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

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ABSTRACT: The properties and morphologies of poly(4-vinylpyridine-*co*-styrene) [P(4VP/St)] lattices, prepared by soap-free emulsion polymerization using the water-soluble initiator 2,2′-azobis(2-amidinopropane) · 2HCl (V50), were greatly affected by the addition of ethyl acetate (EA). The properties and morphologies of the resultant lattices were characterized by measuring the zeta potential, viscosity average molecular weight, particle size and distribution, glass-transition temperature (T_g), and photographs taken by SEM and TEM. The effects of two kinds of monomer feeding modes, that is, the batch and semicontinuous emulsion copolymerization, were also investigated. For batch emulsion copolymerization, by charging EA, the core–shell morphology resulting from the disparate reactivity ratios of the 4VP(1)/St(2) copolymerization system ($r_1 = 1.04$, $r_2 = -0.73$) disappeared. Instead, first a bimodal particle size distribution, with an apparently asymmetric composition structure, and then spherical microspheres were obtained as the amount of EA charged increased from 2 to 10 wt %. The particle size increased twofold by the addition of EA. The zeta potential of particles increased from +64.4 to more than +100 mV, and viscosity average molecular weight decreased from 9.70 to 0.97 × 10⁵ g/mol, as EA increased from 0 to 8 wt %. With the semicontinuous copolymerization, raspberry-like particles were obtained by charging 10 wt % EA, whereas a sandwich-like morphology was obtained without EA. The DSC curves showed one T_g for all the lattices prepared with charging EA, but two T_g's for the latex prepared without using EA, regardless of the monomer feeding modes. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 80: 1988–2001, 2001

Key words: poly(4-vinylpyridine-*co*-styrene); ethyl acetate; disparate reactivity ratio; soap-free emulsion polymerization; zeta potential; morphology

INTRODUCTION

Recent research in our laboratory has been devoted to the control of the morphologies of composite lattices and to use these techniques for practical applications.[1–4] The method of adding

solvents into the polymerization system has been employed both for fundamental studies and applications. For example, hexane was used not only to study the kinetics of the morphology development of PSt/PMMA but also to prepare hollow particles of PSt. Ethyl acetate (EA) has been used as an effective agent to promote the solid content of poly(4-vinylpyridine-*co*-*n*-butyl acrylate) [P(4VP/nBA)] latex to as high as 10 wt %. Unless EA is added, less than 5 wt % of solid content can be

obtained with conventional soap-free emulsion polymerization.[1]

In this study the use of ethyl acetate is discussed, because there are two obvious characteristics of this polymerization system. The first is that, at low concentration, the charged ethyl acetate was considered to be completely soluble in water to lower the polarity of the continuous phase of soap-free emulsion polymerization. Ethyl acetate altered the properties of the continuous phase, rather than (as with conventional additives) acting as a modifier in the production of particles. The second is that the copolymerization reactivity ratios are disparate, that is, for 4VP(1)/nBA(2) $r_1 = 4.3$, $r_2 = 0.23$. These disparate reactivity ratios mean that radicals with either 4VP or nBA chain ends will both add 4VP preferentially to form a 4VP-rich copolymer until 4VP is depleted, after which an nBA-rich copolymer or P(nBA) will be formed. Thus, at all 4VP/nBA ratios, the copolymerization will form a distribution of copolymer compositions comprising a 4VP-rich fraction and an nBA-rich or P(nBA) fraction.

It has been common knowledge in the field of emulsion polymerization that the copolymer composition of such a copolymerization system can be changed by varying the monomer feeding modes.[5–9] Core–shell morphology will be formed by the batch emulsion polymerization, and homogenous copolymer composition can be obtained by employing the semicontinuous emulsion copolymerization, such as power feed[5] and starved monomer feed.[6] In these aspects, Fitch[7] has given a comprehensive review of the experimental results and mechanisms. Furthermore, the quantitative relationship of the monomer feeding rate to the desired copolymer composition, which depends on the copolymerization reactivity ratios, can be solved by employing computer modeling and mathematical simulation.[8,9] As an example, for the vinyl acetate [VAc(1)/butyl acrylate (BuA(2)] copolymerization system, where $r_1 = 0.04$ and $r_2 = 5.5$, even when the initial molar ratio of VAc/BuA is as high as 6/1, it can be predicted[9] that, with batch emulsion copolymerization, copolymers with the same composition ratio as that of monomers cannot be obtained. Only in cases where the monomer feeding rate is controlled to be close to 0 with starved monomer feed, or where the VAc feeding rate is sixfold faster than that of the BuA with a very slow controlled feed, can copolymers with the same composition ratio as that of monomers be obtained.

However, these phenomena seemed not to occur in our previous P(4VP/nBA) batch copolymerization system, where the continuous phase, a mixture of ethyl acetate and water, was different from that of conventional emulsion copolymerization systems.[1] For example, the particle morphology, that is, the phase separation resulting from the inhomogeneous copolymer composition, changed depending on the amount of EA added to the continuous phase. Therefore, it is necessary to study further the effects of ethyl acetate on the soap-free emulsion copolymerization containing an intensively hydrophilic monomer, especially on the emulsion copolymerization with disparate reactivity ratios.

The 4-vinylpyridine/styrene (4VP/St) soap-free copolymerization system was chosen in this work. The reasons for choosing this system are that, first, the system has an extreme disparity of copolymerization reactivity ratios, that is, $r_1 = 1.04$ and $r_2 = -0.73$ [4VP(1)/St(2)].[10] This means that it seems to be highly improbable for polymeric active chains with styrene ends to add styrene molecules. Hence, a homogeneous copolymer composition is unlikely to be obtained, even by the semicontinuous emulsion copolymerization, in which the feed rate and the composition of monomer are carefully selected, in accordance with the prediction of the copolymerization time scale.[9] The second reason is that it has been concluded that the copolymerization reactivity ratios are not affected by the addition of solvent.[11]

EXPERIMENTAL

Materials

Monomers 4-vinylpyridine (4VP) and styrene (St), water-soluble crosslinker ethylene glycol dimethacrylate (EGDMA), oil-soluble crosslinker divinylbenzene (DVB), and solvent ethyl acetate (EA) were purchased from Kishida Chemical Industries (Japan). Water-soluble initiator 2,2′-azobis(2-amidinopropane) · 2HCl (V50) was from Wako Pure Chemicals (Tokyo, Japan). Ethyl acetate (EA) was distilled under atmosphere. 4VP and St were distilled under reduced pressure. EGDMA and DVB were washed with 5% alkaline solution and water, and dried with 4-Å molecular sieves. The initiator V50 was used without further purification.

Water used in all experiments was distilled and deionized (DDI), with a conductivity of 18 MΩ

Table I Typical Recipes of the Soap-Free Emulsion Polymerization of Poly(4-vinyl pyridine/styrene) by Charging Ethyl Acetate into the Continuous Phase

Monomers (wt %)[a]		Ethyl Acetate[b] (wt %)	Initiator V50[c] (wt %)	Water[d] (wt %)
4VP	Styrene			
5	5	0 ∼ 10	2	Variable

[a] Based on the total amount of the resultant latex.
[b] Based on the total amount of the continuous phase.
[c] 2,2′-Azobis(2-amidinopropane) · HCl, based on the amount of monomers.
[d] The amount to maintain the solid content of the resultant latex at 10 wt %.

cm^{-1}, by employing a Milli-Q water purification system (Millipore, Bedford, MA).

Preparation of P4VP/St Latex

P4VP/St latex was synthesized by radical soap-free emulsion polymerization. A standard recipe for polymerization is shown in Table I. Two kinds of apparatus were applied to the polymerization, that is, using a vacuum-sealed ampoule to do the batch emulsion copolymerization and using a separator glass flask with agitator to do the semicontinuous emulsion copolymerization.

For use of the ampoule, a 15-g mixture of ingredients was charged in a 30-ml ampoule and the dissolved oxygen was removed by the freeze/thaw method with liquid nitrogen as a coolant. The heat-sealed ampoule was then fastened to a tumbling device set in a thermostat. The thermostat was heated to the required temperature before the tumbling device was started. The tumbling rate was about 20 rpm.

The semicontinuous emulsion copolymerization was performed in a 500-ml flask, equipped with a stirrer, reflux condenser, dropping funnel, and a nitrogen inlet. The flask was immersed in a thermostat. The monomer mixture was added dropwise into the preheated reaction mixture at a rate of 0.09 g/min. Nitrogen purging was started with the charge of ingredients into the flask and continued to the end of polymerization.

All of the polymerizations were carried out at 70°C for 14 h.

Characterization of Microspheres

The conversion of the monomer was determined by gravimetry, that is, a known amount of latex was dried and weighed. The size and shape of dry microspheres were observed by scanning electron microscopy (SEM; JEOL JSM-5310; JEOL, Peabody, MA) 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 (JFC 1200 Finecoater; JEOL). The particle size was determined by direct measurement of 200 particles/sample on a SEM photo. The ultrathin cross section of a TEM specimen was prepared as follows (MT-7000, Microtome, RMC Inc., Japan): the vacuum-dried latex was embedded in epoxy resin and sliced after the epoxy resin solidified. The thin chips were put on a copper mesh covered with a thin collodion film coated with carbon and then, after drying, were stained with CH_3I vapor in a closed bottle for 3 or 4 days at room temperature.

The latex was diluted with about 500 vol % of DDI water for measurement of zeta potential. The zeta potential was determined by direct measurement of the electrophoretic rate of particles in a 45-V direct-current field and automatically calculated by the equipment (Microtech Nichion, Sony Zeecom, Japan).

The differential scanning calorimeter (DSC; MAC Science DSC-3100, Japan) was used to measure the glass-transition temperature (T_g) of copolymer. The heating rate was 10°C/min and the cooling temperature rate was 20°C/min. The second scanning curve is shown in this study.

To determine the effects of EA on the zeta potential, the latex was dialyzed with DDI water (pH about 6.7) for 3 days, during which treatment water was exchanged three times. The dialyzed latex was diluted to about 20 vol % with the solution of EA/DDI water, and then placed for the required time at room temperature, or heated while being agitated to the required temperature. The other zeta potentials were measured by using the initial latex after dilution without any treatment.

Because there is no proper viscosity constant for the Mark–Houwink–Sakurada equation applicable for the P(4VP/St) copolymer, the molecular weight of the copolymer was estimated by the following equation, which was recommended for pure P4VP.[10] The intrinsic viscosity was determined in 2-butanone/2-isopropanol (6/1 v/v) at 25°C using a Ubbelohde viscometer.

$$[\eta] = 38 \times 10^{-3} \, M^{0.57} \, (mL/g)$$

Table II   Properties of Latex Prepared by Adding Different Amounts of EA

Run	EA[a] (wt %)	Conversion (%)	Diameter (μm)	M_n ($\times 10^{-5}$ g/mol)	ζ Potential (mV)
1149	0	94.7	0.47	9.70	64.4
1202	2	99.6	0.46, 0.97	3.69	75.4
1203	5	96.5	0.93	1.18	95.7
1204	8	97.3	1.05	0.97	>100
1192	10	90.7	1.03	1.04	89.4

[a] Based on the total amount of the continuous phase.

RESULTS AND DISCUSSION

Batch Soap-Free Emulsion Polymerization of P(4VP/St)

Effect of EA on the Properties of Latex

The latex was prepared with an ampoule in the batch polymerization mode. Because the solubility of EA in water is 1 ml/10 ml water (about 8.3 wt %) at 25°C, and less at higher temperatures[12] [an azeotropic mixture with water (6.1 wt %) forms with bp = 70.4°C; therefore, the solubility of EA at the polymerization temperature of 70°C is considered to be in the range from 8.3 to 6.1 wt %], the amount of charged EA was selected as 0, 2, 5, 8, and 10 wt % based on the total amount of the continuous phase. The properties of the resultant lattices are shown in Table II.

Table II shows that the particle size, viscosity-average molecular weight, and zeta potential were considerably affected by the addition of EA. The particle diameter and zeta potential increased, and the viscosity-average molecular weight considerably decreased as the amount of EA increased from 0 to 8 wt %. An exception is the run 1192 sample, for which the particle diameter and zeta potential did not follow the trend of the others.

The obvious and likely primary reason for the variation of zeta potential should be the variation of the surface copolymer composition with EA added. The increase of styrene units in the copolymer would tend to decrease the copolymer chains that are soluble in the continuous phase, and in turn to reduce or collapse the hairy layer on the surface of particles.[13–15] Therefore, the zeta potential increased with the increase of EA. The second reason was considered to be the result of the decrease of permittivity of the continuous phase resulting from the addition of EA. This factor probably contributed to the decrease of zeta

potential when the amount of EA exceeded 8 wt %, the solubility of EA in water. The permittivity of the inner layer of the electrical double layer was considerably decreased by the absorption of the excess EA on the particle surface. Therefore, the effective potential around the particle was decreased.

The formation of a more homogeneous copolymer composition with the addition of EA was confirmed by the morphologies, as shown in the next section. For this section, we were interested in whether the addition of EA (i.e., the decrease of permittivity of the continuous phase) could reduce, or even collapse, the hairy layer that resulted from the dissolution of the hydrophilic P4VP moieties on the surface of P(4VP/St).

It is well known[16] that a maximum appears in the electrophoretic mobility at a certain electrolyte concentration instead of the expected continuous decrease in mobility or in zeta potential with increasing electrolyte concentration. One of the more acceptable mechanisms that explains this anomalous behavior, albeit qualitatively, is the "hairy layer" model.[13–15] This model postulates that on the surface of a particle is a layer of flexible polymer chains with terminal ionic groups. These chains are extended into the distant continuous phase, which varies depending on the electrolyte concentration. At low electrolyte concentration, the extended chains reduce the electrophoretic mobility by displacing the slipping plane farther than in the case where all the charges were on the particle surface. This shifting allows an increase of the surface conduction inside the slipping plane and thus a decrease of zeta potential. As the electrolyte concentration increases, the chains collapse over the surface and the distance between the slipping plane and the bare surface of particle is reduced. The reduction in that distance could also yield a diminution of the surface conductance, and then the mobility

increases. At higher concentrations, classical behavior is observed, because the electrical double-layer compression provokes the complete collapse of the chains over the surface. Based on this model, some authors[17–19] suggested that heating the latex above the T_g of polymer should collapse the hairy layer and, consequently, increase the mobility and zeta potential of particle. This assumption has been confirmed by their experiments.

In this study, the reduction or collapse of the hairy layer was considered to be the result of the decrease of the permittivity of the continuous phase: adding EA will decrease both the permittivity of the continuous phase and the solubility of P4VP in the continuous phase, thereby reducing or collapsing the hairy layer of the P(4VP/St) particles. Also in apparent support of this assumption was that the thickness of the electrical double layer $1/\kappa$ can be written as[20]

$$\frac{1}{\kappa} = \left(\frac{\varepsilon_r \varepsilon_0 kT}{N_A e^2 I} \right)^{1/2}$$

where ε_r is the permittivity of the continuous phase, ε_0 is the permittivity of the free space, I is the ionic strength of electrolyte solution, e is the fundamental unit of electricity, N_A is the Avogadro number, k is the Boltzmann constant, and T is the absolute temperature. Therefore, in this case, if the total ε_r of the continuous phase can be considered as a sum of the volume fraction permittivity of EA and water, the effect of adding EA to the electrical double layer can be estimated with this expression. To obtain the same reduction of the thickness of the electrical double layer at 20°C, the effect of changing ε_r of the continuous phase, with adding EA from 2 to 8 wt %, is nearly equivalent to that of increasing the ionic strength from $1.36I_0$ to $1.96I_0$, where I_0 is the initial ionic strength. This indicates that the addition of EA was powerful enough to compress the hairy layer.

Therefore, several experiments were carried out to detect whether the hairy layer was compressed by the addition of EA and then, if compressed, to what extent. The latex of run 1149 was selected as a sample for these experiments. The reason was that, if it was prepared without using EA, the hairy layer on the particles' surface should not be collapsed by heating during the emulsion polymerization, because the polymerization temperature 70°C was much lower than the T_g of P4VP, 142°C. However, the morphology

of particles formed, as shown in the next section, is a core–shell structure. It should be essential to shorten the time the particles stayed in the EA solution, to avoid EA molecules diffusing into the core, and then changing the diameter of particles by swelling. This was why the following measurements were carried out in relatively short time intervals, generally less than 4 h.

The first experiments were carried out at room temperature to verify whether the addition of EA could compress the hairy layer. If the hairy layer was compressed or perturbed, it should be expected that there must be some macroscopic responses, such as to the electrophoretic mobility and zeta potential. Briefly, the weighed latex of run 1149 was dropped into a bottle containing a solution with a certain concentration of EA. It was stirred for only 30 min, which was considered as the pretreating time, so as to keep as low as possible the effects arising from the EA absorbed in the particles. After the pretreatment, the latex was diluted again with DDI water as quickly as possible. The zeta potential of the diluted latex and the variation with the elapsed time were measured. In these cases, because the latex was diluted to about 1000 vol % with DDI water, the amount of EA in the measured system was less than 10^{-4} (v/v). It was considered to have a negligible effect on the permittivity of the solution in the zeta potential cell. Moreover, the ionic strength was the same for all samples and remained unchanged during the measurement.

Figure 1 shows the results. The variation of zeta potential with the initial concentration of EA seemed irregular, that is, the zeta potentials of 5 and 10 wt % EA were generally lower than that of the others. However, with elapsed time, it can be seen that the zeta potential of the treated samples, although somewhat fluctuating, converged to a constant, about +40 mV, except for that of the sample of 10 wt % EA, which settled to about −30 mV, after 5 h. The zeta potential of the nonpretreated sample (0 wt % EA) slowly and smoothly decreased from +64.2 to +40.6 mV, probably resulting from the gradual expansion of the hairy layer in the water. Because the pretreating time was only 30 min, the fluctuation of zeta potential was considered to be because the hairy layer was not likely to be fully deflated to its limit after being compressed by the EA solution. Therefore, as the compression force was relieved, when the particle was resuspended in water or extremely dilute EA solution, the hairy layer, behaving like a compressed elastomer, fluctuated
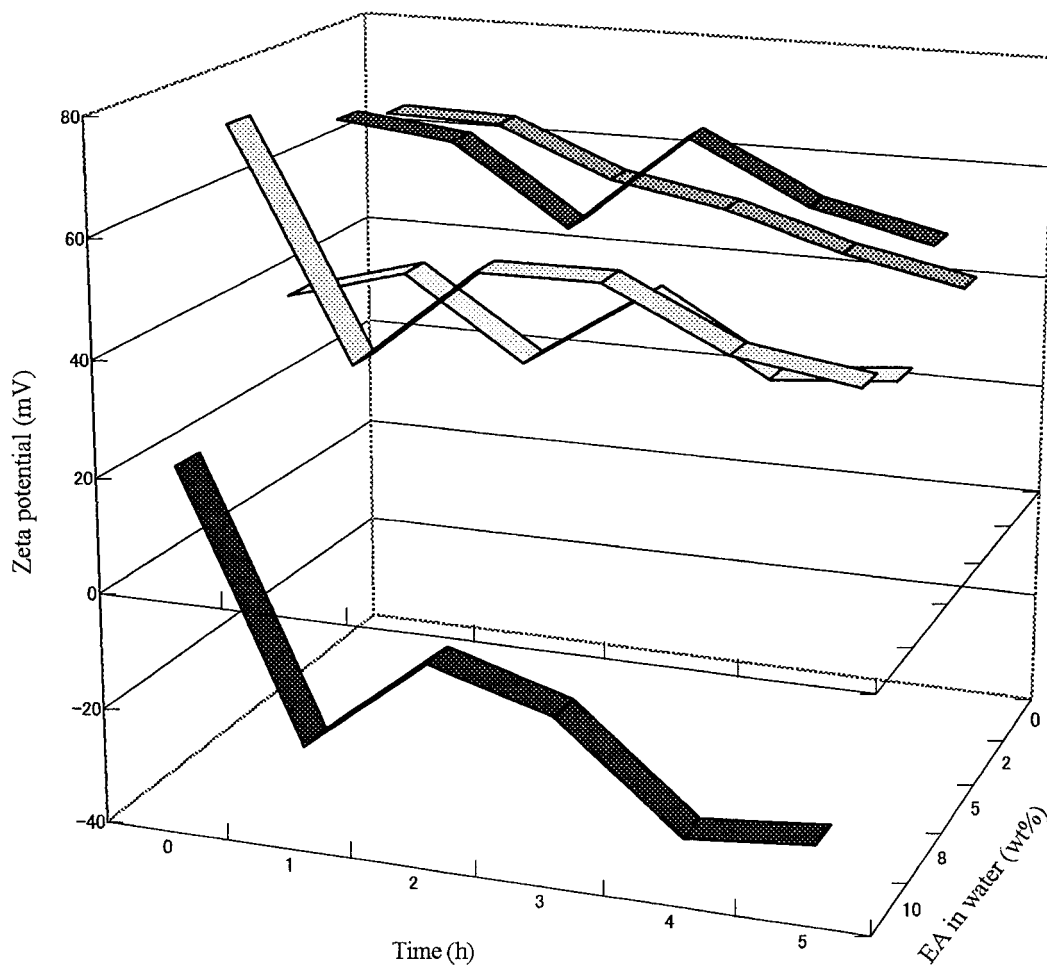
Figure 1 Zeta potentials versus time of run 1149 in water after treatment by EA/water solution.

and gradually expanded again because of the P4VP polymer chains reextending in the water. This was considered to be the reason for the fluctuation of zeta potential. The intensity of fluctuation reflected the compression degree of the hairy layer, which increased as the concentration of EA in the treating solution increased. When the EA concentration was set at 10 wt %, the hairy layer seemed to be compressed so tight that the slipping plane was repelled too far away from the bare surface of particles, where the potential is dominated by the counter-ions. Therefore, the zeta potential became minus with the elapsed time.

To measure to what extent the variant EA solution can compress the hairy layer, the initial latex of run 1149 was diluted with different concentrations of EA solution at room temperature. The zeta potentials of these lattices were measured at certain time intervals, the results of

which are shown in Figure 2. It was observed that the zeta potential increased with time up to 3 h and then stayed at a constant value. Moreover, the constant zeta potential increased as the amount of EA increased up to the solubility level of EA in water (about 8 wt %), then slightly decreased. This implies that the hairy layer attained a new equilibrium after being compressed for 3 h by the EA solution. In this case, it clearly shows that, the higher the concentration, the tighter the hairy layer was compressed to the bare surface; therefore, a higher zeta potential was obtained. The decrease of zeta potential of the sample treated with 10 wt % EA was probably the result of the absorption of the excess EA in the particle surface, hence, the effective potential around the bare surface was decreased because of the lower permittivity of EA.

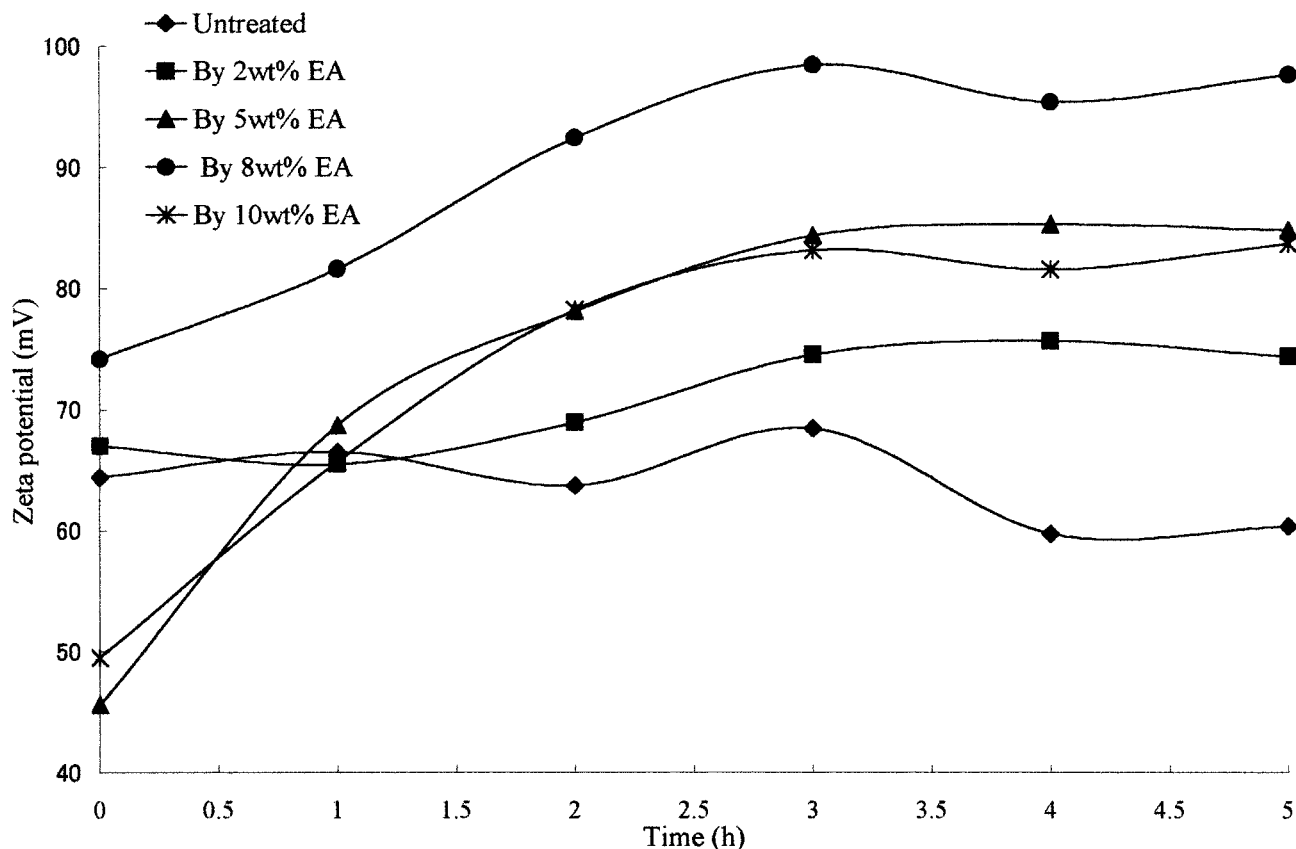In addition those samples, for which the zeta potential attained a constant value, were contin-

Figure 2 Zeta potentials versus time of run 1149 in EA/water solution.

uously heated at 70°C for 3 h. After the heat treatment, the zeta potentials of all the samples remained unchanged, except for that of the untreated sample (0 wt % EA), which slightly increased from +64.2 to +74.2 mV. This implies that the hairy layer was probably not compressed further by heating. On the other hand, it should be expected that the decrease of zeta potentials with the elapsed time in water, as shown in Figure 1, should also take place for the particles in which the hairy layer was collapsed, because of the diffusion of the hydrophilic moieties, P4VP, in the particles' surface. However, this phenomenon was not observed, at least in an interval of 4 h, by using the samples treated with the EA solution for 4 h, which was probably related to the complete collapse of the hairy layer over the surface.

Certainly, situations in practical polymerization systems could be more complicated than those observed in these experiments, such as that the permittivity of the continuous phase also increases with the depletion of the dissolved monomer and the particle size changes as the polymerization progresses. Nevertheless, it can be con-

cluded that the decrease of permittivity in the continuous phase, resulting from the addition of EA, was at least part of the reason for the increase of zeta potential of particles, through compressing or collapsing the hairy layer during emulsion polymerization. It was probably the result of the collapse of the hairy layer, thereby reducing the bridging coagulation of particles resulting from the poly(4-vinylpyridine) hairy layer,[20] that the solid content of poly(4-vinylpyridine-co-n-butylacrylate) latex was successfully promoted from less than 5 to 10 wt % by the addition of EA in the continuous phase.[1]

The increase of particle size with the increase of EA seemed to contradict the results of the increase of zeta potential discussed earlier, provided that it took place in a conventional soap-free emulsion polymerization system. We considered that it was probably related to the following two factors. The first factor was the formation of a more homogeneous copolymer composition because of the addition of EA in the continuous phase, that is, the hydrophobicity of copolymer chains increased as the number of styrene units
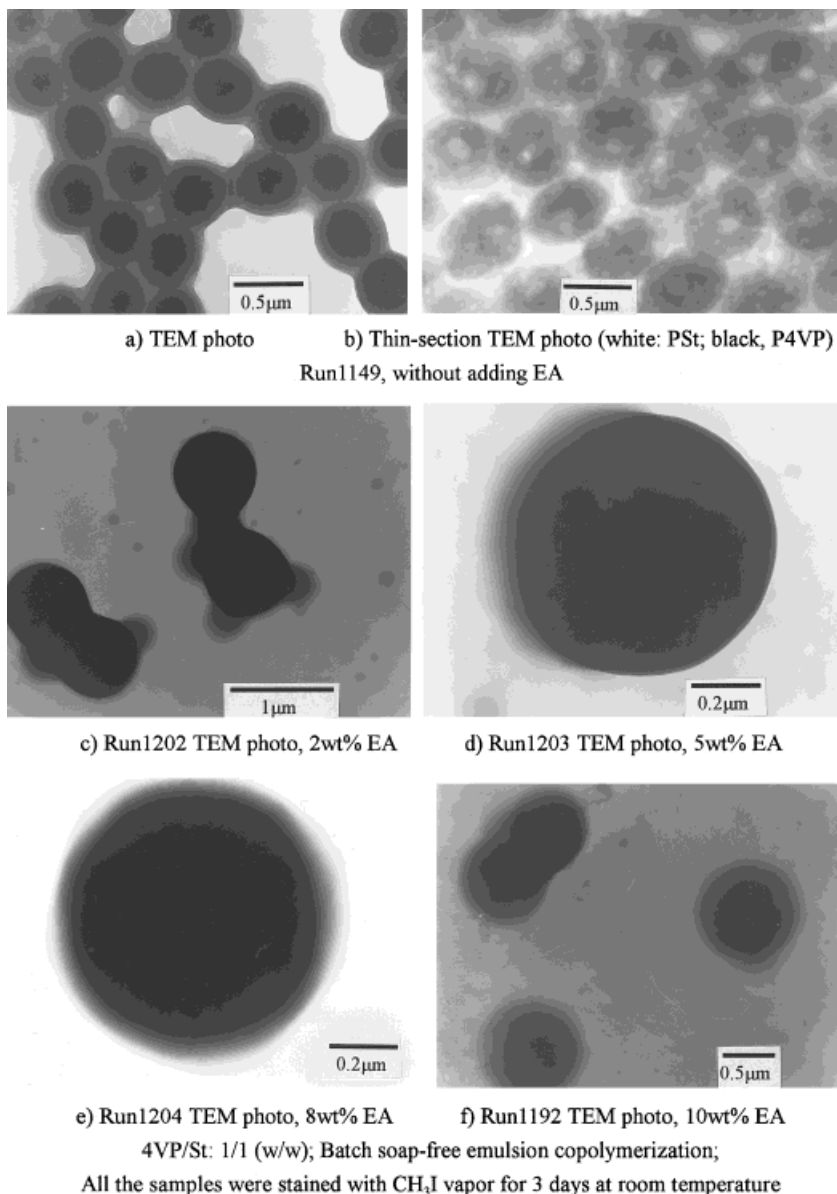
a) TEM photo b) Thin-section TEM photo (white: PSt; black, P4VP)

Run1149, without adding EA

c) Run1202 TEM photo, 2wt% EA d) Run1203 TEM photo, 5wt% EA

e) Run1204 TEM photo, 8wt% EA f) Run1192 TEM photo, 10wt% EA

4VP/St: 1/1 (w/w); Batch soap-free emulsion copolymerization;

All the samples were stained with CH$_3$I vapor for 3 days at room temperature

Figure 3 TEM photographs of latex by batch emulsion polymerization with charging varying amounts of EA.

increased. Therefore, the interfacial tension between the continuous phase and the particles increased, and tended to coagulate to form bigger particles so as to decrease the interfacial tension. The second factor is that the electrostatic repulsion force between the particles decreased as the permittivity of the continuous phase decreased. As for the decrease of molecular weight, it was possibly because of the increase of particle size and the chain transfer behavior of EA in the particles, as the amount of EA increased.

Effect of EA on the Morphologies of Particles

The TEM photographs of the preceding samples are shown in Figure 3. As shown in Figure 3(a) and (b), core–shell morphology was obtained in the absence of EA. However, when EA was added into the polymerization system, it was found that the core–shell structure disappeared. When 2 wt % of EA was added, two kinds of particles were obtained, as shown in Figure 3(c). One was small and less colored, and the other was bigger and darker. When 5 wt % EA was added, as shown in
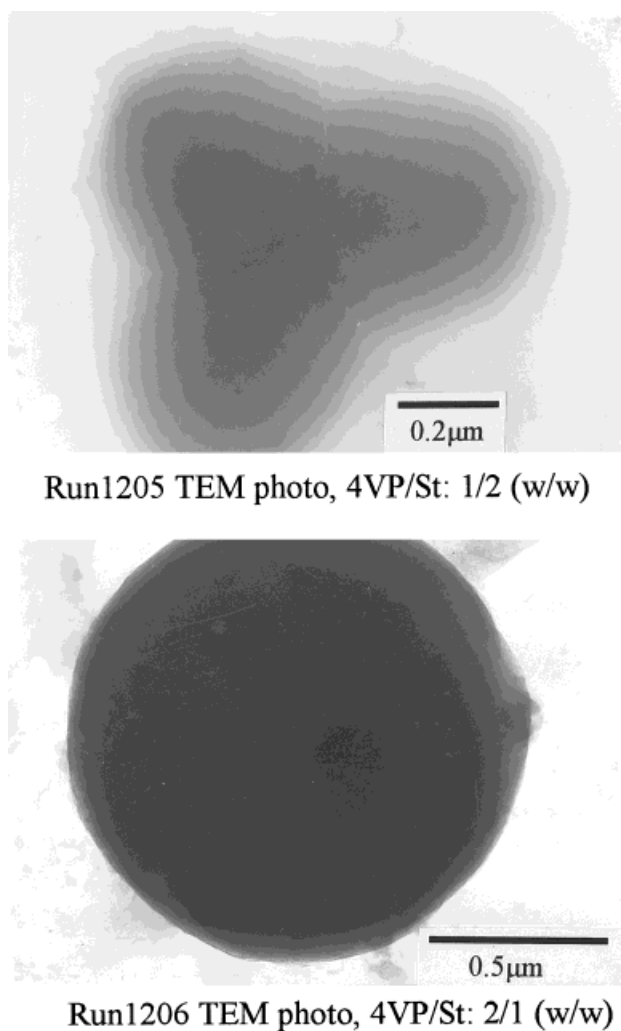
Figure 4   TEM photographs of latex with varying ratios of 4VP/St.

Figure 3(d), a part of the particle (left side) was not so dark and the other part was darker. When the percentage of EA exceeded 5 wt % (i.e., 8 and 10 wt %), the whole particle became light gray, as shown in Figure 3(e) and (f). To determine the morphologies observed earlier, the latex with 4VP/St ratios of 2/1 and 1/2 (w/w) were prepared with adding 10 wt % EA, the TEM photographs of which treatment are shown in Figure 4. It clearly shows that, as the amount of styrene increased, the stained particles became lighter, whereas the particles were darker as 4VP increased. That means the lighter part of the particles originated from the domain rich in styrene units in copolymer molecules. The richer the styrene units in the copolymer chains, the fewer the 4VP units incorporated, and thereby the copolymer was unable to be "densely" stained by CH_3I vapor in the same

conditions. Unfortunately, these finely separated phases were unable to be detected by the corresponding DSC curve (Fig. 5).

The T_g and the DSC curves of these samples are shown in Table III and Figure 5, respectively. There are two T_g's for the latex prepared without adding EA, which are close to the T_g's of pure P4VP and PS, respectively. This agrees well with the core–shell structure as shown in Figure 3(b). When EA was added, only one T_g appeared in the DSC curves for all of the samples. Furthermore, the value of T_g is quite close to the T_g of well-blended P4VP and PSt homopolymers or randomly copolymerized P(4VP/St), which should be in the vicinity of 120°C, according to the Fox equation for the copolymer composition of 4VP/St = 1/1 (w/w). For example, when the percentages of EA were 2 and 5 wt %, the T_g's were the same, about 120°C. This indicated that the copolymer composition, with the addition of EA, was quite different from that without EA. In the absence of EA, two separated domains, mainly comprised of P4VP and PSt, respectively, were formed, whereas in the presence of EA, there were no distinctively separated phases formed in the latex, especially when the percentage of EA exceeded 5 wt %. These observations imply that the copolymerization of 4VP/St tends to form a more homogeneous copolymer composition in the presence of EA.

Effect of EA on the Crosslinked Latex

Two different types of crosslinker, that is, the hydrophilic crosslinker EGDMA and the hydrophobic crosslinker DVB, were used to carry out the polymerization in the presence of 10 wt % EA. For comparison, the reference lattices were also prepared without using EA. The recipes and properties of the resultant latex are shown in Table IV.

The variation of zeta potential, as shown in Table IV, was complicated with the addition of the crosslinker, probably related to the interaction of the crosslinker and EA.

The particle size decreased as EA was added in the continuous phase and, furthermore, it seemed to be independent of the type of crosslinker. In the presence of EA, as shown in Figure 6(a), with the addition of the hydrophilic crosslinker, 0.5 wt % EGDMA, the particle size distribution of the resultant latex was too broad to be measured. In contrast, by adding the hydrophobic crosslinker, DVB, even as high as 5 wt %, the particle size
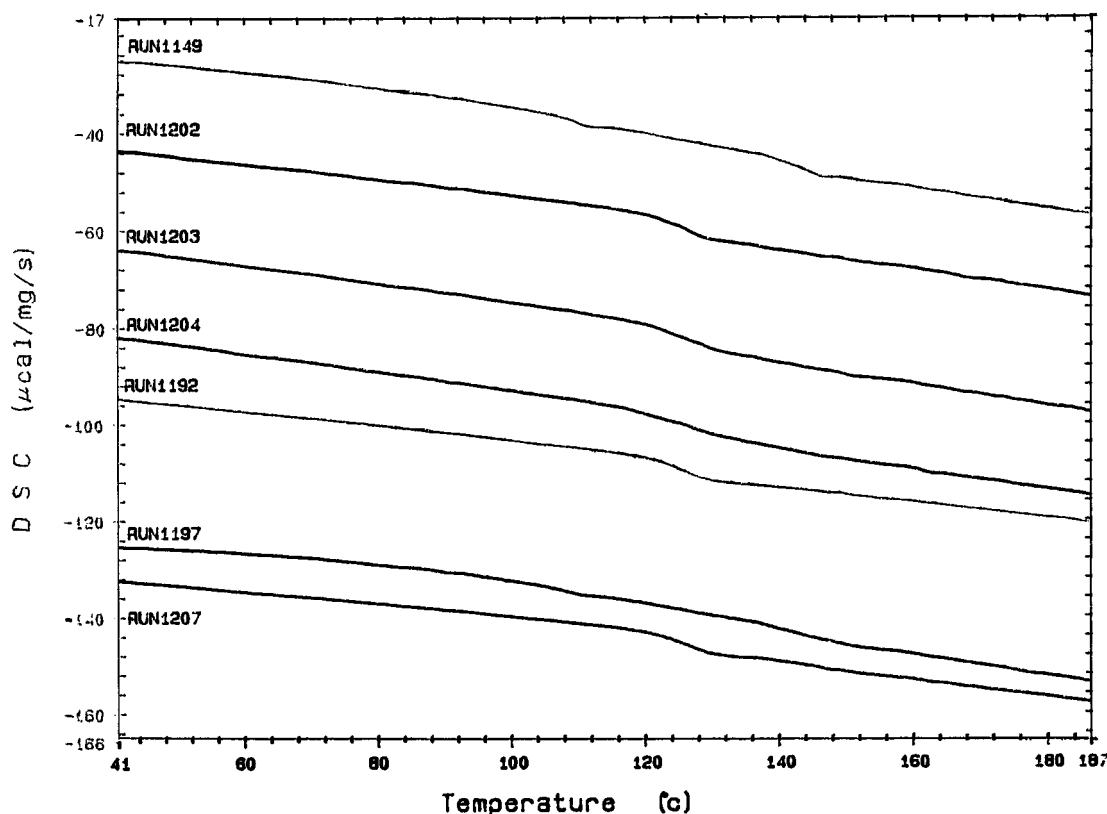
Figure 5 DSC curves of lattices prepared by batch and semicontinuous emulsion polymerization.

distribution was nearly monodispersed. Moreover, the particle size decreased as the amount of DVB increased (runs 1159 and 1153). This result agreed with that of the emulsion polymerization with nondisparate copolymerization reactivity ratios.[20–22]

In the absence of EA [Fig. 6(c) and (d)], the particle sizes were almost the same (the particle size of run 1193 cannot be precisely measured because of the nonspherical shape) and seemed to be unrelated to the amount and type of the crosslinker used. This result implies that the

Table III   Effects of the Amount of EA and the Monomer Feed Modes on the T_g of P(4VP/St) by Soap-Free Emulsion Polymerization

Run	4VP/St (w/w)	EA (wt %)	Monomer Feed Mode[a]	T_g (approx., °C)
1149	1/1	0	B	105, 139
1202	1/1	2	B	120
1203	1/1	5	B	120
1204	1/1	8	B	115
1192	1/1	10	B	116
1205	1/2	10	B	114
1206	2/1	10	B	120
1197	1/1	0	SC	104, 136
1207	1/1	10	SC	122

[a] The ratio of 4-vinyl pyridine and styrene.
[b] Amount of ethyl acetate based on the total amount of the continuous phase.
[c] B, batch; SC, semicontinuous.

Table IV   Effects of EA and Crosslinker on the Properties of P(4VP/St) Latex

Run	EA[a] (wt %)	Crosslinker[b] (wt %)	Conversion (%)	Diameter (μm)	CV[c] (%)	ζ Potential (mV)
1150	10	0.5 (E)[d]	97.8	0.5 (Max)[e]	—	67.7
1194	—	0.5 (E)	93.4	0.85	3.72	75.5
1159	10	0.2 (D)[f]	88.2	0.81	4.78	81.3
1153	10	5.0 (D)	99.6	0.50	5.21	79.6
1193	—	5.0 (D)	90.7	~ 0.82[g]	—	>100
1160	—	0.1E + 0.1D	92.2	0.86	20.9	79.4

The designed solid content of the latex was 10 wt %.
[a] Ethyl acetate, based on the total amount of the continuous phase.
[b] Based on the total amount of monomer.
[c] The distribution of particle size.
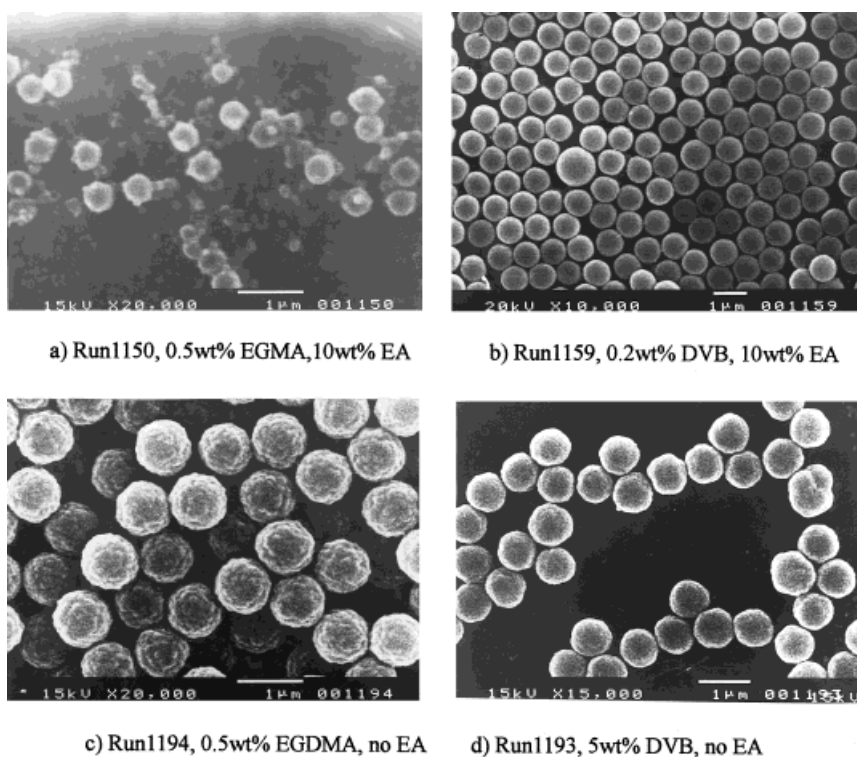[d] Ethylene glycol dimethacrylate.
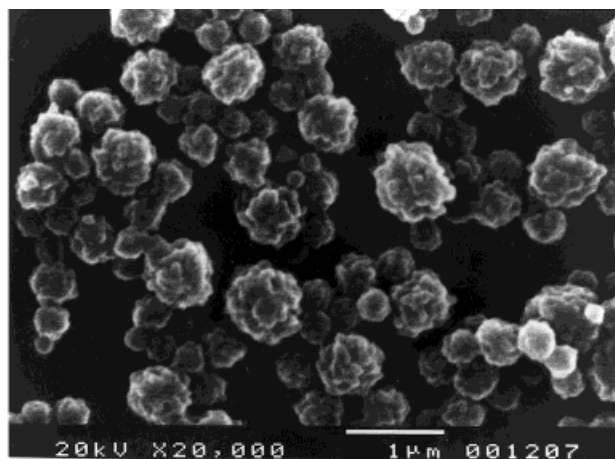[e] Maximum particle size.
[f] Divinylbenzene.
[g] Estimated particle size because of the nonspherical shape.

crosslinker affects only one domain of the particle, that is, either core or shell, rather than the whole particle, because of the disparate reactivity ratios. This is because the phase of PSt in the particle is predominantly crosslinked by DVB and that of P4VP is crosslinked by EGDMA. Two domains of the particle, the P4VP shell and the PSt core, affected the particle size. Therefore, the de-
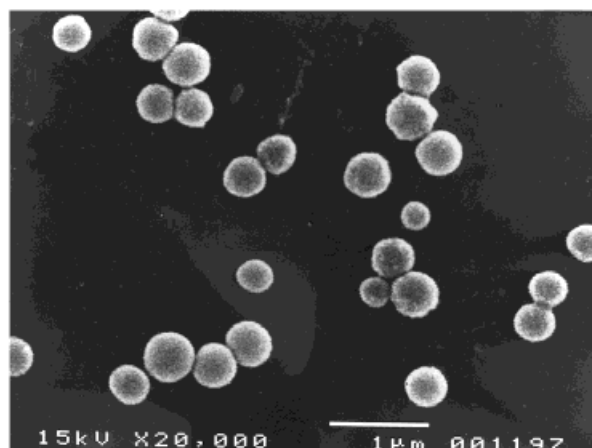
creasing size of either core or shell from being crosslinked, can be compensated by the other phase, which was slightly crosslinked. This assumption seemed to be supported by the observation of morphologies.

The morphologies of these lattices are shown in Figure 6. It was clearly found that, in the presence of EA, as shown in Figure 6(a) and (b), the

a) Run1150, 0.5wt% EGMA,10wt% EA   b) Run1159, 0.2wt% DVB, 10wt% EA

c) Run1194, 0.5wt% EGDMA, no EA   d) Run1193, 5wt% DVB, no EA

Figure 6   SEM photographs of crosslinked latex.

Run1207, 10wt% EA

Run1197, without EA

Semi-continuous emulsion copolymerization, feed rate: 0.09g/min. 4VP/St = 1/1 (w/w)

Figure 7   SEM photographs of lattices by semicontinuous emulsion polymerization.

surface of particles was smooth and the particles were spherical, regardless of the type of crosslinker used. However, in the absence of EA, as shown in Figure 6(c) and (d), the surface was rough when the hydrophilic crosslinker was used and the particles were nonspherical when the hydrophobic crosslinker was used, which resulted from phase separation.

Further investigation of the effects of crosslinker on the morphologies is still in progress. The results shown in this study are intended to prove that the presence of EA in the soap-free emulsion polymerization of comonomers with disparate copolymerization reactivity ratios rendered the copolymer composition homogeneous.

Semicontinuous Emulsion Polymerization

The monomer feed mode in the semicontinuous operation is considered to be an effective way to prepare copolymer with a homogeneous copolymer composition for emulsion polymerization of monomers with disparate copolymerization reactivity ratios.[7,9] Therefore, to investigate the effects of EA further, semicontinuous emulsion copolymerization was also employed, in the absence of EA or in the presence of 10 wt % EA, respectively. The SEM photographs of the resultant latex are shown in Figure 7. It was found that, in the presence of 10 wt % EA, a raspberry-like morphology was obtained,
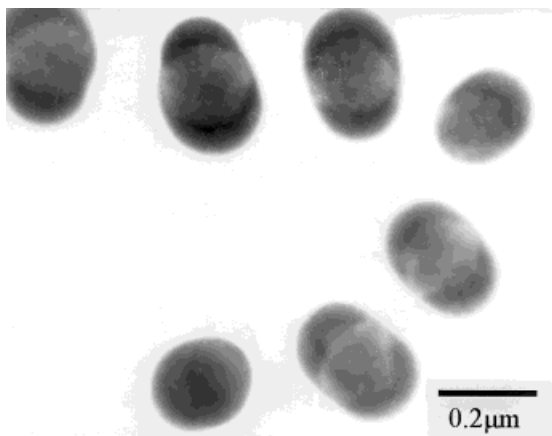
Figure 8 Sandwich-like microspheres.

whereas in the absence of EA spherical particles were formed.

The DSC curves of these two lattices (Fig. 5 and Table III) clearly show that two T_g's appeared for the latex without EA, whereas only one T_g appeared for the latex with using 10 wt % EA. This result indicates that phase separation occurred in the particle prepared without using EA, even though the feed rate was slow, at 0.09 g/min. Moreover, in an attempt to obtain a homogenous copolymer composition without using EA, at the same feed rate, 4VP was added dropwise into the reaction mixture of styrene and water, because the polymerization rate of 4VP is much higher. Interestingly, a homogeneous copolymer composition was not obtained either. Instead, particles of sandwich-like morphology were obtained, as shown in Figure 8. On the contrary, in the presence of EA, even with the batch copolymerization, as discussed earlier, a copolymer composition with only one T_g was obtained.

CONCLUSIONS

It was found that the morphology and properties of poly(4-vinylpyridine-*co*-styrene) [P(4VP/St)] latex prepared by soap-free emulsion polymerization were greatly affected by the addition of ethyl acetate (EA). With the batch polymerization mode, the core–shell morphology was formed without the addition of EA, resulting from the disparate reactivity ratios of the 4VP(1)/St(2) copolymerization system ($r_1 = 1.04$, $r_2 = -0.73$). However, with the addition of EA, the core–shell morphology disappeared, and instead, particles

with a bimodal particle size distribution and apparently asymmetric composition structure and then spherical microspheres were obtained as the charged amount of EA increased from 2 to 10 wt % based on the amount of water. The hairy layer of the particle can be compressed or collapsed by the addition of EA. Therefore, the particle size was increased up to twofold by the addition of EA, and the zeta potential of particles increased from +64.4 mV to more than +100 mV as EA increased from 0 to 8 wt %. The estimated viscosity-average molecular weight decreased from 9.70 to 0.97 $\times 10^5$ g/mol, as EA increased from 0 to 8 wt %. The results, obtained from the addition of crosslinker in this polymerization system, further proved the assumption that the addition of EA to the continuous phase favored the formation of a more homogeneous copolymerization composition, but lower molecular weight. For the semicontinuous monomer feed mode, raspberry-like particles were obtained by adding 10 wt % EA, whereas sandwich-like particles were obtained without using EA. The DSC curves revealed only one T_g for all the latex prepared with the addition of EA, but two T_g's appeared for the latex prepared without using EA, regardless of the monomer feeding modes.

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