more

Table 4 Formation and characteristics of high-solid content latex

Run	Seed	Tem	CR%	Large population		Small population	
				d_p (nm)	%V	d_p (nm)	%V
1501	487	75	1.33	564	86.5	90	13.5
1502	487	80	0.91	550	81.6	103	18.4
1503	487	85	1.02	525	76.3	115	23.7

Where $m(\text{SE}, 487 \text{ nm}) = 125 \text{ g}$, $m(\text{SDS})/m(\text{OS-15}) = 1.5/0.5$, $m(\text{APS}) = 0.23 \text{ g}$, $m(\text{SBC}) = 0.23 \text{ g}$, $m(\text{Mon}) = 100 \text{ g}$, stir rate was 250 r/min. Since it is reached reaction temperature, mixed monomer began to be added by dropwise

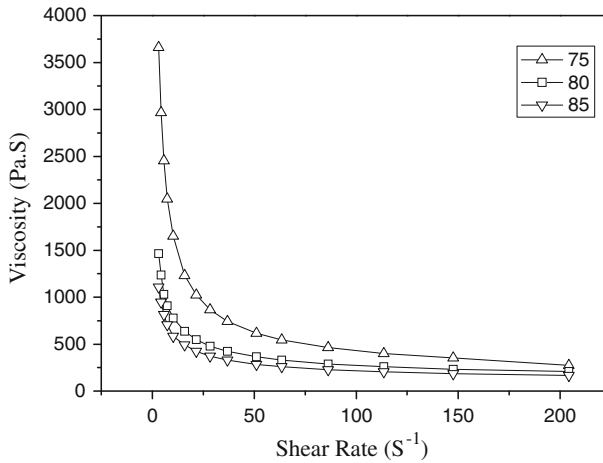


Fig. 11 Viscosity of HSC latex prepared at different temperature (75, 80, and 85 °C) as a function of shear rate

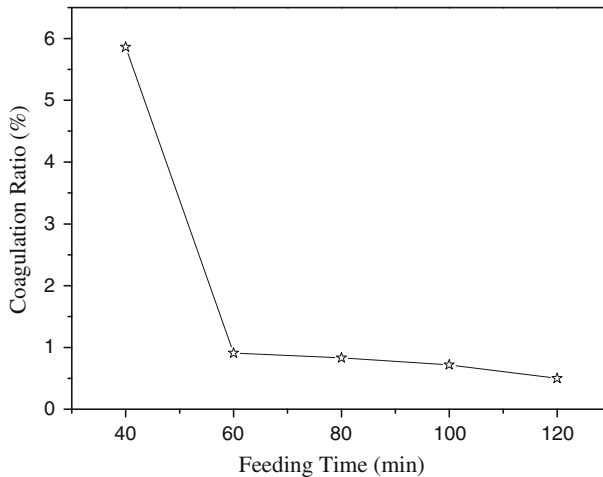


Fig. 12 Influence of the feeding time on the coagulation ratio of HSC Latex. Where $m(\text{SE}, 487 \text{ nm}) = 125 \text{ g}$, $m(\text{SDS})/m(\text{OS-15}) = 1.5/0.5$, $m(\text{APS}) = 0.23 \text{ g}$, $m(\text{SBC}) = 0.23 \text{ g}$, $m(\text{Mon}) = 100 \text{ g}$, stir rate was 250 r/min. Since the temperature reached 80 °C, mixed monomer began to be added by dropwise

coagulum than other runs. Actually, under a circumstance of high polymer concentration, added monomer would prefer to anchor around large particles rather than diffuse to enter micelle. High flow rate of mixture monomers might provoke a violent re-nucleation susceptible to destabilize the entire system. Feeding rate of monomer far outweigh the diffusion velocity of monomer, thereby seeded colloidal particles were easily swelled by unreacted monomers, most of monomers used for undesired growth of seeds that aroused a bad change on particle size and their PSD. On the other hand, as mentioned previously, the larger the feed rate was, the more

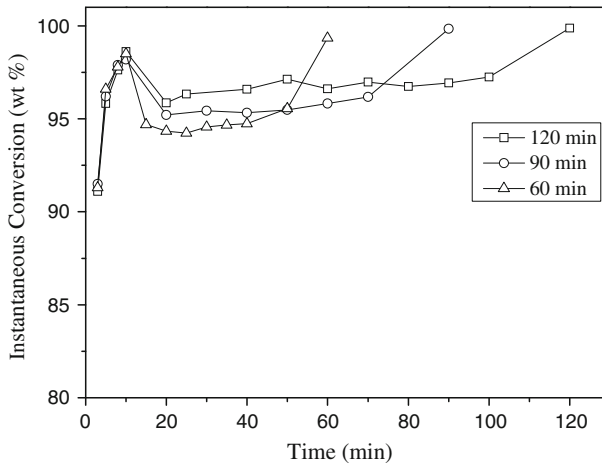


Fig. 13 Instantaneous conversion of HSC Latex during the monomer feed stage. Where $m(\text{SE}, 487 \text{ nm}) = 125 \text{ g}$, $m(\text{SDS})/m(\text{OS-15}) = 1.5/0.5$, $m(\text{APS}) = 0.23 \text{ g}$, $m(\text{SBC}) = 0.23 \text{ g}$, $m(\text{Mon}) = 100 \text{ g}$, stir rate was 250 r/min . Since the temperature reached $80 \text{ }^\circ\text{C}$, mixed monomer began to be added by dropwise

the monomer located on the particle surface, and hence softer the particle which was more prone to agglomeration. Naturally, a large number of coagulum would be caused in a short time.

The above results are related to polymerization kinetics, instantaneous conversion curves with different feeding rate are showed in Fig. 13, it helps us to understand the fact that different feeding rates would have different impacts on stability of polymerization. As we can see, polymer conversion increase gradually as time goes on, the final polymer content of all three runs can still reach more than 98 wt%. The polymerization reaction with longer feeding time (120 min) seemed more stable and meanwhile kept a higher instantaneous conversion than other ones. Besides, polymerization reaction with short feeding time kept a much lower conversion, because it had more unreacted monomers in its reactor. In addition, it was necessary to note that the reaction temperature was risen to $85 \text{ }^\circ\text{C}$ for 15 min at the last stage, that was the reason why instantaneous conversion increased sharply at the last minutes.

Conclusion

Several key influence factors of the stability during preparation of HSC P(MMA/BA/AA) latex was investigated. It was observed that particle sizes and their distribution exercised a great influence on latex's ability throughout secondary nucleation. It was verified that the PSD was greatly determined by factors such as ingredient, proportion of surfactant, monomer composite, seed particle size, reaction temperature, and feeding rate. And at the later period of polymerization reaction,

strong particle–particle interaction also would be aroused by particles PSD, which directly caused the stability of the final latex.

It seemed that when $m(\text{SDS})/m(\text{OS-15})$ was 1.5/0.5, the seed particle size was 487 nm, the content of MMA and AA in monomer was about 40 and 3 wt%, respectively, reaction temperature was 80 °C, and feeding time was more than 60 min (feeding rate was 1.67 g/min), the colloidal system was able to provoke a compliant re-nucleation, and maintain an excellent growth of subsequent particles. Naturally, these process conditions would provide a desired PSD and obtain a HSC latex with low-viscosity and high-stability.

Acknowledgments This work was supported by the Natural Science Foundation of Education Department of Hubei Province (No. 2002D00005). The authors wish to thank our colleagues for their kind help and encouragement.

References

1. van Herk AM (2005) Chemistry and technology of emulsion polymerization. Blackwell Publishing Ltd, UK
2. Ai ZQ, Deng R, Zhou QL, Liao SJ and Zhang HT (2010) High solid content latex: Preparation methods and application. *Adv Colloid Interface Sci.* doi:10.1016/j.cis.2010.05.003
3. Zhang HT, Huang JX (2007) New technology and application in emulsion polymerization. Chemical Industry Press, Beijing, China
4. Chu F, Graillat C, Guyot A (1998) High solid content multisized emulsion copolymerization of styrene butyl acrylate and methacrylic acid. *J Appl Polym Sci* 13:2667–2677
5. Chu F, Guillot J, Guyot A (1998) Study of poly(St/BA/MAA) copolymer latexes with bimodal particle size distribution. *Polym Adv Technol* 12:851–857
6. Chu F, Guillot J, Guyot A (1998) Study of poly(St/BA/MAA) copolymer latexes with trimodal particle size distribution. *Polym Adv Technol* 9:844–857
7. Schneider M, Graillat C, Guyot A, McKenna TF (2002) High solids content emulsions. II. Preparation of seed lattices. *J Appl Polym Sci* 10:1897–1915
8. Schneider M, Graillat C, Guyot A, McKenna TF (2002) High solids content emulsions IV. Improved strategies for producing concentrated lattices. *J Appl Polym Sci* 10:1935–1948
9. Schneider M, Graillat C, Guyot A, McKenna TF (2002) High solids content emulsions. III. Synthesis of concentrated lattices by classic emulsion polymerization. *J Appl Polym Sci* 10:1916–1934
10. Boutti S, Graillat C, McKenna TF (2005) High solid content emulsion polymerization without intermediate seeds Part III. Reproducibility and influence of process condition. *Polymer* 46: 1223–1234
11. Sajjadi S, Brooks BW (2000) Unseed semibatch emulsion polymerization of butyl acrylate: bimodal particle size distribution. *J Polym Sci Part A Polym Chem* 38:3612–3630
12. Sajjadi S, Brooks BW (1999) Semibatch emulsion polymerization of butyl acrylate. I. Effect of monomer distribution. *J Appl Polym Sci* 74:3094–3110
13. Sajjadi S (2001) Particle formation under monomer-starved conditions in the semibatch emulsion polymerization of styrene I. Experimental. *J Polym Sci Part A Polym Chem* 39:3940–3952
14. Guyot A, Chu F, Schneider M, Graillat C, McKenna TF (2002) High solid content latexes. *Prog Polym Sci* 27:1573–1615
15. Gonzalez I, Asua JM, Leiza JR (2007) The role of methyl methacrylate on branching and gel formation in the emulsion copolymerization of BA/MMA. *Polymer* 48:2542–2547
16. Parouti S, Kammona O, Kiparissides C, Bousquet J (2003) A comprehensive experimental investigation of the methyl methacrylate/butyl acrylate/acrylic acid emulsion terpolymerization. *J Polym React Eng* 11:829–853
17. Ai ZQ, Zhou QL, Zhang HT, Xie CS (2005) Preparation and property study of high-solid content and low-viscosity P(MMA/BA/AA) emulsion. *Acta Polym Sin* 5:754–759

18. Ai ZQ, Zhou QL, Xie CS, Zhang HT (2007) In situ preparation and properties of high-solid-content and low-viscosity poly(methylmethacrylate/*n*-butylacrylate/acrylic acid)/poly(styrene/acrylic acid) composite latexes. *J Appl Polym Sci* 3:1815–1825
19. Chen YZ, Shao YL, Ying G, Jin SM (2007) Random-design for the technology of emulsion polymerization with high solid content and the statistical analysis of the resultant data. *Iran Polym J* 16:417–423
20. Deng R, Wang ZY, Chen C, Ai ZQ (2010) Progress in rheological properties of high-solid-content latex. *Chin Polym Bull* 2:52–57
21. Chu F, Guillot J, Guyot A (1998) Rheology of concentrated multisized poly(St/BuA/MAA). *Colloid Polym Sci* 276:305–312
22. Urretabizkaia A, Asua JM (1994) High solids content emulsion terpolymerization of vinyl acetate, methyl methacrylate, and butyl acrylate I. Kinetics. *J Polym Sci Part A Polym Chem* 32:1761–1778