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ORIGINAL PAPER

Preparation and characterization of stable and high solid content St/BA emulsifier-free latexes in the presence of AMPS

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Abstract Stable and high solid content (about 50 wt%) St/BA emulsifier-free latexes were successfully synthesized using emulsifier-free emulsion polymerization with the addition of a small amount of reactive emulsifier AMPS. Properties of the latexes, such as the average particle diameter and its distribution, the morphology of latex particles, and stability were investigated. Physical properties of the latex films, i.e., glass transition temperature (T_g), water resistance, and solvent resistance were investigated as well. The size of latex particles is 400–600 nm in diameter, which is larger than that prepared by conventional emulsion polymerization. And the particle size distribution is narrow and uniform. It was found that the diameter of the latex particles decreases with the increasing content of the initiator KPS and the reactive emulsifier AMPS. Compared with the film prepared by conventional emulsion polymerization, water resistant and solvent resistant of the films prepared by emulsifier-free emulsion polymerization are improved greatly.

Keywords Emulsifier-free · Emulsion polymerization · Styrene · 2-Acrylamido-2-methylpropane sulfonic acid · Water resistance

Introduction

Compared with the conventional emulsion polymerization, latex particles prepared by emulsifier-free emulsion polymerization are uniform, well-distributed, and have clean surfaces. Also emulsifier-free emulsion polymerization successfully avoids the drawbacks that emulsifiers bring in the conventional emulsion polymerization

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[1–6]. Due to these advantages, much attention has been drawn to emulsifier-free emulsion polymerization. Recently, reactive emulsifiers have attracted considerable attention in the industrial applications, such as paints, coatings, inks etc. Reactive emulsifier is a kind of polymerizable reactive surfactant molecule, which used not only as a surfactant but also a comonomer [7]. And the buzz word “surfmers,” which derives from surfactant monomers, is used to refer to it [8]. Some surfmers have been synthesized and used in emulsifier-free emulsion polymerizations of different monomers. And the use of surfmers has been shown to improve the water resistance in comparison to conventional emulsifiers [9, 10]. Abele et al. [11] synthesized polymerizable cationic and zwitterionic dialkyl maleates with different hydrophobic chain lengths ($R = C_{10}H_{21}$, $C_{12}H_{25}$, $C_{16}H_{33}$, $C1_{8}H_{37}$) and different counterions (I, Br, HSO_4) for the cationic hydrophilic part, and used them in batch and seeded emulsion polymerization of styrene (St) and butyl acrylate (BA). Hong et al. [12] used an effective polymerizable poly(ethylene glycol)-ethyl ether methacrylate (PEG-EEM) macromonomer to prepare monodisperse copolymer particles of St, *n*-butyl acrylate, and methacrylic acid by emulsion copolymerization. Tang et al. [13] synthesized 3-allyloxy-2-hydroxyl-propanesulfonic (AHPS) salt and used it as a hydrophilic comonomer for the MMA/BA emulsifier-free emulsion copolymerization system to obtain stable and high solid content latexes. Zhang et al. [14] investigated the behavior of emulsifier-free emulsion copolymerization of St and sodium 1-allyloxy- 2-hydroxypropane sulfonate (SAHS). SAHS possessed a negative charged group and can polymerize with St to form a stable polymer colloids. However, up to today, reports on preparing stable and high solid content St/BA emulsifier-free emulsion polymerization system are limited. Chang et al. [15] used the AMPS (2-acrylamido-2-methylpropane sulfonic acid) as a reactive emulsifier to the St/BA emulsion polymerization system, the solid content of the obtained latex is less than 40 wt%.

2-acrylamido-2-methylpropane sulfonic acid is a reactive, hydrophilic, sulfonic acid acrylic monomer capable of imparting a number of distinctive high-performance characteristics to a wide variety of anionic polymers. Compared with the conventional emulsifier SDS (sodium dodecyl sulfate), AMPS exists as a kind of reactive monomer component and can be chemically bonded onto the particle surfaces. The structure of AMPS can be seen in Fig. 1. The purpose of this study is to prepare stable and high solid content St/BA emulsifier-free latexes which have a potential application in coating. With the addition of AMPS, stable and high solid content (about 50 wt%) emulsifier-free latex were obtained. Then, factors that influence properties of the latexes were investigated, and physical properties of the films were investigated as well.

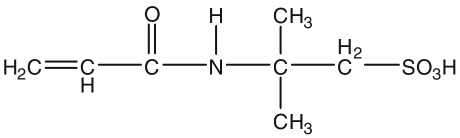

Fig. 1 The structure of AMPS

Experimental

Materials

Styrene, BA, and SDS were purchased from Tianjin Chemical Regent Co. (Tianjin, China); Potassium persulfate (KPS) was recrystallized; 2-acrylamido-2-methylpropane sulfonic acid (AMPS) was purchased from Zhenhui Chemical plant (Henan, China); Sodium Bicarbonate ($NaHCO_3$) was purchased from Rainbow Chemical plant (Shanghai, China); and Deionized water was applied for all polymerization and treatment processes.

Polymerization

The St/BA emulsifier-free emulsion polymerization was carried out in a 250 mL four-necked flask equipped with stirrer, thermometer, reflux condenser, nitrogen inlet, and dropping funnel. The stirring rate was controlled at 350 rpm. The polymerization flask was placed in a water bath at 80 °C. The preparing process could be described as follow: first, water, $NaHCO_3$, 1/6 of St/BA mixture monomers, and a certain amount of AMPS were added to the flask that had been purged with nitrogen for 20 min. The reactor was then heated to the reaction temperature of 80 °C. After that 1/3 of KPS solution was added to the flask. The rest KPS solution, AMPS solution, and St/BA mixture monomers were fed into the flask for 3–4 h. Finally, the polymerization was kept at 85 °C for 2 h. As for the conventional emulsion polymerization, it was carried out with the same conditions as above except that the AMPS was replaced by SDS. Recipes for the emulsion polymerization are presented in Table 1.

Characterization

Morphologies and latex particle size

A transmission electron microscope (TEM FEI tecnai G20, U.S.A. FEI Corp) was used to observe the morphologies of the obtained latexes. The obtained dispersions were diluted and ultrasonicated for 10 min, and then dried onto carbon-coated copper grid and dried in air before observation.

The average diameters of the obtained latexes were measured with PCS (Malvern Zetasizer Nano S, UK) Instruments. Each sample was repeated for three times to give the average particle size.

Stability tests

Stability against electrolytes was tested by adding different concentration salts and kept at room temperature for 10 days [16]: 0.1 M NaCl, 0.5 M NaCl, 1.0 M NaCl; 0.1 M $CaCl_2$, 0.5 M $CaCl_2$, 1.0 M $CaCl_2$. That is, taking 2 g emulsions, adding the same amount of electrolyte solution. Immediate flocculation or flocculation after certain time was observed visually.

Table 1 Recipes for the polymerization

No.	BA (g)	St (g)	AMPS (g)	Water (g)	KPS (g)	$NaHCO_3$ (g)
0	33	27	(SDS 0.9 g)	60	0.36	0.10
1	**27**	**33**	0.9	60	0.36	0.10
2	**30**	**30**	0.9	60	0.36	0.10
3	**33**	**27**	0.9	60	0.36	0.10
4	**36**	**24**	0.9	60	0.36	0.10
5	33	27	**0.6**	60	0.36	0.10
6	33	27	**0.9**	60	0.36	0.10
7	33	27	**1.2**	60	0.36	0.10
8	33	27	**1.5**	60	0.36	0.10
9	33	27	**1.8**	60	0.36	0.10
10	33	27	0.9	60	**0.24**	0.10
11	33	27	0.9	60	**0.30**	0.10
12	33	27	0.9	60	**0.36**	0.10
13	33	27	0.9	60	**0.42**	0.10
14	33	27	0.9	60	**0.48**	0.10

No. 0: conventional emulsion polymerization; No. 1–4: emulsifier-free emulsion polymerization with different St/BA ratios; No. 5–9: emulsifier-free emulsion polymerization with different contents of AMPS; No. 10–14: emulsifier-free emulsion polymerization with different contents of KPS

Bold value indicates that it is different from other recipes

For the freeze/thaw test, some latex (about 10 mL) was kept at −8 °C for a certain time. After another 24 h at room temperature, the flocculation of the latex was observed.

Glass transition temperature measurements

Glass transition temperature (T_g) of the copolymer was investigated by a Perkin Elmer DSC 60 differential scanning calorimeter (DSC) with a heating rate of 20 °C min^{-1} under a nitrogen atmosphere and quench-cooled.

Water resistance of the latex films

Water resistance was characterized by soaking the latex films at 25 °C in water and weighing the amount of water absorbed at a preset time period. Water uptake is defined as $\text{wt\%} = (W_1 - W_0)/W_0$, where W_0 is the weight before soaking and W_1 is the weight after soaking. (Latex films subjected to the physical properties test were cast at room temperature, then vacuum dried at 50 °C for 72 h and kept at room temperature for 24 h).

Solvent resistance of the latex films

Solvent resistance was characterized by soaking the latex films in bottles with petroleum ether for 24 h and weighing the amount of solvent absorbed. Swelling ratio is defined as wt% = $(W_3 - W_2)/W_2 \times 100\%$, where W_2 is the weight before soaking and W_3 is the weight after soaking.

Results and discussion

Morphologies and latex particle size

The results of emulsion polymerization are shown in Table 2 and Fig. 2. It can be seen clearly that the contents of coagulum are low, and the monomer conversion ratios are high enough. The polydispersity index of emulsifier-free latex is lower than that of conventional latex, and the average diameter of emulsifier-free latex particle is larger than that of conventional latex. This is attributed to the difference in latex particle formation mechanism. In conventional emulsion polymerization, latex particles formed are chiefly by micelle nucleation mechanism which was proposed by Harkins. And in emulsifier-free emulsion polymerization, latex particles formed are mainly by homogeneous nucleation mechanism which was proposed by Fitch. Fitch et al. proposed the homogeneous nucleation mechanism, in which a growing oligomeric free radical precipitates from the aqueous phase when it reaches a critical chain length (n^*) to form a primary particle [13]. The number of particles formed in emulsifier-free system is limited; therefore, particle size is larger

Table 2 Results of the emulsion polymerization

No.	Conversion (%)	Average diameter (nm)	PDI	Coagulum (%)
0	96.5	243	0.15	1.162
3	97.8	494	0.01	0.637

No. 0: conventional emulsion polymerization; No. 3: emulsifier-free emulsion polymerization

AMPS = SDS = 0.9 g; other conditions are the same

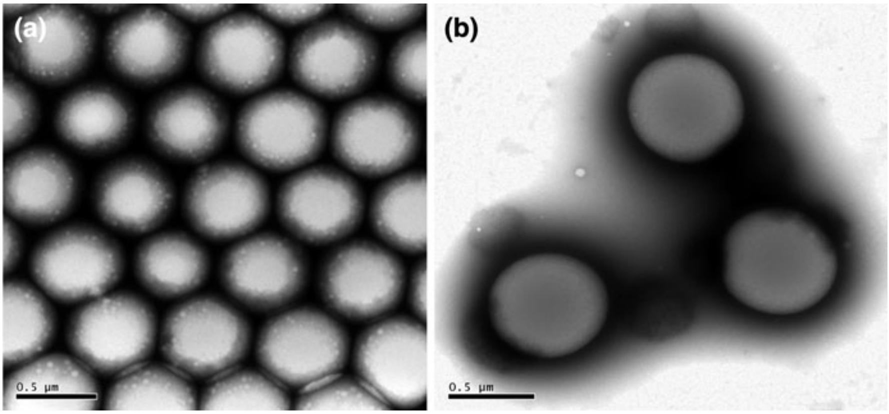

Fig. 2 TEM photographs of the emulsifier-free latex particles

than that of the conventional latex. In addition, as can be seen in Fig. 2a, b particles of emulsifier-free latex are almost the same size, about 500 nm. And particle size distribution is very narrow and uniform. It demonstrated the monodisperse emulsifier-free latex can be obtained successfully.

Influence of the content of AMPS and KPS on the size of latex particles

In traditional emulsion polymerization, initiator and emulsifier concentrations greatly influence the size of latex particles. As seen from Figs. 3 and 4, the diameter of the latex particle decreases with the increasing content of AMPS and KPS that was added to the emulsifier-free emulsion polymerization system. According to the homogeneous nucleation mechanism [13], a growing oligomeric free radical precipitates from the aqueous phase when it reaches a critical chain length (n^*) to form a primary particle. Then, the polymerization is continued in the particles. Higher AMPS and initiator concentration can lead to forming more oligomeric free radicals, and then more primary particles are produced in the system. The content of monomers is limited; therefore, the particle size is smaller. So the size of the latex particle decreases with the increasing content of AMPS and KPS accordingly.

Stability tests

The results of the latex stability against electrolytes are displayed in Table 3. The latex stabilized with AMPS has better stability against electrolytes than that stabilized with SDS. In the case of addition of 0.1 M NaCl and 0.1 M $CaCl_2$, the latex stabilized with SDS and AMPS are both stable. And the latex stabilized with AMPS can resist a higher concentration salt. However, the latex stabilized with SDS

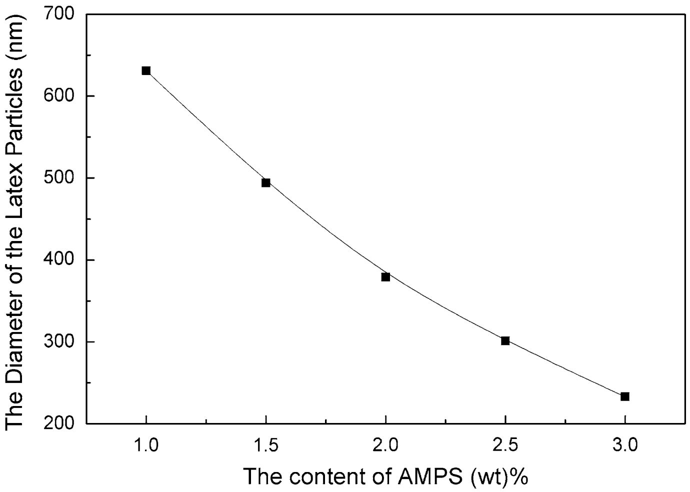

Fig. 3 Effect of AMPS content on the diameter of the latex particles (the content of AMPS is based on total monomers)

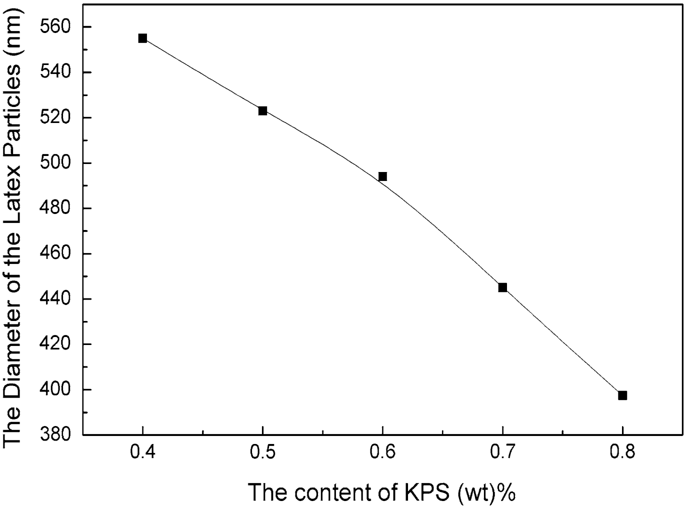

Fig. 4 Effect of KPS content on the diameter of the latex particles (the content of KPS is based on total monomers)

Table 3 Stability against electrolytes

No.	0.1 M NaCl	0.5 M NaCl	1.0 M NaCl	0.1 M $CaCl_2$	0.5 M $CaCl_2$	1.0 M $CaCl_2$
0	+	++	+++	+	+++	+++
3	+	+	+	+	+	+

No. 0: conventional emulsion polymerization; No. 3: emulsifier-free emulsion polymerization

AMPS = SDS = 0.9 g; other conditions are the same

+ stable for 1 week; ++ some flocculation after certain time (30 min to 4 days); +++ flocculation immediately

could not resist a higher concentration salt and has some flocculation after certain time or has flocculation immediately. It is because AMPS can be bonded onto the surface of the latex particles or polymerized in water phase acted as polyelectrolyte hydrosoluble chains, greatly improve the surface-charge densities of the latex particles and therefore lead to the latex stable. So the latex stabilized with AMPS has better stability against electrolytes [15].

The freeze/thaw tests of the latex cause flocculation in all cases. None of the latex can resist the freeze/thaw test. It is not very clear why all the latex samples are flocculation in these tests.

Glass transition temperature

The data of T_g from theory calculation and DSC measurement in different St/BA ratios are shown in Table 4. The results indicate that the observed T_g is about 30 K higher than that of the theory calculation according to the Fox equation. In addition, T_g of the copolymer that was prepared by emulsifier-free emulsion polymerization is

Table 4 Data of T_g from theory calculation and DSC measurement in different St/BA ratios

No.	0	1	2	3	4
St/BA ratio	4.5/5.5	5.5/4.5	5.0/5.0	4.5/5.5	4.0/6.0
Theoretical T_g (K)	268	283	275	268	261
Observed T_g (K)	297	309	306	298	286

equal to that of the copolymer that was prepared by conventional emulsion polymerization at the same St/BA ratio. This indicates that polymerization methods have no influence on T_g at the same St/BA ratio.

Water resistance of the latex films

Water uptakes of the copolymers are shown in Figs. 5 and 6. The results show that water uptakes of the films prepared by emulsifier-free emulsion polymerization are much lower than that of the conventional emulsion polymerization sample. It can be explained that conventional emulsifiers used to stabilizing the latex are only physically absorbed on the surface of latex particles, bringing about the high amount of water uptakes. Also we can find that water uptakes of the copolymers rise with the increase of the AMPS and KPS concentration in Figs. 5 and 6. It is because the more the AMPS and KPS were added to the emulsifier-free emulsion polymerization system, the more the hydrophilic groups were introduced into the copolymers, the easier the water uptakes increased. In our study, we found that to some extent the latex stability is influenced by the amount of the KPS and AMPS. So if we want to prepare stable latex making sure the copolymers are high water resistant, the amount of initiator and ionic comonomers (AMPS) should be taken into account.

Solvent resistance of the latex films

As can be seen from Table 5, swelling ratios of films prepared by emulsifier-free emulsion polymerization are lower than that of the conventional emulsion polymerization sample. Polymerizable emulsifier AMPS can be more effective than conventional emulsifier SDS on improving the solvent resistance of latex films. It can be explained that the functions of the two types of agent are different. SDS is only physically absorbed on the surface of latex particles, whereas AMPS exists as a kind of monomer component and can be chemically bonded onto the particle surfaces. Thus, AMPS is more effective than SDS on preventing solvent into the films.

Conclusions

Stable and high solid content (about 50 wt%) St/BA emulsifier-free latexes were successfully synthesized with the addition of a small amount of AMPS. The size of latex particles is 400–600 nm in diameter, which is larger than that prepared by conventional emulsion polymerization. And the particle size distribution is narrow

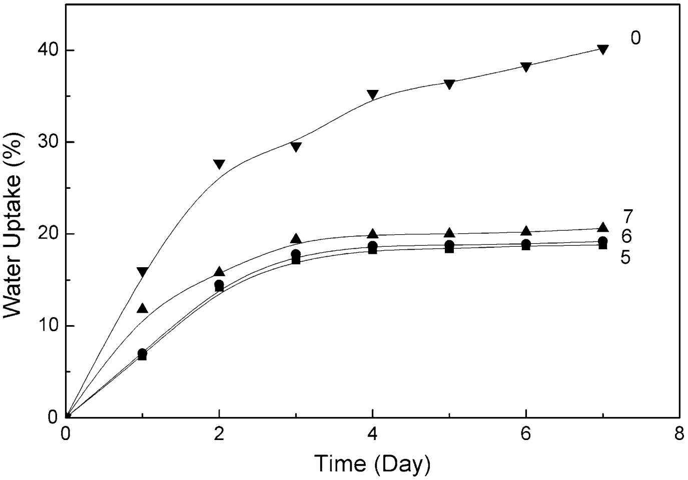

Fig. 5 Influence of AMPS concentration on water resistance of the films and a comparison with conventional emulsion film

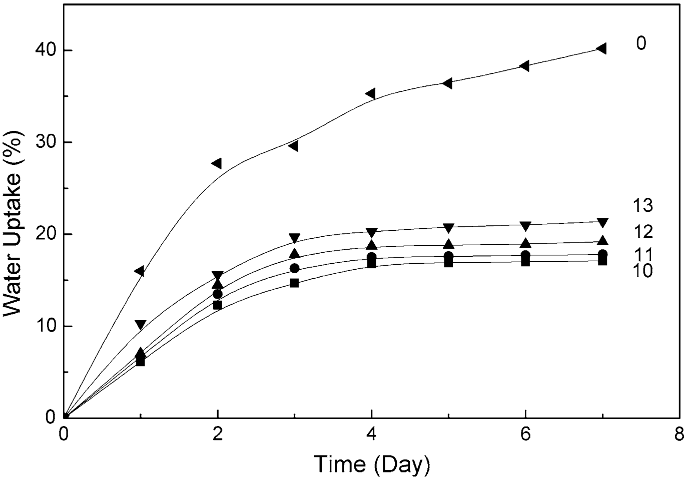

Fig. 6 Influence of KPS concentration on water resistance of the films and a comparison with conventional emulsion film

Table 5 Effect of AMPS and SDS content on the solvent resistance

No.	5	6	7	8	9	0
AMPS (wt%)	1.0	1.5	2.0	2.5	3.0	(SDS) 1.5
Swelling ratio (%)	28.4	20.3	25.8	23.3	26.3	32.1

Other conditions are the same; wt% of AMPS is based on total monomers and uniform. The diameter of the latex particles decreases with the increasing content of KPS and AMPS. Compared with the film prepared by conventional emulsion polymerization, water resistant and solvent resistant of the film prepared by emulsifier-free emulsion polymerization are improved greatly.

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