

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

I. Aspects of the Mechanism

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ABSTRACT: A series of experiments were carried out on the soap-free emulsion polymerization mechanism of 4-vinyl pyridine (4VP)/styrene (St) and the solvent, ethyl acetate (EA), by using the cationic initiator, 2,2'-azobis(2-amidinopropane) 2HCl (V50). To investigate the mechanism of polymerization in detail, a particular quasi-static polymerization system—the reaction mixture in a sealed bottle allowed to stand without agitation during the whole polymerization period—was employed. The partition of monomers at ambient and solid content of the latex during the quasi-static polymerization in the presence of 8 wt % EA was measured by $^1\text{H-NMR}$, and the variation of particle size was observed by scanning electron microscopy (SEM). The solubility of 4VP and St in water decreased as the amount of EA increased. Meanwhile, most of the EA was partitioned in the oil phase, even in the cases where the charged amount of EA was much lower than the solubility of EA (~ 8 wt %) in water at ambient. The solubility of EA in water was also affected by the composition of 4VP and St (i.e., increased as the fraction of 4VP increased, but decreased as the fraction of St increased). This observation, as well as the quantitative analysis of the quasi-static emulsion polymerization, indicated that the initial reaction in the soap-free emulsion polymerization was closely related to the disturbance of the interface of monomer/water phase, which triggered the generation of monomer droplets. Therefore, a new mechanism was proposed for the nucleation of soap-free emulsion polymerization, namely, the nucleation was performed in the droplets. The droplets absorbed the oligomeric radicals generated in the aqueous phase to continue the polymerization, as well as to promote the colloidal stability of the droplets. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 2679–2691, 2001

Key words: mechanism of soap-free emulsion polymerization; cationic water-soluble initiator; quasi-static polymerization; ethyl acetate; 4-vinyl pyridine/styrene

INTRODUCTION

In our previous work,¹ ethyl acetate (EA) was employed to increase the solid content of soap-free emulsion polymerization of poly(4-vinyl pyridine-*co-n*-butyl acrylate). Also, for investigating the

effects of EA on the soap-free emulsion polymerization,² the 4-vinyl pyridine [4VP(1)] and styrene [St(2)] copolymerization system, of which the copolymerization reactivity ratios were disparate, $r_1 = 1.04$, $r_2 = -0.73$ ³ was selected. The study on the properties and morphologies of resultant latices, which were carried out with ampoules, indicated that, with the addition of EA, the copolymer composition tended to be homogeneous irrespective of the disparate copolymerization reactivity

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ratios. Therefore, continuing work was devoted to reveal the effects of EA on the mechanism of P(4VP/St) soap-free emulsion polymerization in detail.

In the past decades, the mechanism of emulsion polymerization was widely investigated for almost all the factors that possibly affected polymerization behavior.^{4,5,6} Three well-known models, as comprehension of these works, were postulated, although some details of these mechanisms are still disputed. They are micellar nucleation, homogeneous nucleation, and mini-emulsion mechanisms. On the basis of these mechanisms, much work devoted to mathematical treatment has been published.⁷⁻¹¹

However, both in the mechanisms and in the mathematical equations, a term that directly reflected the influence of agitation on the process of nucleation and particle size development could not be found. This was inconceivable, because the agitation, to some extent, was the original driving force for the emulsion polymerization. In many cases, without agitation, a successful emulsion polymerization cannot be performed. Particularly in the industrial scale production of emulsion latex, it was common knowledge that agitation was related to both the amount of coagulum and the end properties of latex.⁴ Much work has been devoted to the design of the stirrer, from the shape of impeller to the mode of installation in a reactor.¹²⁻¹⁶

In fact, attempts to introduce the agitation factors in the models have been done from earlier times until now. The studies were mainly focused on the effect of agitation on the particle number, because the particle number is related to the polymerization rate and affects the outcome of coagulation of particles during the polymerization.^{4,17-23} For example, with the emulsion polymerization of St, Omi et al.^{17,18} found that the final particle number decreased as the agitation increased, using sodium oleate as emulsifier, whereas Nomura et al.¹⁹ suggested that the size of monomer droplet decreased as the agitation rate increased, using sodium lauryl as emulsifier. As for the soap-free emulsion polymerization of MMA in a pilot scale reactor, Kawase²² found that the particle size increased as the agitation rate increased from 50 to 272 rpm. The size distribution was nearly monodisperse at the initial stage, but broadened at high conversion at the lower agitation rate, whereas at the higher agitation rate, the size distribution became narrow. Chen and Chang²³ found the particle number at the high agitation rate was higher than that at

the low agitation rate; therefore, he proposed that the shear force had an important role in the nucleation stage of the soap-free emulsion polymerization of St with a low amount of 2-hydroxyethyl methacrylate (HEMA). However, no further details were given for the effects of agitation on the nucleation.

The other important effect of the agitation on the mechanism of emulsion polymerization is the size of monomer droplets and the transport of monomers to the reaction loci. The classical theory of Harkins^{24,25} describes the role of droplets as a reservoir of monomers which supplies monomers to the growing particles by the diffusion process through the aqueous phase. The normal size and number of monomer droplets are around 1–10 μm and on the order of $10^{11}/\text{L}$ -latex, respectively; hence the possibility of them becoming reaction loci is negligible compared to the soap micelles, the number of which is 10^{20} – $10^{21}/\text{L}$ -latex. His theory has been considered to be sufficient to elucidate the experimental results of emulsion polymerization conducted with hydrophobic monomers such as St. It seems to the present authors that his theory, for the diffusion process of monomer in particular, has been overextended without much dispute as to the emulsion polymerization involving more hydrophilic monomers.

It should be reasonable to presume that there is no thermodynamic restriction for a hydrophilic monomer, such as 4VP, to form smaller droplets than that of St. Besides, two facts seemed to be ignored in the emulsion polymerization system. The first is that the collision of particles with the monomer droplets, especially in the initial stage at which the macroscopic volume or cross-sectional area of monomer droplets cannot be negligible, although their number is fewer than that of the particles. The second is that the monomer droplets are also capable of absorbing the oligomeric radicals, thereby starting polymerization in the monomer droplets.⁴⁻⁶

Under the limitations of the monomer diffusion process, some authors encountered a difficult choice to explain their experimental results that the initial copolymer chains were more abundant in a hydrophobic monomer despite the disparate reactivity ratios.²⁶⁻³² Either the copolymerization reactivity ratios obtained from the bulk copolymerization were not applicable²⁶⁻²⁹ or the hydrophobic monomer diffused much faster than that expected in the emulsion copolymerization system.³⁰⁻³² Therefore, the most recent article published by Samer and Schork³⁰ proposed that there was a substantial driving force for monomer

transport other than the diffusion in the copolymerization of methyl methacrylate (MMA)/2-ethylhexyl acrylate (EHA). In this context, related experiments should be cited here that were designed to detect the exit of radicals from a particle.⁶ Although it was realized that the oligomeric radicals had difficulty exiting from a particle, as well as the reentry to a particle via water phase because of their hydrophobicity, the diffusion was yet regarded as a unique way for the transport of oligomeric radicals. One might wonder why mass exchange could not occur at the moment of collision between two particles.

Therefore, to investigate the effect of agitation as well as the role of monomer droplets in the emulsion polymerization system, a unique experiment, called quasi-static polymerization, was carried out. Namely, the reaction mixture in a sealed bottle was allowed to stand without any agitation during the whole polymerization period. This experiment originated from an occasional observation that the polymerization preferentially occurred at the upper layer of the aqueous phase just below the interface of monomer/water phase, when the 4VP/St polymerization system (initiator, V50) stood still for a long time in a room where the temperature was only slightly changed. This observation was not coincidental with that expected from homogeneous nucleation,⁵ according to which the polymerization should homogeneously take place in the aqueous phase. Moreover, there is only one monomer droplet (i.e., the monomer phase during the polymerization because mechanical agitation was not imposed). It is beneficial for us to clarify the function of monomer droplets and that of agitation in the polymerization system. Additionally, as preliminary work for these studies, the partitions of monomers and EA were also measured.

EXPERIMENTAL

Materials

The following monomers, 4-vinylpyridine (4VP), styrene (St), methyl methacrylate (MMA), and solvent ethyl acetate (EA), were purchased from Kishida Chemical Industries Co., Ltd. Water-soluble initiator 2,2'-azobis(2-amidinopropane), 2HCl (V50), and potassium persulfate (KPS) were supplied by Wako Chemical Industry Co., Ltd. EA was distilled under atmosphere. The other reagents were distilled under reduced pressure, ex-

Table I Typical Recipe for the Experiments and Measurements of Partition

Monomer (wt %)		EA ^a (wt %)	Water (wt %)	Initiator ^b (wt %)
St	4VP			
5	5	8	82	2
	MMA			
	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.

cept the initiators V50 and KPS, which were used without further purification.

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

Methods of Experiments

A standard recipe for polymerization is shown in Table I.

Partitions of Monomers and EA

The mixture, which was formulated as shown in Table I, was fully mixed with a pipette at ambient and then allowed to stand for 2 h at 25°C. The partitions of monomers and EA were determined by ¹H-NMR (ALPHA-500, JEOL). The typical spectra and calculating methods are shown in the appendix.

Quasi-Static Soap-Free Emulsion Polymerization

The quasi-static emulsion polymerization was employed in this study. It can be defined as follows: the monomers, EA and water (total weight: 80 g), in a 100-mL screw bottle were fully mixed with a pipette at ambient and allowed to stand at 25°C for 4 h. The bottle was then immersed in a 70°C water bath without any agitating. As shown in Figure 1, approximately 0.1 mL latex was withdrawn from a layer with a syringe at each sampling. Because 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.

Characterization

The partition, conversion, and concentration of the monomers, as well as the composition of co-

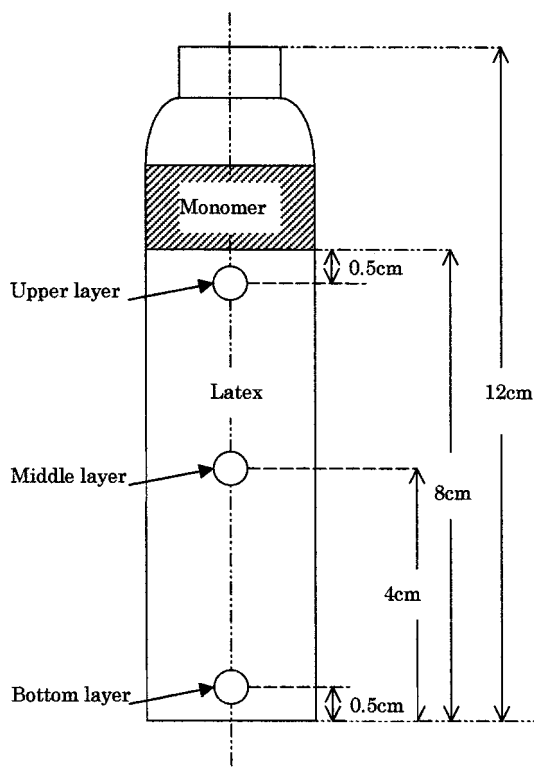


Figure 1 Illustration of sampling position in the quasi-static polymerization system.

polymers, were all determined by $^1\text{H-NMR}$ operated at 500 MHz, 30°C , for which the methods of calculation are shown in the appendix. The sample, withdrawn from the polymerization system by a syringe, was directly injected into the NMR tube and then diluted with approximately $10\times$ vol deuterated methanol (CD_3OD), as soon as possible. The NMR samples were stored at 5°C before measurements.

The size and shape of the dried microspheres were observed by scanning electron microscopy (SEM) (JEOL JSM-5310) and transmission electron microscopy (TEM) (Hitachi H-700H). The SEM sample was prepared as follows: one drop of diluted 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 direct measurement of 200 particles/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, stained with CH_3I vapor in a closed bottle at room temperature for 3 or 4 days.

All of the phenomena and experiments were reproducible.

RESULTS AND DISCUSSION

Partition of Monomers and EA

The partition coefficients for various monomers in the copolymerization system are important parameters for the kinetic analysis⁴⁻⁶ with an accurate estimation of monomer composition in the polymer particles. In the present work, the partition of 4VP and EA had to be measured at ambient because 4VP polymerized readily at high temperature, especially in the presence of initiator, V50.

The variation of 4VP concentration in the aqueous phase, as EA was added from 0 to 10 wt %, is shown in Figure 2. It was found that, with the increase of EA in the polymerization system, the solubility of hydrophilic monomer in the aqueous phase, 4VP, decreased. On the other hand, as shown in Figure 2, most of the 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 (~ 8 wt %).³³

Further investigation indicated that the concentration of EA in the aqueous phase shown in Figure 2 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.

The peak for St in NMR spectrum of the aqueous phase was very weak because of its low solubility. Hence, the error accumulated from the cal-

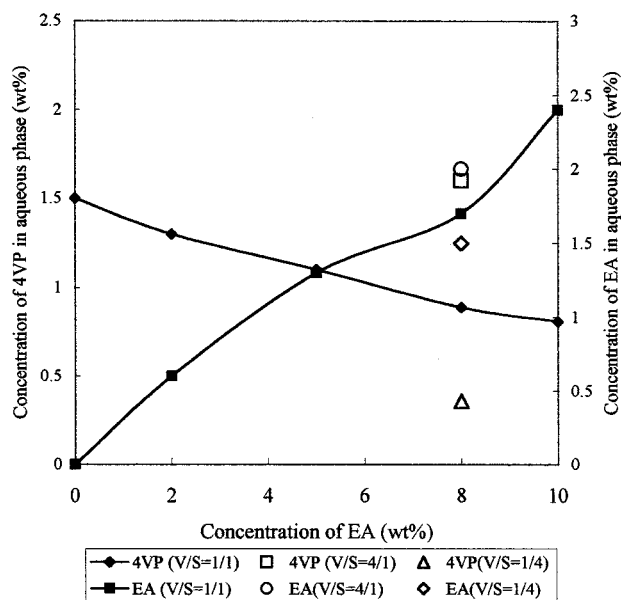


Figure 2 Partition of 4VP, St, and EA in the aqueous phase.

culuation was considerable. However, the tendency of the solubility of St in water seemed also to decrease as EA increased.

As a result, it is too complicated to calculate the partition coefficient for monomers, because the concentrations of 4VP, St, and EA in the aqueous phase were dependent on the feed composition. However, it was clear that the solubilities of monomers in the aqueous phase were controlled by the amount of EA.

In many publications,^{1-2,27-31} 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 may be taken for granted and should be reconsidered according to the results shown in Figure 2. For these results, we decided to investigate several factors from the very beginning of polymerization that probably affect the kinetic behavior of polymerization in detail.

Quasistatic Polymerization

This experiment was intended to investigate the nucleation process and the transport mechanism of monomers, because there was only one big droplet (i.e., the oil phase of monomer existed on top of the aqueous phase). If the monomer molecules diffused from the monomer phase into the aqueous phase, it was reasonable to assume that a concentration gradient from the interface of monomer/water to the aqueous phase existed. This concentration gradient was expected to be detectable.

Phenomena of Experiments

As shown in Figure 3(a), the apparent nucleation reaction took place preferentially in the layer just below the interface of the oil/water phase. Furthermore, as time elapsed, the nucleation reaction in the bottom layer of the aqueous phase (i.e., the process where the transparent aqueous phase became blue) was not observed. Instead, as shown in Figure 3(b), the milky-white latex formed in the upper aqueous layer settled down to the bottom layer. This phenomenon was dependent on the amount of added EA and the time of standing still. The more the added EA and the longer the standing time, the more enhanced the phenomenon was. Apparently, this phenomenon was not in agreement with that expected by the homogenous nucleation mechanism postulated by Fitch,⁵

where the nucleation reaction should occur uniformly, because the concentration of water-soluble monomer and initiator is uniform in the aqueous phase.

Two possibilities may be considered to account for this anomalous phenomenon based on the homogenous nucleation mechanism. One may be that the solubility of 4VP increased as the temperature was elevated. Thereby, the concentration of monomer in the layer just below the interface of the oil/water phase was higher than that elsewhere. The second possibility may be that the initially formed water-soluble oligomeric radicals precipitated readily because of the higher concentration of EA in the upper layer of the aqueous phase. However, it should be noted that this anomalous phenomenon was also observed both in the soap-free emulsion polymerization of St and in that of MMA, using V50 as an initiator [Fig. 3(c,d)]. Therefore, the latter possibility was rather remote.

To verify the influence of the former factor, the solubilities of 4VP as well as that of MMA in the aqueous phase were measured. As shown in Table II, the data strongly imply that both the solubilities of 4VP and the MMA decrease at higher temperatures.

Other factors, thus, must be found to explain this anomalous phenomenon. We considered that it was probably related to the convective flux generated in the polymerization system at the beginning of heating, thereby disturbing the interface of monomer/water phases.

The quasi-static experiments were designed to reveal the effects of disturbance of the interface of the monomer/water phase on the nucleation process. The mixture of MMA and water was allowed to stand in a 70°C water bath for 1 h. Then, the aqueous solution of V50 was charged into the polymerization system by two modes: injected into the bottom layer of the aqueous phase and added dropwise from the monomer phase above. With the former mode, the disturbance of the interface, if there was any, was distant from the layer where the initiator solution was added, whereas, with the latter mode, the interface was disturbed by the addition of initiator solution. It was found that the reaction started soon after the initiator was added with the latter mode, although with the former initiator-charging mode, it took about 5 min until the reaction began. Additionally, the reaction took place locally somewhere above, rather than in, the layer where the initiator solution was injected. Although it was unavoidable to dilute the local concentration of

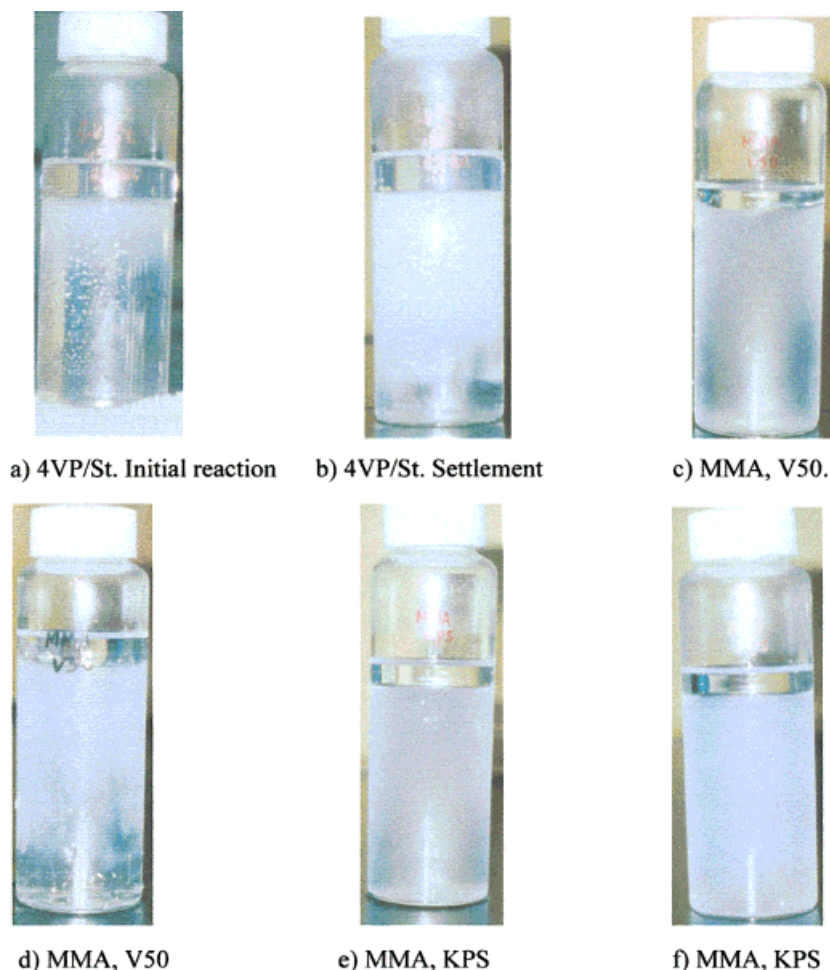


Figure 3 Progress of quasi-static experiments shown by photographs: (a) Initial reaction; (b) settlement of particles; (c) settlement of monomer droplets before the initial reaction occurred; (d) initial reaction; (e) settlement of monomer droplets before the initial reaction occurred; (f) initial reaction.

monomer due to the injection of initiator solution with the former mode, it was the best solution we could find to cancel the effect of the formation of monomer droplets, which were possibly generated

Table II Solubility of 4VP and MMA in the Aqueous Phase at Different Temperatures

	Temperature (°C)		
	5	25	70 (0.5 h)
4VP (wt %)	1.27	0.84	0.93
EA (wt %)	2.63	1.97	1.70
MMA (wt %)	1.48	1.18	1.09

Formulated according to the recipe shown in Table I, except for the addition of initiator. Time of stand still was 2 h, except for 70°C.

(the volume of estimated bottom layer/the volume of V50 solution = $\sim 30 \text{ mL}/4 \text{ mL}$).

It could be concluded that the nucleation took place solely, or at least, preferentially in the area near the disturbed interface of monomer/aqueous phase. Consequently, the properties of the interface of monomer/aqueous phase are important to the progress of initial reaction.

On the basis of these results, we suggest that this anomalous phenomenon was related to the droplets formed from the disturbance of the interface of monomer/aqueous phase by the convective flux, and likely, by the decrease of solubility of monomer in the aqueous phase while the temperature increased. This suggestion is envisaged in Figure 4(a). An area supersaturated by the monomer was generated because of the disturbance of convective flow to the interfacial layer or the de-

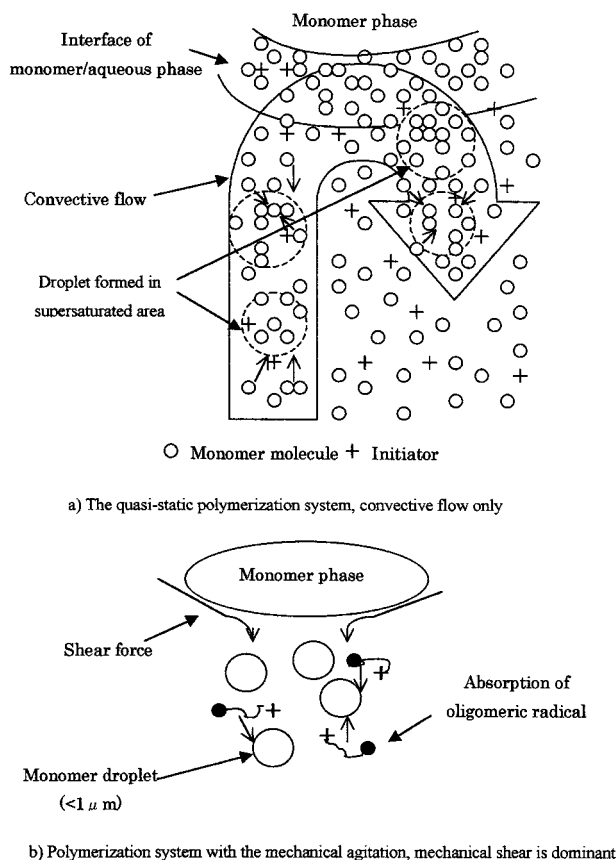


Figure 4 Scheme of the initial reaction in the quasi-static polymerization system.

crease of the solubility of monomer. The monomer droplets formed and absorbed the oligomeric radicals generated in the convective flow or in the aqueous phase elsewhere.

Other relevant evidence to support this postulation may be obtained from the different behaviors arising from the types of initiator, V50 and KPS, respectively. In the case of using V50, as shown in Figure 3(c,d), a layer, likely comprising a large amount of monomer droplets, was observed originating from the interface of monomer/water phase and extending to the aqueous phase [Fig. 3(c)]. The reaction took place before it spread over the whole aqueous phase because of the higher decomposition rate of V50 (70°C ; $k_d = 1.15 \times 10^{-4} \text{ s}^{-1}$ ^{28,34,35}). Figure 3(d) evidently shows that the polymerization preferentially occurred in the upper layer of the aqueous phase, and then the formed particles settled down. However, in the case of using KPS, due to the slower decomposition rate (70°C ; $k_d = 2.33 \times 10^{-5} \text{ s}^{-1}$ ³⁵), as shown in Figure 3(e,f), the layer comprising monomer droplets spread over the aqueous phase before the occurrence of reaction [Fig. 3(e)]. A

nucleation reaction similar to that expected by homogeneous nucleation⁴ was thus observed [Fig. 3(f)].

This mechanism sketched in Figure 4 seems to resemble the micellar nucleation mechanism postulated by Goodall et al.³⁶ and the two-stage mechanism by Kawaguchi et al.^{26,27} However, some substantial differences existed among them. In Goodall's micellar nucleation mechanism, the initial oligomeric polymer, which was supposed to be surface-active, precipitated to form a large number of micelles; thereafter the monomer molecules diffused into these micelles. However, the observations in Figure 3 strongly implied that the droplets existed prior to the formation of micelles.

In fact, a good suggestion was given in the two-stage mechanism postulated by Kawaguchi et al.^{26,27} They claimed that the homogeneous reaction in the aqueous phase was just a transitional period during which the main reaction locus was transferred from the aqueous phase to the particles. The propagating oligomeric radicals would provide preferential loci for the condensation of hydrophobic monomer, such as St, because of decreasing hydrophilicity. After the hydrophobicity of propagating oligomeric radicals reached a certain extent, they precipitated to form the nuclei. Obviously, this mechanism was proposed to explain why the composition of hydrophobic monomer was so high in the initial copolymer reported by Kawaguchi et al.^{26,27,31,32} and Chen and Chang.²³ However, if the condensation of St in the loci created by the hydrophilic oligomeric radicals really occurred, at that time the accumulated monomers surrounding the hydrophilic oligomeric radical must grow to form a monomer droplet, because the hydrophilic monomer should also condense even more rapidly due to the higher diffusion rate.

Quantitative Analysis

This experiment was designed to confirm quantitatively the phenomena observed above. Meanwhile, as suggested by the results of partition measurements, the transport of monomer was regarded as quite different depending on the presence of EA. The macroscopic mass transfer or the process of monomer transferring to the aqueous phase during the polymerization can be detected, because there was only one big monomer droplet (i.e., the oil phase existed in the quasi-static emulsion polymerization system).

Briefly, the results of the experiment with 8 wt % EA are shown as an example, because the pro-

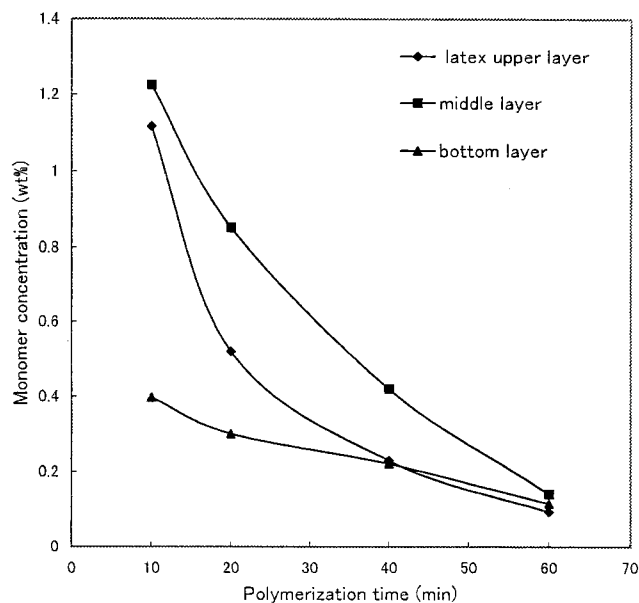


Figure 5 Variation of total concentration of 4VP and St in various layers of latex.

files obtained from adding various amounts of EA coincided with those shown in this article.

The variations of concentration and composition of comonomer in three layers of the latex phase (see Fig. 1) versus the polymerization time are shown in Figures 5 and 6, respectively. It clearly shows in Figure 5 that the concentration of comonomer in the upper layer of the latex rapidly decreased in the initial stage. Meanwhile, the concentration of comonomer in the bottom layer is lowest with a gradual decrease. The concentration of comonomer in the middle layer was the highest because of the increase of St, as shown in Figure 6. These results coincide with the scheme shown in Figure 4(a).

The polymerization occurred preferentially in the upper layer, and then the formed particles started to settle in the lower aqueous phase. The rapid decrease of monomer in the upper layer was due to the high polymerization rate and the settling of particles. The middle layer, obviously, acted as an accumulating hub for the species coming down from the upper layer and coming up from the bottom layer due to the convective flux. The most noticeable characteristic of the middle layer was that the concentration of St was very high, compared with the other layers. This implies that most of the species were transferred from the upper layer, because the concentration of St in the aqueous phase prior to the polymerization was very low. The droplets, originating from the disturbance of the interface of monomer/

water phase, contained a higher concentration of St. They moved down to the middle layer by convective flow, and St was accumulated because of the higher polymerization rate of 4VP. The species in the bottom layer were transferred from the middle layer. Therefore, the concentration of monomer was the lowest.

Other evidences to further support the above results are the variation of solid content and particle number during the polymerization. As shown in Figures 7 and 8, both the solid content and the particle number in the bottom layer were much higher than those in the other layers within the first 10 min. This means that the initial settling rate of particles was very fast because of the high rate of convection at the beginning of heating. After 10 min, as shown in Figure 8, the particle number in the bottom layer decreased until 40 min, during the polymerization. It implies that the settling rate from the middle layer decreased because of the decrease of convective flow, and the coagulation of particles occurred during this period. This was the reason that the quasi-static polymerization could not continue for a longer time. After 40 min, the particle number in the bottom layer dramatically increased again, obviously because of the settling of a great number of particles from the middle layer compensating for the formation of coagulum. On the other hand, the particle number of the upper layer shown in Figure 8 was almost constant after 10 min,

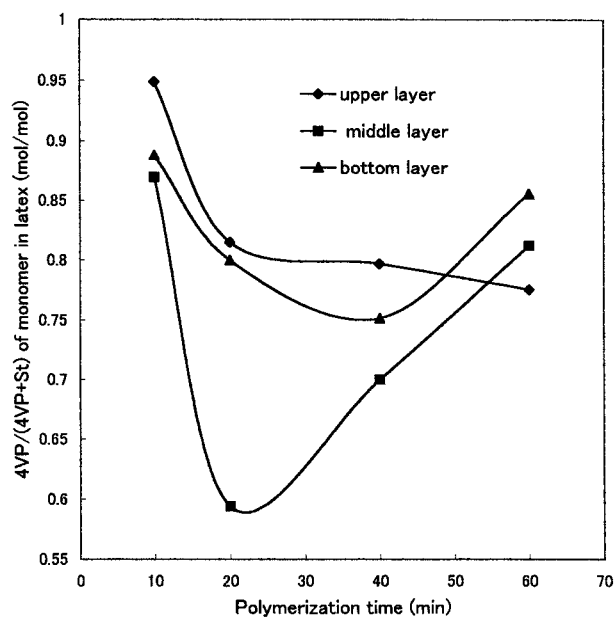


Figure 6 Variation of 4VP monomer molar fraction at various layers of latex.

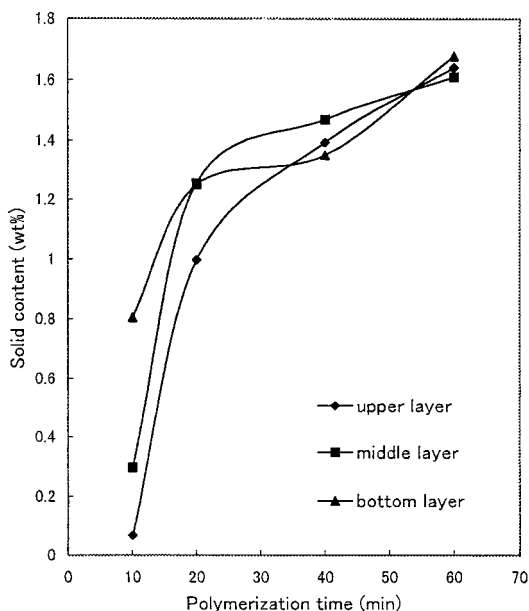


Figure 7 Solid content in various layers of latex versus polymerization time.

whereas the solid content shown in Figure 7 continuously increased. This indicated that the settling of particles from the upper layer gradually decreased because the driving force i.e., the convection flow disappeared. Moreover, it seemed that the generation of new particles in the upper layer also ceased. It should be recalled that the particle number generated in the quasi-static emulsion polymerization was on the order of $10^{14}/\text{L-Lx}$, which was on the same order as those prepared by mechanical agitation.^{31,32,37} The particle diameters were in the range of $0.30\text{--}0.55\ \mu\text{m}$ with 8% EA and $0.38\text{--}0.47\ \mu\text{m}$ without EA, respectively. The SEM micrographs of these particles are shown in Figure 9, where a kind of fuzzy morphology was found in the presence of EA. It was probably due to the etching effects of EA existing both in the particles and in the aqueous phase during the preparation of SEM samples.

The concentration of EA in the polymerization system was also determined as shown in Figure 10. It was found that the concentration of EA in the bottom layer was the lowest among the three layers up to 20 min after the polymerization started. This result possibly reflected the fact that EA was not a good solvent for copolymer with high 4VP content. It means that, in the droplets or growing particles with a high concentration of monomer, EA could exist in a considerable amount, but as the monomer was consumed, EA would probably be excluded from the particles,

because of the high fraction of 4VP in the initial polymer ($\sim 97\ \text{wt}\%$). Hence, in the first 10 min, the concentration of EA in the bottom layer stayed almost unchanged with that at the equilibrium prior to the polymerization (Table II), although a great number of particles had settled. After 10 min, the increase of EA in the bottom layer probably depended on the diffusion of EA from the aqueous phase of the middle layer in accordance with the partition relationship discussed above, because the monomer concentration in the aqueous phase of bottom layer was very low. The increase of EA in the aqueous phase of the bottom layer may be related to the coagulation of particles in this layer (Fig. 8), because the permittivity of the aqueous phase decreases with the increase of EA.^{2,6}

The variation of concentration of EA in the upper and middle layer was complicated because of the existence of monomer both in the particles and in the aqueous phase. However, compared to the solubility of EA shown in Table II, the higher concentration of EA in these layers implies that most of the EA existed in the particles because of the higher concentration of monomer in the initial stage. This was probably the reason for the decrease of molecular weight with the increase of EA, resulting in the reaction of chain transfer in the polymerization system.² The decrease in concentration of EA, as the polymerization progressed, indicated that EA tended to attain equilibrium solubility in the aqueous phase when the monomer was consumed.

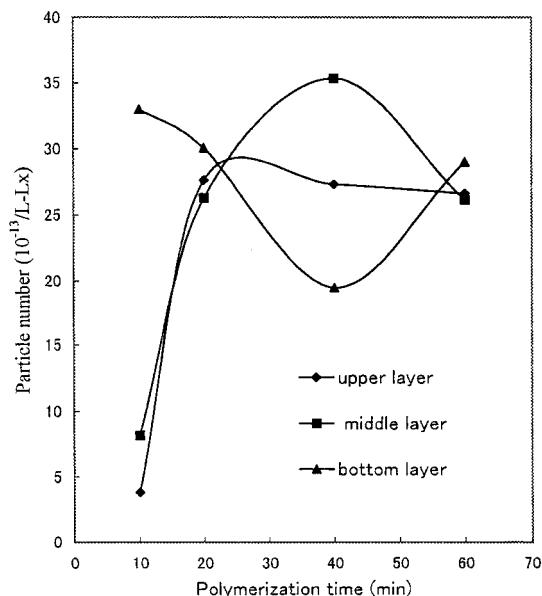
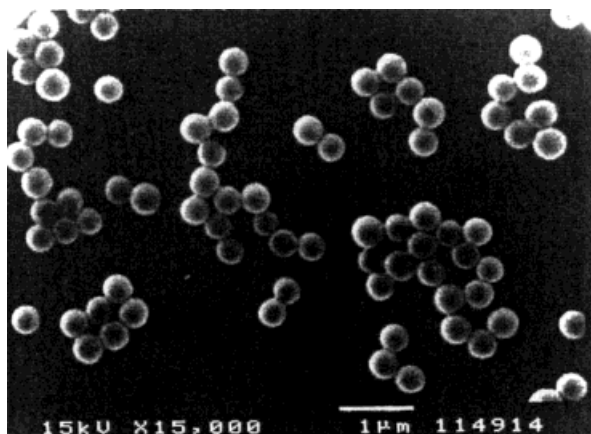
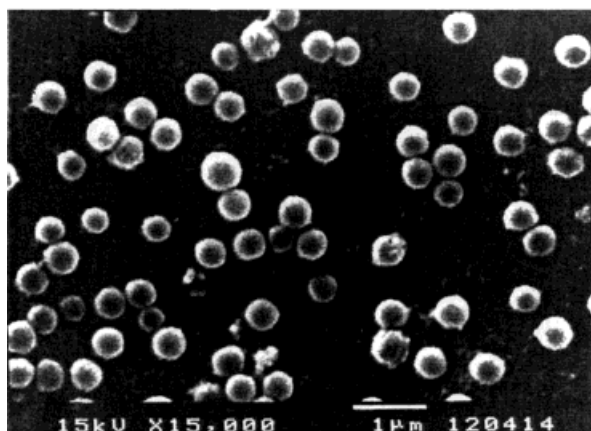


Figure 8 Particle number in various layers of latex versus polymerization time.



No EA, 60min, Conversion: ca 21wt%



8wt% EA, 60min, Conversion: ca 16wt%

Figure 9 Micrographs of particles prepared by quasi-static emulsion polymerization.

The process of monomer transport promoted by the concentration gradient of monomer was not a major factor in this experiment. Furthermore, the expected apparent decrease of the volume of monomer phase, resulting from the monomer diffusion, was not observed yet, even though this polymerization was continued for 3 days in the 70°C water bath (latex coagulated). Instead, a film was formed at the interface of monomer/latex phases. It was readily understood that, without agitation, the oligomeric radicals formed in the aqueous phase were absorbed by the monomer droplets and propagated onto the surface of monomer droplets to form a film. This reaction was considered one of the reasons for the coagulum build-up in practical emulsion polymerization.^{3,4,5} Therefore, a reasonable deduction should be that the interface of the monomer droplet/aqueous

phase must be dynamic for successful emulsion polymerization; namely, the surface of droplets must be continuously renewed by the shear force and/or collision with particles resulting from the agitation. What would happen while renewing the surface of droplets in a polymerization system with mechanical agitation is illustrated in Figure 4(b).

CONCLUSION

The solubility of 4VP and St in water decreased, as the amount of EA increased, in the soap-free emulsion polymerization system. Meanwhile, most of the added EA partitioned in the oil phase, even in cases where the charged amount of EA was much lower than the solubility of EA in water at ambient. The solubility of EA in water was also affected by the composition of 4VP and St (i.e., it increased as the fraction of 4VP increased, but decreased as the fraction of St increased).

These phenomena, as well as the quantitative analysis of the quasi-static emulsion polymerization, indicated that the initial reaction in the soap-free emulsion polymerization was closely related to disturbance of the interface of monomer/water phase, thereby the generated droplets of monomer. Therefore, a new proposal is given for the nucleation reaction of soap-free emulsion polymerization. Namely, the nucleation occurs in

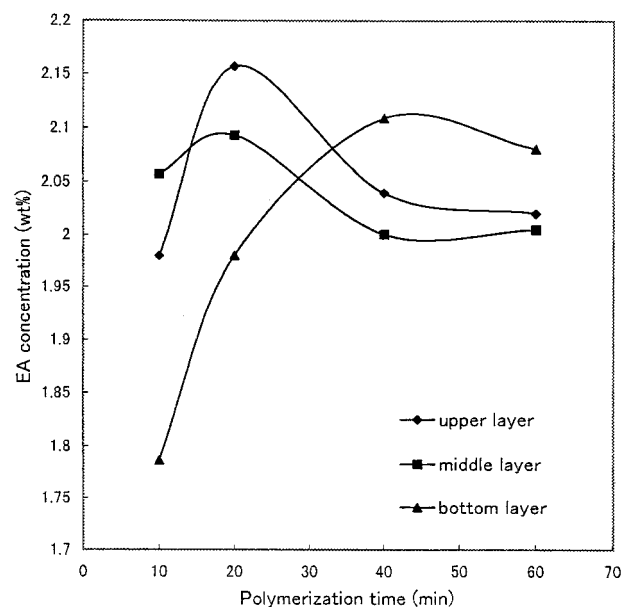
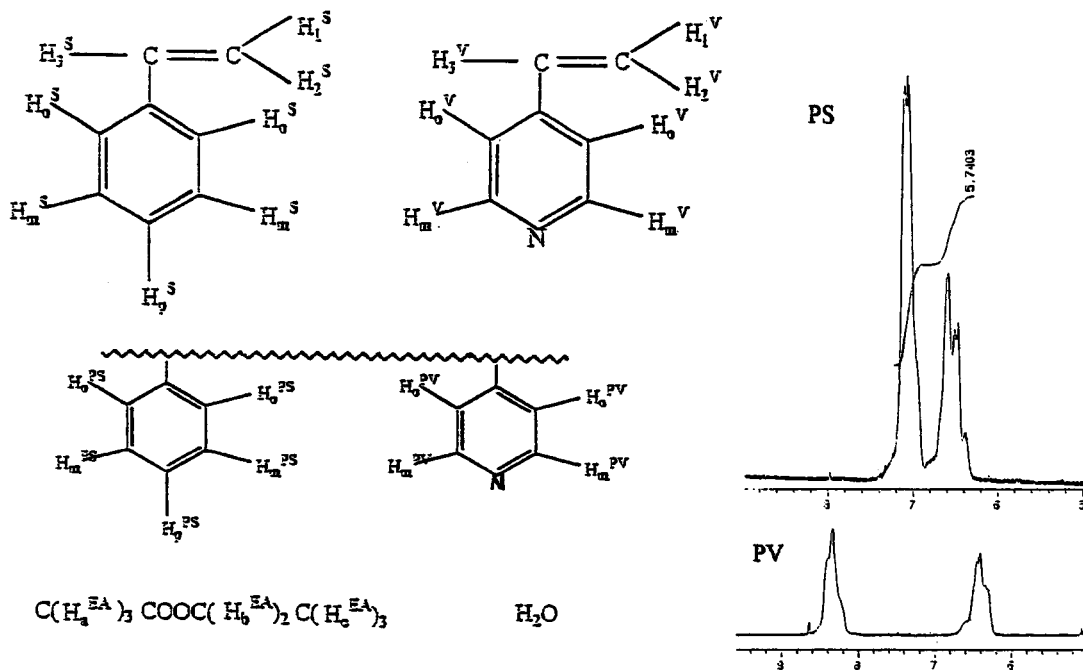


Figure 10 Concentration of EA in various layers of latex versus polymerization time.

Molecular Structure



RUN1204 SAMPLING, 200gram, 50min, SE4 MG, 120423

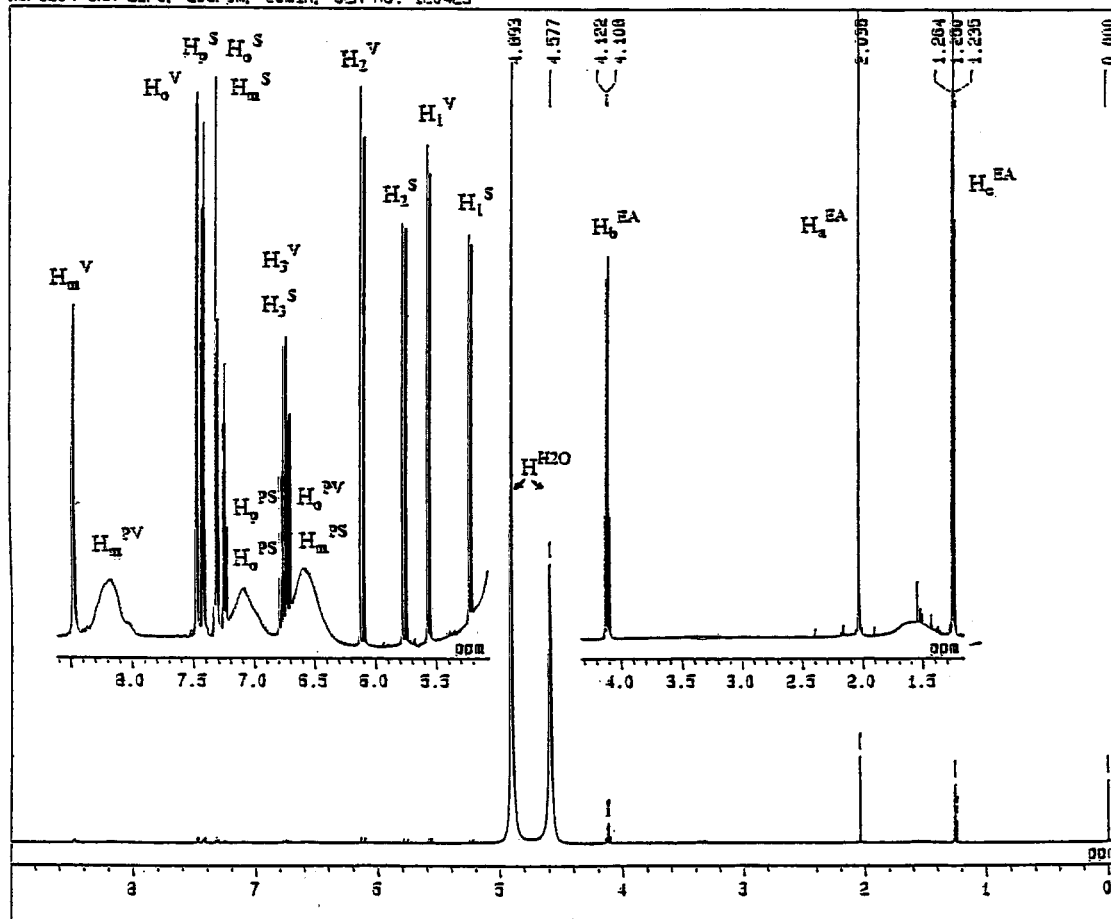


Figure A.1 Typical ¹H-NMR spectrum and the assignment of peaks.

Table A.I Comparison of Data Derived from NMR and Gravimetry

Specimen ^a (Run 1204, 100 rpm)	NMR (Solid Content, wt %)	Gravimetry (Solid Content, wt %)
90 min	3.56	3.67
120 min	4.65	4.53
240 min	5.90	5.72
Initiator, V50 ^b	5.25, 5.46, 5.87	5.56

^a Specimens sampled during the polymerization at different time (for details see ref. 37).

^b Aqueous solution prepared with gravimetry.

the droplets. The droplets absorb the oligomeric radicals generated in the aqueous phase to continue the polymerization. The oligomer meanwhile acts as emulsifier molecules promoting the colloidal stability of droplets by decreasing the interfacial tension of monomer droplets.

APPENDIX

The typical ¹H-NMR spectrum and assignment of peaks are shown in Figure A.1.

The area of peak was calculated automatically by the machine because the peaks used, as shown in Figure A.1, were isolated from each other.

For example, the average molar composition of the copolymer, $x_{4VP/St}$, was calculated as

$$x_{4VP/St} = \frac{\frac{1}{2}A_{\delta=8.3 \text{ ppm}}}{\frac{1}{3}A_{\delta=7.1 \text{ ppm}}}$$

where $A_{\delta=8.3 \text{ ppm}}$ is the integrated area of peak at the chemical shift ~ 8.3 ppm, which was considered to be the contribution of two ¹H adjacent to the N atom in the pyridine ring. $A_{\delta=7.1 \text{ ppm}}$ is the integrated area of peak at ~ 7.1 ppm contributed by the three ¹H (*para*- and *ortho*-) of the benzene ring.

The solid content of latex, wt %, was calculated as

$$\begin{aligned} \sum Wt &= M_v A_{\delta=8.3} + M_s A_{\delta=7.1} \frac{2}{3} + M_w A_{\delta=4.9-5.0} \\ &\quad + M_v 2A_{\delta=6.2} + M_s 2A_{\delta=5.8} + M_e A_{\delta=4.4} \\ \text{wt \%} &= \frac{M_v A_{\delta=8.3} + M_s A_{\delta=7.1} \frac{2}{3}}{\sum Wt} \times 100\% \end{aligned}$$

where the constants of M_v , M_s , M_w , and M_e are the molecular weights of 4VP, St, water, and EA,

respectively. The results of calculation were made to three significant figures because the difference of integrated areas of the equivalent peaks, such as $A_{\delta=6.2 \text{ ppm}}$ and $A_{\delta=5.6 \text{ ppm}}$, usually started from the third figure.

However, two cases were confronted in practice. Case one was that the specimen, generally in the beginning of polymerization, was soluble in CD₃OD. In this case, the concentration of monomer, solid content, and composition of monomer and (co)polymer were calculated via one NMR spectrum. Case two was that the specimen was insoluble in CD₃OD when the content of St in polymer reached a certain level. In this case, the concentration and composition of monomers as well as the concentration of EA were derived by the same method as Case one, although an error was unavoidable, resulting from the insoluble polymer. However, this error was negligible, because the total solid content of polymerization system was just 10 wt %, and the maximum error was estimated to be lower than 5%.

In Case two, deuterated chloroform (CDCl₃) was used to dissolve the dried latex, and then the composition of copolymer was calculated. Meanwhile, the conversions were determined by gravimetry.

Because two different methods were used in Case two (i.e., NMR and gravimetry) to determine the conversion of monomer, it was necessary to investigate if the data derived from the two methods were comparable with each other. Table A.I shows the results derived from the two methods. It was found that the data agreed well.

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