

Effects of Ethyl Acetate on the Soap-Free Emulsion Polymerization of 4-Vinylpyridine and Styrene. II. Aspects of the Mechanism

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ABSTRACT: The kinetics of the soap-free emulsion polymerization of 4-vinylpyridine and styrene, as well as the morphology development during the polymerization, were investigated with $^1\text{H-NMR}$, scanning electron microscopy, transmission electron microscopy, and differential scanning calorimetry. To clarify the process of particle nucleation and particle growth, we focused on the effects of the addition of ethyl acetate (8 wt %) combined with lower rates of agitation (100 and 200 rpm). The results showed that both the nucleation and the growth of particles were related to the monomer droplets stemming from the interface of the monomer and aqueous phases by the disturbance by agitation and/or from the condensation of monomers dissolved in the aqueous phase. Besides the diffusion of monomer molecules through the aqueous phase, the incorporation, among the species previously formed, of monomer droplets was a major cause of monomer transport in the emulsion polymerization system. The particle morphology was controlled by the miscibility of the monomers and (co)polymer, rather than the phase separation due to the different compositions of the copolymers in the particles. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 2692–2708, 2001

Key words: poly(4-vinyl pyridine-co-styrene); ethyl acetate; monomer droplet; morphology development; soap-free emulsion polymerization; agitation rate; emulsion polymerization

INTRODUCTION

The mechanism of soap-free emulsion copolymerization, particularly the copolymerization system of a hydrophobic monomer combined with a hydrophilic one, has been widely studied.^{1–10} All these studies are focused on factors, such as the pH of the aqueous medium and the employment of ionic or nonionic monomers, that affect the overall hydrophilicity of the comonomer and (co)polymer initially formed. This is possibly because the hydrophilicity of the monomer or (co)polymer is very important for nucleation according to the

prevalent Fitch–Tsai theory,^{11,12} well known as homogeneous nucleation. The initial hydrophilic polymeric chains must incorporate enough of the hydrophobic monomer units before they precipitate. The emulsion polymerization of a 4-vinylpyridine (4VP)/styrene (St) system was also employed for this purpose by Kawaguchi et al.^{2,3} In their studies, the effects of the amount of non-ionic emulsifier and monomer feed ratios, as well as the pH of the polymerization medium, were investigated, with the anionic initiator potassium persulfate (KPS). They claimed that the polymer particles were not discernible in electron micrographs of latex prepared with soap-free emulsion copolymerization before the fractional conversion of 4VP was higher than 40%. These phenomena were attributed to the degree of dissociation of

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basic 4VP under basic and acidic conditions. Similar results were also observed in the soap-free emulsion copolymerization of St and acrylamide (AA)/St.^{4,5}

Chen et al.¹⁰ reported an anomalously low content of hydrophilic monomer units in the initial (co)polymer, in which St and a nonionic hydrophilic monomer, 2-hydroxyethyl methacrylate, were employed with the anionic initiator KPS. However, this anomalous phenomenon was not observed in the soap-free emulsion copolymerization system of St and AA derivatives reported by Pichot et al.,⁷⁻⁹ who used the cationic initiator 2,2'-azobis(2-amidino-propane) dihydrochloride (V50). In this work, this anomalous observation was not always observed, as reported later. With respect to the experimental conditions of Kawaguchi et al.,^{2,3} this work is different in several ways, although the same copolymerization system of 4VP/St was employed. First, a cationic initiator, V50, was used in this work. This means that the polymerization was performed under an acidic medium, even though the pH of the aqueous phase was intentionally not adjusted before the polymerization. Second, the effects of agitation and the addition of ethyl acetate (EA) were stressed as the two main foci in this work. Moreover, the development of the morphologies was also elucidated during the polymerization. This study was intended to investigate the mechanism of soap-free emulsion copolymerization from a different angle for a better understanding of the role of hydrophilic monomer.

In another article,¹³ we reported on a phenomenon that occurred as well as the results of a quantitative analysis in a quasistatic emulsion polymerization system; that is, a sealed glass bottle containing the reaction mixture was allowed to stand in a thermostat without mechanical agitation. Only a convective flow provided transport for the ingredients. On the basis of our observations, a new mechanism was postulated, that the nucleation was related to the monomer droplets generated by the disturbance of the interface between the monomer and water phases. In this article, we investigate how this mechanism works in a dynamic (with mechanical agitation) emulsion polymerization system.

EXPERIMENTAL

Materials

The monomers 4VP and St and the solvent EA were purchased from Kishida Chemical Indus-

Table I Typical Recipe for the Experiments

Monomer (wt %)		EA ^a (wt %)	Water (wt %)	Initiator ^b (wt %)
St	4VP			
5	5	8 or 0	82.8 or 90	2

^a Based on the amount of water.

^b Based on the amount of monomer. The total amount of the reagents was 300.0 ± 0.2 g.

tries Co., Ltd. (Tokyo, Japan). The water-soluble initiator V50 was provided by Wako Chemical Industry Co., Ltd. (Tokyo, Japan). EA was distilled under atmosphere. Other reagents were distilled under reduced pressure, except for the initiator V50, which was used without further purification.

Water used in all experiments was distilled and deionized with a conductivity of 18 MΩ cm⁻¹ with a Milli-Q water purification system (Millipore, Tokyo, Japan).

Methods

A standard recipe for polymerization is shown in Table I. All the ingredients except the V50 solution were put in a 300-mL, four-necked, round-bottom reactor equipped with an anchor-type agitator (adjusted at a height of 10 mm from the bottom of the vessel), a condenser, a nitrogen inlet, and a rubber stopper for sampling. Nitrogen was bubbled through the mixture of reagents for 1 h before the temperature was elevated, and a nitrogen blanket was maintained during the polymerization. The V50 solution, freed of oxygen by the same procedure used for the other ingredients, was added when the temperature of the reaction mixture reached 70°C. A small amount of latex (ca. 0.1 mL) near the bottom of the reactor was withdrawn when the latex was soluble in deuterated methanol (CD₃OD), and about 2 mL was withdrawn when the latex was insoluble.

For the measurement of the monomer conversion by gravimetry, about 2 mL of the sample was precipitated with several drops of a dilute solution of NaOH (0.1 wt %) and then dried by vacuum after centrifugation, with hot water washing repeated twice.

Characterization

The solid content of latex, the concentrations of the monomers, and the compositions of the co-

polymers were all determined with $^1\text{H-NMR}$ (Alpha-500, JEOL, Tokyo, Japan) at 500 MHz and 30°C combined with gravimetry, for which the details are shown in the appendix of another article.¹³ The specimen, withdrawn from the polymerization system with a syringe, was directly injected into the NMR tube and then diluted with about 10 times the volume of CD_3OD as soon as possible. The NMR samples were stored at 5°C before measurements

The size and shape of dried microspheres were observed with scanning electron microscopy (SEM; JEOL JSM-5310) and transmission electron microscopy (TEM) (Hitachi H-700H, Tokyo, Japan). The SEM sample was prepared as follows: one drop of dilute latex (1×10^{-4} g/mL) was cast on a stage covered with an aluminum film; after being dried at room temperature, it was coated with a thin gold film. The particle size was determined by the direct measurement of 200 particles per sample on a SEM photo. The TEM specimen was prepared as follows: one drop of dilute latex (1×10^{-4} g/mL) was cast on a copper mesh covered with a thin collodion film coated with carbon, and then, after drying, was stained with CH_3I vapor in a closed bottle for 3 or 4 days at room temperature.

Differential scanning calorimetry (DSC; Mac Science DSC-3100, Tokyo, Japan) was used for measuring the glass-transition temperature of the copolymer. The heating rate was $10^\circ\text{C}/\text{min}$, and the cooling rate was $20^\circ\text{C}/\text{min}$. The second scanning curve is shown in this article.

All of the experiments were reproducible.

RESULTS AND DISCUSSIONS

Morphology Development during the Polymerization

In another article,¹³ we postulated that the initial nucleation was related to the monomer droplets generated by the disturbance of the interface between the monomer and water phases and the condensation of the monomer in the aqueous phase due to the decreased solubility of the monomer. The first task of this study, therefore, was to examine whether monomer droplets could be found in the emulsion polymerization system with mechanical agitation. This is the reason the morphology development of the particles during the polymerization is considered first. However, because mixing resulting from the convective flux

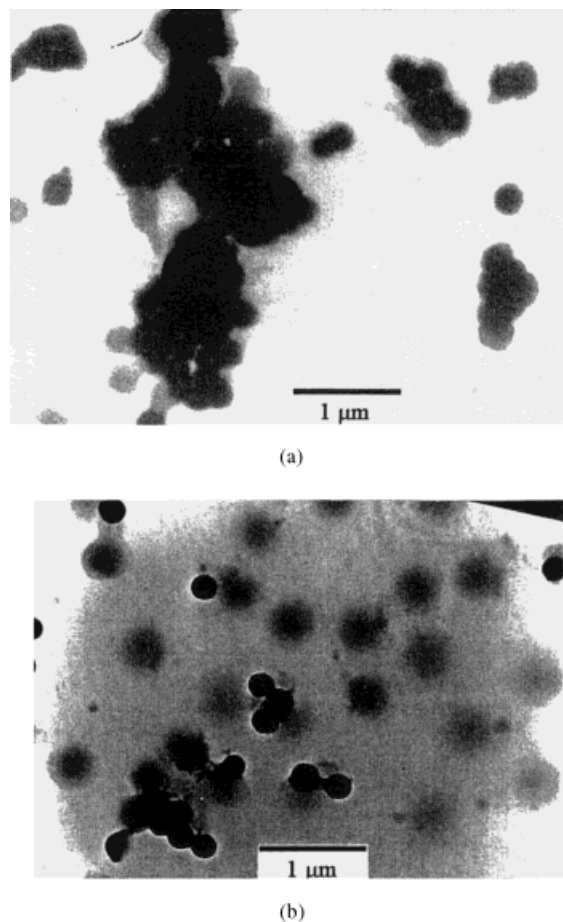


Figure 1 Morphologies of the initial particles (without EA, 200 rpm): (a) gray particles, 10 min, 0.24 wt % solid content, and (b) black particles and gray particles, 20 min, 0.75 wt % solid content. The samples were dried for a month in a desiccator and then stained with CH_3I vapor for 3 days at room temperature.

in the quasistatic emulsion polymerization may be very weak, for this article, a low agitation rate (100 ± 20 rpm) and a more intensive agitation rate of 200 ± 20 rpm were employed for the polymerization as well.

The morphologies of the initial particles are shown in Figure 1. The most noticeable characteristic of the morphology in the initial stage was that the particles were composed of species with low electron density and anomalous shapes, regardless of the addition of EA and the agitation rate (for simplicity, the particles with lower electron density are called gray particles in context). These particles became denser against the electron beam (black) and more spherical as the polymerization progressed, as shown in Figure 1(b). Some authors^{8,14} reported that particles with

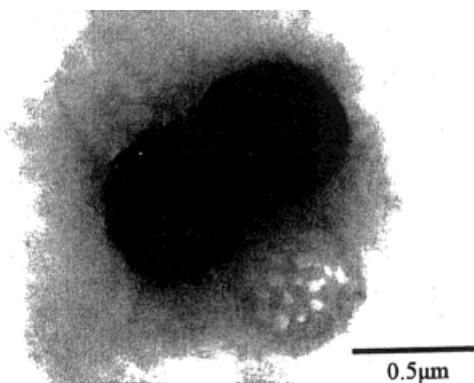


Figure 2 Morphologies of the initial particles exposed under a strong electron beam (without EA, 100 rpm, 20 min, 2.0 wt % solid content). The particles were exposed to the intensive electron beam for 2 min. The samples were stained with CH_3I vapor for 3 days at room temperature.

lower electron density species formed in the initial stage, but none of them gave a definite explanation.

We considered that the gray particles were related to the concentration of the monomer swollen in the particles. The higher the concentration of the monomer was, the softer the particles became. Therefore, the particles with a higher concentration of monomers would spread out, rather than keeping a spherical shape during the preparation of TEM samples, when water and volatile monomer evaporated at room temperature. Consequently, the particles allowed more transmission of the electron beam and thus became gray. Goodall et al.¹⁴ also observed anomalous morphologies during the soap-free emulsion polymerization of St. The emission of a substance from the gray area was not observed under exposure of the electron beam of TEM. However, in this work, as shown in Figure 2, there were remnants of monomer-swollen particles from which volatile substances were stripped, and the skeleton of the polymers remained. The stripped substances are likely to be compounds with low molecular weights. For St,¹⁴ it was evaporated by vacuum before the particle was detected in the TEM field, whereas for 4VP, the complicated reaction of 4VP with oxygen occurred readily during the drying process (4VP was readily oxidized and/or reacted by other means to form a red solid at ambient temperature).

It could be concluded, therefore, that the initial entities contained much more monomer (mainly 4VP) and that they grew into the particles with

the progression of polymerization [as shown in Fig. 1(b), the black ones were smaller than the gray ones]. In other words, the particles were generated from the entities with higher concentrations of monomer. It is hard to imagine that the particles with lower solid contents (the gray particles) contained higher concentrations of monomer than those with higher solid contents (black particles), if one considers the swelling equilibrium. Therefore, the gray particles were proposed to be the monomer droplets stabilized by the absorption of surface-active oligomers (monomer droplets without stabilizers should not be observed because they would dissolve in a large amount of water during the preparation of TEM samples).

After the initial stage, the effects of the agitation rate and the addition of EA became pronounced. With an agitation rate of 200 rpm, as shown in Figure 3(a), in the absence of EA, gray particles existed up to 40 min after the polymerization started, but the smaller particles appeared in the micrograph. In the presence of 8 wt % EA, the development of the morphologies included the generation of new particles at 40 min with the appearance of hemispheric particles [Fig. 3(b)] from 60 to 180 min and the evolution to egglike particles [Fig. 3(c)].

Conventionally named new particles (smaller particles, also gray against the electron beam) were generated in the earlier stage and then grew during the polymerization. Additionally, the generation of new particles, as reported later, seemed to be related solely to the agitation rate, regardless of the addition of EA.

The prevalent explanation for the anomalous morphology is that phase separation occurred in the particles because of the copolymers formed with different compositions.^{8,10} However, this explanation is inadequate for the explanation of the phase separation because a core-shell structure should be formed, rather than the anomalous shape, in view of the variation of interfacial tensions, particularly in the copolymerization of a hydrophilic monomer and a hydrophobic one, as discussed in this work. Furthermore, the anomalous morphologies were also found in the soap-free emulsion homopolymerization of St.¹⁴ This implies that there may be an uninvestigated event in the process of particle growth that was probably obscured by vigorous agitation.

The morphology development of particles during polymerization with an agitation rate of 100 rpm is shown in Figures 4 and 5. In the absence of

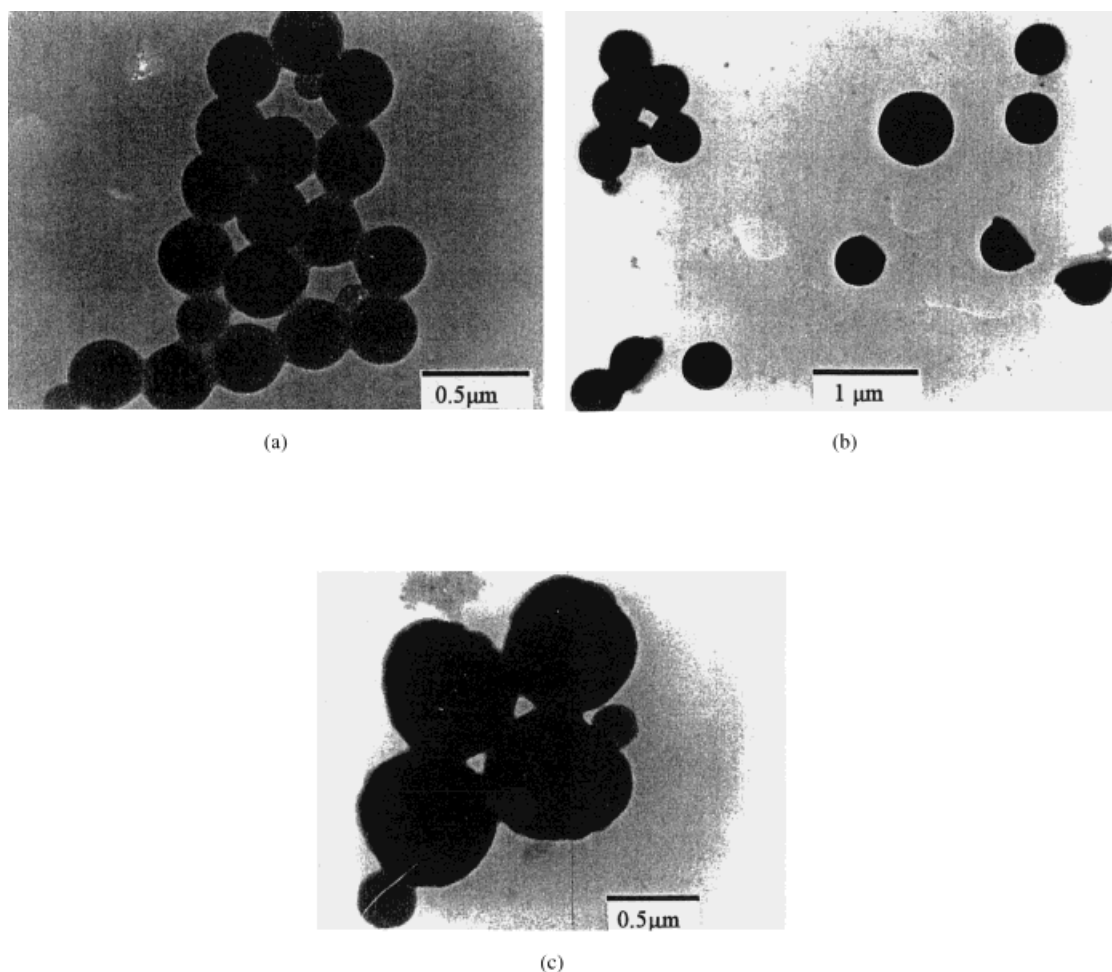


Figure 3 Morphology development with an agitation rate of 200 rpm: (a) generation of new particles, no EA, 40 min, 23 wt % conversion; (b) hemispheres, 8 wt % EA, 60 min, 45 wt % conversion; and (c) egglike particles, 8 wt % EA, 360 min, 97% conversion. All the samples were stained with CH_3I vapor for 3 days at room temperature.

EA, as shown in Figure 4, gray particles were observed until 90 min after the polymerization started. This period, as reported later, was dominated by the polymerization of 4VP. It is proposed that the gray particles were monomer droplets stabilized by oligomers in the initial stage, but it would be more appropriate to consider that the gray particles were particles swollen with monomers because of the collision with monomer droplets during the polymerization. The incorporation of a black particle into the gray ones is shown in Figure 4(a). Such an incorporation of particles was not found between two black particles. As a result of incorporation, particles with anomalous shapes appeared in the micrographs [Fig. 4(b)]. Finally, the formation of hemispheric particles and the converted core-shell structure [some particles were possibly composed of a poly-

styrene core covered with a thin poly(4-vinylpyridine) (P4VP) layer] should occur, while St dominated the later polymerization stage [Fig. 4(c,d)]. This incorporation is probably the main reason for postulation of the core-shell particle growth mechanism by Chen et al.¹⁰

Similar morphology development was also found in the presence of 8 wt % EA, as shown in Figure 5. However, gray particles existed for a longer time in the polymerization system because of the lower transfer rate of 4VP to the aqueous phase, and apparently a core could be found in the gray particles [Fig. 5(a)]. Although St dominated the later polymerization, hemispheric particles were formed [Fig. 5(b)], that, in fact, were dumbbell-like microspheres shown in Figure 5(c) in the SEM micrograph. This means that St was localized and polymerized in a half part of the particle.

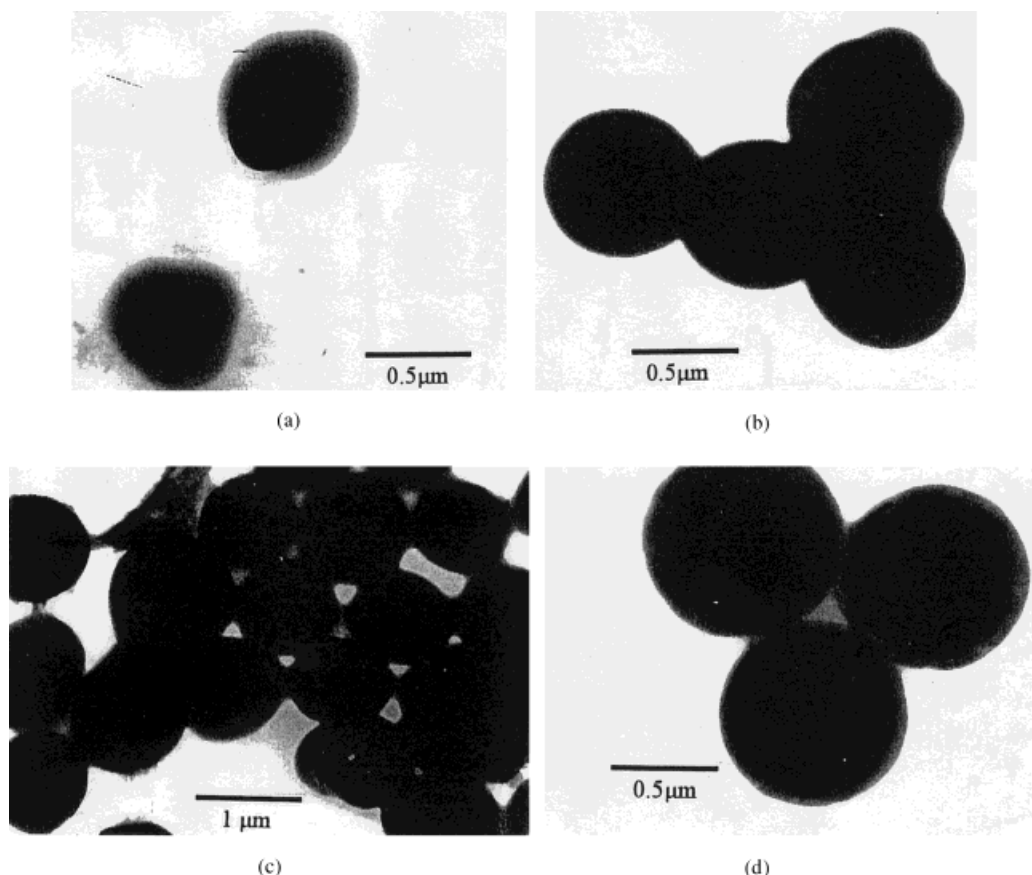


Figure 4 Morphology development in the absence of EA with an agitation rate of 100 rpm: (a) incorporation of particles, 40 min, 43 wt % conversion; (b) anomalous particles, 60 min, 52 wt % conversion; (c) hemispheres, 240 min, 89 wt % conversion; and (d) converted core-shell, 360 min, 93 wt % conversion. All the samples were stained with CH_3I vapor for 3 days at room temperature.

New particles, that is, the very small particles observed with an agitation rate of 200 rpm, were not observed.

The morphology development strongly implies that the collision and subsequent incorporation of particles with particles rich in monomers (or stabilized monomer droplets) was one possible route for the particles to obtain monomers. As evidence for this speculation, an assumption^{12,15} should be mentioned that is usually used to simulate the polymerization process. The assumption is that the composition of the comonomer in the particles is equal to that of monomer droplets during the emulsion polymerization. This assumption is undisputed for a thermodynamic equilibrium system, but it does not seem to be realistic for a dynamic system, such as this 4VP/St polymerization system in particular, where 4VP should diffuse and be consumed more rapidly than St. However, the results of a simulation based on this

assumption were often reported to agree well with the experimental results.^{16–19} The reason may be that this assumption is the reality of what happens in a polymerization system; that is, the monomer transport is predominantly controlled by the incorporation of monomers through collision with monomer droplets, rather than via monomer diffusion through water.

With this proposition, in addition to the postulation for the nucleation process in another article,¹³ all these anomalous morphologies can be explained.

New particles were generated at agitation rates of 100 and 200 rpm. The difference was that the new particles generated at 200 rpm were much smaller. Therefore, the difference in the particle size between the mature particles and the new particles was more pronounced at an agitation rate of 200 rpm than at a rate of 100 rpm. For the generation of secondary particles, a dual nucleation mechanism, as postulated for the soap-

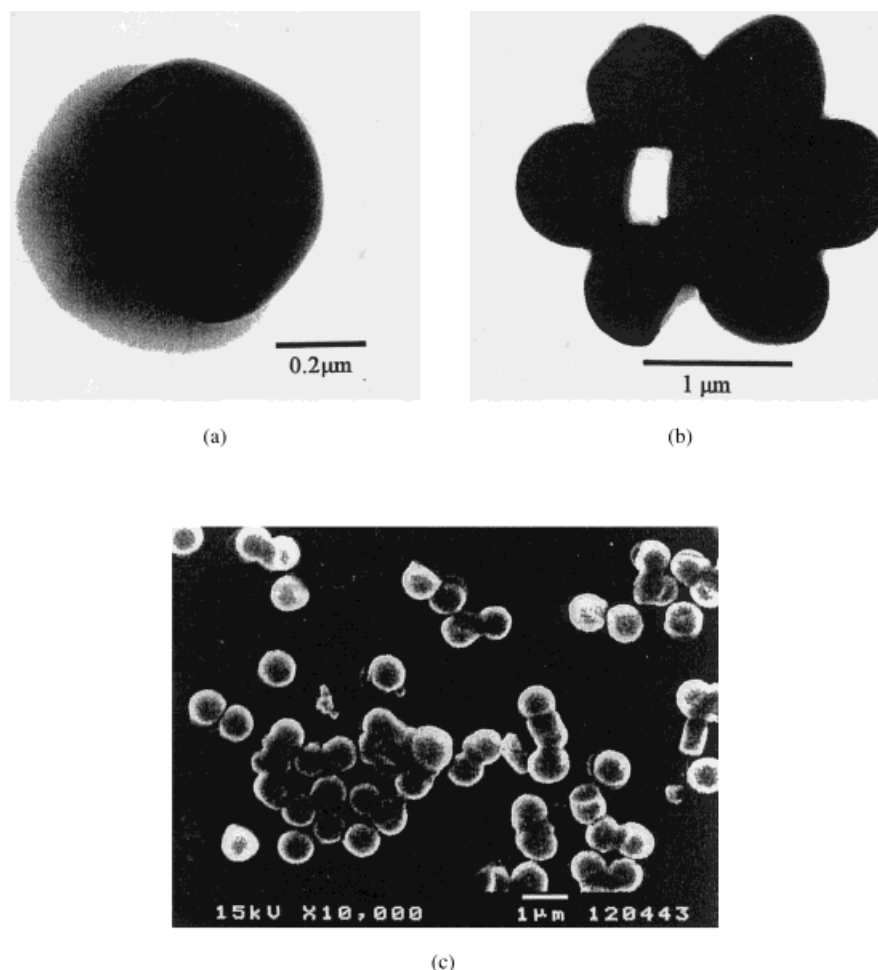


Figure 5 Morphology development in the presence of EA with an agitation rate of 100 rpm: (a) incorporation of particles, 120 min, 45 wt % conversion; (b) hemispheres, 540 min, 78 wt % conversion; and (c) SEM micrograph of dumbbell-like particles, 540 min. All the TEM samples were stained with CH_3I vapor for 3 days at room temperature.

free emulsion polymerization of St, in the presence of a high concentration of sodium styrene sulfonate (NaSS), should be considered.²⁰ That is, homogeneous nucleation occurred at the initial stage of polymerization, and then micellar nucleation occurred at the end of polymerization because an excess amount of NaSS remained in the aqueous phase. This mechanism suggests that new particles or secondary particles were generated at the end of polymerization. However, as shown in Figure 3, new particles were generated almost at the beginning of the polymerization. Furthermore, secondary particles (conventionally very small particles), as discussed later, were likely to be generated in the upper layer and then settle to the bottom layer of the latex phase with an agitation rate of 100 rpm. Therefore, the reaction of hydrophilic monomer in the aqueous phase plays a

somewhat limited role of providing the surface-active species to the particles and monomer droplets.

The formation of hemispheric particles and other anomalous particles indicated that there must be a repulsive force for one particle to incorporate the other or monomer droplets, which existed between the monomer-rich area and the polymer-dominating area. Goodall et al.¹⁴ reported that anomalous particles appeared at the lower temperature (<323 K) but did not appear at the higher temperature (>348 K) of the soap-free emulsion polymerization of St. This result is a result of our proposal. We believe that the lower the temperature is, the higher the viscosity in a particle is and the lower the diffusion rate of a monomer is. Therefore, the monomer diffused slowly from the stabilized monomer droplets to the particles.

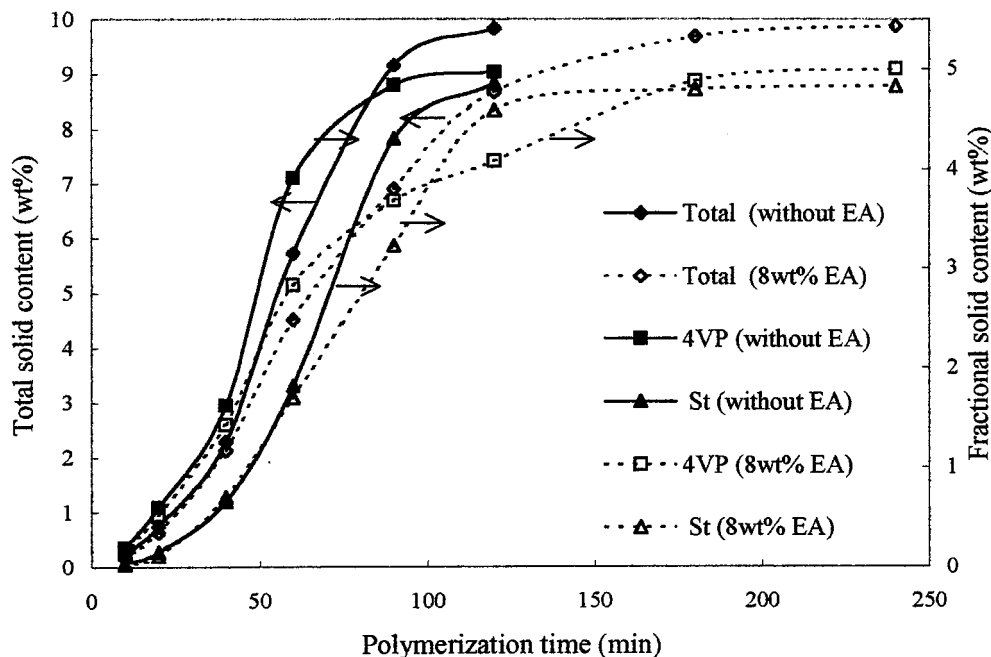


Figure 6 Solid content versus polymerization time at an agitation rate of 200 rpm. The solid contents are based on the amount of all species in the latex phase.

With the higher agitation rate, the possibility of particles colliding with the monomer phase (bigger monomer droplets) increased, so that most of the monomer in supersaturated areas, as considered in another article,¹³ could directly condense on the surface of colliding particles. For the lower agitation rate, larger monomer droplets were generated, but the lower frequency of collision led to a higher concentration of polymer in the monomer droplets before they incorporated the particles [Fig. 5(a)]. Consequentially, anomalous morphologies were observed during the polymerization (Figs. 4 and 5).

Kinetics of Polymerization

Agitation Rate of 200 rpm

The variations of the solid content and concentration of monomer in the latex versus the polymerization time are shown in Figures 6 and 7, respectively. The most noticeable characteristic of the conversion–time curves is that the fractional conversion of St increased rapidly, although slightly slower than the fractional conversion of 4VP, regardless of the addition of EA. This implies that the distribution of the composition of the copolymer formed should be narrow. Meanwhile, as

shown in Figure 7, the concentration of St also increased rapidly in the latex phase.

In this article, the phrase *latex phase* is used, meaning that the monomer phase (the oil phase), not the conventional monomer droplets dispersed in the aqueous phase, existed at the top of the latex phase or at least at the moment of sampling with a short interruption of agitation (tens of seconds). In fact, the oil phase clearly existed during polymerization at an agitation rate of 100 rpm, especially in the presence of 8 wt % EA.

In articles written by Kawaguchi et al.,^{2–5} the fraction of 4VP in the (co)polymer varied from about 40 to 30% and about 70 to 25% during polymerization with feed ratios of 4VP (f_{VP}) of 0.30 and 0.25 at pH 11 and 2, respectively, with an agitation rate of 300 rpm. Similarly, the anomalous low fraction of hydrophilic monomer in the copolymer was also observed in other copolymerization systems.^{4,5,10} In this work, we found that the copolymer composition was correlated with the agitation rate. As shown in Figure 8, the initial fraction of 4VP in the copolymer was about 82 mol % with an agitation rate of 200 rpm. However, with an agitation rate of 100 rpm, the initial fraction of 4VP was about 91 mol % and then slightly increased to about 94 mol %, regardless of the addition of EA.

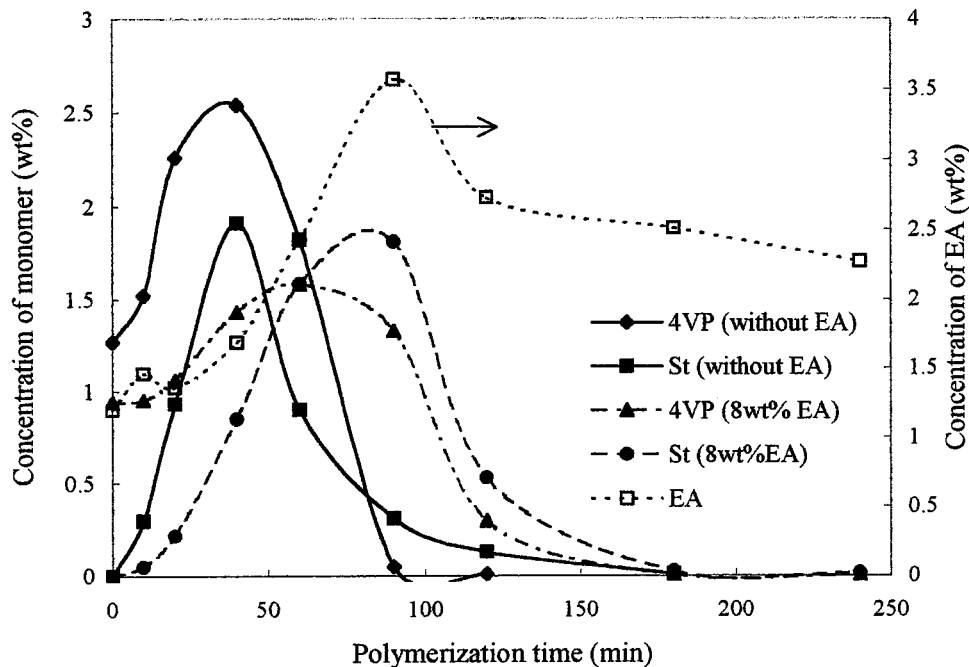


Figure 7 Concentrations of 4VP, St, and EA in the latex phase versus the polymerization time at an agitation rate of 200 rpm. The weight percentage on the perpendicular axis is based on the latex phase.

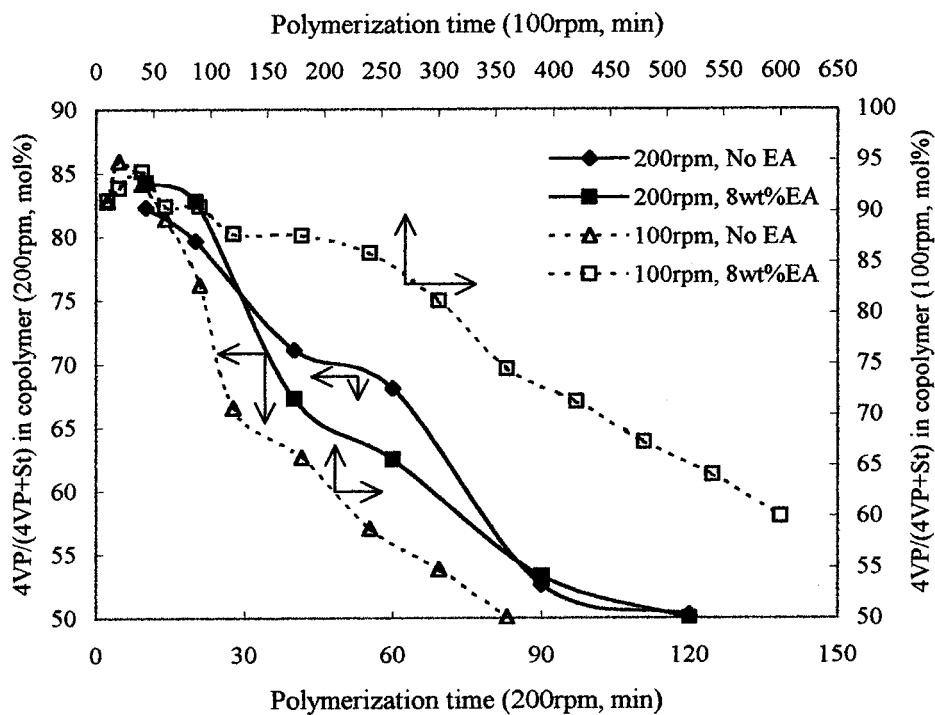


Figure 8 Composition of the latex polymer versus the polymerization time. The initial monomer feed ratio was $f_{VP} = 0.5$.

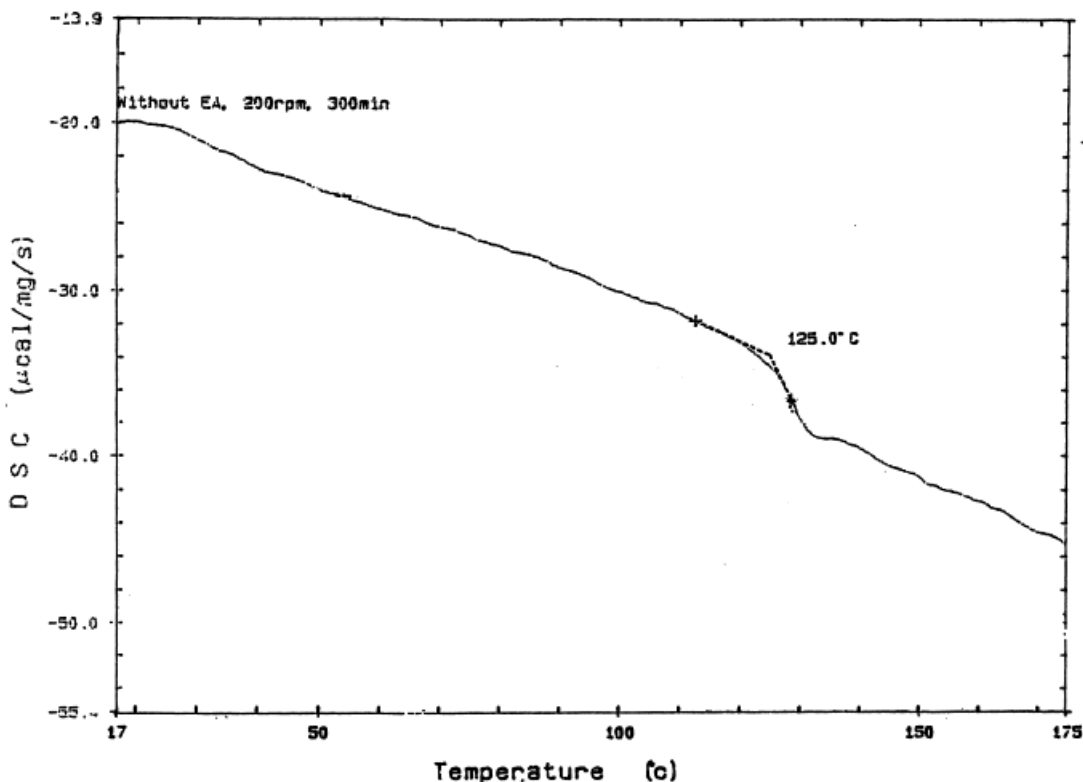


Figure 9 DSC curve of latex (without EA, 200 rpm). The lattice was withdrawn from the polymerization system at a total conversion of 98 wt % (300 min, without EA, 200 rpm). The heating rate was 10°C/min.

The anomalous low fraction of hydrophilic monomer in the initial polymer cannot be explained by the homogeneous nucleation mechanism,¹¹ even when modified with the two-stage mechanism postulated by Kawaguchi et al.² All the factors, including nucleation, diffusion rate, and reactivity ratios, according to the mechanism of homogeneous nucleation predicted that the initial copolymer composition should be close to the pure polymer of P4VP. Furthermore, this anomalous observation would disappear with a decreased agitation rate. For example, in the quasi-static polymerization, the initial fraction of 4VP in the copolymer was about 97 wt %.¹³ This result indicated that the composition of the initial copolymer during the nucleation changed with the background situation.

The DSC curve of the copolymer without the addition of EA is shown in Figure 9. It clearly shows that there were no macroscopic domains dominated by P4VP or polystyrene in the latex, although the 4VP(1)/St(2) reactivity ratios ($r_1 = 1.04$, $r_2 = -0.70$ ²¹) are disparate. Generally, only with starved feeding in the semicontinuous

process can a homogeneous composition of the copolymer latex be obtained for a comonomer with such disparate reactivity ratios.^{11,12,15,22,23} Accordingly, it is reasonable to deduce that polymerization in the particles may have also progressed under a condition of starved monomer in this work. This deduction was supported by observations of the morphology development.

It should now be clear that nucleation took place in the monomer droplets, in which St existed at a certain level. Moreover, the transport of monomer should be discontinuous because of collision. Because the monomer droplets readily absorbed the oligomeric radicals generated in the aqueous phase due to the lower surface charge density, the high nucleation rate, simultaneously combined with the lower fraction of hydrophilic monomer in the initial polymer, was understandable, despite the disparate reactivity ratios of the comonomer. Also, a homogeneous composition of the latex was obtained instead of the core-shell structure that usually results from disparate reactivity ratios^{22,23} because of the discontinuous transfer of monomer.

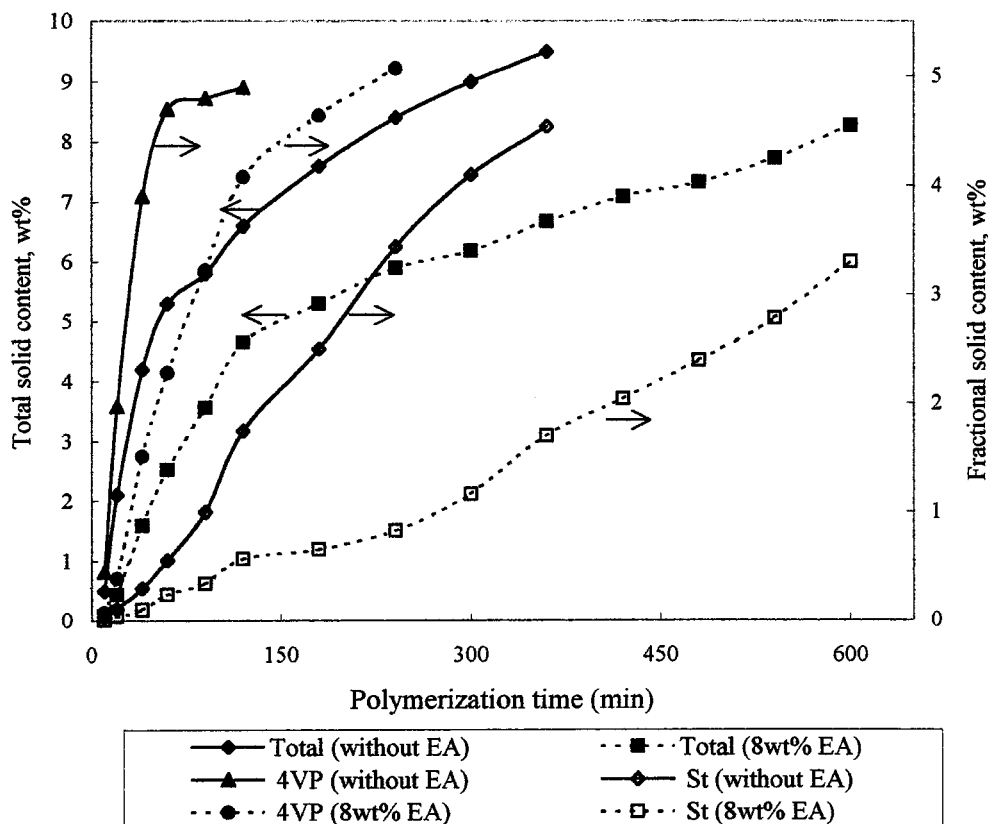


Figure 10 Solid content versus polymerization time at an agitation rate of 100 rpm. The solid contents are based on the latex phase.

Agitation Rate of 100 rpm

The solid content and monomer concentrations in the latex phase are shown in Figures 10 and 11, respectively, with an agitation rate of 100 rpm. The fractional solid content of St increased much more slowly than those shown in Figure 7 with an agitation rate of 200 rpm. Meanwhile, as shown in Figure 11, the variation of the monomer concentration in the latex phase could be divided into two stages. In the first stage, the concentration of 4VP was higher but rapidly decreased as the polymerization progressed. In the second stage, the concentration of 4VP was very low, but the concentration of St increased abruptly in the absence of EA, whereas it gradually increased in the presence of 8 wt % EA.

The concentration of EA in the latex phase, as shown in Figure 11, revealed a minimum at 60 min after the polymerization started. This minimum appeared at 20 min with an agitation rate of 200 rpm (Fig. 7). An interpretation for the decrease of EA in the latex phase is that EA was expelled from the particles. In other words, EA

was preferentially partitioned in the particles while a certain amount of monomer existed and was expelled from the particles because of the immiscibility of EA and the copolymer with a high content of 4VP. This is an important argument for established that the accepted theory (that monomers are transported by diffusion and are considerably swollen in particles) does not always hold for all copolymerization systems. The miscibility between the comonomer and copolymer is an important factor for the aforementioned scenario, especially in a copolymerization involving a highly hydrophilic monomer with a hydrophobic one. The formation of hemispheres and converted core-shell structures, as shown in Figure 4(c,d), in the absence of EA was probably due to poor miscibility between St monomer and the copolymer with a high content of 4VP and the high viscosity in the particle.

Because EA initially existing in the particles would be expelled when 4VP was consumed, the morphologies shown in Figures 3(b,c) and 5, that is, egglike and hemispheric particles, can be ex-

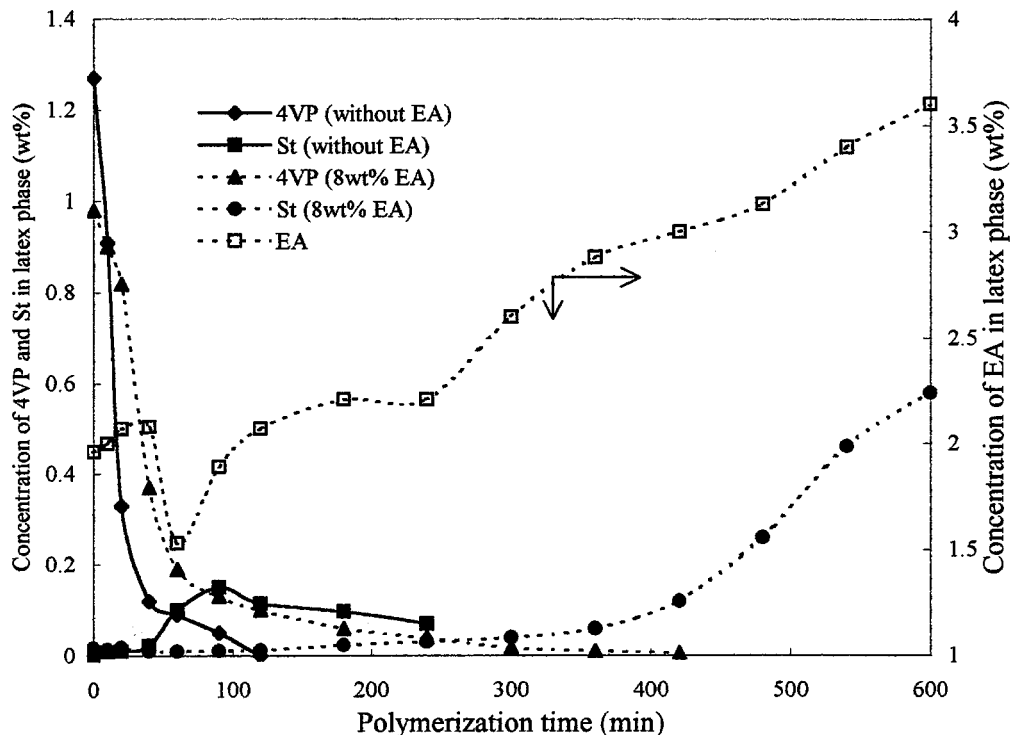


Figure 11 Concentrations of 4VP, St, and EA in the latex phase versus the polymerization time at an agitation rate of 100 rpm. The concentrations are based on the latex phase.

plained. The monomer droplets, mainly consisting of St and EA, engulfed particles that had a high content of 4VP in the copolymer; the diffusion of St to the particles was constrained by EA; and, therefore, egglike and hemispheric particles (dumbbell-like particles) were formed. The fraction of St in the copolymer determined the compatibility between EA and copolymer, thereby determining the extent of phase separation.

Number and Size Distribution of Particles

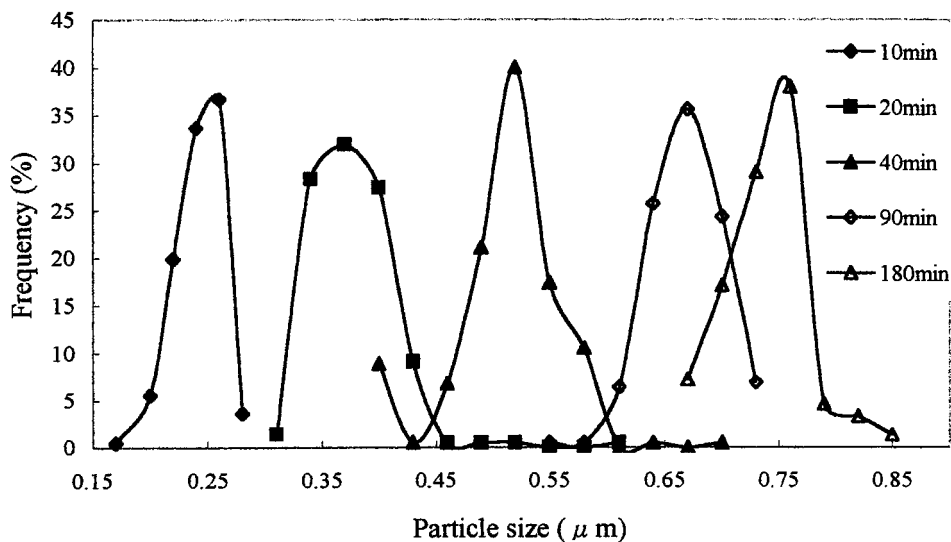
Generally, the particle number in emulsion polymerization is important for determining the mechanism of the emulsion polymerization.^{12,15} However, in this work, as shown in Figure 1, it was very difficult to estimate the particle number in the initial stage because the particle size could not be determined precisely. This problem probably exists in other polymerization systems because, if the particle was significantly swollen by the monomer at low conversion, the particle must be soft enough to spread out rather than keep a spherical shape during the preparation of SEM or TEM samples. In this case, the measured diameter of particles must be overestimated, and this

results in a decrease in the calculated number of particles. Also, the determination of the particle size at a higher monomer conversion is difficult because of the nonspherical shape of the particles. For this reason, the estimated maximum number of particles during polymerization is shown in Table II (with the diameter averaged over all the diameters of particles, including nonspherical particles). Apparently, as shown in Table II, the maximum particle number increased as the agitation rate increased. This is coincident with the results reported by Chen et al.¹⁰ and Kawase.²⁶

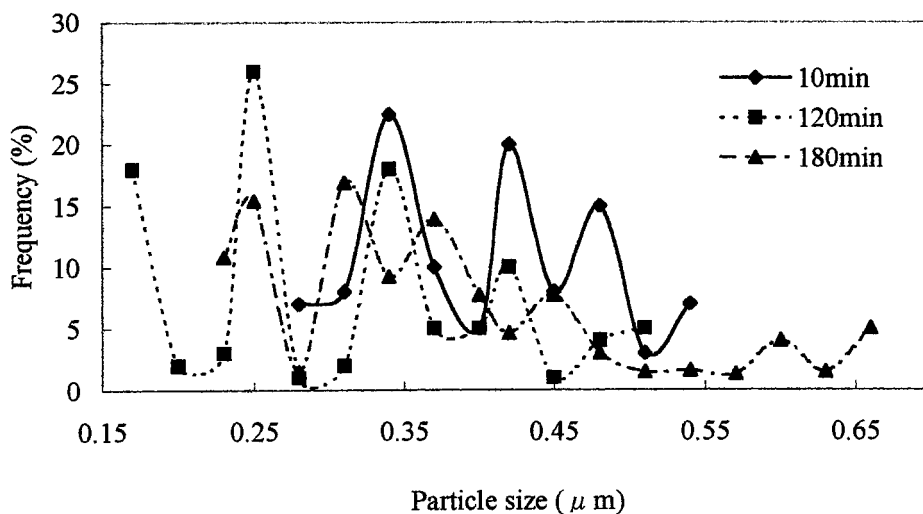
The distributions of particle size during polymerization, for example, are shown in Figures 12

Table II Maximum Particle Number of Latex Prepared with the Agitation Rates of 100 and 200 rpm

Agitation Rate (rpm)	200		100	
	No EA	EA	No EA	EA
Maximum particle number (10^{-14} /L of latex)	5.5	4.8	2.7	3.7



(a)



(b)

Figure 12 Distribution of particle size versus the polymerization time (without EA, 200 rpm): (a) distribution of normal particle size (200 rpm, 8 wt % EA) and (b) distribution of anomalous particle size (200 rpm, 8 wt % EA).

and 13. Bimodal or even multimodal distribution of particle size was observed from the very beginning of the polymerization both for 200 and 100 rpm, regardless of the addition of EA. On the basis of the results from the morphology development (the gray and black particles and the incorporation of polymer particles by monomer droplets), we concluded that the difference in particle size during polymerization mainly originated from the difference in the concentration of monomer and EA in the particles.

Table III shows the development of the average diameter of particles derived from peaks of size distribution shown in Figures 12(a) and 13. Obviously, as shown in Table III, the average volume ratio of particles, based on the one observed at 10 min of polymerization, increased by an integral multiple. For example, at an agitation rate of 200 rpm, the integral multiples are 4, 8, and 16, whereas at an agitation rate of 100 rpm, the integral multiples are 3, 5, and 8. It is clear that the higher the agitation rate is, the greater the num-

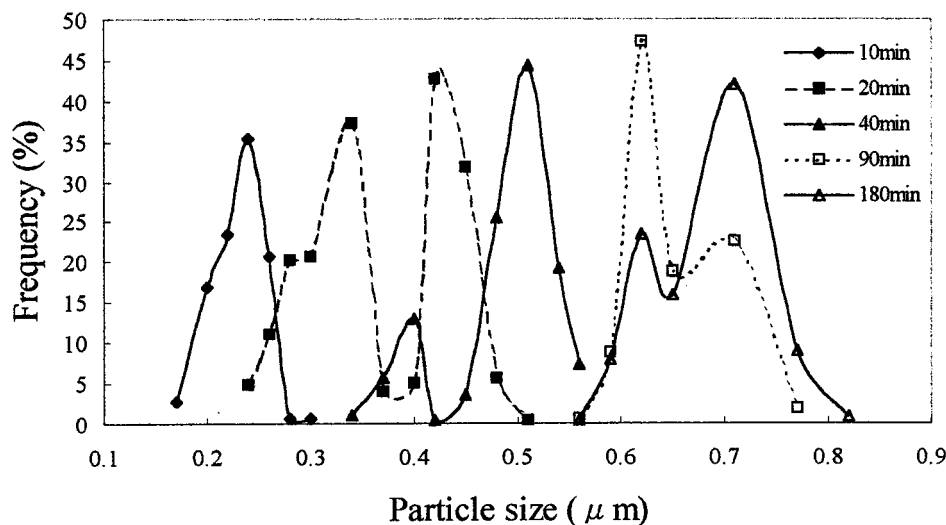


Figure 13 Distribution of particle size versus the polymerization time (100 rpm, 8 wt % EA).

ber of incorporated particles is. Interestingly, the particle number still increased dramatically at this stage, as long as it was calculated from the diameters of all the particles. This implies that the rate of new particle generation, which originated from the monomer droplets initially,¹³ was much faster than that of the consumption for the growth of particles. In other words, the monomer droplets engulfed the mature particles and was the major cause of monomer transport, at least in the earlier stage, which was postulated to be the cause of monomer transport in miniemulsion polymerization.^{12,27}

These results are summarized in a model given in Figure 14. At 200 rpm, monomer droplets generated at the interface of the monomer and aqueous phases were fully mixed with mature particles immediately because of the higher agitation

rate. At the initial stage, some monomer droplets remained to form the smaller particles because of the smaller number of particles [Fig. 14(a)]. However, as the number of the particles increased, the incorporation among mature particles and monomer droplets became dominant. With the greater average number of incorporated species in a particle, as shown in Table III, the possible modes increased for the combination of species, as shown in Figure 14(b). In the absence of EA, these different modes of combination were averaged over all particles as polymerization progressed and resulted in a rather narrow size distribution of final particles. However, in the presence of EA, this might lead to the generation of particles with anomalous sizes (oversized or smaller particles), as shown in Figure 12(b), due to the differences in the EA concentrations of mature particles and

Table III Development of Particle Volume During the Polymerization

Time (min)	200 rpm				100 rpm			
	No EA		8 wt % EA		No EA		8 wt % EA	
	D_i	V_i/V_{10}	D_i	V_i/V_{10}	D_i	V_i/V_{10}	D_i	V_i/V_{10}
10	0.23	1	0.24	1	0.45	1	0.24	1
20	0.36	4 (3.8)	0.38	4 (4.0)	0.67	3 (3.3)	0.34	3 (2.8)
40	0.46	8 (8.0)	0.50	8 (9.0)	0.78	5 (5.2)	0.42	5 (5.4)
60	0.59	16 (16.9)	0.58	16 (14.1)	0.88	8 (7.5)	0.48	8 (8.0)
							0.52	10 (9.6)

D_i = diameter averaged from the largest diameter peak in Figures 12 and 13; V_i = volume of particles; V_{10} = volume of particle at 10 min. Figures in parentheses are the calculated data.

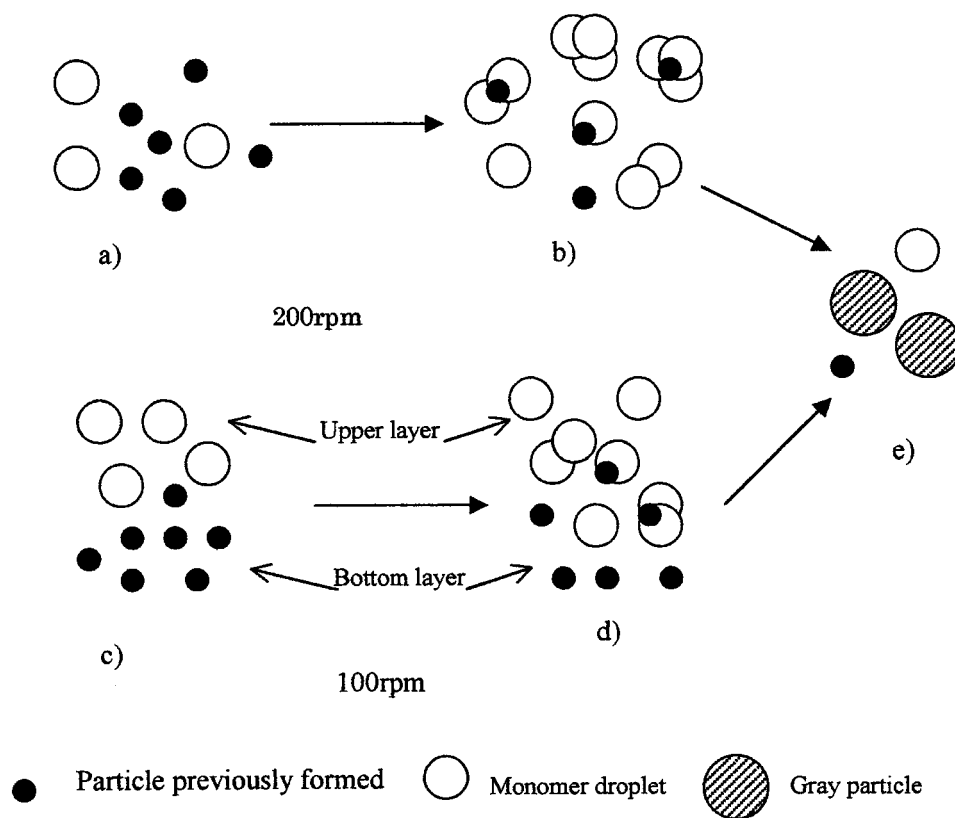


Figure 14 Model for the growth of particles.

monomer droplets and in the concentrations among the monomer droplets themselves during polymerization.

The bimodal size distribution of particles at 100 rpm is related to the fact that monomer droplets were generated in the upper layer and then settled down to the bottom layer of the latex because of the low agitation rate. Hence, the narrow distribution of particles is readily understandable because of the smaller number of particles at the initial stage [Fig. 14(c)]. As the number of particles increased, a majority of the monomer droplets settled down in the bottom layer, mainly to engulf the particles previously formed [Fig. 14(d)]. Consequentially, this resulted in the bimodal distribution of particle sizes shown in Figure 13 (the peaks at 90 and 180 min should be noted). Additionally, on the basis of the model shown in Figure 14, the results reported by Kawase²⁶ for the soap-free emulsion polymerization of MMA can be explained. At the higher agitation rate, the size distribution was broader at the initial stage and converged to a narrow one at the end, whereas at the lower agitation rate, the size distribution was narrow at the initial stage but broader at the end of polymerization.

Polymerization Rate

The polymerization rates are shown in Figure 15, combined with the total concentrations of monomers in the latex phase. As shown in Figure 15(a), at an agitation rate of 200 rpm, the polymerization rate is generally proportional to the concentration of monomers. In the presence of 8 wt % EA, the polymerization rate slightly decreased, whereas the total comonomer concentration was highest. This likely happened because the content of St in the comonomer was higher than that of 4VP, as shown in Figure 7. However, at an agitation rate of 100 rpm, as shown in Figure 15(b), the variation of the polymerization rate can be divided into two stages. First, the polymerization rate was higher in the earlier stage when 4VP controlled the polymerization, although the concentration of monomers dramatically decreased. The second stage began from the abrupt decrease in the polymerization rate to the end of polymerization. In the second stage, St controlled the polymerization, and so the polymerization rate was lower. These results are rather unexpected if we consider those observed in a conventional emulsion polymerization system. However, if we

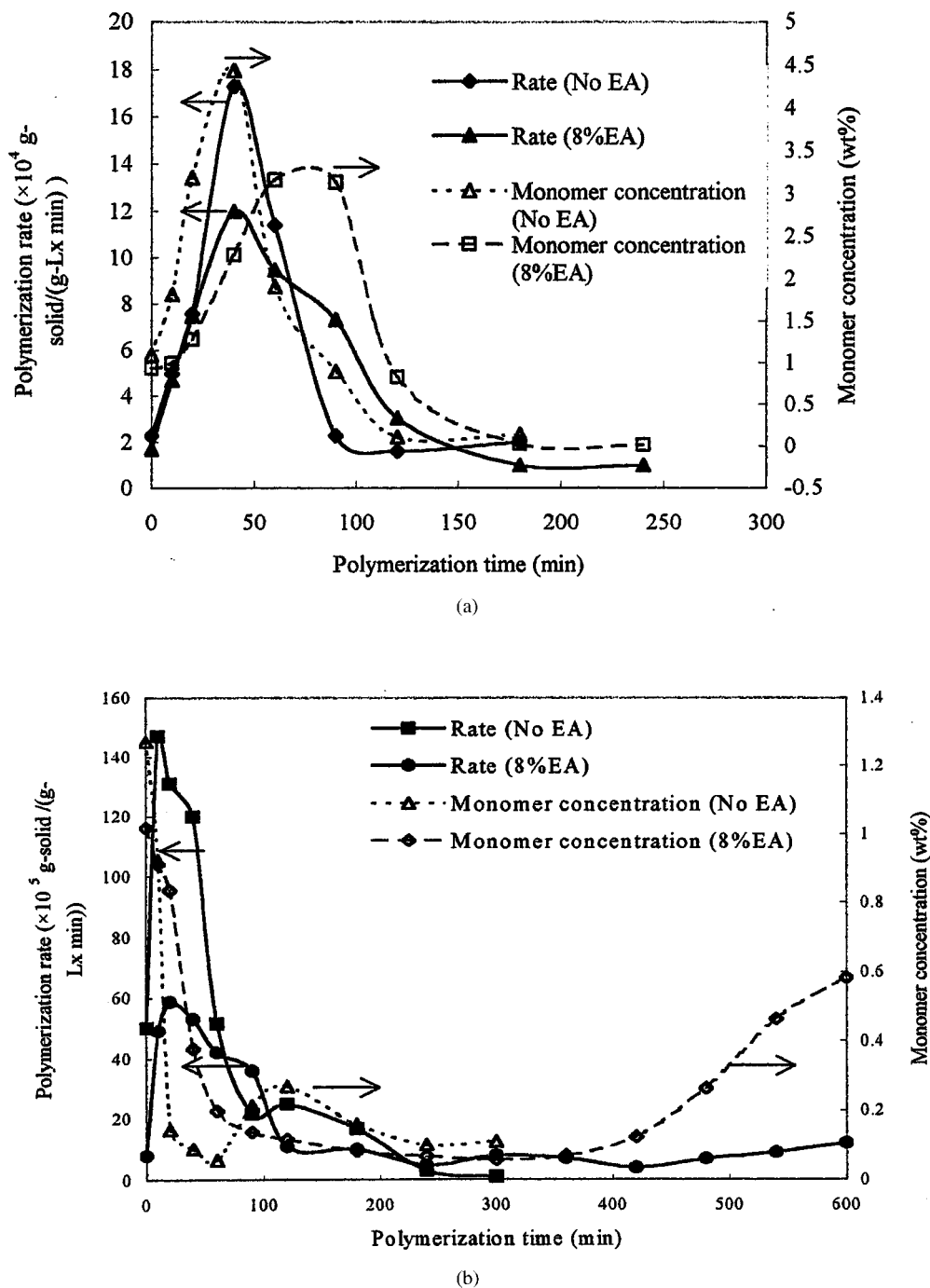


Figure 15 Polymerization rate and total concentration of the monomers in the latex phase versus the polymerization time: (a) 200 and (b) 100 rpm. The monomer concentrations are based on the latex phase.

consider the results obtained in the quasistatic soap-free emulsion polymerization,¹³ that particles generated in the upper layer and then settled down to the bottom layer of the aqueous phase, the aforementioned results may be readily understood. As mentioned in the Experimental section

of this article, the latex near the bottom of the reactor was sampled. At an agitation rate of 100 rpm, the latex phase may not be fully mixed because of the weak agitation. Therefore, most of the particles shown in this article were collected from the settled ones initially generated in the

layer just below the interface of the monomer and latex phases. This implies that the monomer droplets may always be generated during polymerization because of agitation, and so the comonomer concentration and solid content are different in the different layers of the latex phase, which was discussed in detail for quasistatic emulsion polymerization.¹³ In this case, both the polymerization rate and the monomer concentration just reflected what happened in the bottom layer of the latex, rather than the whole latex phase.

Nevertheless, the results obtained at 100 rpm established a bridge to connect quasistatic polymerization and conventional emulsion polymerization. Therefore, quasistatic emulsion polymerization¹³ can be used as an effective model system for investigating the mechanism of emulsion polymerization.

CONCLUSIONS

From the previous discussions, we can conclude the following:

1. Particles were generated in monomer droplets that formed from the interface of the monomer and aqueous phases because of the disturbance of the agitation or the condensation of the monomer molecules dissolved in the aqueous phase.
2. The incorporation among the species previously formed and the monomer droplets was a major cause of monomer transport in the emulsion polymerization system, in addition to the diffusion of monomer molecules through the aqueous phase.
3. At the higher agitation rate, smaller monomer droplets were generated, and so the particle number increased.
4. The particle morphology was determined from the miscibility between the monomer and polymer in the particles, rather than the phase separation due to the different copolymer compositions in the particles.
5. Quasistatic emulsion polymerization can be used as an effective model system for investigating the mechanism of emulsion polymerization.

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