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Mechanism of Soap-Free Emulsion Polymerization of Styrene and 4-Vinylpyridine: Characteristics of Reaction in the Monomer Phase, Aqueous Phase, and Their Interface

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ABSTRACT: The characteristics of reactions in the monomer phase, aqueous phase, and the interface of monomer/aqueous phase of soap-free emulsion polymerization of 4-vinylpyridine (4VP) and styrene (St) system were evaluated by using the different types of initiators, addition of organic solvents, and changes of agitation rate. The oil-soluble initiators 2,2'-azobis(2,4-dimethylvaleronitrile) (ADVN), benzoyl peroxide (BPO), and 2,2'-azobis(isobutyronitrile) (AIBN), the organic water-soluble initiator, 2,2'-azobis(2-amidinopropane) dihydrochloride (V50), and the inorganic water-soluble initiator, potassium persulfate (KPS), were used. ¹H NMR and scanning electronic microscopy (SEM) were employed for the characterizations. As a result, the mechanism of interfacial particle formation was supported. Namely, the minimonomer droplets were generated by the disturbance in the interface of monomer/aqueous phase due to the agitation. The minimonomer droplets were stabilized by the adsorption of surface-active oligomer generated by the reactions in both the aqueous phase and the interface. The monomer transfer from the bulk monomer phase to the growing particles was via the coalescence of minimonomer droplets with particles. The role of reaction in the aqueous phase was proposed to just provide the surface-active oligomer for the stabilization of particles. The rapid reaction in the aqueous phase due to the high concentration of hydrophilic monomer produced longer hydrophilic chains and led to the coagulation of particles by a bridging-coagulation effect. On the basis of this mechanism, the coagulum-free stable latices with high monomer conversion were prepared by using KPS and AIBN and, theoretically, can be prepared by using any type of initiators at a high level of solid content and feed ratio of hydrophilic monomer.

Introduction

By far, the loci of reaction in an emulsion polymerization system were mechanically divided into three parts in general,^{1–3} i.e., the aqueous phase, the particles or micelles, and the bulk monomer phase. The reaction in the aqueous phase was regarded as the initial locus of the reaction, which governed the formation of particles and then supplied the oligomeric radicals to the growing particles. The reaction in the particles or micelles led to the propagation of polymeric chains, whereas the reaction in the bulk monomer phase resulted in the generation of coagulum. On the basis of this consideration, some disputable assumptions must be given while studying the kinetics of a practical emulsion polymerization system. For example, in the soap-free emulsion polymerization system of hydrophobic monomer such as styrene by using a water-soluble initiator like potassium persulfate, an assumption was established to deal with the contradiction between the high polymerization rate and very low concentration of hydrophobic monomer in the aqueous phase. Namely, the constant of initial reaction in the aqueous phase must be much higher than that of normal propagation reaction.^{1–3} When an oil-soluble initiator such as BPO was used, an assumption is required that the radicals must escape from the monomer phase to the aqueous phase so as to initiate the monomer dissolved in the aqueous phase.^{2–4} Moreover, the factor of agitation

cannot be introduced into the kinetic expressions of emulsion polymerization.² However, as we know, the emulsion polymerization cannot be performed without agitation in the practice. Therefore, the loci of reaction in an emulsion polymerization system should be further disputed.

It is common knowledge in the interfacial science that,⁵ in order to lower the interfacial tension between oil droplets and water, the oil droplets tend to adsorb the ions on their surface. Meanwhile, the hydrophilic component preferentially distributes on the surface of oil droplets when the oil droplets are comprised of a hydrophilic component and a hydrophobic one. This implies that both the concentration of initiator and monomer may be high in the interface of the monomer/aqueous phase, even when the inorganic salt was used as an initiator. For example, in the soap-free emulsion polymerization system of styrene, the inorganic water-soluble salt such as potassium persulfate may not solely exist in the water phase. Both the monomer droplets of styrene and particles of polystyrene may adsorb the $S_2O_8^{2-}$ anions to lower their interfacial tensions. When a small amount of sodium styrenesulfonate (NaSS) was used, it is also reasonable to assume that most of NaSS molecules may be adsorbed on the surface of monomer droplets, to some extent, being similar to the emulsifier molecules. Combining these interfacial factors, it may be helpful to further understand the mechanism of emulsion polymerization. In fact, the interface has been suggested to be the locus of initial reaction for the thermally initiated emulsion polymerization.^{6,7} Therefore, the role of reaction in the interface of monomer/

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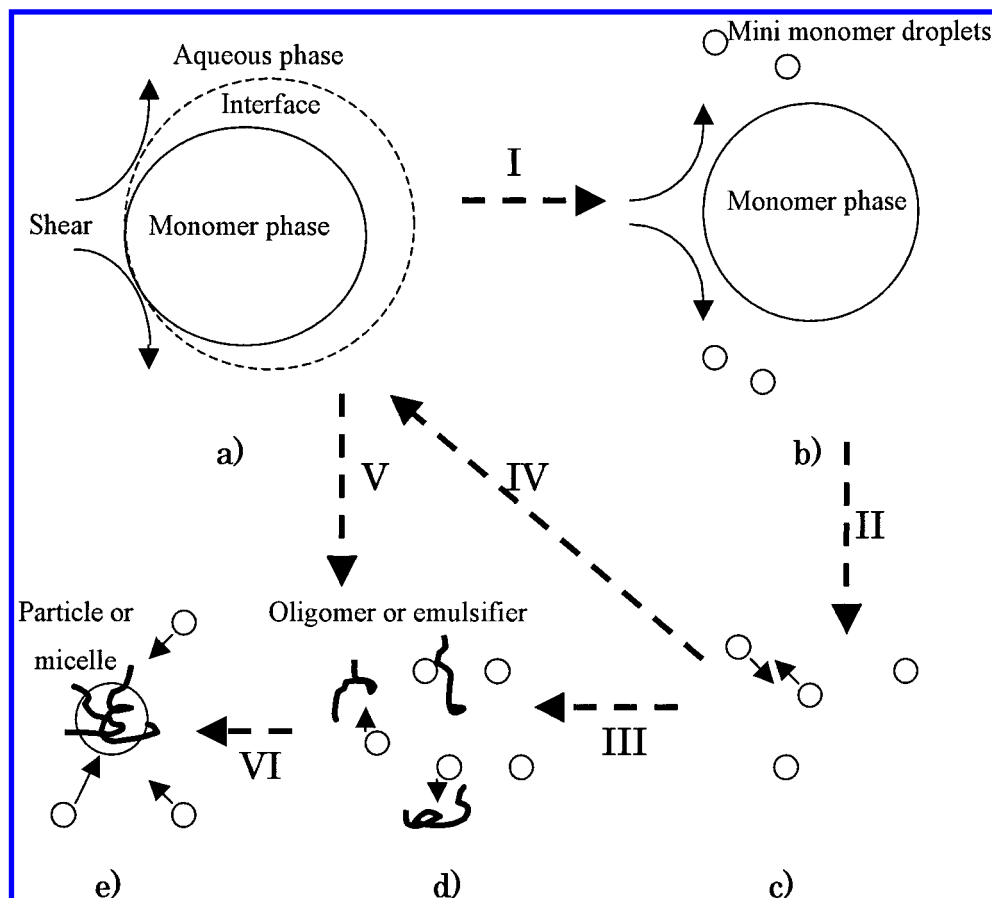


Figure 1. Interfacial particle formation mechanism.

aqueous phase should be evaluated in all the mechanistic study of emulsion polymerization, though the thickness of interface is just on the order of tens molecular size.⁵

In our previous papers,^{8–10} we have attempted to postulate a unified mechanism called interfacial particle formation mechanism for all the types of emulsion polymerization based on the experimental results of 4VP and St soap-free emulsion polymerization, especially those of the quasi-static emulsion polymerization. As shown in Figure 1, the mechanism begins with the deformation of the interface of monomer/aqueous phase in the shear field, by which a supersaturated area of monomer relative to the surrounding aqueous phase is created (Figure 1a). The minidroplets of monomer form in the supersaturated area due to the condensation of monomer molecules (Figure 1b). The life span of these minidroplets of monomer existing in the aqueous phase is determined by the interfacial tension of minidroplets/aqueous phase. Obviously, when the interfacial tension is high, they may return to the monomer phase by ripening soon after they were born (Figure 1, path IV). In a conventional emulsion polymerization where the emulsifier was used, the existence of emulsifier favors the survival of the minidroplets. The emulsifier molecules adsorbed on the surface of minidroplets will not only drastically lower the interfacial tension but also provide electrostatic repulsion or steric hindrance against the ripening of the minidroplets. When the concentration of effective emulsifier is high or powerful enough to prevent the micelles from collision incorporation, it is expected that the miniemulsion will be formed (Figure 1d,e). This is also the reason that the total amount of styrene in the micelles is just 1–2% of the charged

amount of monomer in a conventional emulsion polymerization system.²

In the soap-free emulsion polymerization system, the stabilization of minidroplets of monomer depends on the adsorption of initiator molecules (including ions) or the hydrophilic monomers if they are added. The stabilizing effects of these species may be weak. However, at the polymerization temperature, the situation may change because both the reactions in the aqueous phase and the interface may provide sufficient amount of emulsifier for the stabilization of minidroplets. The reaction in the interface may be most important for the formation of particles in many cases, because the oligomer generated in the interface may act as a nucleus for the condensation of monomer in the supersaturated area (Figure 1, paths V and VI). Therefore, the rate of generation of particles is related to the rate of reaction in the interface, which is determined by the concentration of initiator in the interface. Because of the characteristics of interface as mentioned above and additionally some reaction in the aqueous phase, it is consequential that the initial copolymer of emulsion copolymerization is rich in the more hydrophilic component.^{1–3,11–13} And also, it does not contradict the observations that the particles began to appear just when the content of hydrophobic component in the copolymer attained higher level.^{14–17}

Meanwhile, the process of monomer transfer from the bulk monomer phase to the growing particles was also suggested in this mechanism. Namely, when there is large number of particles existing in the emulsion polymerization system, the monomer in the supersaturated area can directly condense on the surface of particles at the moment when the particles collide with

the bulk monomer phase. Or in other words, as a model (Figure 1e), the particles collide with and then are incorporated into minidroplets of monomer. In this way, first, the morphology development of particles^{8,18} as well as the transfer of a large amount of dye with intensive hydrophobicity to the resultant particles during the polymerization^{19,20} can be easily explained. Second, the two-stage nucleation^{14–17} and core–shell growth mechanism^{13,21} observed by many authors are the consequence of this mechanism under some special conditions. Meanwhile, the process of emulsion polymerization, where the monomer such as acrylonitrile is a poor solvent for its own polymer, is clarified. At last, when the generating rate or the charged amount of emulsifier is low, the monodispersed distribution of particle size may be expected because of the lower stability of minidroplets and the averaged equal possibility of collision of per particle.

This mechanism not only naturally introduced the effects of agitation into the kinetics of emulsion polymerization but also clarified some disputable assumptions in the conventional mechanisms such as those mentioned above. On the other hand, it presents a new method of thinking to deal with the problems arising from the emulsion polymerization. For example, how does one extinguish the coagulation while using the oil-soluble initiator in a soap-free emulsion polymerization? It is possible that, ensuring the stability of particles, the stable latices without coagulation should be prepared by using any type of initiators as soon as they can be moved into the interface of monomer/aqueous phase according to this mechanism. Moreover, the mathematical model of this mechanism in our next paper will present the details of how to control the number, size, and its distribution of resultant particles as well as the rate of polymerization.

As the applications as well as the supporting evidence of this mechanism, in this paper, we will discuss the characteristics of the reactions in the different phases of soap-free emulsion polymerization. Then, by controlling these reactions, the coagulum-free stable latices with high content of hydrophilic monomer, 4VP, were prepared by using any type of initiators in the absence of emulsifier.

Experimental Section

Materials. Monomers 4-vinylpyridine (4VP) and styrene (St) and solvent ethyl acetate (EA) and toluene were purchased from Kishida Chemical Industries Co. Ltd. Water-soluble initiators, 2,2'-azobis(2-amidinopropane) dihydrochloride (V50) and potassium persulfate (KPS), oil-soluble initiators benzoyl peroxide (BPO), 2,2'-azobis(isobutyronitrile) (AIBN), and 2,2'-azobis(2,4-dimethylvaleronitrile) (ADVN) were offered by Wako Chemical Industry Co. Ltd. Ethyl acetate (EA) and toluene were distilled under the atmospheric pressure. Other reagents were distilled under reduced pressure except for the initiators, which were used without further purification.

The distilled and deionized (DDI) water with the conductivity of 18 MΩ·cm⁻¹ by employing a Milli-Q water purification system (Millipore) was used.

Methods of Experiments. A standard recipe for polymerization is shown in Table 1. The pH 2 was the consequence of using the initiator, V50, as reported in the previous papers.^{8–10} It was calculated from the amount of HCl attached on V50. Therefore, for better comparison, the pH of water was adjusted to 2 when using the oil-soluble initiators.

Both the batch and semibatch emulsion polymerization were employed and performed in a 300 mL four-neck, round-bottom reactor equipped with an anchor-type agitator (adjusted at the

Table 1. Standard Recipe for the Emulsion Polymerization of 4VP and St

monomer (wt %)		EA ^a (wt %)	water (wt %)	initiator ^b (wt %)
St	4VP			
5	5	8	82	2
10		90		2

^a Variable (0–10) for measuring the partition of comonomer. The amount of water changed simultaneously. ^b Based on the amount of monomer.

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 elevating the temperature, and the nitrogen blanket was maintained throughout the polymerization. For the batch polymerization, while KPS was used as initiator, the KPS solution free of oxygen by bubbling nitrogen for 1 h was added when the temperature of reaction mixture attained 70 °C. However, while using oil-soluble initiators, the initiators first was dissolved in the monomer and then added the monomer into the water free of oxygen (70 °C). For the semibatch polymerization, the monomer containing initiator was equally divided into three parts (10 g/part). Each part was added dropwise into the reactor (70 °C) within 2 h. The three parts were continuously added without any time intervals.

The monomer conversion was measured by gravimetry. The latex (ca. 2 mL) was precipitated with 0.5 N KOH solution containing 0.01 wt % hydroquinone (HQ) and then dried by vacuum after repeating twice the cycle of centrifugation–hot water washing.

Characterization. The partition of monomer and solvent was determined by ¹H NMR (ALPHA-500, JEOL) operated at 500 MHz, 30 °C, for which the details were shown in the Appendix of the previous paper.⁸ The pH of water was adjusted by adding KOH or HCl and measured with a pH/ion meter (HORIBA F-23, Horiba Ltd. Co., Tokyo, Japan). The solid content of latex was determined by gravimetry.

The size and shape of dried microspheres were observed by scanning electron microscopy (SEM) (JEOL JSM-5310). 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.

All of the experiments were reproducible.

Results and Discussion

A. Preliminary Experiments. 1. Partition of Monomer and Solvent. The partition of 4VP and EA was measured at ambient temperature because 4VP polymerized readily at high temperature. The variation of 4VP concentration in the aqueous phase, as EA was added from 0 to 10 wt %, is shown in Figure 2. It shows that, with the increase of EA in the polymerization system, the solubility of hydrophilic monomer in the aqueous phase, 4VP, was decreased and drastically decreased as low as about 0.3 g/100 g water at the monomer feed ratio, 4VP/St = 1/4 in the presence of 8 wt % EA. On the other hand, as shown in Figure 2, most of EA was also partitioned in the oil phase, even when the amount of added EA was lower than the solubility of EA in water at ambient temperature (ca. 8 wt %).²² Additionally, the concentration of EA in the aqueous phase was also affected by the composition of monomers. It decreased as the fraction of 4VP increased and increased as the fraction of St increased in the comonomer.

This result indicates that the solubility of hydrophilic monomer in the water is controlled by the amount of hydrophobic ones. The larger the amount of hydrophobic monomer, the less the amount of hydrophilic monomer

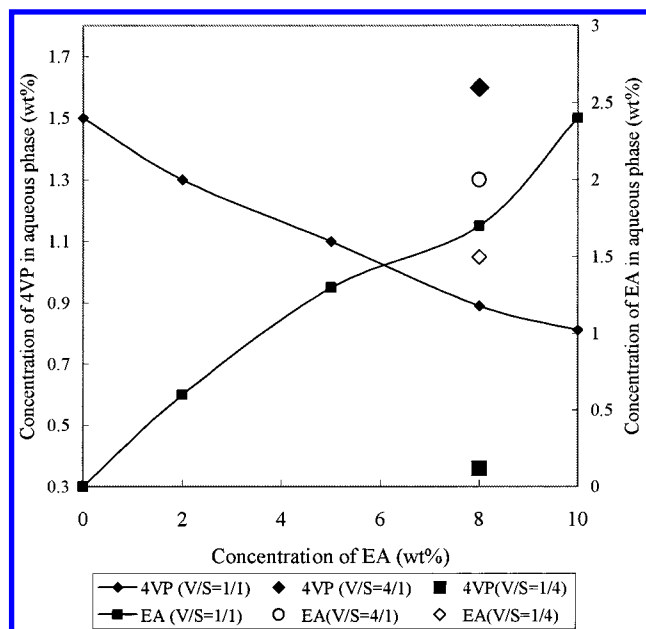


Figure 2. Partition of monomer and EA in the aqueous phase.

dissolved in the aqueous phase. In other words, if 4VP in the monomer phase was consumed by the polymerization, the monomer phase would withdraw 4VP from the aqueous phase. In many publications,^{11–17,23–25} an assumption was frequently applied for explaining the unexpectedly fast transport of hydrophobic monomers. The solubility, thereby the diffusion rate, of hydrophobic monomer was increased by the dissolution of hydrophilic monomer in the aqueous phase. This assumption should be reconsidered according to the above results.

2. Thermal Background Initiation. Thermal background initiation has been considered as one of the paths of particle formation in the emulsion polymerization system.² It referred to the contribution of polymerization resulting from the thermally initiated polymerization of monomers in aqueous phase and particles or maybe including those in the monomer phase.

In this paper, because the oil-soluble initiator was used, and as we know, its concentration in the aqueous phase was very low, it was necessary to clarify how the thermal background polymerization contributed to the emulsion polymerization. For this purpose, the thermally initiated soap-free emulsion polymerization with the standard recipe (excluding initiator) was performed at pH 2, 200 rpm for 24 h.

The result showed that there was no particle found in the aqueous phase, but the coagulum floating on the top of the aqueous phase. The composition of coagulum was tested with its solubility in methanol. It was observed that the polymer in coagulum was dominantly comprised of the 4VP unit because the polymer dissolved in methanol, forming a transparent solution.

It is understandable because the thermally initiated polymerization occurring whether in the aqueous phase or in the monomer phase will create the copolymer dominated by 4VP. The concentration of 4VP in the aqueous phase is much higher than that of St, and furthermore, the bulk copolymerization reactivity ratios of 4VP (1) and St (2) ($r_1 = 1.43$, $r_2 = -0.71$)²⁶ favor the formation of homopolymer of 4VP even in the monomer phase. Nevertheless, the result definitely indicated that the background thermal polymerization did not contribute to the generation of particles; moreover, the particles

could not be formed by the precipitation of polymer from the monomer phase to the aqueous phase.

3. Quasi-Static Emulsion Polymerization Using BPO and AIBN. The quasi-static emulsion polymerization was also employed to test the aqueous phase reaction using the oil-soluble initiators in this paper. That is to say, the monomers, initiator, and water (formulated as the standard recipe, total weight 80 g) in a 100 mL screw bottle were fully mixed with a pipet at ambient. Allowed to stand still at 25 °C for 4 h, the bottle was immersed in a 70 °C water bath without any agitation. Because the convection, resulting from the heat flux and the sampling, was not avoidable in the polymerization system, it was called quasi-static soap-free emulsion polymerization.

In the previous paper,⁸ the phenomena of quasi-static emulsion polymerization using V50 and KPS were reported. The phenomenon that the particles formed nearby the interface and settled down to the bottom of bottle was observed while using V50. Whereas, the minidroplet-like monomer first settled down to the bottom of bottle from the interface, and then the phenomenon that the reaction took place across the whole aqueous phase was found while using KPS. The reasons for these different phenomena were attributed to the different concentration of initiators at the interface and the rate of decomposition of initiators. Namely, V50 molecules were preferentially adsorbed on the surface of 4VP/St monomer phase because V50 molecules were positively charged and with higher decomposition rate constant.

In this paper, the oil-soluble initiators, AIBN and BPO, were used, and the quasi-static emulsion polymerization was performed for 8 h. Although the minidroplet-like monomer layer was observed to settle down from the interface, the reaction in the aqueous phase and the particles formed nearby the interface were not found. This result indicates that the reaction in the aqueous phase hardly takes place due to the extremely low concentration of AIBN and BPO (the solubility in water, 50 °C: AIBN, 0.036 g/100 g; BPO: 0.001 g/100 g water).^{2,27} Moreover, the decomposition rates may be too low to initiate the polymerization in the minidroplets of monomer before they returned to the monomer phase (70 °C, in styrene, k_d (s⁻¹) of AIBN and BPO is on the order of 10⁻⁵).²⁶

4. Swelling of 4VP to Particle of PSt. It is considered as a principle in all the mechanisms postulated by far; i.e., the monomer molecules diffuse into the growing particles until the swelling equilibrium and then polymerize in the particle.^{1–3} In this paper, the swelling behavior of 4VP to PSt particles was investigated. The thermally initiated seed emulsion polymerization of 4VP (PSt was used as seed particles, monomer/seed polymer = 1/1 (wt/wt)) was carried out at 70 °C for 24 h. It was observed that the 4VP monomer induced the phase separation from the PSt latex throughout the polymerization process, and the final size of particles was not changed compared with that of the seed particles.

This result showed that the swelling degree of a hydrophilic monomer, 4VP, to a hydrophobic polymer, PSt, was very low. The reasonable thermodynamical explanation may be that the change of Gibbs free energy favors the polar molecules of 4VP to exist in the aqueous phase as well as in its own phase rather than in a nonpolar environment of PSt particles. It implies that

Table 2. Solid Content of Resultant Latex Using Different Types of Initiators

run	EA (wt %)	initiator	pH	solid content of resultant latex (wt %)
1242	8	KPS	11	0
1243	8	KPS	2	0
1244	0	KPS	2	0
1149	0	V50	2 ^a	9.8
1228	0	AIBN	2	4.92
1232	0	BPO	2	3.09
1238	0	ADVN	2	0.75

^a Calculated value. Agitation rate: 200 rpm; 4VP/St = 1/1 (wt/wt).

the hydrophilic monomer transfers into the growing particles by another means because, as we know, the locus of polymerization is the particles after the stage of nucleation. Considering the partition behavior of hydrophilic monomer, we propose that the hydrophilic monomer transferred by the means of adsorption to the hydrophobic interface.

B. Batch Emulsion Polymerization with Different Types of Initiators. The solid content of latex prepared by the batch polymerization of 4VP and St with using different types of initiators is shown in Table 2. It was observed that the latex could be prepared by using all the types of initiators except KPS. The solid content of the latex increased in the order V50 > AIBN > BPO > ADVN. Since the aqueous phase was adjusted to pH 2 prior to the polymerization (except for V50, which carries HCl itself), it should be reasonable to consider that the stability of particles contributed by the protonated 4VP groups was equal in all the cases.

V50 should be partitioned preferentially in the aqueous phase and the interface of monomer/aqueous phase. The interface dominantly comprised of 4VP molecules tends to adsorb the cation and the hydrophobic monomer phase consisted of most of St may object the entrance of polar molecules. Therefore, the reactions in the aqueous phase and the interface should be noticeable.

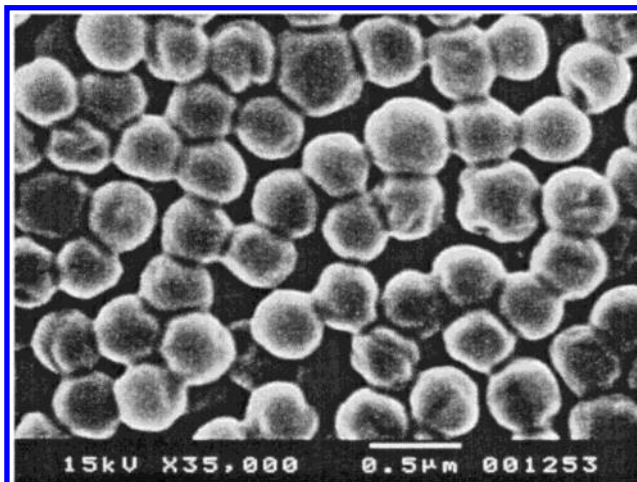
The polymerization in the aqueous phase should not be different from a conventional solution or bulk polymerization where the rate of polymerization and the molecular weight are determined by the concentrations of monomer and initiator. Generally, the concentration of monomer in the aqueous phase is very low in the emulsion polymerization system of styrene, hence just the short polymeric chains generated in the aqueous phase. These short chains may act as emulsifier molecules to stabilize the growing particles. However, when the concentrations of monomer and initiator are fairly high, the polymeric chains with higher molecular weight will form. The long polymeric chains not only increase the viscosity of the aqueous phase but also become entangled, leading to the bridge coagulation of particles. An example²³ to show such an effect is that the particles of P(4VP/*n*-butyl acrylate) (4/1 wt/wt) could be prepared without coagulation only in the presence of 8 wt % or more EA based on the amount of aqueous phase. The addition of EA, as shown in Figure 2, was to lower the concentration of 4VP in the aqueous phase. Other examples are the reports by other authors in which it was claimed that the coagulation would take place when the amount of hydrophilic component increased up to a certain level.^{13–17}

This result indicates that the polymerization in the interface should contribute to the formation of particles.

Table 3. Recipe for the Preparation of Coagulum-Free Latex Using KPS^a

monomer (g)		toluene (g)	water (g)	KPS (g)
St	4VP			
15	15	30	240	0.6

^a Agitation rate: 200 rpm; pH = 11; polymerization at 70 °C for 14 h.

**Figure 3.** Microspheres prepared by using KPS.

Both KPS and V50 are ionic and water-soluble initiators, but the effects of using these two types of initiators are completely different. As shown in Table 2, in the use of KPS, the latex could not be prepared even by adding 8 wt % EA and adjusting the pH to 2. The question seemed to arise from the charge of initiator fragment. Namely, the fragment derived from the decomposition of KPS is negatively charged, whereas the protonated 4VP groups on the surface of particle is positively charged. Therefore, the particle will not be stable while simultaneously posing opposite charges on its surface. However, this did not seem to be the substantial reason because increasing the pH value of emulsion polymerization system could deplete the protonation of 4VP. For example, Ohtsuka et al.¹⁷ reported that, by using KPS, the soap-free emulsion polymerization of 4VP and St could perform without coagulation under the conditions of monomer feed ratio, $f_{4VP} < 0.25$ (wt/wt) at pH 2 and $f_{4VP} < 0.30$ (wt/wt) at pH 11. From Figure 2, it can be deduced that in such low f_{4VP} 's the concentration of 4VP in the aqueous phase must be very low.

In light of our mechanism, $S_2O_8^{2-}$ of KPS does not favor the preferential absorption of surface of monomer phase where 4VP molecules dominate. Most of $S_2O_8^{2-}$ is partitioned in the aqueous phase. Therefore, the unique way to prepare the stable latex without coagulation is to improve the properties of interface of monomer phase, meanwhile, to reduce the concentration of monomer in the aqueous phase as low as possible. Accordingly, as shown in Table 3, the recipe was designed referring to that of Ohtsuka et al.; i.e., toluene was used to replace 2/3 weight of styrene in Ohtsuka's recipe.

The coagulation-free stable latex of 4VP/St (1/1 w/w) with the zeta potential of -35.3 mV was successfully prepared. Obviously, the fragment ions derived from the decomposition of KPS stabilized the particles. The SEM photo of particles is shown in Figure 3.

On the basis of these discussions, it should be clear that the reaction in the interface directly contributes

Table 4. Solid Content of Resultant Latex Using AIBN and BPO under Various Conditions

run	4VP/St (g/g)	EA (wt %)	initiator	agitation (rpm)	pH	solid content of latex (wt %)
1225	1/1	8	AIBN	100	7	1.60
1226	1/1	8	AIBN	200	7	1.77
1227	1/1	8	AIBN	200	2	5.18
1228	1/1	0	AIBN	200	2	4.92
1229	1/1	8	AIBN	350	2	4.04
1230	1/1	0	AIBN	350	2	4.12
1231	1/1	8	BPO	200	2	3.10
1232	1/1	0	BPO	200	2	3.09
1233	1/1	0	AIBN	100	2	2.24
1234	1/1	0	AIBN	350	2	4.12
1235	4/1	0	AIBN	200	2	2.91
1236	1/4	0	AIBN	200	2	4.88
1256 ^a	1/1	0	AIBN	200	2	3.05

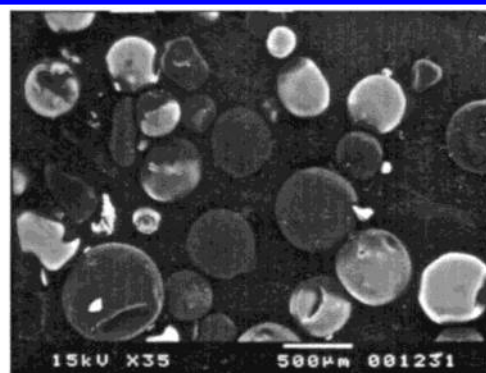
^a Polymerization temperature: 80 °C. All the polymerization performed at 70 °C for 24 h.

to the formation of particles. Whereas, the reaction in the aqueous phase just provides the surface-active oligomers for the stabilization of entities, i.e., particles and minidroplets of monomer. When the long polymeric chains formed in the aqueous phase due to high concentration of monomer, the bridging-coagulation of particles may take place.

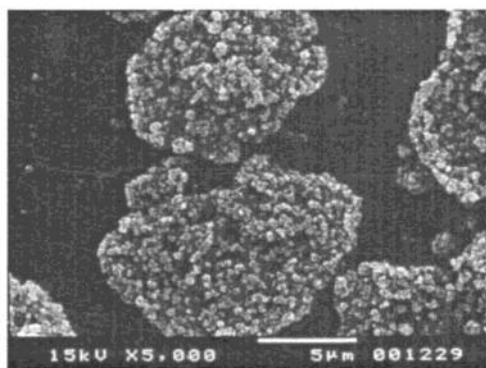
In the cases of using oil-soluble initiators, the polymerization in the aqueous phase may be negligible because of the extremely low concentration of initiator. Additionally, the thermal background initiation as performed the preliminary experiments did not contribute to the formation of particles. Therefore, the reactions in the monomer phase and the interface of monomer/aqueous phase should be only considered.

Many authors have reported the use of oil-soluble initiators in the emulsion polymerization,^{2,28,29} recently in the miniemulsion polymerization systems in particular.^{30–32} However, most of them focused on the emulsion polymerization systems in the presence of emulsifier and rarely on the soap-free emulsion polymerization system. The probable reason was that the polymerization in the monomer phase was inevitable, which consequently led to the formation of coagulum based on the conventional mechanisms of emulsion polymerization. For example, Kim et al.³³ reported that the amount of coagulum was 39% and 43% in the batch soap-free emulsion polymerization of styrene with a small amount of NaSS, while using AIBN and BPO, respectively. Torii et al.³⁴ investigated the effects of water-soluble, nonionic azo-initiators on the emulsion polymerization (VA-080, 082, 086, 088). They found that these initiators could not be used for the soap-free emulsion polymerization of styrene, but the latex could be prepared without coagulation by adding 30% acrylamide (AAm). The generation of coagulum in the batch soap-free emulsion polymerization of St/AAm (7/3 w/w) was not correlated to the solubility of initiator in water but to the stabilizing ability of fragments derived from the decomposition of initiators, the decomposition rate, and the efficiency of initiators. However, the partition of initiator in the different phases of the polymerization system was not discussed.

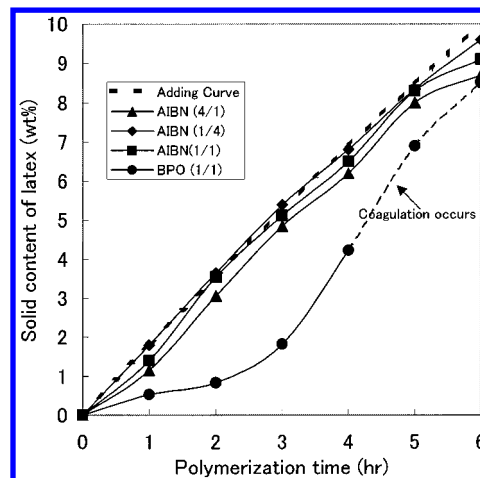
In our views, ADVN should be more hydrophobic than AIBN according to their chemical structures. Therefore, compared with AIBN, ADVN is more difficult to enter the polar interface. Moreover, the k_d of ADVN is much higher ($k_d(70\text{ °C})$, ADVN in toluene, $1.9 \times 10^{-4}\text{ s}^{-1}$; AIBN in styrene, $4.72 \times 10^{-5}\text{ s}^{-1}$; $k_d(74.8\text{ °C})$, BPO in



a) Beads of coagulum by bulk polymerization in monomer phase



b) Coagulum formed by the incorporation of particles

Figure 4. Coagulum derived from bulk polymerization and incorporation of particles.**Figure 5.** Solid content vs polymerization time of the semi-batch polymerization using BPO and AIBN.

styrene, $1.83 \times 10^{-5}\text{ s}^{-1}$).²⁶ These two factors determined that the bulk polymerization rate is much higher than that in the interface, as shown in Table 2, which led to much more amount of coagulum in the batch emulsion polymerization. This explanation seemed to be also applicable for the results obtained by Ohtsuka et al. For example, the k_d 's of initiators are VA-080 > 082 > 086 > 088, but the polarity is VA-080 < 082 < 086 < 088. The k_d of AIBN is a little larger than that of BPO, but the solubility in water shows that AIBN is much more polar, and therefore the concentration of AIBN in the interface is higher than that of BPO. This is the reason that the solid content of latex obtained by using AIBN was higher than that by using BPO.

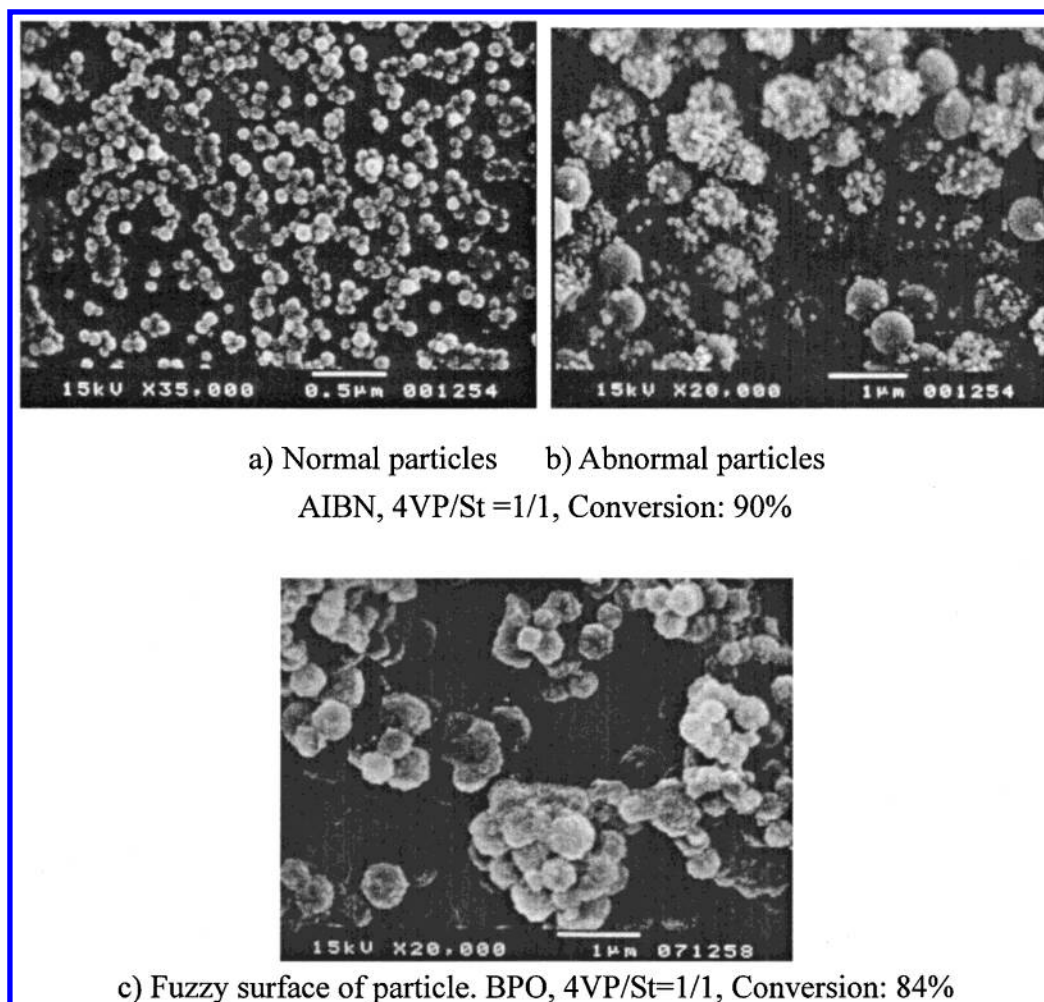


Figure 6. Microspheres prepared by using BPO and AIBN with the semibatch polymerization.

In the following section, the use of oil-soluble initiators will be further discussed.

C. Batch Emulsion Polymerization Using AIBN and BPO. The effects of various operation factors on the final solid content of batch emulsion polymerization using AIBN and BPO are shown in Table 4.

As shown in Table 4, the solid content was drastically increased with the decrease of pH value from 7 to 2 (runs 1226 and 1227). Interestingly, the solid content was slightly affected by the addition of EA (runs 1227–1232) but dramatically decreased as the feed ratio of comonomer, 4VP/St, increased from 1/4 to 4/1 (w/w) (runs 1235, 1228, and 1236). Moreover, with 4VP/St = 4/1, there was approximately 1.2 wt % of 4VP monomer (ca. 15% of charged 4VP monomer) left in the final latex, while with 4VP/St = 1/4, the concentration of 4VP monomer left in the final latex could not be measured. It indicates that, first, the polymerization in the aqueous phase may be negligible due to the extremely low concentration of initiator. Second, as discussed in the part of preliminary experiments, 4VP molecules can hardly diffuse into the growing particles. When the hydrophobic surface of monomer phase disappears due to the bulk polymerization, 4VP molecules dissolved in the aqueous phase may by no means enter the particles.

The effects of agitation rate were also investigated. It was observed that the solid content increased as the agitation rate increased from 100 to 200 rpm and then decreased at 350 rpm. The reason for the decrease of solid content at 350 rpm is that a large amount of

foamlike coagulum formed besides the beadlike coagulum. As shown in Figure 4b, the foamlike coagulum consisted of a large number of small particles. It implies that the higher agitation rate favors the generation of particles but does not favor the stability of particles.

The solid content was not increased by the increase of polymerization temperature (run 1256).

D. Elimination of Coagulum and Kinetics Using AIBN and BPO. On the basis of the above results as well as according to our mechanism, the preparation of stable latex without coagulation was attempted by employing the oil-soluble initiator. The semibatch emulsion polymerization was employed because the polymerization in the bulk monomer phase was the source of coagulation. The dropwise adding monomer phase would be rapidly divided into minidroplets, and the minidroplets could not coalesce in each other by collision to form the bulk monomer phase due to the small number.

The conditions of the polymerization was selected as: pH 2, 250 rpm, and 70 °C. The rate of addition was controlled artificially.

The results are shown in Figure 5. Obviously, by using BPO, the rate of polymerization was much slower than those using AIBN. The coagulum was also observed in the interval of 4 and 5 h, and the final latex was not stable. The particles in the final latex (polymerized for 24 h) precipitated soon after the polymerization. The SEM photo of such particles is shown in Figure 6c. The fuzzy surface was observed. We suggest that the mobility of particle decreased due to the adsorption of

water-soluble oligomers on its surface. The monomer accumulated to form the monomer phase due to the low polymerization rate. The concentration of 4VP in the aqueous phase was high. Therefore, a large amount of water-soluble oligomer would form by the thermally initiated polymerization, thereby the bridging-coagulation of particles occurred. The slower feed rate of monomer thus should be required for the preparation of stable latex without coagulation in the case of BPO.

For the use of AIBN, the polymerization rate was fast. The difference of rate due to the different monomer feed ratio was not observed within the experimental errors.

While 4VP/St = 4/1, the solid content seemed always lower than those of others, probably due to a part of 4VP dissolved in the aqueous phase.

It is interesting to note that a large amount of coagulum would be generated while using V50 as initiator in the semibatch emulsion polymerization (V50 dissolved in the aqueous phase prior to the polymerization). However, as shown in Figure 5, the stable latices were successfully prepared without coagulation by using AIBN and semibatch emulsion polymerization. The difference was possibly that a lot of water-soluble polymeric chains would be formed in the aqueous phase in the case of V50.

A multidispersed distribution of small particle size (ca. 50 nm) was obtained with either the batch or semibatch emulsion polymerization whenever the oil-soluble initiators were used (Figure 6a). This result implies that the particles generated throughout the process of polymerization as soon as the interface was formed. Recently, Klein et al.^{35,36} investigated the effects of various factors such as cmc of SDS and monomer/water ratios on the emulsion polymerization of styrene using the reaction calorimeter. They pointed out that the particles generated throughout the emulsion polymerization even after the monomer phase was depleted because of the dual nucleation mechanism. However, as shown in the preliminary experiments, the nucleation in the aqueous phase was impossible due to the extremely low concentration of AIBN. And also, the thermally initiated polymerization did not contribute to the nucleation even though the concentration of 4VP in the aqueous phase may be fairly high.

On the other hand, as shown in Figure 6b, the most noticeable fact is that there were many particles with abnormal size (around 0.5 μm) in the latex prepared by semibatch emulsion polymerization. We considered that these particles were formed via the bulk polymerization in the monomer phase because the shear force imposed on the surface of monomer phase decreased with the consumption of monomer phase (diameter of bulk monomer droplet decreased). In other words, the polymerization in the bulk monomer phase contributed to the formation of particles, too.

Conclusions

The characteristics of polymerization in the aqueous phase, monomer phase, and their interface were clarified by using the soap-free emulsion polymerization of 4VP/St and different types of initiators. The short-chain oligomers generated by the polymerization in the aqueous phase may act as the emulsifier to stabilize the particles, but the long-chain oligomers formed due to the high concentration of monomer and initiator, dissolved in the aqueous phase, and led to the bridging-coagulation of particles. The polymerization in the

interface of monomer/aqueous phase was the direct source to generate the particles. Whereas the polymerization in the monomer phase would lead to the generation of coagulum in the batch polymerization in general, particles may form in the semibatch polymerization where the monomer phase became a droplet with the micron size due to the mechanical shear force.

The monomer was transferred from the monomer phase to growing particles by the incorporation of particles into minidroplets of monomer. However, the hydrophilic monomer dissolved in the aqueous phase entered the particles via the adsorption on the hydrophobic surface.

The coagulum-free stable latices of 4VP and St with high content of 4VP (more than 50 wt %) were prepared by using the anionic initiator, KPS, with batch polymerization and by using the oil-soluble initiator, AIBN, with semibatch polymerization.

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