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# Two-stage mathematical model of ultrasonically initiated emulsion polymerization part one, stage I

Nianwei Yin, Keqiang Chen *

*State Key Laboratory of Polymer Materials Engineering, Polymer Research Institute of Sichuan University, Chengdu 610065, People's Republic of China*

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**Abstract**

A new two-stage mathematical model of ultrasonically initiated emulsion polymerization, only acceleration and deceleration stages, was proposed in this paper. This model took into account homogeneous, micelle and monomer droplet nucleation mechanisms. According to this model, the reason of constant velocity stage disappeared is due to very abundant small size monomer droplets nucleation after the surfactant exhausted. Moreover, for St and MMA, the model predicts that as the ultrasonic intensity increases the monomer conversion and polymerization rate at stage I will rapidly increase while the ending time of stage I rapidly decrease. However, as the monomer content increases the monomer conversion and polymerization rate at stage I will rapidly decrease while the ending time of stage I rapidly increase. For the two monomers mentioned above, the model predictions are both very excellent agreement with the experimental data from the literatures.

*Keywords:* Ultrasonic; Emulsion polymerization; Mechanism

## 1. Introduction

Harkins [1,2] was the first to propose a qualitative three intervals mechanism based on free radical penetration into monomer-swollen emulsifier micelles. Duck [3] and Roe [4] consummated this theory. Except the micelle-entry nucleation mechanism, Priest [5] and Fitch [6–8] proposed the homogenous nucleation mechanism, and Hansen and Ugelstead [9–11] and Durlin et al. [12] proposed the third nucleation mechanism, that is, monomer droplets nucleation mechanism. Later, Song and Poehlein [13] developed a theory included all three particle nucleation mechanisms in a mathematical model. They all considered that the course of emulsion polymerization could be considered as involving three intervals.

Interval I, where particle formation takes place. The end of this interval is not dependent upon the degree of conversion, but on the total amount of polymer formed. With usual recipes, it ends at about 1–5% conversion. Interval II lasts from the end of Interval I to monomer droplets disappeared. In this interval, the particle number is usually found to be constant, the particle volume increases proportional to conversion, the monomer concentration in the particles is approximately constant, and therefore the termination is also constant within the particles. Interval III, which is the deceleration stage, starts when the monomer disappears as a separate phase. In Interval III the monomer concentration steadily decreased with increasing conversion, and the particle volume decrease slightly due to contraction by polymerization.

Recently, ultrasonically initiated emulsion polymerization of methyl methacrylate [14,15], styrene [16] and butyl acrylate/vinyl acetate [17] has attracted more attention. Compared to conventional emulsion polymerization, ultrasonically initiated emulsion polymerization can produce faster polymerization, higher monomer conversion and molecular weight. However, due to the introduction of the ultrasound, the polymerization mechanisms become more complex. Different from the conventional emulsion polymerization, where the course could be divided into three intervals, many researchers [16,18] found there only existed two stages, the acceleration stage and deceleration stage. However, no theory explained why the stage of the constant velocity was disappeared.

Because there is no chemical initiator, so any polymerization mechanism must explain where the free radicals come from. According to previous work [15,19–21], Xia and Wang [22] summarized that there were mainly four kinds of free radicals: (1) $H^{\cdot}$ and $OH^{\cdot}$ coming from water, (2) coming from the decomposition of the monomer, (3) coming from the decomposition of the emulsifier, and (4) coming from the degradation of macromolecules. They [22] considered that the

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* Corresponding author. Tel.: +86 28 85401398; fax: +86 28 85402465.
*E-mail address:* yinnianwei@163.com (K. Chen).

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free radicals coming from water and monomers could be neglected in the ultrasonically initiated emulsion polymerization. In our previous paper [23], we proposed a new theory, which detailedly discussed the particles nucleation mechanism of the ultrasonically initiated emulsion polymerization according to Poehlein's [24] comprehensive picture of mechanisms for particle nucleation of the emulsion polymerization. In this paper, we proposed a two stages polymerization model and detailedly discussed the first stage of ultrasonically initiated emulsion polymerization. About the discussion of the second stage can see another paper [25].

## 2. Theory

Similar to the conventional emulsion polymerization, there also exist three kinds nucleation fashion in the ultrasonically initiated emulsion polymerization, which are the micelle-entry nucleation, homogeneous nucleation and monomer droplets nucleation. However, due to the introduction of ultrasound, the role of monomer droplets nucleation will be evidently increased for the size of monomer droplets is so small, 50–200 nm [26] compared to 2–10 μm [27] in the conventional emulsion polymerization. So the number of particles will continuously increase even though the micelles have been exhausted. In this course, the polymerization rate will continuously increase due to the new particle formed. Only after monomer droplets are disappeared, the number of particles will maintain a constant and the polymerization rate will decrease. Thus, different from the conventional emulsion polymerization, there only exist the acceleration and deceleration stage in the ultrasonically initiated emulsion polymerization. Many researchers [16,18] have observed this phenomenon. In this paper, we proposed a two-stage mathematical model of the ultrasonically initiated emulsion polymerization.

### 2.1. The number of particles at stage I

The number of particles at stage I of ultrasonically initiated emulsion polymerization was developed in a previous paper [23]

$$N = N_A[P] = \frac{Q_1 + \beta Q_2}{1 - \beta} \tag{1}$$

$$\beta = \frac{Q_0 - Q_1}{Q_0 + Q_2} e^{-(Q_1+Q_2)\delta_0 t} \tag{2}$$

where

$$Q_1 = \frac{\sqrt{(\delta_1 - \delta_2[\mathrm{CS}])^2 + 4\delta_0(\delta_4[\mathrm{CS}] - \delta_3[\mathrm{CS}]^2)} + (\delta_1 - \delta_2[\mathrm{CS}])}{2\delta_0} \tag{3}$$

$$Q_2 = \frac{\sqrt{(\delta_1 - \delta_2[\mathrm{CS}])^2 + 4\delta_0(\delta_4[\mathrm{CS}] - \delta_3[\mathrm{CS}]^2)} - (\delta_1 - \delta_2[\mathrm{CS}])}{2\delta_0} \tag{4}$$

where $[P]$ is the particle concentration, $N_A$ is Avogadro's number, [CS] is the mole concentration of cavitation, and the parameters $\delta_0$, $\delta_1$, $\delta_2$, $\delta_3$ and $\delta_4$ are constant and their definition can see our previous papers [23].

### 2.2. The monomer conversion at stage I

Now we considered a particle existed in the system, so the polymerization rate in a particle, $d\Omega/dt$, can be acquired,

$$\frac{d\Omega}{dt} = \frac{k_p}{N_A}[M_p]i \tag{5}$$

where $\Omega$ is the mole mass of monomer converted to polymer in a particle; $k_p$ is the propagation rate constant in the particle; $N_A$ is the Avogadro's number; $t$ is the time; $[M_p]$ is the monomer concentration in the particle; and $i$ is the radical number in a particle.

The $[M_p]$ can be defined by following equation:

$$[M_p] = \frac{\phi_m}{V_M} \tag{6}$$

where $\Phi_m$ is the volume fraction of monomer in a particle, and $V_M$ is the molar volume of monomer.

For a monomer-swollen particle, its radius can be calculated by following equation,

$$r_p^3 = \frac{3}{4\pi} \frac{V_M d_m}{d_p(1 - \phi_m)} \Omega \tag{7}$$

where $d_m$ and $d_p$ are the density of monomer and polymer, respectively.

In the first stage, when a monomeric radical enters into a monomer-swollen micelle or a monomer droplet, the value of $\Phi_m$ should be equal to one for the total monomer-swollen micelle or monomer droplet. However, if we consider the nearby area of the monomeric radical existed, the value of $\Phi_m$ should be close to that of $\Phi_m$ in the monomer-swollen polymer. Thus, in the first stage, the value of $\Phi_m$ always maintains constant. So, differentiating Eq. (7) gives,

$$\frac{dr_p^3}{dt} = \frac{3}{4\pi} \frac{V_M d_m}{d_p(1 - \phi_m)} \frac{d\Omega}{dt} \tag{8}$$

Substituting Eq. (5) into Eq. (8) gives,

$$\frac{dr_p^3}{dt} = \frac{3}{4\pi} \frac{k_p}{N_A} \frac{d_m \phi_m}{d_p(1 - \phi_m)} i \tag{9}$$

Let,

$$K = \frac{3}{4\pi} \frac{k_p}{N_A} \frac{d_m \phi_m}{d_p(1 - \phi_m)} \tag{10}$$

Then, the Eq. (9) can be rewritten as,

$$\frac{dr_p^3}{dt} = Ki \tag{11}$$

At stage I, because the size of particles is very small and the diffusing path of free radical in the particles is very short, so the termination reaction in the particles is instantaneous. Thus, the radical number in a particle should be a constant.

Above equation indicates that the volume propagation rate of a particle is a constant. If a particle forms at time $\tau$, until time $t$, its volume can be calculated by following equation,

$$v(\tau) = \frac{4}{3}\pi K i(t-\tau) + v'_0 \tag{12}$$

where $v'_0$ is the volume of the monomer-swollen micelle or monomer droplets. Within $\mathrm{d}\tau$ interval, the total volume of particles per liter water, $v_\tau$, can be calculated by following equation,

$$v_\tau = \left(\frac{4}{3}\pi K i(t-\tau) + v'_0\right)\dot{N}(\tau)\mathrm{d}\tau \tag{13}$$

where the item $\dot{N}(\tau)\mathrm{d}\tau$ represents the total particles number formed at $\mathrm{d}\tau$ interval. Integrating above equation from $t=0$ to $t=t$ gives

$$v_{\mathrm{pt}} = \int_0^t \left(\frac{4}{3}\pi K i(t-\tau) + v'_0\right)\dot{N}(\tau)\mathrm{d}\tau \tag{14}$$

where $v_{\mathrm{pt}}$ is the total volume of particles formed until time $t$. The monomer conversion at time $t$ before the monomer droplets disappeared, $X_t$, can be calculated by following equation

$$X_t = \frac{d_{\mathrm{p}}(1-\phi_{\mathrm{m}})}{m_0}\int_0^t \left(\frac{4}{3}\pi K i(t-\tau) + v'_0\right)\dot{N}(\tau)\mathrm{d}\tau \tag{15}$$

where $m_0$ is the monomer mass charged. Substituting Eqs. (1) and (10) into above equation gives

$$\begin{aligned} X_t = {} & \frac{d_{\mathrm{p}}(1-\Phi_{\mathrm{m}})N_{\mathrm{A}}v'_0}{m_0}\left(\frac{Q_2+Q_1\beta}{1-\beta} - (Q_0+Q_2-Q_1)\right) \\ & + \frac{k_{\mathrm{p}}d_{\mathrm{m}}\Phi_{\mathrm{m}}I}{m_0}\left(\frac{1}{\delta_0}\ln(1-\beta) + (Q_1-Q_0)t \right. \\ & \left. - \frac{1}{\delta_0}\ln\left(\frac{Q_1+Q_2}{Q_0+Q_1}\right)\right) \end{aligned} \tag{16}$$

where $I$ represents the average radical number in one particle, and the relationship of $I$ and $i$ can be declared by the following equation

$$I = \sum_{i=0}^{\infty} iN_i / \sum_{i=0}^{\infty} N_i.$$

In the above equation, the value of $v'_0$ should be more detailedly discussed. Once a monomeric radical entered into a monomer-swollen micelle or a monomer droplet, they would become a particle. Except for the nearly region of the monomeric radical existed, however, the other region of the monomer-swollen micelle or monomer droplets cannot influence the monomer conversion. So, the total volume of the particle cannot be applied for calculating the monomer conversion and only the nearby area of the monomeric radical existed could be used. So, the value of $v'_0$ should be equal to zero. Thus, the Eq. (16) can be written as,

$$X_t = \frac{k_{\mathrm{p}}d_{\mathrm{m}}\Phi_{\mathrm{m}}I}{\delta_0 m_0}\left(\ln(1-\beta) + (Q_1-Q_0)\delta_0 t - \ln\left(\frac{Q_1+Q_2}{Q_0+Q_2}\right)\right) \tag{17}$$

### 2.3. The polymerization rate at stage I

At stage I, the polymerization rate at time $t$, $R_{\mathrm{pt}}$, should continuously increase due to the sustained particle formation and can be calculated by differentiating Eq. (17),

$$R_{\mathrm{pt}} = \frac{k_{\mathrm{p}}d_{\mathrm{m}}\Phi_{\mathrm{m}}I}{m_0}\left(\frac{Q_1+Q_2}{1-\beta} - (Q_2-Q_0)\right) \tag{18}$$

### 2.4. The ending time of stage I

The monomer conversion as the nucleation ends, $X_{t0}$, can be determinate by following equation,

$$X_{t0} = \frac{d_{\mathrm{p}}(1-\Phi_{\mathrm{m}})}{d_{\mathrm{p}}(1-\Phi_{\mathrm{m}}) + d_{\mathrm{m}}\Phi_{\mathrm{m}}} \tag{19}$$

So the ending time of stage I, $t_0$, can be determined by Eqs. (17) and (19).

## 3. Results and discussion

The mathematical model developed in the above section was used for computer simulation. The kinetic parameters of two monomers employed, styrene (St) and methyl methacrylate (MMA), in the simulation are listed in Table 1. All the radical desorptions from particles, micelles and monomer droplets are neglected in the simulation for simplicity. According to Smith and Ewart's [28,29] theory, for the conventional emulsion polymerization, the average radical number is about 0.5 in interval I and II. So for an alone particle, if it has 0.5 monomeric radical all the time, its radius will increase within 1 h from zero to about 38 nm for St and 59 nm for MMA, respectively. However, the actual radii are only about 10 nm for St [18] and 25 nm for MMA calculated from Chou's [15] experimental data. So the average radical number must be far-forth less than 0.5. There are two factors leading to the average radical number far-forth less than 0.5. The first is desorption of radical from particles. The second is the particle number increasing. In fact the average radical number should be influenced by the cavitation concentration, that is, the larger cavitation concentration, the larger value of the average radical number. However, for simplifying the model, we assumed it as a constant value 0.1.

### 3.1. Variation of cavitation concentration [CS]

Figs. 1 and 2, for St and MMA, respectively, are the computer simulative curves of the monomer conversion with reaction time at different cavitation concentration. They show that monomer conversion increases with the cavitation

Table 1
Kinetic data used in calculation and the model parameters calculated

| Monomer | St[a] | MMA[a] | Ref. |
|---|---|---|---|
| $M_w$ (mol/L) | 0.0035 | 0.15 | [30] |
| CMC (mol/L) | 0.0076 | 0.0076 | [31] |
| $r_p$ (nm) | 21 | 21 | [32] |
| $r_m$ (nm) | 5 | 5 | [31] |
| $r_d$ (nm) | 50 | 50 | [b] |
| $n^*$ | 5 | 66 | [33,7] |
| $n_1$ | 2 | 2 | [b] |
| $I$ | 0.1 | 0.1 | [b] |
| $k_p$ (L/(mol S)) | 60.3 | 251 | [34,35] |
| $k_{tw}\times10^{-7}$ (L/(mol S)) | 2.74 | 1.74 | [34,7] |
| $C_m\times10^5$ | 5 | 1 | [34,35] |
| $k_{trm}\times10^3$ (L/(mol S)) | 3.2 | 2.51 | [34,35] |
| $D_w\times10^{10}$ (dm$^2$/s) | 2.86 | 2.86 | [36] |
| $\Phi_m$ | 0.6 | 0.6 | [31] |
| $d_m$ (g/L) | 906 | 942 | |
| $d_p$ (g/L) | 1050 | 1190 | |
| $K_f$ (L/(mol S)) | 100 | 100 | [b] |
| $\alpha_p\times10^5$ | 5.57 | 395 | |
| $\alpha'_p\times10^5$ | 5.57 | 395 | |
| $B$ | 1.36 | 1.36 | |
| $k_d\times10^{-8}$ (L/(mol S)) | 1.36 | 1.36 | |
| $t_1$ | 0.000264 | 0.000105 | |
| $t_2$ | 0.00144 | 0.00933 | |
| $\mu_1$ | 546 | 218 | |
| $\mu_2$ | 0 | 0 | |
| $\gamma_t$ | 0 | 0 | |
| $K_c\times10^{-8}$ | 4.55 | 4.55 | |
| $K_{md}\times10^{-8}$ | 1.08 | 1.08 | |
| $\delta_0$ | 100 | 100 | |
| $\delta_1$ | 0 | 0 | |
| $\delta_2\times10^{-11}$ | 2.48 | 2.56 | |
| $\delta_3\times10^{-12}$ | 8.18 | 5.54 | |
| $\delta_4\times10^{-6}$ | 2.07 | 2.07 | |

[a] Recipe: monomer (10 wt%), water (89 wt%), and SDS (1%) at 30 °C.
[b] Assumed.

concentration increasing. The reason is the more cavitation in the reaction system, the more free radical formation and the smaller the monomer droplets. So there will be more monomer droplets nucleation and particle growing [23]. Different from the conventional emulsion polymerization, which existed a constant velocity reaction stage, no such stage appeared in the ultrasonic initiated emulsion polymerization from Figs. 3 and 4 that were the computer simulative curves of the polymerization rate with reaction time of stage I at different cavitation concentration for St and MMA, respectively. However, when the cavitation concentration exceeded $5\times10^{-15}$ mol/L, there existed a constant velocity stage for St. This phenomenon was not consistent with the experimental result gained by Ooi and

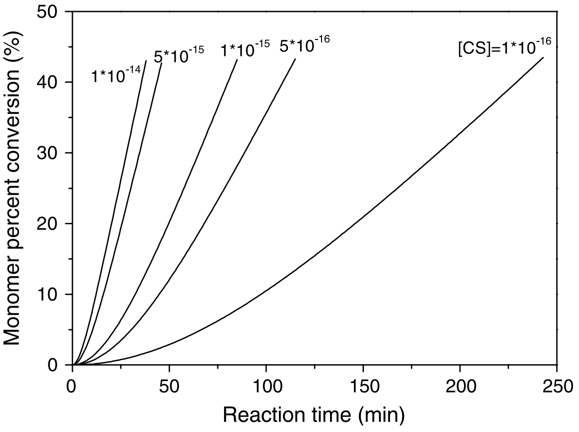

Fig. 1. The curves of monomer percent conversion versus reaction time of different [CS] at stage I for St.

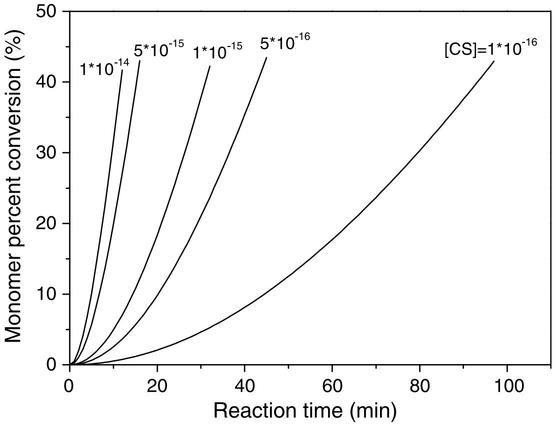

Fig. 2. The curves of monomer percent conversion versus reaction time of different [CS] at stage I for MMA.

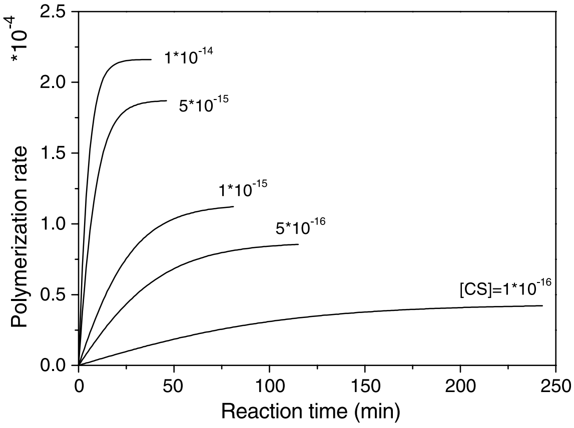

Fig. 3. The curves of polymerization rate versus reaction time of different [CS] at stage I for St.

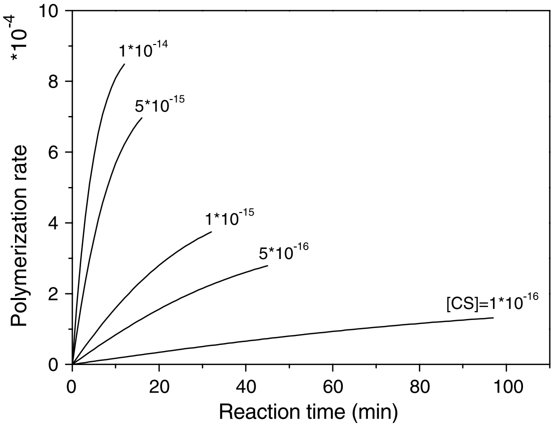

Fig. 4. The curves of polymerization rate versus reaction time of different [CS] at stage I for MMA.

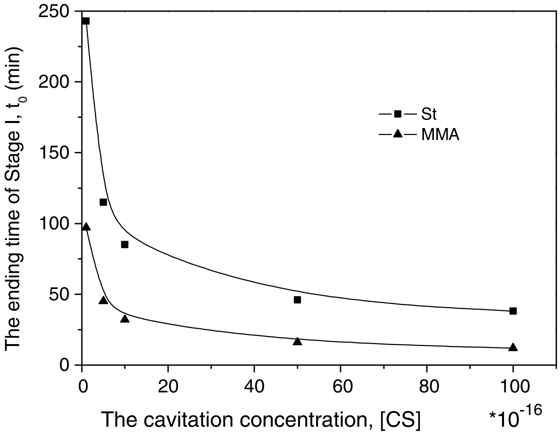

Fig. 5. The curves of the ending time of stage I versus the cavitation concentration.

Biggs [16,18], where no constant velocity stage. The cavitation concentration of Ooi and Biggs's [16,18] reaction system, however, was only $3.4\times10^{-16}$ mol/L that was far-forth less than $5\times10^{-15}$ mol/L. In such low cavitation concentration, no constant velocity stage appears from Fig. 3. The reason appeared the constant velocity stage as the cavitation concentration exceeded a value may be that the larger the cavitation concentration, the more free radical formed lead to mostly monomer droplets converting to particles within very short time, that means the nucleation time is shortened. Because the monomer solubility of MMA (about 1.5 wt%) is far-forth larger than that of St (about 0.035 wt%), there will exist homogeneous nucleation after all the monomer droplets converted to particles in the MMA reaction system. So even though the cavitation concentration achieves a larger value ($1\times10^{-14}$ mol/L), no constant velocity stage is appeared.

At the same cavitation concentration, the polymerization rate of MMA is larger than that of St. The ending time of stage I of MMA is also shorter than that of St from Fig. 5, which is the curves of the ending time with the cavitation concentration for St and MMA. The reason is that the propagation rate constant $k_p$ of MMA (about 251 L/(mol S)) is larger than that of St (about 60.3 L/(mol S)). Larger value of $k_p$ will lead to more monomer converting to polymer. If the homogeneous nucleation is neglected, after monomer droplets disappeared due to polymerization, the nucleation stage, that is, stage I will be end.

### 3.2. Variation of monomer content

In the conventional emulsion polymerization system, the monomer droplets only serve as a monomer reservoir to maintain a nearly constant concentration of monomer in the aqueous phase and the thermodynamic equilibrium of monomer between the aqueous phase and polymer phase. In the ultrasonically emulsion polymerization system, however, besides serving as a monomer reservoir, the monomer droplets will be an important nucleation locus, especially after the micelles are disappear. So the monomer content in the reaction system will greatly influence the monomer conversion and polymerization rate. Figs. 6–9 are the curves of monomer percent conversion and polymerization rate versus reaction time of different monomer content at stage I for St and MMA. All the calculation data come from Table 1 and only the monomer content value are changed. For both two kinds of monomer, St and MMA, no constant velocity stage appears. As the monomer content decrease, the monomer conversion and polymerization rate rapidly increase. Monomer content has two kinds of contrary effect to influence the monomer conversion and polymerization rate. More monomer charged will form more monomer droplets and offer more polymerization loci, so the monomer conversion will increase with monomer content increasing. On the other hand, for acquiring same monomer conversion, more monomer content need more monomer converting to polymer, so it would decrease the monomer conversion.

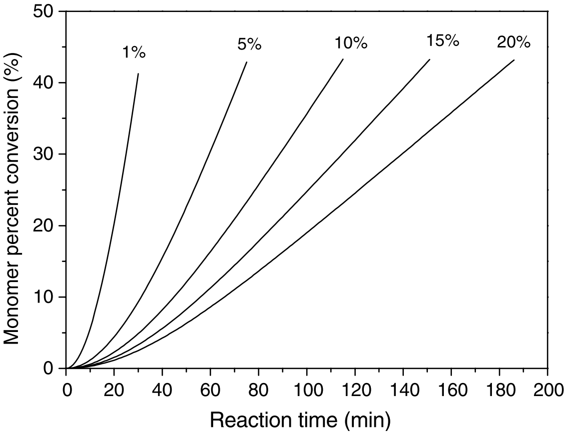

Fig. 6. The curves of monomer percent conversion versus reaction time of different monomer content at stage I for St.

Fig. 10 is the curves of the ending time of stage I versus the monomer content for St and MMA. The ending time of stage I almost linearly increase with the monomer content increasing both St and MMA. The slopes are about 8.053 and 2.711 for St and MMA, respectively. This show that the ultrasonically initiated emulsion polymerization of St is more tend to be

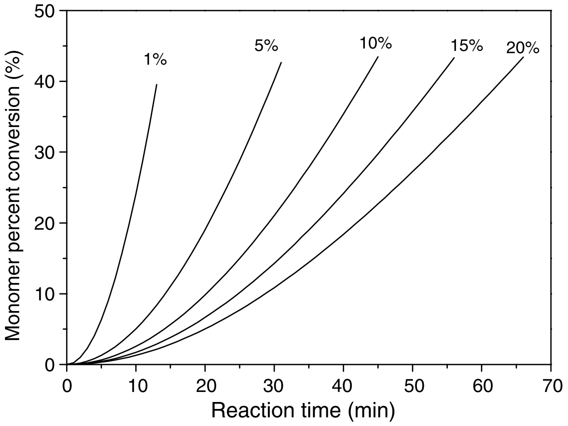

Fig. 7. The curves of monomer percent conversion versus reaction time of different monomer content at stage I for MMA.

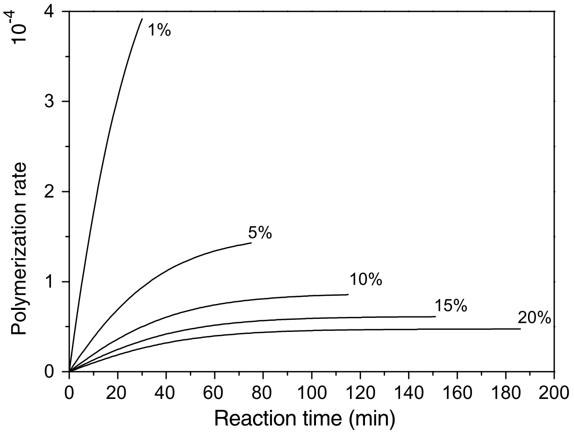

Fig. 8. The curves of polymerization rate versus reaction time of different monomer content at stage I for St.

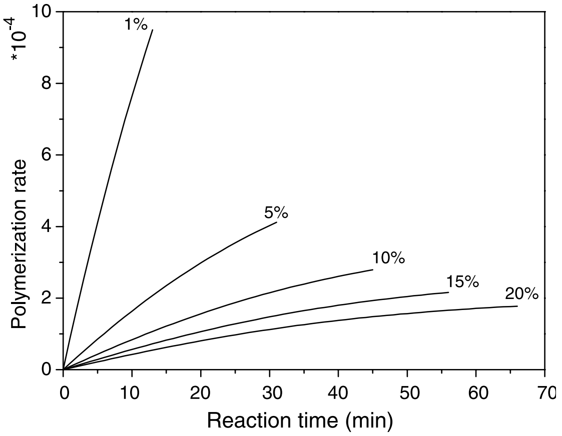

Fig. 9. The curves of polymerization rate versus reaction time of different monomer content at stage I for MMA.

influenced by monomer content. The reason may be that the monomer solubility and propagation rate constant of St are far-forth less than those of MMA.

### 3.3. Experimental test of the model

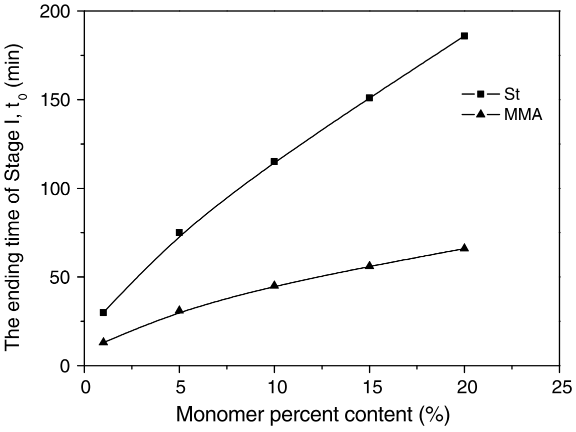

Fig. 10. The curves of the ending time of stage I versus the monomer content.

Table 2
The monomer conversion data of St at stage I

| Acoustic intensity (W cm$^{-2}$) | Reaction time (min) | Monomer conversion (%w/w) |
|---|---|---|
| 20.3 | 30 | 7.44 |
| 20.3 | 60 | 14.58 |
| 20.3 | 90 | 19.92 |
| 20.3 | 120 | 33.24 |
| 35.5 | 30 | 3.17 |
| 35.5 | 60 | 13.32 |
| 35.5 | 90 | 32.31 |

Recipe: styrene (5 wt%), water (94 wt%) and SDS (1 wt%) at 30 °C.

The experimental data of Ooi [18] for St and Chou [15] for MMA are listed in Tables 2 and 3, respectively. Recipes and reaction conditions of the experiments are also listed in the tables. The kinetic data for model simulation come from Table 1 except that the monomer percent content is changed from 10 to 5% and 20% for St and MMA, respectively. The calculations of cavitation mole concentration are based on the Eq. (59) of Ref. [23]. The cavity nuclei number $N_1$ of St is also assumed as 2000. However, due to the monomer solubility (about 1.5 wt%) and monomer content (20 wt%) of MMA are both larger than those (about 0.035 and 5 wt%) of St, so the cavity nuclei number $N_1$ of MMA should be also larger than that of St and we assume it as 10,000. Moreover, according to above-mentioned reason in previous part, the average radical number in one particle should be far-forth less than 0.5 and we assume it as 0.1 for computer simulation. However, the value of average radical number evidently is influenced by ultrasonic intensity. Larger ultrasonic intensity should produce more free radical and lead to larger value of $I$. So assuming different value of $I$ for different ultrasonic intensity, which is listed in Table 4, should be reasonable. Although the input ultrasonic intensity of St are larger than those of MMA, the actual cavitation concentration in aqueous phase of St are less than

Table 3
The monomer conversion data of MMA at stage I

| Acoustic intensity (W cm$^{-2}$) | Reaction time (min) | Monomer conversion (%w/w) |
|---|---|---|
| 6.8 | 10 | 1.2 |
| 6.8 | 15 | 4.3 |
| 6.8 | 20 | 9.6 |
| 6.8 | 25 | 14.5 |
| 6.8 | 30 | 20.2 |
| 6.8 | 35 | 25.5 |
| 6.8 | 40 | 29.5 |
| 11.0 | 10 | 2.2 |
| 11.0 | 15 | 5.2 |
| 11.0 | 20 | 12.5 |
| 11.0 | 25 | 18.9 |
| 11.0 | 30 | 25.9 |
| 11.0 | 35 | 31.2 |
| 14.4 | 10 | 5.1 |
| 14.4 | 15 | 10.2 |
| 14.4 | 20 | 19.1 |
| 14.4 | 25 | 30.5 |
| 14.4 | 30 | 38.2 |

Recipe: MMA(20 wt%), water (79 wt%) and SDS (1 wt%) at −10 °C.

Table 4
The value of $I$ under different ultrasonic intensity

| Monomer | Ultrasonic intensity (W cm$^{-2}$) | Cavitation concentration, $10^{-16}$ (mol/L) | Average radical number in one particle $I$4 |
|---|---|---|---|
| St | 20.3 | 2.61 | 0.06 |
| St | 35.5 | 3.07 | 0.075 |
| MMA | 6.80 | 9.23 | 0.11 |
| MMA | 11.0 | 10.8 | 0.12 |
| MMA | 14.4 | 11.8 | 0.18 |

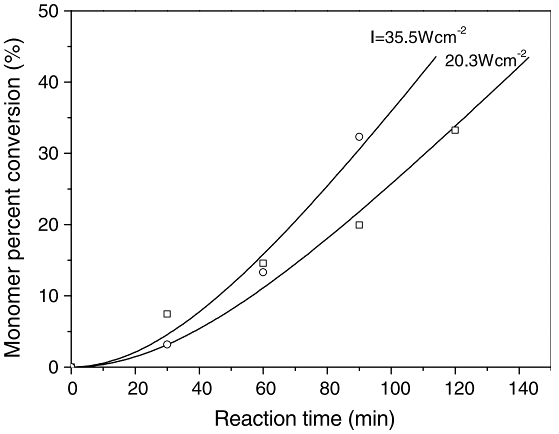

Fig. 11. Comparison of the model prediction (solid line) with the experimental data of St.

those of MMA. So it is reasonable that the average radical number in one particle of St is less than those of MMA.

Due to the strong agitation and crashing effect of ultrasound, the rate constant of particle coagulation $K_f$ should be less than that in the conventional emulsion polymerization. It is not unreasonable that the two systems, St and MMA, would have the same value of $K_f$ for the almost same particle size. Here we assume them as 100. The Figs. 11 and 12 are comparison of the model prediction (solid line) with the experimental data of St by Ooi [18] and MMA by Chou [15], respectively. They show that, for the St and MMA systems, both the model predictions are excellent agreement with the experimental data.

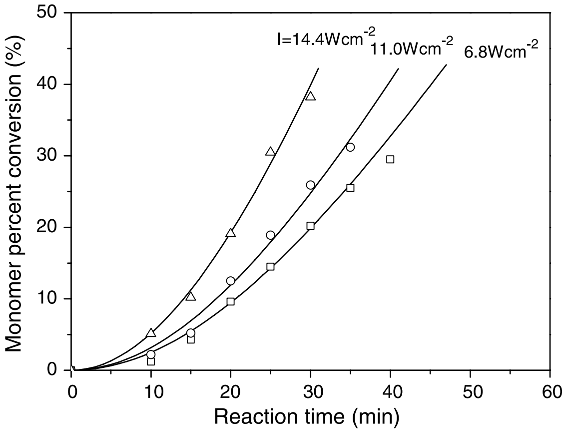

Fig. 12. Comparison of the model prediction (solid line) with the experimental data of MMA.

## 4. Conclusions

Different from the conventional emulsion polymerization, where the reaction course is divided into three intervals, that is, acceleration, constant velocity and deceleration region, a new two-stage mathematical model, only acceleration and deceleration stages, was proposed in the ultrasonically initiated emulsion polymerization. This model takes into account homogeneous, micelle and monomer droplet nucleation mechanisms. Chain transfer to monomer and termination in the aqueous phase, capture of oligomer radicals by particles, and coagulation of particles are also included in the model. According to this model, the reason of constant velocity stage disappeared is due to very abundant small size monomer droplets nucleation after the surfactant exhausted. Moreover, for both sparingly water-soluble monomer, St, and water-soluble, MMA, the model predicts that as the ultrasonic intensity increases the monomer conversion and polymerization rate at stage I will rapidly increase while the ending time of stage I rapidly decrease. However, as the monomer content increases the monomer conversion and polymerization rate at stage I will rapidly decrease while the ending time of stage I rapidly increase. For the two monomers mentioned above, the model predictions are both very excellent agreement with the experimental data from the literatures.

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