

STUDY ON THE FORMATION MECHANISM OF MONODISPERSE PARTICLES IN THE EMULSIFIER-FREE EMULSION POLYMERIZATION OF METHYL METHACRYLATE AND BUTYL ACRYLATE

Mao-gen Zhang^a, Zhi-xue Weng^b, Zhi-ming Huang^b and Zu-ren Pan^b

^a College of Chemistry and Environment Science, Nanjing Normal University, Nanjing 210097, China

^b Institute of Polymer Engineering, Zhejiang University, Hangzhou 310027, China

Abstract The formation mechanism of monodisperse polymer latex particles in the emulsifier-free emulsion polymerization of methyl methacrylate and butyl acrylate with potassium persulfate as initiator was investigated. A multi-step formation mechanism for the monodisperse polymer particles was proposed. The nucleation mechanism is considered to be the coagulation of the precursor particles by homogeneous nucleation when the primary particles reach a critical size with high surface charge density and sufficient stability. It had been proved by a special experiment that the early latex particles formed by the coagulation were stable. The primary particles grow by absorbing monomers and radicals in the polymerization system and then become colloidally unstable again due to the understandable decrease of particle surface charge density, which leads to the aggregation of the growing particles and the formation of larger latex particles therefrom. After the nucleation period, the preferential aggregation of the smaller particles in the propagation process leads to the change of the particles towards a uniform size and narrower particle size distribution. The coexistence and competition of homogeneous nucleation, coagulation, propagation and aggregation result in the increase of the polydispersity index ($U = D_{43}/D_{10}$) in the first stage, then its decrease in the later stage because of the competition of propagation and aggregation, and the gradual formation of the monodisperse particles.

Keywords Emulsifier-free emulsion polymerization, Latex, Monodisperse particle, Particle formation mechanism, Acrylate

INTRODUCTION

Recently, much attention has been paid to emulsifier-free emulsion polymerization (EFEP) as a newer process of emulsion polymerization. Academic and practical interests^[1] have prompted study of the nucleation mechanism and the preparation of highly pure monodisperse latex particles.

Several nucleation mechanisms of particles in EFEP have been proposed: (1) Homogeneous nucleation proposed by Fitch^[2, 3] — primary particles are formed from the precipitation of growing oligomeric radicals in the aqueous phase when they reach a critical polymerization degree (n_{cr}); (2) Coagulative nucleation of the growing free radicals proposed by Arai^[4] — the growing oligomeric radicals undergo termination followed by particle nucleation through coagulation of these dead species; (3) Micellization nucleation of the growing oligoradicals — primary particles are formed when the growing oligomeric radicals reach a certain size and concentration at which they become surface active and undergo micellization, as proposed by Van der Hoff^[5], Goodall^[6], Cox^[7], Chen and Piirma^[8], and Vanderhoff^[9]; (4) Coagulative nucleation of the precursor particles — the latex particles are formed from the coagulation nucleation of the precursor particles which are formed from homogeneous nucleation of growing oligomeric radicals^[10–13]; (5) *In situ* micellization mechanism proposed by Song and Poehlein^[14, 15] — the particle nucleation period can be divided into two stages. A large number of oligomer micellar particle nuclei are produced in stage 1.

* Corresponding author: Mao-gen Zhang (张茂根), E-mail: maogenzhang@hotmail.com

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Munro^[16] suggested that the nucleation mechanisms in EFEP of polar and nonpolar monomers were different; none of the above mechanisms can be used to describe the particle nucleation mechanism of various kinds of monomers.

The growth mechanism of the particles in EFEP was believed similar to that in traditional emulsion polymerization. However, some questions were still unclear. When does the nucleation period end in EFEP? How are the monodisperse particles formed in EFEP? What is the growth mechanism of the polymer particles?

In this paper, the formation and growth mechanism of the monodisperse polymer particles was investigated in the emulsifier-free emulsion copolymerization of methyl methacrylate and butyl acrylate.

EXPERIMENTAL

Raw Materials

Methyl methacrylate (MMA) and butyl acrylate (BA) were CP grade and purified by distillation under reduced pressure before use. Potassium persulfate (KPS, AR grade) used as initiator was recrystallized from water.

Polymerization

The EFEP of MMA/BA was carried out in a batch process. The reactor was a 500 mL double wall four-necked glass flask equipped with a stirrer, condenser, nitrogen inlet and thermometer. All of the monomers and deionized water were placed in the flask at the beginning, and then the KPS solution was added to start the polymerization at a certain temperature.

After the polymerization was started, several aliquot portions of the reaction mixture were taken at a certain time interval for the measurement of monomer conversion (X_p) and particle diameter. Two samples were taken every time for parallel measurement of X_p . The sample was placed in a weighed bottle containing three drops of a short-stopping solution (5% phenol in water-alcohol solution) and dried. The conversion was determined gravimetrically and calculated from the weight of the dried sample divided by the total weight of the mixture used.

The sample for the measurement of particle diameter was placed in a separating funnel containing three drops of the short-stopping solution, and left to stand for the separation of monomer and latex phase. The latex phase was separated off for the measurement of the particle diameter.

Characterization

The average particle diameter and particle size distribution (PSD) were measured by a Beckman Coulter LS 230 Enhanced Laser Diffraction Particle Size Analyzer, which was linked to a computer. The accuracy and resolution of the LS 230 submicron data had been demonstrated by the analysis of a trimodal latex mix (83, 204 and 503 nm) provided by Beckman Coulter Inc. The instrument can separate and size each individual component. The measurement baseline was automatically calibrated every hour by the computer system linked to the instrument. The reproducibility error of the instrument was less than 1% and the particle size accuracy of the LS 230 has also been confirmed by electron microscopy.

The average particle diameter, D_{pq} , is defined as follows^[17]:

$$D_{pq} = \left(\frac{\sum_{i=1}^k n_i D_i^p}{\sum_{i=1}^k n_i D_i^q} \right)^{\frac{1}{p-q}} \quad (1)$$

The particle size was characterized by D_{43} , D_{30} and D_{10} ^[17]. The particle size distribution index was characterized by the polydispersity index^[17, 18], $U = D_{43}/D_{10}$. The smaller the U value (tends to 1.000), the narrower the particle size distribution, and the better the monodispersity of the latex particles. The monodispersity or polydispersity can also be observed by the PSD scheme given by LS 230 Analyzer.

Based on the analysis of the statistical meanings of D_{pq} , D_{30} is the volume average diameter^[18], D_v , D_{10} is the number average diameter^[17], D_n .

Calculation of the Particle Number Density of the Polymer Latex Particles Containing no Monomers

N_p , the polymer latex particle number density in 1 mL water, was calculated from the average particle diameter, D_p , in EFEP. For the polymer emulsifier-free latex particles, when containing no monomers, N_p can be calculated by the following equation^[18]:

$$WX = \pi D_p^3 \rho N_p V / 6 \quad (2)$$

Where W (g) is the weight of monomer used; X (%), monomer conversion; π , circumferential ratio; ρ (g/cm³), polymer density; V (mL), the volume of water used.

Based on the analysis of the statistical meanings of D_p in Eq. (2), it should be the volume average particle diameter^[17]. So we have: $D_p = D_v = D_{30}$. And we get:

$$N_p = 6 WX / (\pi D_v^3 \rho V) \quad (3)$$

Calculation of N_p of the Polymer Latex Particles Swelled with Monomers

N_p of the polymer latex particles swelled with monomers can be calculated by the following equation^[19]:

$$N_p = 6 WX / (\pi D_v^3 V \rho_{ps} \omega_p) \quad (4)$$

where ρ_{ps} is the average density of the polymer latex particles swelled with monomers; ω_p is the polymer weight fraction in the latex particles swelled with monomers.

Calculation of ρ_{ps}

In the polymerization process, the average density of the polymer latex particles swelled with monomers, ρ_{ps} , can be calculated for the two stages.

(a) When liquid monomer drops exist in the system, the polymer latex particles can be considered as swelled with saturate monomers, so ω_p and ρ_{ps} are constant, respectively. ρ_{ps} can be calculated approximately^[20]:

$$\rho_{ps} = [\omega_p / \rho_p + (1 - \omega_p) / \rho_m]^{-1}, \quad X \leq X_C \quad (5)$$

Where X_C is the critical monomer conversion when the monomer drops disappear.

(b) After the liquid monomer drops disappear, ω_p and ρ_{ps} will change with the monomer conversion. ρ_{ps} can be calculated approximately by the following equation^[20]:

$$\rho_{ps} = [X / \rho_p + (1 - X) / \rho_m]^{-1}, \quad X \geq X_C \quad (6)$$

Where ρ_p and ρ_m are the density of the polymer and monomers, respectively.

Comparing Eqs. (5) and (6), we can see that, $\omega_p = X$, after disappearance of the liquid monomer drops.

The Critical Monomer Conversion When the Monomer Drops Disappear

In the EFEP of MMA/BA with the MMA weight fraction of 0.60–0.90, X_C was 0.23 on the assumption that X_C is determined by MMA^[19]. In the EFEP of BA^[20], $X_C = 0.39$. In the emulsion polymerization of MMA/BA in the presence of sodium lauryl sulfate^[21], with the MMA molar fraction of 0.50, $X_C = 0.35$.

In this paper, for the EFEP of MMA/BA, with the MMA weight fraction of 0.50, or the MMA molar fraction of 0.56, similar to the MMA/BA system with the MMA molar fraction of 0.50, we might assume $X_C = 0.35$. This was found to be approximately correct in the experiment. The reaction mixture was sampled at a certain time interval, and left to stand in a separating funnel for the separation of monomer and latex phase. Because there are no extra emulsifiers in the EFEP, the separation of monomer and latex phase is easy to observe if only there are monomer droplets.

Calculation of ρ_p and ρ_m

In the copolymerization system of MMA/BA, ρ_p and ρ_m can be approximately calculated from the average density of copolymer and monomers, respectively, by the following equations:

$$1/\rho_m = W_{BA}/\rho_{BA} + W_{MMA}/\rho_{MMA} \quad (7)$$

$$1/\rho_p = W_{PBA}/\rho_{PBA} + W_{PMMA}/\rho_{PMMA} \quad (8)$$

Where W_{BA} and W_{MMA} are the weight fractions of monomer BA and MMA, respectively, and W_{PBA} and W_{PMMA} are the weight fractions of polymer PBA and PMMA, respectively.

In this paper, the MMA weight fraction is 0.50, that is, $W_{BA} = W_{MMA} = 0.50$, and $W_{PBA} = W_{PMMA} = 0.50$. We took: $\rho_{MMA} = 0.94$, $\rho_{PMMA} = 1.21$, $\rho_{BA} = 0.90$, $\rho_{PBA} = 1.055$ based on the literature^[19, 20].

So we can calculate: $\rho_m = 0.92$, $\rho_p = 1.127$.

Calculation of $\rho_{ps}\omega_p$

In the polymerization process, the value of $\rho_{ps}\omega_p$ in the polymer latex swelled with monomers can be calculated for the two stages:

(a) When monomer droplets exist in the system

The polymer latex particles can be considered as swelled with saturation monomers, so ω_p and ρ_{ps} are constant, respectively, $\omega_{PMMA} = 0.32$ and $\omega_{PBA} = 0.38$ ^[19]. For the copolymerization system of MMA/BA with MMA weight fraction of 0.50, ω_p is approximately taken from the average of ω_{PMMA} and ω_{PBA} . This, $\omega_p = 0.35$.

From Eq. (5), we can get $\rho_{ps} = 0.98$.

Let $F = \rho_{ps}\omega_p$. Then, we have:

$$F \equiv \rho_{ps}\omega_p = 0.34, \quad X \leq X_C = 0.35 \quad (9)$$

(b) After the monomer droplets have disappeared, ω_p and ρ_{ps} will change with the monomer conversion. ρ_{ps} can be calculated approximately from the Eq. (6), and $\omega_p = X$. So we have:

$$F = \rho_{ps}\omega_p = X[X/1.127 + (1 - X)/0.92]^{-1}, \quad X \geq X_C = 0.35 \quad (10)$$

Thus, the calculation equation for the particle number density, Eq. (4), can be rewritten as:

$$N_p = 6WX/(\pi D_v^3 V F) \quad (11)$$

RESULTS AND DISCUSSION

The change of particle size distribution of the latex samples in the process of the batch EFEP of MMA/BA is shown in Fig. 1.

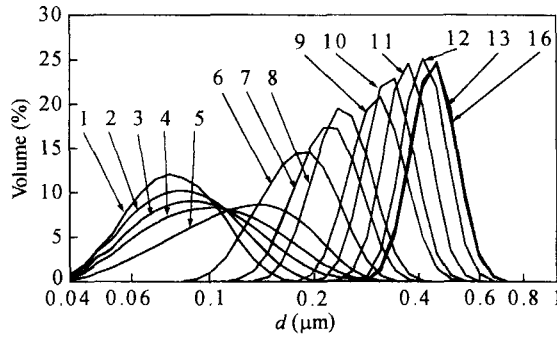


Fig. 1 Dynamic scheme of particle size distribution in the whole process of MMA/BA batch emulsifier-free emulsion copolymerization

The change of monomer conversion (X_p), the particle size (D_{43} , D_{30} and D_{10}), the polydispersity index (U), and the particle number density (N_p) of the latex particles in the full process are shown in Table 1.

Table 1. The data of X_p , D_{43} , D_{30} , D_{10} , U and N_p of the latex particles in the full process in the MMA/BA emulsifier-free emulsion polymerization*

Run	t (min)	X_p (%)	D_{43} (nm)	D_{10} (nm)	U	D_{30} (nm)	F	N_p
0	0	0	-	-	-	-	-	-
1	5	1.21	85.9	67.9	1.265	73.3	0.34	3.453E13
2	10	2.35	93.1	69.2	1.345	76.1	0.34	5.994E13
3	15	3.05	105	71.6	1.466	80.5	0.34	6.579E13
4	20	4.22	115	74.5	1.544	85.3	0.34	7.638E13
5	25	5.32	136	83.7	1.625	98.5	0.34	6.261E13
6	35	8.35	193	162	1.191	172	0.34	1.844E13
7	45	12.69	233	206	1.131	215	0.34	1.435E13
8	55	17.28	256	231	1.109	239	0.34	1.423E13
9	65	25.39	323	296	1.091	305	0.34	1.006E13
10	75	33.01	350	326	1.074	334	0.34	9.958E12
11	85	46.19	393	368	1.068	376	0.46	7.151E12
12	95	72.76	439	414	1.060	422	0.77	4.789E12
13	105	88.54	466	437	1.066	446	0.97	3.921E12
14	115	90.45	468	439	1.066	449	1.00	3.827E12
15	125	91.28	469	439	1.068	449	1.01	3.794E12
16	150	92.05	470	441	1.066	451	1.02	3.763E12

* MMA, 60 g; BA, 60 g; H₂O, 600 g; APS, 0.68 wt% based on monomers; 70°C; 250 rpm

Change of Particle Size Distribution

It may be noted from Fig. 1 that the particle size distribution curves of the latex particles are rather broad at the early stage such as in run 1, and then they become broader until run 5, which is a sample still containing some very small particles. The curve of run 5 is the broadest. From run 6, very small particles disappeared, and then the distribution curves become narrower and narrower with the increase of monomer conversion and particle size, and finally the curves remain almost unchanged. That is to say, the monodisperse particles are gradually formed at a higher conversion, but not at the early stage of the polymerization.

The change of U value with the monomer conversion is shown in Fig. 2. The U value changes first from an intermediate to a maximum value rapidly, then decreases rapidly to a smaller value, and finally it levels off.

Change of Particle Size before and after the Monomer Droplet Disappearance

The D_{43} versus conversion curve is similar to a parabola, as shown in Fig. 2. The increase of D_{43} with conversion is fast before X_C (about 35%), and becomes slower after X_C .

The diagram of the change of D_{43} with time is similar to the change of conversion with time, as shown in Fig. 3. It is shown that the increase of D_{43} with time is synchronous with X_p . The increase of conversion and D_{43} with time is slow at the early stage, and fast in the auto-accelerating polymerization period. When the monomer conversion levels off, D_{43} becomes almost unchangeable.

Note the data in Table 1. D_{43} increases slowly with time at first, and D_n changes a little, leading to the increase of $U (= D_{43}/D_{10})$ value up to a maximum. Then, D_n increases faster than D_{43} , leading to the decrease of U value, and the formation of almost monodisperse particles finally.

The increase of the particle size results from two contributory aspects: the propagation contribution due to the chain propagation of monomers continuously entering into the latex particles from water phase, and the aggregation contribution due to the aggregation of the growing particles. The propagation and aggregation contributions are both important for the increase of particle size before X_C , so the increase of D_{43} with conversion is fast.

The aggregation contribution is the only possible aspect for the increase of particle size after X_C . The propagation contribution for the increase of particle size is not any longer; on the contrary, the polymerization in a latex particle would result in the decrease of particle size for the constriction of particle volume because the density of monomer is less than that of polymer. The constriction of particle volume would increase the surface charge density and the stability of latex particles. The polymerization in a latex particle would result in an

increase of the viscosity in the particles with the decrease of monomer concentration, and lead to an increase of aggregation tendency under the polymerization condition. As the particle size is still increasing slightly after X_C , the aggregation contribution to the increase of particle size is more prominent than the decrease of particle size by the constriction of particle volume. The particle size tends to be hardly changeable when the monomer conversion levels off. It is suggested that under the polymerization conditions the latex particles are not stable enough and tend to aggregate until they reach an ultimate conversion. The final latex is rather stable.

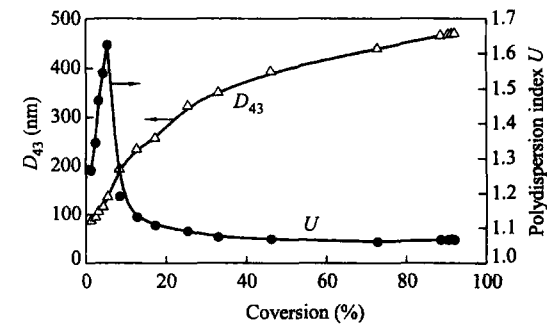


Fig. 2 D_{43} and U versus conversion in the full process of MMA/BA batch emulsifier-free emulsion copolymerization

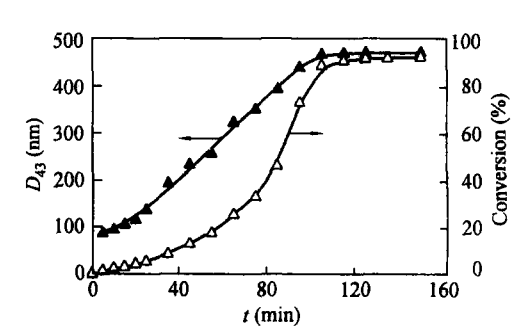


Fig. 3 D_{43} and conversion versus time in the full process of MMA/BA batch emulsifier-free emulsion copolymerization

Morphology of the Latex Particles

The TEM photographs of some latex samples in the polymerization process are shown in Fig. 4. The apparent diameter of the particles after 5 min polymerization is about 50–70 nm, and is not uniform. The morphology of the latex particles is approximately round, but the particle surface is rough. The particle surface of the other samples in the polymerization process, such as after 25 and 35 min polymerization, are rough and irregular also. However, the surface of the final particles is smooth and regular.

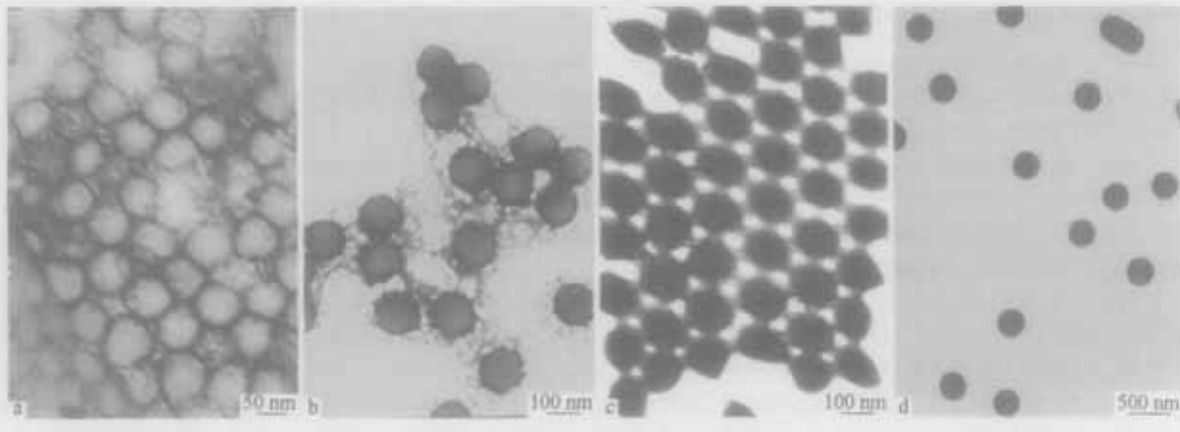


Fig. 4 TEM photographs of P(MMA/BA) latex particles at different polymerization times
a) run 1, 5 min; b) run 5, 25 min; c) run 6, 35 min; d) run 16, 150 min

Change of N_p

The change diagram of N_p with conversion is somewhat similar to that of U value with conversion, as shown in Fig. 5. The N_p value changes first with the conversion from a moderate value to a maximum rapidly, then decreases rapidly to a smaller value, and gradually levels off to a minimum.

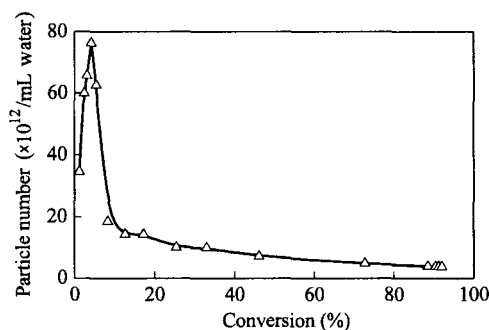


Fig. 5 Change of particle number density versus conversion in the whole process of MMA/BA batch emulsifier-free emulsion copolymerization

As the polymerization starts, the nucleation rate and the formation rate of relatively stable latex particles is fast, therefore N_p will increase rapidly at the early stage until it reaches a maximum. In the subsequent polymerization period, the aggregation of growing particles due to the decrease of surface charge density of the particles will lead to the rapid decrease of N_p . After the nucleation period has ended, the preferential aggregation of the smaller particles in the propagation process leads to the gradual decrease of the particle number density until it reaches the almost unchangeable minimum.

Nucleation Mechanism of the Stable Primary Particles

In the batch EFEP of MMA/BA, the nucleation mechanism is usually considered to be the coagulation nucleation of the precursor particles by homogeneous nucleation^[10–13]. This might be reasonable in EFEP with the considerably water-soluble monomer (the solubility of MMA and BA in water at room temperature is 1.5% and 0.16%, respectively). In the early stage of the polymerization, the radicals generated in the aqueous phase initiate the monomers; the latex particles are formed from the coagulation nucleation of the precursor particles, which are formed from homogeneous nucleation of growing oligomeric radicals when they reach a critical chain length. The size and the surface charge density of the precursor particles are usually very small, so they are colloiddally unstable and easily undergo coagulation until they reach a size with high surface charge density and are therefore stable enough to form stable primary particles.

In other words, the latex particles formed by the coagulation should be stable if they were isolated from the polymerization system. This has been proved by a special experiment. The early latex sample taken from the polymerization system was terminated by the short-stopping solution, left to stand for the separation of monomer and latex phase, and then the latex phase was separated out. It was found that the run 1 latex so obtained was really very stable, D_{43} and D_{10} of run 1 after 5 min polymerization being 85.9 and 67.9 nm, respectively, *i.e.* quite big. The values were the same, whether they were determined just after separation from the polymerization system or several days later. The latex was stable even after three freeze-thaw cycles. This constitutes evidence for the above nucleation mechanism.

Propagation and Aggregation of Latex Particles

Once the latex particles have been formed, they continue to grow via further propagation by absorbing monomers and radicals in the polymerization system. The increase in particle size would result in a decrease in surface charge density. Then the particles become colloiddally unstable again, leading to the aggregation of the growing particles and to the formation of larger latex particles. Accordingly, there are some particles bigger or smaller in the subsequent polymerization period, as shown in Fig. 1, such as run 4 and 5. This is a stage of the coexistence and competition of nucleation, coagulation, propagation and aggregation of the particles. The U value would increase with the conversion at this stage.

When does the nucleation period end? From the diagram of the peak of particle size distribution in Fig. 1, it can be found that the very small particles had disappeared since run 6. It can be considered that the nucleation

period ended then. The U value would decrease with the conversion after this time.

Formation Mechanism of Monodisperse Particles

We think that all the above facts are related to the following polymerization mechanism. It is proposed that the monodisperse particles are formed by a multi-step mechanism. The coexistence and competition of nucleation, coagulation, growth and aggregation results in the formation of the monodisperse latex particles.

The homogeneous nucleation and coagulation of precursor particles are the main processes in the early stage. It is suggested that the new latex particles are formed continuously in the nucleation period. Therefore, D_n changes slightly, because D_n is determined mainly by smaller particles. The coexistence of bigger and smaller particles results in the slow increase of D_{43} ; D_{43} is determined mainly by bigger particles.

When the latex particles are growing by absorbing the monomers from the aqueous phase, the smaller the particles, the faster the decrease of particle surface charge density and the higher the particle aggregation rate, because the smaller particles have bigger curvature radius and higher surface energy. The smallest particles will disappear first in the polymerization. The decrease of smaller particles will result in a remarkable increase of D_{10} . After the nucleation period has ended, the preferential aggregation of the smaller particles in the propagation process leads to the result that the particles gradually change towards a uniform size and so the PSD becomes narrower. Eventually, fairly monodisperse latex particles are obtained.

Therefore, the coexistence and competition of homogeneous nucleation, coagulation, propagation and aggregation result in the increase of U value in the early stage. After the nucleation period, the coexistence and competition of propagation and aggregation lead to the decrease of the U value and the gradual formation of monodisperse particles gradual.

Universality of the Formation Behavior for the Monodisperse Polymer Particles

A similar tendency for the formation process of monodisperse latex particles can be seen in the EFEP of other systems as well. It was found in our experiments that the changes in particle size, particle size distribution, particle number density with conversion are similar in the different EFEP systems, whether the experiments were with or without a comonomer, and even though the structure, amount and addition mode of the comonomer, and the polymerization conditions were different from each other. Consequently, there might be something similar in the formation process of the monodisperse polymer particles in EFEP, *i.e.* the formation mechanism of the monodisperse polymer latex particles.

CONCLUSIONS

It has been shown in this paper that the colloiddally stable monodisperse latex particles are formed by a multi-step process by tracking of the change of the particle size and particle size distribution (PSD) in the EFEP. The PSD of the latex particles is rather broad at the early stage. Then it becomes broader with some very small particles and bigger particles. Then the very small particles disappear, and the distribution curves gradually become narrower and narrower with the increase of particle size, and the monodisperse particles are formed finally. The diagram of the change of D_{43} with time is similar to that of conversion with time, and the D_{43} versus conversion curve is similar to a parabola, being fast at low conversion, and leveling off gradually to a final size at high conversion. D_{43} and D_{10} in the very early stage are quite big, and the particle surface is rough. The particle number density (N_p) rapidly increases with the conversion at first, then rapidly decreases and gradually levels off to a minimum.

A multi-step formation mechanism of the monodisperse polymer particles has been proposed. The nucleation mechanism is considered to be the coagulation of the precursor particles by homogeneous nucleation when the primary particles reach a size with high surface charge density and sufficient stability. It has been proved by a special experiment that the latex particles formed by coagulation at the very early stage are stable. The primary particles propagate through absorbing monomers and radicals in the polymerization system and then become colloiddally unstable again due to the understandable decrease of particle surface charge density, which leads to the aggregation of the growing particles and the formation of larger latex particles therefrom. After the

nucleation period ends, the preferential aggregation of the smaller particles in the propagation process leads to the result that the particles gradually verge towards a uniform size and the PSD becomes narrower. The coexistence and competition of homogeneous nucleation, coagulation, propagation and aggregation results in an increase of the U value in the first stage, while the competition of propagation and aggregation leads to a decrease of the U value in the later stage, and the gradual formation of monodisperse particles.

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