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Ultrasonically initiated emulsifier-free emulsion copolymerization of *n*-butyl acrylate and acrylamide. Part I: Polymerization mechanism

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Abstract

The polymerization mechanism of ultrasonically initiated emulsifier-free emulsion copolymerization of *n*-butyl acrylate (BA) and acrylamide (AM) was investigated. A four-step polymerization mechanism of the ultrasonically initiated emulsifier-free emulsion was put forward based on the monomer conversion and the main reaction locus. Improving the power output would increase the monomer conversion and the rate of polymerization. However, when the reaction temperature was 30 °C and the concentration of $\mathbf{Na_2SO_4}$ was 0.1%, the monomer conversion and the rate of polymerization achieved maximum. The FTIR spectra showed that the sample obtained by this way was the copolymer of BA and AM, but not the blend of poly(butyl acrylate) and polyacrylamide.

Keywords: Ultrasonic irradiation; Emulsifier-free emulsion polymerization; *n*-Butyl acrylate and acrylamide

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1. Introduction

Emulsion polymerization without conventional emulsifier is of academic and practical interest for it provides one or more of the following advantages [1,2]: no emulsifier migration during film formation, monodisperse particle size distribution, and excellent shear stability. It is also used for some medical and biochemical purposes because of cleanness of the disperse medium and functionality due to the on-surface groups.

The following methods have been adopted to obtain such emulsifier-free polymer latices from the dispersions of hydrophobic monomers: (1) polymerization by use of ionic group containing initiators, for example, potassium persulfate (KPS) [3], azobis(alkylimidine hydrochloride) [4–6], potassium peroxydiphosphate [7], etc.; (2) polymerization in the presence of amphiphilic polymer or oligomer; (3) copolymerization with hydrophilic monomers. The hydrophilic comonomers used so far are carboxylic monomers [8,9], acrylamide and its derivatives [1,10]; and (4) copolymerization with ionic hydrophilic monomers such as sodium styrene sulfonate (NaSS) [11], sodium salt of 2-sulfoethyl methacrylate (NaSEM) [11], 1,2-dimethy 5-vinylpyridinium methylsulfate (DVPM) [12]. A monomer with its high hydrophilicity could make ease of homogeneous nucleation as it was used in an emulsifier-free emulsion polymerization. The formation of stable latex particles in the absence of emulsifiers might follow a homogeneous nucleation mechanism [13,14], or an oligomer micellization mechanism [15], or the coagulation mechanism [16,17]. However, the micellar nucleation mechanism was proposed only for the system without comonomer (i.e. Styrene(St)/KPS/H_2O) [15]. According to the variety of critical chain length n^*, Song [18,19] proposed two-stage model in the St/KPS/H_2O emulsifier-free emulsion polymerization. The first stage was characterized by a time dependent critical chain length n^* and rapid particle nucleation through in situ micellization. And the second stage was characterized by a constant n^* and a decrease in particle number due to particle coagulation.

Ultrasonic irradiation was widely used in chemical synthesis. When an ultrasonic wave passed through a liquid medium, a large number of microbubbles formed, grew, and collapsed in a very short time of about a few microseconds, and this process was called ultrasonic cavitation. Sonochemical theory calculations and the corresponding experiments suggested that ultrasonic cavitation could generate local temperatures as high as 5000 K and local pressures as

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high as 500 atm, with heating and cooling rates greater than 10^9 K/s, a very vigorous environment which could induce some chemical reactions that couldn't take place under normal conditions [20]. Therefore, ultrasound had been extensively applied in dispersing, emulsifying, crushing, and activating of particles. Recently, more attention has been focused on ultrasonically initiated emulsion polymerization, such as methyl methacrylate [21,22], styrene [23] and butyl acrylate/vinyl acetate [24]. In these emulsion polymerizations induced by ultrasound, there was not any additive chemical initiator, which was absolutely necessary in classical emulsion polymerization.

In the present work, acrylamide (AM), a monomer with strong hydrogen bonding, was used as the comonomer in the polymerization of butyl acrylate (BA) in ultrasonically initiated emulsifier-free polymerization without any conventional chemical initiator. And the polymerization mechanism as well as its affecting factors was studied.

2. Experimental

2.1. Materials

Ion-exchanged and distilled water was used in all the polymerization. *n*-Butyl acrylate (BA) (Tianjin Chemical Reagents Company, AR) was washed three times with 10% aqueous solution of sodium hydroxide, and three times with distilled water to remove the inhibitor (hydroquinone), then dried with anhydrous sodium sulfate, and distilled by vacuum. Acrylamide (AM) (Chengdu Kelong Chemical Reagents Company, AR) was purified by recrystallization from benzene. Sodium sulfate (Na_2SO_4) was obtained from Chengdu Kelong Chemical Reagents Company and used as received. Potassium persulfate was obtained from Aijian Chemical Reagents Company and used as received. Hydroquinone was obtained from Chongqing Beibei Fine Chemical Company and used as received.

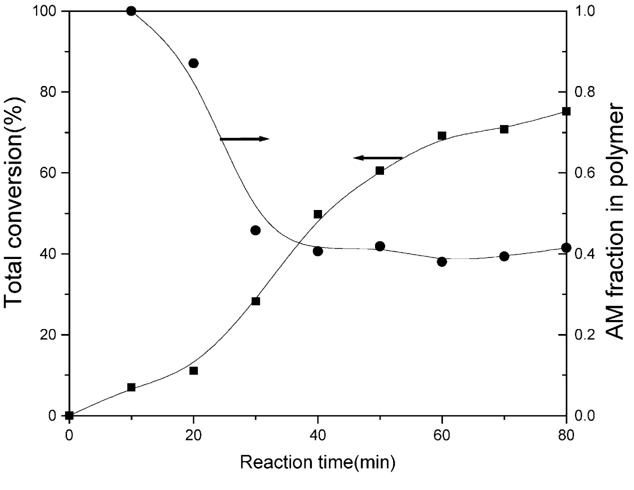

Fig. 1. Total conversion, and AM fraction in accumulated polymer with reaction time. (Output power: 600 W, reaction temperature: 25 °C, the conc. of Na_2SO_4: 0.5%).

2.2. Apparatus

The equipment employed in this search is a 20 KHz ultrasonic generator, Sonics and Material Modal VC-1500, with a standard titanium horn and a replaceable flat titanium tip. The ultrasonically initiated emulsifier-free emulsion polymerization apparatus used are shown schematically in Fig. 1 of Ref. [25]. The oscillator power was set at various points in a range from 10 to 50 (on a scale of 100), and cooling air was blown over the ultrasonic horn to prevent overheating. Ultrasonic irradiation of the emulsifier-free emulsion polymerization was conducted with the probe of the coupling horn, which was immersed directly in the emulsion system. During polymerization, thermostatted water was circulated to maintain a constant temperature. The reaction temperature was measured with a digital thermometer.

2.3. Ultrasonically initiated emulsifier-free emulsion copolymerization of BA and AM

Typically, 5.5 g BA, 5.5 g AM, and 0.1–0.5 g Na_2SO_4 was added into about 100 ml distilled water. The system was deoxidated by bubbling oxygen-free nitrogen while held at constant temperature. The polymerization was then initiated by subjecting this emulsion to ultrasonic irradiation with power output of 150–750 W. No extra stirring was required due to the rapid agitation induced by ultrasound. During polymerization, the flow rate of nitrogen was kept 20 ml/min. After ultrasonic irradiation for a certain time, the polymerization was stopped. The polymer latex was placed in refrigerator at least 24 h and then poured into ice-cold anhydrous ethanol, and the precipitated polymer was filtered, washed to remove the inorganic salts, and dried under vacuum.

2.4. Conventional emulsifier-free emulsion copolymerization of BA and AM

Typically, 10 g BA, 10 g AM and about 156 ml distilled water were introduced into a 300 ml flask fitted with a stirrer. Nitrogen was bubbled through the reaction mixture for about 1 h to remove the oxygen, and then about 0.0135 g initiators, potassium persulfate, was added to the flask. The reaction temperature was held at 70 °C. Small amounts of the samples were withdrawn from the flask at various time intervals for determination of the conversion. After reaction for a certain time, the polymerization was stopped. The polymer latex was placed in refrigerator at least 24 h and then poured into ice-cold anhydrous ethanol, and the precipitated polymer was filtered, washed to remove the inorganic salts, and dried under vacuum.

2.5. Characterization

The total monomer conversion of BA and AM copolymer was measured by weighing method, and calculated with the following equation:

$$x\% = \frac{(w_2 - w_0)/(w_1 - w_0) - A}{B} \times 100$$

where x is the total monomer conversion; w_0 is the weight of the weighing bottle; w_1 is the weight of the copolymer latex with the weighing bottle; w_2 is the weight of the dried copolymer with the weighing bottle; A is the weight percent of Na_2SO_4; B is the weight percent of the total monomer in the recipe. The residuary AM in the polymerization system could be volatized by heating 4 h under 110 °C. So the influence of residuary AM in the conversion measured could be neglected.

The amount of AM that was not polymerized in reaction system was measured by the Bromine titration method, and calculated with the following equation:

$$\mathrm{AM} = (V_1 - V_2) \times C \times 0.03554$$

where V_1 is the volume of the sodium hyposulfite of the blank experiment; V_2 is the volume of the sodium hyposulfite which was consumed by the sample; C is the concentration of the sodium hyposulfite.

The structure of BA and AM copolymer obtained by ultrasonically initiated emulsifier-free emulsion polymerization was analyzed by FTIR. FTIR spectra were recorded on a Nicolet 560 FTIR spectrometer (Nicolet Instrument Corp., USA). The weight-average sizes of the latex particles and particles size distribution were measured by laser light scattering using a SALD-2001 Laser Diffraction Particles Size Analyzer (Shimadzu Corp).

The weight-average particle number (N_p) per milliliter of water was calculated from the following equation:

$$N_p = \frac{m_0 \times (\frac{1}{6}x_1 + x_2)}{\rho v} \times \frac{3}{\pi D_w^3}$$

where m_0 is the mass of the monomer; v is the volume of distilled water; x_1 and x_2 are AM and BA conversion, respectively; D_w is the weight-average size; ρ is the average density of particle. In the present work, we did not measure the average density of particles. However, we could use BA and AM conversion data and their respective homopolymer density to estimate the value of ρ.

Tamai and his co-workers [26] found that the AM amounts copolymerized with St were about one-sixth of the AM conversion in the St and AM emulsifier-free emulsion polymerization system. So we also estimated that there were only about one-sixth of the AM molecules connecting on the particles surface in this research, and the others creating polyacrylamide dissolved in the aqueous phase. So the calculation of the average density of particle (ρ) could be according as following equation:

$$\rho = \frac{\frac{1}{6}x_1\rho_1 + x_2\rho_2}{\frac{1}{6}x_1 + x_2}$$

where ρ_1 and ρ_2 are the density of polyacrylamide, 1.302 g/cm^3, and poly(butyl acrylate),1.05 g/cm^3, respectively.

3. Results and discussion

3.1. Polymerization mechanism

Results for the copolymerization of BA and AM in an ultrasonically initiated emulsifier-free aqueous medium are shown in Fig. 1. From the shape of AM fraction in accumulated polymer versus time curve, at the earlier reaction stage (reaction time less than 20 min), polymerization of AM proceeded in preference to that of BA, and gradually lost its preference. At this stage, the color of reaction system became gradually from offwhite to creamwhite. After reaction time exceeded to 40 min, the value of AM fraction in accumulated polymer maintained constant, about 0.4.

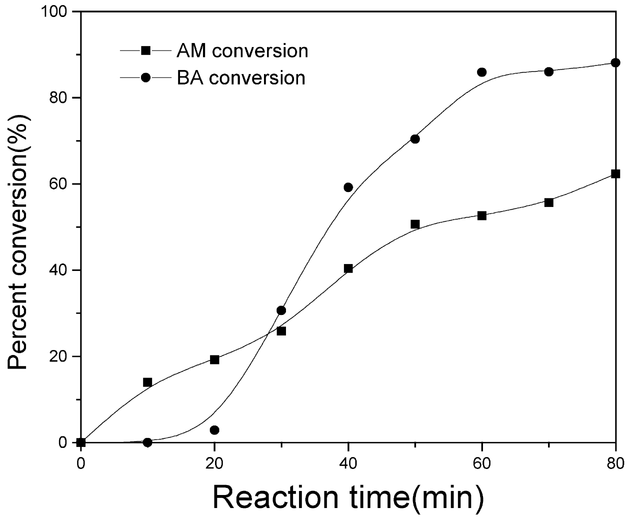

Fig. 2. BA conversion and AM conversion on reaction time. (Output power: 600 W, reaction temperature: 25 °C, the conc. of Na_2SO_4: 0.5%).

The changes of conversion of BA and AM with time are shown in Fig. 2. Within the reaction time range, AM reaction was similar to ultrasonic solution polymerization, and the reaction rate almost keeps invariability in total reaction period, about 0.0117 mol l/s. However, the polymerization of BA could be considered the conventional emulsion polymerization in the presence of emulsifier. It also involved three stages those were the acceleration stage, the constant rate stage and the deceleration stage, respectively. And the polymerization rate at the constant rate stage was about 0.0147 mol l/s.

The total conversion, AM conversion × 0.5 and AM fraction in accumulated polymer with reaction time in conventional emulsifier-free emulsion copolymerization of BA and AM are shown in Fig. 3. Compare to the two reaction systems, the conventional emulsifier-free emulsion and the ultrasonically initiated emulsifier-free emulsion of BA and AM, they should have the similar polymerization mechanism. However, because of the intensive agitation of the ultrasonication, which would produce many small droplets that consumedly increased the nucleation of the monomer droplets, so the latter reaction system had higher polymerization rate.

Juang and Krieger [11] studied the emulsifier-free emulsion copolymerization of St with sodium styrenesulfonate (NaSS) and divided the polymerization course into four stages. And Ohtsuka [27] also proposed a three-stage polymerization mechanism in the St-AM emulsifier-free copolymerization according to the main reaction locus. The copolymerization mode of the ultrasonically initiated emulsifier-free emulsion of BA and AM system seems to resemble that of Ohtsuka's St-AM system [27]. Judging from the dependence of the conversion and polymer composition on the reaction time, the ultrasonically initiated emulsifier-free emulsion of BA and AM copolymerization course is divided four stages as follows.

3.1.1. The first stage of polymerization

The cavitation bubbles produced by ultrasonic irradiation would induce AM molecules in aqueous phase to polymerize preferentially And the AM polymerization behavior in the aqueous phase could be similar to the ultrasonic solution polymerization mode. As the AM free radicals produced by ultrasonic were hydrophilic, they could not enter into the lipophilic BA monomer droplets. So the nucleation of the monomer droplets could be neglected at this stage. This stage was resembled Juang and Krieger's [11] first stage. And it would be continued to the AM conversion about 15%, as the reaction time was about 13 min. At the same time there were some white foam formed in the reaction vessel. At the termination of this stage, BA conversion was almost zero.

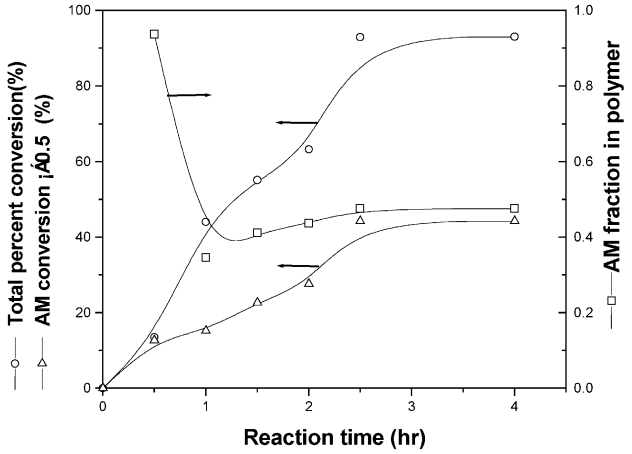

Fig. 3. Total conversion, AM conversion × 0.5 and AM fraction in accumulated polymer with reaction time in conventional emulsifier-free emulsion copolymerization of BA and AM.

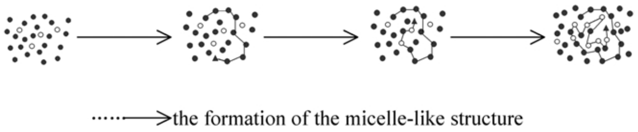

Fig. 4. Mechanism of the micelle-like structure: ● AM; ○ BA; ▲ radical.

3.1.2. The second stage of polymerization

As the reaction went on, some BA molecules added on the polyacrylamide chain and resulted in the hydrophilicity of polyacrylamide decreasing rapidly, correspondingly its lipophilicity increasing. The conversion curve of BA at this stage could be considered acceleration stage, which seemed to resemble the acceleration stage in the conventional emulsion polymerization in the presence of emulsifier. The rate of polymerization of BA increased from 3.06×10^{-4} mol/l s at 10 min to 2.5×10^{-3} mol/l s at 20 min. This indicated that BA molecules began to react with the polyacrylamide chain. Finally the micelle-like structure, in which the inside part was composed of BA chains and the outside part was composed of AM chains, would be produced. Because of the hydrophilicity of AM chains, the micelle-like structure formed by this way could attain stabilization in the aqueous phase. Besides of the formation of the micelle-like structure at this stage, the nucleation of the monomer droplets, which would quicken up the BA polymerization, was consumedly increased. This stage was the second stage of polymerization.

In the present work, the first and second stage resembles Ohtsuka's first stage [27]. The two stages should be regarded as a transitional period during which the main reaction locus transferred from the aqueous phase to the micelle-like structure or the BA monomer droplets, and the micelle-like structure was inferred to be formed by the mechanism envisaged in Fig. 4. From the reaction phenomena, as the BA conversion achieved to about 2% and the reaction time was about 20 min, the second stage would end. At the same time the total reaction vessel became cream white.

3.1.3. The third stage of polymerization

After the micelle-like structures formed in the aqueous phase, they began to offer the loci for BA to be concentrated. Concentration of BA around the micelle-like structures would accelerate polymerization of BA and the composition would shift to a BA-rich one rapidly. Differently the conventional emulsifier-free emulsion copolymerization of BA and AM, besides of the nucleation of the micelle-like structures, the nucleation of the BA monomer droplets would make *an* important role. This would observably increase the polymerization rate. The AM fraction in accumulated polymer reduced from 0.87 at 20 min to 0.41 at 40 min, then kept almost constant shown in Fig. 1. When the BA fraction in micelle-like structures exceeded a critical level, micelle-like structures precipitated to nucleate latex particles. Similarly, conventional emulsion polymerization in the presence of emulsifier, the BA polymerization in this stage could be considered constant rate stage, and the average polymerization rate was about 0.0147 mol/l s.

Ohtsuka observed a leveling-off in AM conversion at his second stage of the St-AM emulsifier-free emulsion polymerization system. However, in the present work, no leveling-off in AM conversion was observed. The AM conversion increased continuously from 19.19% at 20 min to 52.63% at 60 min. The reason may be the cavitation bubble produced by ultrasound continuously induced AM molecules in water to form abundance radicals, but in Ohtsuka's system the radicals produced by chemical initiator was limited.

Fig. 5 is the curves of the number of particles and the particles size on reaction time. Differently the conventional emulsion in presence of emulsifier, in which the number of particles kept constant after the stage of nucleating, the number of particles continuously increased at the third stage of polymerization. This also suggested that the BA molecules were necessary in the formation of the particles. As the nucleation region lasted to the end of the third stage and the little particles continuously produced, so the weight-average size also continuously decreased.

3.1.4. The fourth stage of polymerization

The beginning of the fourth stage was characterized by gradually slowdown of BA polymerization. This showed that the main reaction locus returned to the aqueous phase. The change of main reaction locus would be concerned with the disappearance of the BA droplets. The droplets supplied BA molecules to the particles through the aqueous phase. Their disappearance caused a decrease in the concentration of BA not only in the particles but also in the aqueous phase. The decrease in the latter retarded the change of the hydrophilicity of growing radicals, which consequently stayed longer in the aqueous phase and facilitated the reaction with AM in the aqueous phase. In contrast to this, the decrease of the BA concentration in the particles and the aqueous phase caused BA polymerization to slow down although the slowdown might be canceled out by the gel effect at the beginning of the fourth stage. So the increasing of the total conversion was mainly attributed to the AM polymerization in the aqueous phase. In this stage, there were not enough BA molecules to form the new particles (the BA conversion about 85%), so the particle number shown in Fig. 5 did not continuously increase.

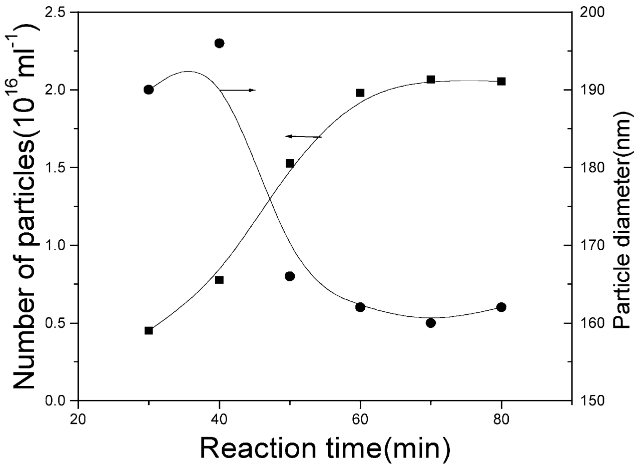

Fig. 5. The curves of the number of particles and particles diameter on reaction time. (Output power: 600 W, reaction temperature: 25 °C, the conc. of Na_2SO_4: 0.5%).

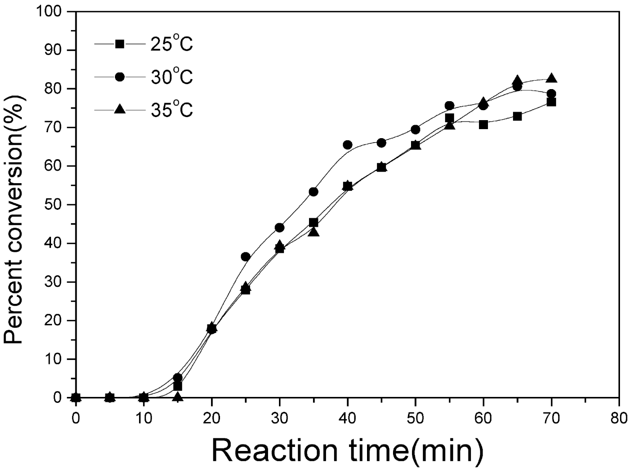

Fig. 6. Conversion vs sonic time curves during ultrasonic copolymerization of BA/AM at different reaction temperature. (Output power: 450 W; Conc. of Na_2SO_4: 0.5%).

3.2. Effects of temperature and concentration of Na_2SO_4 on polymerization

The conversion-time curves at different reaction temperature were shown in Fig. 6. The conversion-time curves

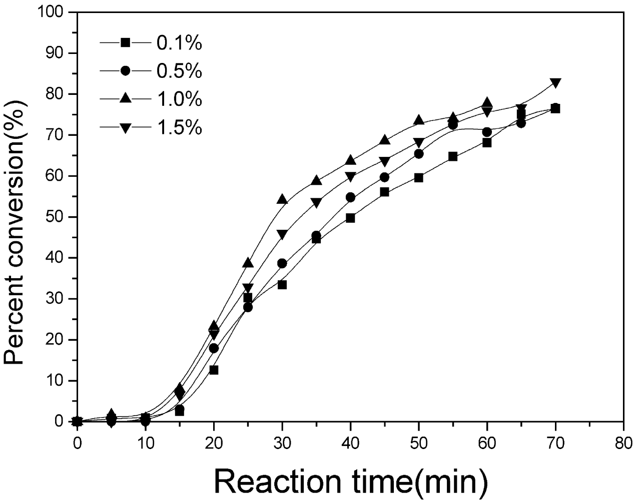

Fig. 7. Conversion vs sonic time curves during ultrasonic copolymerization of BA/AM at different conc. of Na_2SO_4. (Output power: 450 W; 25 °C).

were almost coincided at 25 and 35 °C, only as conversion more than 70%, high temperature could promote reaction conversion. The reason was that at the high temperature, the BA or AM molecules could easily diffuse into particle to react. In the present work, elevation of the reaction temperature could bring two different effects. (1) to accelerate production of the cavitation bubbles and increase the reaction capacity of monomer. This effect would increase the reaction conversion. (2) to reduce the affection of cavitation bubbles to the reaction medium. And the same time high temperature could promote the dissolvability of macromolecule chain and decrease the aggregation of the macromolecule chains. These would decrease the final conversion.

As shown in Fig. 7, the concentration of Na_2SO_4 also affected the conversion of the polymerization. In case of no Na_2SO_4 in the reaction system, no polymer product can be acquired. This showed that the inorganic salt plays a very important role stabling particles especially in the initial stage via forming the electrical double layer. While the concentration of Na_2SO_4 was about 1%, the conversion of polymerization achieved maximum. The effect of the concentration of Na_2SO_4 on polymerization also was two different sides. One side was that the elevation of the concentration of Na_2SO_4 could increase the stability of particles in the aqueous phase, and the rate and the places of nucleation, which would increase the reaction conversion. Another side was that excessive organic salt would destroy the emulsion system, which would reduce reaction conversion.

Table 1
Weight average particle size at different power output

Power output (W)	150	300	450	600	750
D_W (nm)	222	169	161	289	292

Conc. of Na_2SO_4: 1.0%; 25 °C 60 min.

3.3. Effect of ultrasonic power output on polymerization

In an ultrasonically initiated emulsifier-free emulsion polymerization system, an important parameter influencing the formation of radicals was the ultrasonic intensity. However, quantitatively determining the ultrasonic intensity was difficult. For a relative comparison, we used the power output to study the effect of ultrasonic intensity on ultrasonically initiated emulsifier-free emulsion polymerization. The conversion versus time curves on the power output of 300, 450, 600 W were shown in Fig. 8. It was clear that with increasing the power output, the conversion of the monomer increased. Generally, increasing ultrasonic intensity led to an increase of the number of radicals produced through ultrasonic irradiation in the range of the cavitation threshold (the minimum acoustic intensity for ultrasonic cavitation) and cavitation peak values (the maximum acoustic intensity for ultrasonic cavitation). In the present work, it could be assumed that the ultrasonic intensity used for the BA and AM system falls in that range.

We also observed the influence of the ultrasonic power output on particles size and particles size distribution. The data were shown in Table 1 and Fig. 9, respectively. When the power output was 450 W, the particles size was minimum and the particles size distribution was narrowest. Increasing ultrasonic intensity would increase the stirring effect, which would lead to enhancing aggregation among particles. So the particles size and particles size distribution would increase by increasing ultrasonic intensity. However, low ultrasonic intensity would decrease the producing rate of radicals and the nucleation rate. Correspondingly, the aggregation rate among particles was increased, which also led to an increase of the particles size and particles size distribution.

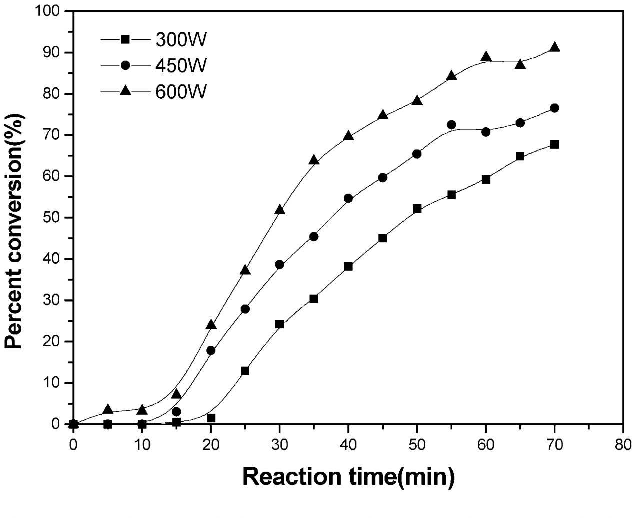

Fig. 8. Conversion vs sonic time curves during ultrasonic copolymerization of BA/AM at different power output (Conc. of inorganic salt: 0.5%; 25 °C).

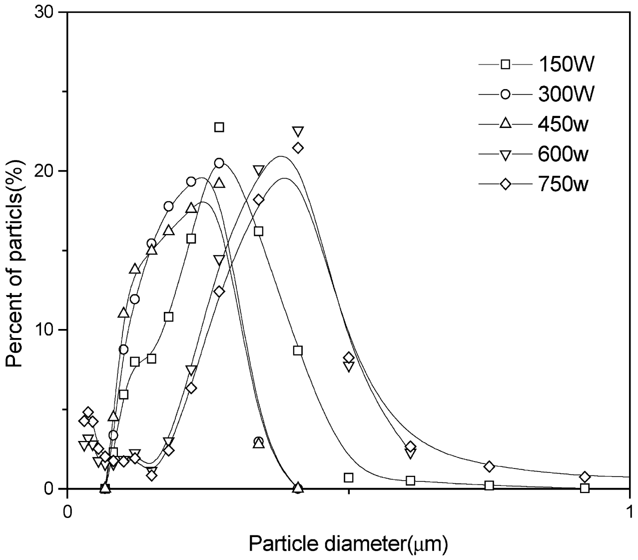

Fig. 9. Weight average particle size distributions at different power output.

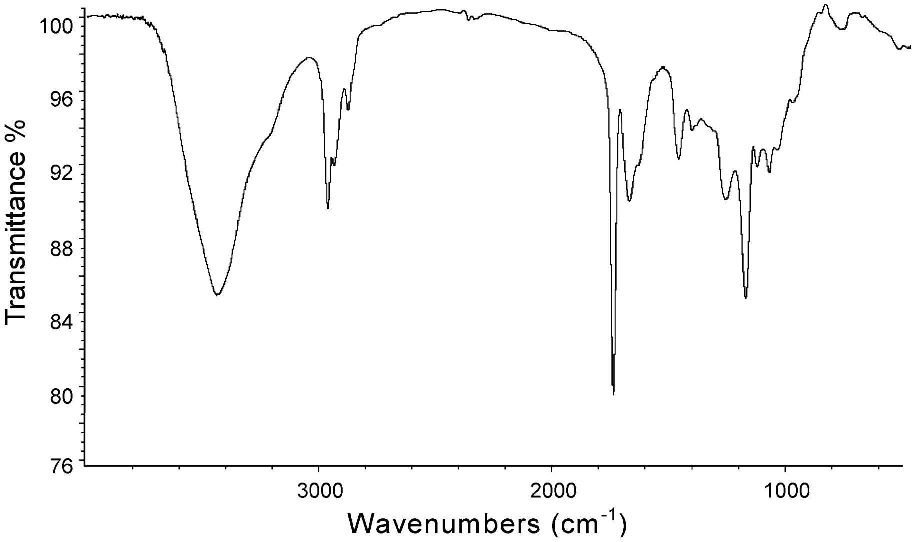

Fig. 10. FTIR spectrum of copolymer of BA and AM obtained by ultrasonically initiated emulsifier-free emulsion polymerization after extracted 48 h by water and 48 h by acetone, respectively.

3.4. Structure characterization

Fig. 10 shows the FTIR spectrum of the sample obtained through ultrasonically initiated emulsifier-free emulsion polymerization of BA-AM after extracted by water for 48 h and acetone for 48 h, respectively. The characteristic peaks of BA at 1735, 2960, 2873, and 964 cm^{-1} and AM at 1666, 3435, 1398, and 1166 cm^{-1} appear in the FTIR spectrum. This shows that after extracted by water for 48 h and acetone for 48 h, the sample obtained by this way is the copolymerization of BA and AM, but not the blend of poly(butyl acrylate) and polyacrylamide.

4. Conclusion

Ultrasonically initiated emulsifier-free emulsion copolymerization of BA and AM has been successfully carried out. The ultrasonically initiated emulsifier-free emulsion and the conventional emulsifier-free emulsion of BA and AM had the similar polymerization mechanism except that the former had higher polymerization rate due to the strong agitation of the ultrasonication. The polymerization course was divided into four stages considered the monomer conversion and the main reaction locus of BA and AM, respectively. (1) At the beginning, AM molecules polymerized preferentially in the aqueous phase. As the chain length of polyacrylamide increased, its hydrophilicity rapidly depressed. (2) So the BA molecules could react with polyacrylamide chain and form the micelle-like structure. (3) After the particles formation by the aggregation of the micelle-like structure, BA polymerized exclusively in the particles, but the AM continuously mainly polymerized in the aqueous phase because of the cavitation bubble produce by ultrasound. (4) After the disappearance of BA droplets, the sources of BA supply to the particles, the main reaction locus was transferred from the particles to the aqueous phase.

Improving the power output would increase the monomer conversion and the rate of polymerization. However, when the reaction temperature was 30 °C and the concentration of Na_2SO_4 was 0.1%, the monomer conversion and the rate of polymerization achieved maximum. Increasing or decreasing the reaction temperature and the concentration of Na_2SO_4 all would lead to the decrease of the conversion. The FTIR spectrum showed that after extracted by water for 48 h and acetone for 48 h, the sample obtained by this way was the copolymer of BA and AM, but not the blend of poly(butyl acrylate) and polyacrylamide.

Acknowledgements

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References

[1] Kawaguchi H, Ohtsuka Y, Sugi Y. J Appl Polym Sci 1981;26:1637.
[2] Ceska GW. J Appl Polym Sci 1974;18:427.
[3] Song Z, Poehlein GW. J Polym Sci, Part A: Polym Chem 1990;25: 2359–92.
[4] Liu L-J, Krieger IM. In: Becker P, Yudenfreund MN, editors. Emulsions, latices, and dispersions, New York: Marcel Dekker; 1978. p. 41.
[5] Goodwin JW, Ottowill RH, Pelton R. Colloid Polym Sci 1979;257:61.
[6] Sakota K, Okaya T. J Appl Polym Sci 1976;20:1725–33.
[7] Goodall AR, Hearn J, Wilkinson MC. Br Polym J 1978;10:141.
[8] Cesca GW. J Appl Polym Sci 1974;18:427.
[9] Sakota K, Okaya T. J Appl Polym Sci 1976;20:1745–52.
[10] Kawaguchi H, Ohtsuka Y, Sugi Y. J Appl Polym Sci 1981;26:1649.
[11] Juang MS, Krieger IM. J Polym Sci, Polym Chem Ed 1976;14:2089.
[12] Liu LJ, Kreger IM. J Polym Sci, Polym Chem Ed 1981;19:3013.

[13] Arai M, Arai K, Saito S. J Polym Sci, Polym Chem Ed 1979;17:3655–65.
[14] Fitch RM, Prenosil MP, Sprick KJ. J Polym Sci, Part C 1969;27:95.
[15] Goodall AR, Wilinson MC, Hearn J. J Polym Sci, Polym Chem Ed 1977;15:2193–218.
[16] Lichiti G, Gilbert RG, Napper DH. J Polym Sci, Polym Chem Ed 1983;21:269–91.
[17] Feeney PJ, Napper DH, Gilbert RG. Macromolecules 1987;20:2922–30.
[18] Song Z, Poehlein GW. J Colloid Interface Sci 1989;128:489.
[19] Song Z, Poehlein GW. J Colloid Interface Sci 1989;128:501.
[20] Suslick KS. Science 1990;247:1439–45.
[21] Liu Y, Chou H, Stoffer JO. J Appl Polym Sci 1994;53:247.
[22] Chou H, Stoffer JO. J Appl Polym Sci 1999;72:797.
[23] Biggs S, Grieser F. Macromolecules 1995;28:4877.
[24] Cooper G, Grieser F, Biggs S. J Colloid Interface Sci 1996;52:184.
[25] Xia H, Wang Q, Liao Y. Ultrason Sonochem 2002;9:151–8.
[26] Tamai H, Murakami T, Suzawa T. J Appl Polym Sci 1985;30:3857–66.
[27] Ohtsuka Y, Kawaguchi H, Sugi Y. J Appl Polym Sci 1981;26:1637–47.