A NEW KINETIC MODEL OF EMULSIFIER-FREE EMULSION POLYMERIZATION

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SUMMARY: A new kinetic model was built to fit the conversion of emulsifier-free emulsion polymerization. It was found that the fit was satisfying, and that important parameters could be obtained, such as the maximum polymerization rate, average nucleation rate, average polymerization rate in the steady stage and the conversions at the end of the nucleation and steady stage. Therefore, the whole polymerization process can be understood in detail. TEM tracking verifies that the kinetic model is reliable and accurate.

Introduction

Emulsifier-free emulsion polymerization can be used to synthesize clean and uniform latex particles having functional groups exposed on the surface for biomedical and catalytic support applications. It has been extensively investigated in the last decade, and details can be found in recent reviews by Pichot *et al.*[1-2]. But the kinetic model of emulsifier-free emulsion polymerization has seldom been studied. In general, the kinetics was investigated by two methods. One is seeking the relationship of particle number density (N_p) with various polymerization parameters;[3-4] the other is working out the slope of the conversion curve at the steady stage (within the conversion range of 20%-70%) by linear regression, then finding the relationship of the polymerization rate (the slope) with the polymerization parameters[5]. The two methods are troublesome and can only be used to investigate the steady stage.

In this presentation, a new kinetic model - Integrated Gamma Function - was devised according to the kinetic characteristics of emulsifier-free emulsion polymerization, and it was employed to investigate the copolymerization systems: styrene (St) - methyl methacrylate (MMA), St - AA (acrylic acid). Further more, the kinetic model was verified by the TEM tracking of St - MMA-AA emulsifier-free copolymerization.

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Experiment

Materials. St, MMA and AA were distilled under reduced pressure and stored under nitrogen at 4 ^{0}C if not used immediately. Water was freshly deionized. APS was recrystallized from deionized water.

Experimental Procedure. Emulsifier-free emulsion polymerizations were carried out in one batch at 84 ^{0}C in a 500-mL four-neck receptor purged continuously with nitrogen and equipped with a Teflon stirrer, condenser, thermocouple, and with one neck capped with a rubber septum for taking samples. The stirring rate for all runs was 200 rpm and the reaction time was 12 hours to assure a complete reaction. Typical recipe is listed in Table 1. Latex stability was good since no coagulum adhered on the reactor and no separation or coagulation was observed on standing for six months. Conversions were determined by gravimetry. The average diameter (D_w) and morphology of the latex particles were determined from electron micrographs with a JEM-100SX TEM. The particle number density (N_p) was estimated by use of the mass balance and the corresponding data of D_w and conversion.

Table 1. Recipes of the emulsifier-free emulsion polymerization

	[AA]	[APS]	T	St	MMA	H_2O
Run	10^{-2}mol/L	mmol/L	^{o}C	mL	mL	mL
St-AA	15.191	4.570	84	45.00	0.00	240.00
St-MMA-AA	15.191	4.570	84	30.00	15.00	240.00
St-MMA	0	4.570	84	30.00	15.00	240.00

Construction of the kinetic model

In general, the conversion curve of emulsifier-free emulsion polymerization has the following characteristics:

A. The conversion and the polymerization rate are zero at the beginning of the reaction.

B. The conversion and the polymerization rate increase with the reaction proceeding, then the polymerization rate decreases after reaching a maximum.

C. Finally, the polymerization rate is zero and the conversion levels off at a limiting conversion.

According to the characters of the conversion curve, the model function of the conversion vs. the reaction time should have the following characteristics:

A. There exists a parameter t_0, for which $G(t)=0$ if $t \leq t_0$ and $G(t)>0$ if $t>t_0$

B. $G(t)$ monotonously ascends in $[t_0, +\infty)$

C. $G(t)$ is upper bounded, that is to say $\lim_{t\to\infty} G(t) = M < +\infty$

Therefore, we have chosen an Integrated Gamma Function as the kernel of model function. The definition of Gamma Function is $g(x, c) = x^{c-1}e^{-x}$ for $x\geq 0$ and $c>0$. The integration of $g(x, c)$ along the x coordination from $-\infty$ to $+\infty$ is a constant $\Gamma(c)$ and the limitation of $g(x, c)$ is zero while x tends to $+\infty$. i.e.,

$$\int_{-\infty}^{+\infty} g(x,c)dx = \Gamma(c) \quad , \quad \lim_{x\to\infty} g(x,c) = 0$$

where c is named shape parameter and e is the Euler constant. Integrate Gamma Function $G(x, c)$ is defined as integration of $g(t, c)$ from $-\infty$ to x, where the variable in Gamma Function is substituted by a formal parameter t, i.e., $G(x,c) = \int_{-\infty}^{x} g(t,c)dt$. Apparently, the derivative of the above-defined Integrated Gamma Function is a Gamma Function. Gamma Function is a well-behaved function, continuous and derivable. The first order derivative of it is $g'(x,c) = (c-1-x)x^{c-2}e^{-x}$. When $c\leq 1$, $g'(x,c) \leq 0$, i.e., $g'(x,c)$ monotonously descends within its definition domain. Apparently, $c\leq 1$ is not appropriate for simulation of the polymerization rate. For $c>1$, we have $g'(x,c) > 0$ when $x < c-1$ and $g'(x,c) = 0$ when $x = c - 1$, and $g'(x,c) < 0$ when $x > c-1$, i.e., $g(x, c)$ monotonously ascends till $x=c-1$ where it meets a maximum, then it monotonously descends, which fits the character of the polymerization rate. So we assume $c>1$.

In order to study in a detailed manner the variations of the polymerization rate along with the reaction process, we consider the second order derivative of $g(x, c)$ when $c>1$.

1) for $c\neq 2$

$$g''(x,c) = x^{c-3}e^{-x}((x-(c-1))^2 - (c-1))$$

Let $g''(x,c) = 0$, we have $x = c - 1 \pm \sqrt{c-1}$, i.e., two inflexions of $g(x, c)$.

2) for $c=2$

$$g''(x,c) = (x - 2)\, e^{-x}$$

Let $g''(x,c) = 0$, we have $x = 2$, i.e., the sole inflexion of $g(x, c)$.

Parameter design

While designing parameters, we have to take complexity, adaptation, estimation accuracy and some other items into consideration. The more the parameters, the more the degree of freedom and the more flexible and the more accurate is the fit of the function conversion versus time of the reaction. However, more parameters means more variables to be estimated, which makes the function more complicated, and more samples are necessary. On the contrary, too few parameters make the simulation by the function difficult and it cannot reflect its intrinsic factors. Here we have chosen $F(t) = b_0 * G(b_1 * t + b_2, c)$, which contains four parameter, as our fitting function, where c is the shape parameter of the Gamma Function, b_0 is the limiting conversion parameter, b_1 and b_2 are the linear adjusting parameters of polymerization time.

Calculation

We estimate the parameters b_0, b_1, b_2 and c through samples gained during the reaction by Least Square analysis.

Limiting Conversion $F(+\infty) = b_0$.

Curve of Polymerization Rate: $f(t) = F'(t) = b_0 * b_1 * g(b_1 * t + b_2, c)$

We calculate the first order derivative of the polymerization rate curve and resolve the equation $f'(t) = 0$, giving access to the time at which the polymerization rate reaches the maximum t_m, the corresponding conversion Conv_m and the maximum polymerization rate $(gL^{-1}m^{-1})$: MV $= f(t_m) * M_0$, where M_0 is the initial total concentration of the monomers taking part in the reaction (g/L). We then calculate the second order derivative of polymerization rate curve and resolve the equation $f''(t) = 0$. We get the two inflexions t_1, t_2 and their corresponding conversion $Conv_1$ and $Conv_2$. We define ΔCONV = $Conv_2 - Conv_1$, the average polymerization rate $(gL^{-1}m^{-1})$ of the steady period AV=$M_0 * \Delta \mathrm{CONV}/(t_2 - t_1)$ and the average nucleation rate NV=$M_0 * Conv_1/t_1$ $(gL^{-1}m^{-1})$.

Fitting the conversion-time curves

The fits of conversion-time curves for St-AA, St-MMA-AA and St-MMA emulsifier-free emulsion copolymerization obtained by using the kinetic model are shown in Fig. 1. Important parameters such as: MV, AV, the corresponding conversions, times when the nucleation and the steady stage stop, and the fit errors (residual) are shown in Table 2.

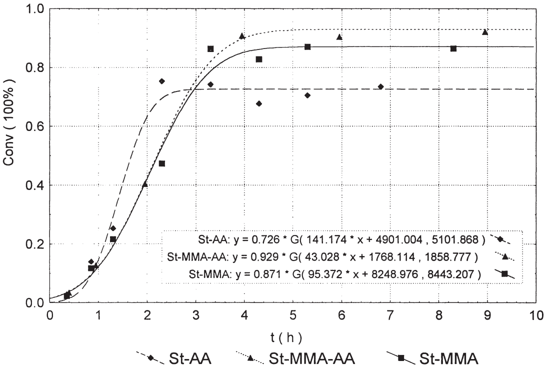


Fig. 1:. Fit of conversion-time curves for St-MMA-AA, St-MMA and St-AA emulsifier free emulsion polymerization.

Table 2. Numerical values used for fitting the curves in Fig. 1.

	MV	t_m	$Conv_m$	t_1	$Conv_1$	t_2	$Conv_2$	AV	Residual
	$gL^{-1}m^{-1}$	h	100%	h	100%	h	100%	$gL^{-1}m^{-1}$	%
St-AA	1.4713	1.42	0.3603	0.91	0.1127	1.92	0.6083	1.2583	0.0211
St-MMA-AA	0.9509	2.08	0.4938	1.08	0.1422	3.09	0.7764	0.8133	0.0016
St-MMA	0.9273	2.03	0.4330	1.06	0.1370	2.99	0.7305	0.7917	0.0112

The efficiency of the fit is very good, as shown in Fig. 1 and Table 2. In all cases, there exists a limiting conversion. As shown in Fig. 1 the conversion curves initially ascend and then level off at a limiting conversion of about 0.75-0.95. The occurrence of the limiting conversion is due to polymerization in a shell-region and monomer diffusion-controlled polymerization at high conversion as proposed by Chen *et al*(3-4). This suggests that the built kinetic model is consistent with the shell growth mechanism for emulsifier-free emulsion polymerization. From Table 2, the whole polymerization process can be clearly understood. For example, take the copolymerization of St – MMA: after it polymerizes 2.03 h, the polymerization rate reaches a maximum (0.9273 $gL^{-1}m^{-1}$), and the corresponding conversion is 43.30%; after 1.06 h the nucleation stage ceases and the corresponding conversion is 13.70%; after 2.99 h the steady stage is completed, the corresponding conversion is 73.05% and the average polymerization rate during the steady stage is 0.7917 $gL^{-1}m^{-1}$. Therefore, properties of St – MMA – AA latex particles can be controlled through feeding AA at different polymerization stage of St – MMA copolymerization(6). More testing work of this kinetic model can be found for St – MMA – AA copolymerization systems(7,8). Studies are being done regarding the microscopic process of the polymerization (*e.g.* propagation rate coefficients, water solubility of various species, termination mechanisms *etc.*) with this kinetic model, and will be published in the near future.

Particle size and morphology

In order to verify the reliability of the kinetic model, size and morphology of the particles were monitored continuously by TEM and the solid content was measured all along the polymerization process. Figure 2 shows TEM photographs of the particles at different reaction time (stained by pH 6.4 phosphotungstic acid). D_w and N_p determined by TEM and the conversions at different reaction time are shown in Table 3 and the curve fits are shown in Figure 3. In addition, the numerical characteristics of the fits are shown in Table 4.

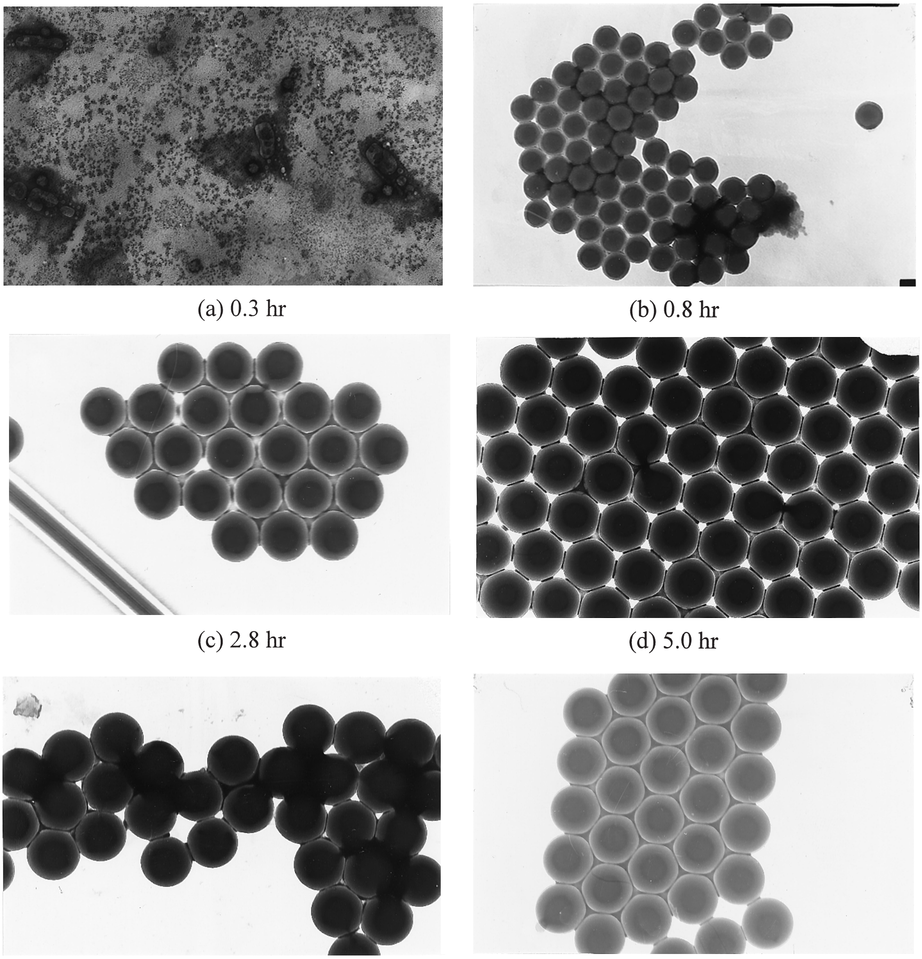
Table 3. Average diameter (D_w), number of particles (N_p) and conversion

t (h)	D_W (nm)	N_P (10^{16}/L)	Conv (%)
0,3	~5.0	3317,20	2,40
0,8	121,0	1,42	10,80
1,8			47,00
2,8	211,2	1,35	70,30
5,0	224,0	1,17	74,10
6,8	225,1	1,03	74,97
8,8	230,5	0,98	75,80
10,3	231,8	0,97	77,60

Table 4. Numerical values used to fit Fig. 3

	MV (nm/m) ($gL^{-1}m^{-1}$)	t_m h	D_{wm}_$Conv_m$ (nm-100%)	t_1 (h)	D_{w1}_$Conv_1$ (nm-100%)	N_{p1} (10^{16}/L)	$Conv_1$_D_{w1} (100%-nm)	t_2 (h)	D_{w2}-$Conv_2$ (nm-100%)	AV (nm/m) ($gL^{-1}m^{-1}$)
D_w	5,4376	0,728	97,72	0,455	22,97	460,00	0,0383	1,001	175,15	5,4010
Conv	1,0221	1,562	0,3391	0,806	0,0857	1,4200	122,88	2,318	0,5996	1,0190

Figure 2 shows that the stable particles are spherical and uniform. At the beginning of the reaction, there are lots of hairy materials as shown in (a). This suggests that the nucleation occurs mainly via a homogeneous nucleation mechanism. Since phosphotungstic acid at pH 6.4 stains hydrophilic domains of the particles, the hairy materials are water-soluble polymers produced in the homogeneous nucleation period. From (b) to (f), the particles are all of core-shell structure and with the polymerization proceeding, the shell thickness grows gradually while the size of the core keeps constant. This provides strong evidence for the occurrence of a shell growth mechanism in the present system.



(a) 0.3 hr

(b) 0.8 hr

(c) 2.8 hr

(d) 5.0 hr

(e) 6.8 hr

(f) 10.3 hr

Fig. 2. TEM photographs of the latex particles at different reaction time

Figure 3 shows that, at the beginning of the reaction, N_p emerges as a very high peak. This indicates that a large number of collisions occurred between the primary particles at the beginning of the reaction thus further confirming that particles are generated via a homogeneous nucleation mechanism. After coagulation, newly formed particles are more stable due to an increase of surface charge density. Therefore, N_p stays constant. Due to the coagulation, the stable particles have a uniform size and a large diameter. As shown in Table 4, the corresponding t_l of the $Conv_l$ is 0.806 h, which corresponds to the time when N_p begins to be constant, as shown in Figure 3. This suggests that the first inflexion t_l of the polymerization rate curve is the time at which nucleation stops and the steady stage starts. This result implies that our model function is reliable and accurate.

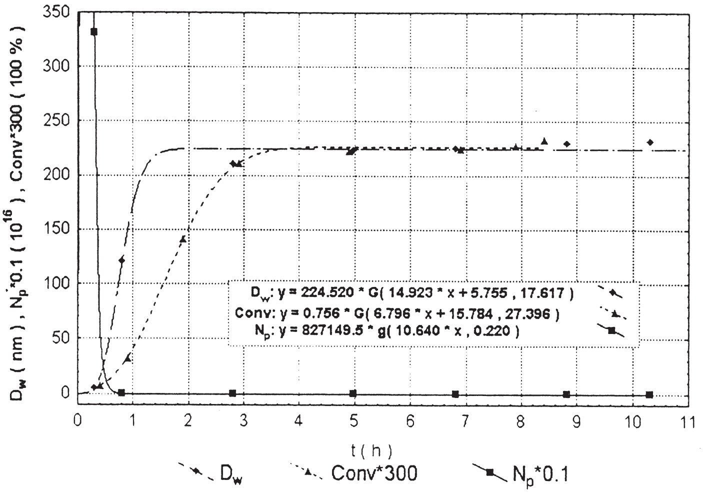


Fig.3 The fitting curves of D_w, N_p and conversion of the polymerization of St-MMA-AA

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