

Novel Method to Prepare Charged Mosaic Membrane by Using Dipole-Like Microspheres. I. Preparation and Characterization of Poly(4-vinylpyridine/*n*-butyl acrylate) Seed Latex with High Solid Content by Soap-Free Emulsion Polymerization

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ABSTRACT: The stable latex of poly(4-vinylpyridine-*co-n*-butyl acrylate) (P4VP/*n*BA) with a solid content as high as 10 wt % was prepared by a modified soap-free emulsion polymerization. A mixture of water and organic solvents was employed as the continuous phase for increasing the solid content of the latex. Several organic solvents were investigated and, among them, ethyl acetate (EA) and diethyl ether (DE) were effective. The stable latex with 10 wt % solid content was prepared by charging 10 wt % EA or a EA/DE mixture (5 wt % each); however, more than 10 wt % solid content of the stable latex could not be obtained even by charging more than 10 wt % EA or a EA/DE mixture. The stable latex with 10 wt % solid content, which was crosslinked with less than 0.5 wt % (based on monomer) of ethylene glycol dimethacrylate, was prepared by charging 10 wt % of EA. In this case, however, the pH of the continuous phase had to be adjusted to lower than 4. The effects of EA on the characteristics of the resulting uncrosslinked latex were investigated by employing ζ -potential measurements and scanning electron microscopy. It was found that the mass of coagulum decreased as the EA increased. At 8 wt % of EA, a stable latex of 10 wt % solid content without any coagulum was obtained. The ζ potential of particles increased from -100 up to 45.7 mV as the EA increased from 0 to 10 wt %. The effects of batch and semicontinuous copolymerization on the morphology of the microspheres were investigated by using DSC and ultrathin cross-sectional transmission electron microscopy photos. A core-shell structure was not found, despite the batch copolymerization of 4VP(1)/*n*BA(2) ($r_1 = 4.3$, $r_2 = 0.23$), even with disparate reactivity ratios. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 76: 1731–1740, 2000

Key words: charged mosaic membrane; poly(4-vinylpyridine-*co-n*-butyl acrylate) microspheres; soap-free emulsion polymerization; ethyl acetate; high solid content

INTRODUCTION

Charged mosaic membranes consist of parallel domains of anion-exchange and cation-exchange

elements through the membranes. It is predicted from phenomenological theory¹ that ionized substances of low molecular weight are very permeable through a charged mosaic membrane while nonionized ones are not. That is to say, compared with a conventional ion-exchange membrane, a current circuit, which results from cationic and anionic substances simultaneously passing through

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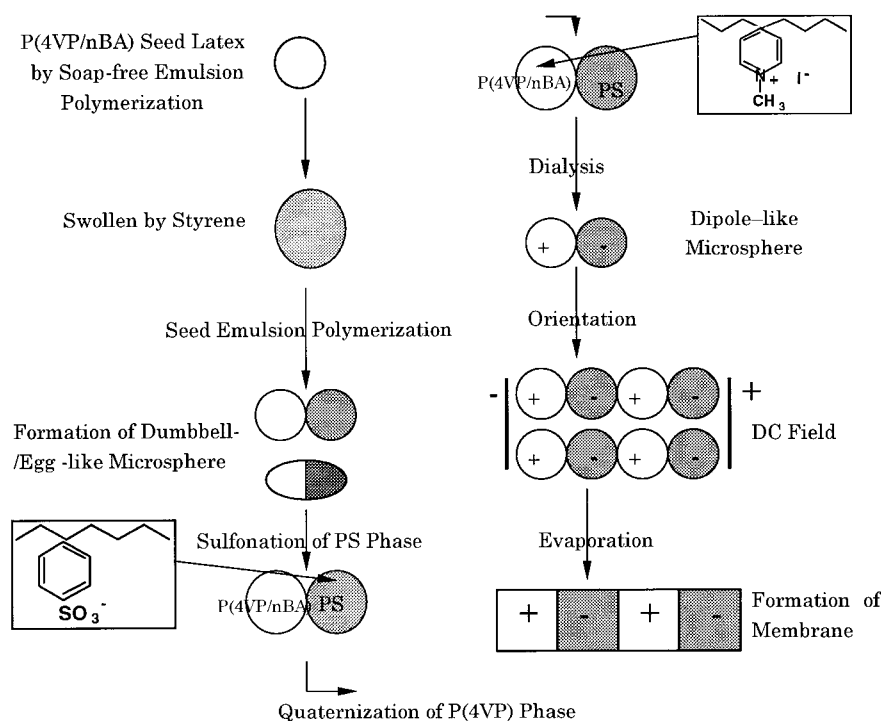


Figure 1 The schematic process of the preparation of a charged mosaic membrane by employing dipole dumbbell- and egg-like microspheres.

the membrane, accelerates the transportation of charged substances. Thus, the charged mosaic membrane is thought to be an effective, energy-saving, clean separation membrane, particularly for use for desalination of seawater.

Since being proposed by Söllner² in connection with biological phenomena, several workers³⁻⁵ investigated the preparation of charged mosaic membranes using the microphase separation of block/graft copolymers, where the membrane contains alternating regions of positive and negative charges. However, several fatal defects were found in the membranes prepared by these methods. For example, the membranes need a support matrix because of their low mechanical strength, some charged domains cannot pass uninterrupted and yet perpendicularly through the membrane, and the surface of the membrane is usually covered by the phase with lower hydrophilicity.

We have been engaged for some years in the investigation of preparation and characterization of polymeric microspheres.⁶⁻⁸ Based on the knowledge of polymeric microspheres, we propose a new method to prepare charged mosaic membranes by using polymer microspheres, as schematically shown in Figure 1. In this method, at first the dipole-like microspheres orient before the

formation of a membrane. Hence, order in which the negatively charged domains and positively charged domains alternately appear should exist not only inside the resulting membrane, but also on the surface of the membrane. Moreover, the orientation of microspheres favors uninterrupted phase growth⁵ perpendicularly through the membrane. In addition, the microspheres can be easily modified (e.g., crosslinking between and inside the microspheres) to enhance the mechanical properties. This method is thus theoretically expected to overcome the defects of the charged mosaic membrane mentioned above.

Poly(4-vinylpyridine) (P4VP) was selected for this purpose because its chemical properties, such as acidity, basicity, and hydrophilic and hydrophobic properties, can be easily modified. In this study it was modified by introducing cations into the polymer chains that have been commonly applied to the preparation of cation ion-exchange resins. Furthermore, they can also be easily crosslinked within and between microspheres. This property would be expected to favor the enhancement of the mechanical properties of the resulting membrane. The addition of *n*-butyl acrylate (nBA) lowers the glass transition temperature (T_g) of P4VP because the T_g of the P4VP

homopolymer is as high as 142°C, which is unfavorable for the preparation of a membrane because a high temperature is required. The high temperature is harmful to the orientation of dipole-like microspheres in a direct current field. Furthermore, the resulting membrane is brittle. The ratio of 4VP/nBA of 4/1 was selected because the T_g of the resulting copolymer is about 80°C, which is close to the T_g of polystyrene (PS) in accordance with the Fox equation. Conventionally, PS is used to introduce the sulfonic anion into polymer chains by sulfonation for the preparation of an anionic ion-exchange resin.

In the preparation of microspheres, emulsion^{9,10} or soap-free polymerizations¹¹⁻¹⁵ are the most popular, because the monodispersed microspheres can be easily synthesized by such polymerization. Especially with the soap-free polymerization method, one can take advantage of the fact that the surface of the microsphere is not stained by the emulsifier. Water is usually used as the continuous phase in soap-free polymerization. With this continuous phase, however, this method cannot be applied to the preparation of P(4VP/nBA) with more than 5 wt % solid content as we will report later. Rembaum et al.¹⁶ reported on the preparation of P4VP microspheres with cobalt γ radiation. In their cases the maximum solid content was 3 g/100 mL when water was employed as the continuous phase and 8 g/100 mL when 30% methanol/water (w/w) was employed, even though 0.4% (w/v) poly(ethylene oxide) (PEO) was charged in both cases. Obviously, their method is not feasible in the laboratory, nor is the use of PEO as a surfactant. Ma and Fukutomi¹⁷ claimed that adding a partially quaternized P4VP to the polymerization system could solve this problem. But even in their cases, the solid content of the reported latex was less than 5 wt %, which is unsatisfactory for the demands of industrial production. It is thus necessary to establish preparative methods for a latex with a higher solid content.

The addition of organic solvents to change the polarity of the continuous phase was considered to increase the solid content of the P4VP latex in this work. Because the considerable hydrophilicity of P4VP probably results in the formation of a "hairy layer" on the surface of the microspheres, it will make the latex unstable as the polymerization progresses. Two methods have been considered to be effective in solving this problem. The first is modifying the properties of the microsphere surface, for example, charging various sur-

factants to decrease the hydrophilicity of the microsphere surface or increasing the charge density of the microsphere surface to enhance the repulsive force between the microspheres. The second is decreasing the polarity of the continuous phase to decrease the solubility of the microsphere surface. Ma and Fukutomi's¹⁷ work is an example of the first method where P4VP microspheres were stabilized by increasing the charge density of the microsphere surface. However, the second method has not been reported on until now. That is why we employed it here and expected to prepare a P4VP latex with a higher solid content. It is a new attempt to prepare a P4VP latex with a higher solid content by soap-free polymerization with a water/organic solvent as the continuous phase. The success of this method would possibly provide a new method to prepare a higher solid content latex of other intensively hydrophilic polymers, such as *p*-styrene sulfonic acid, sodium salt.

For the preparation of dumbbell-like microspheres we employed seed emulsion polymerization because it is the most popular method applied to the preparation of microspheres with different morphologies. Cho and Lee,¹⁸ Sheu et al.,¹⁹ and Berg et al.²⁰ published some advanced work on experiments and theory of this method, although they predominantly employed the PS/PS or poly(methyl methacrylate)/PS copolymerization systems. The work on a P4VP/PS copolymerization system has not been reported, especially when employing a mixture of water and solvent as the continuous phase. We will report on it in our next article and subsequently report on the preparation of a dipole-like microsphere and the charged mosaic membrane.

In this article we report on the preparation and characterization of a seed latex of P4VP/nBA with a high solid content by employing a mixture of water and solvent as the continuous phase.

EXPERIMENTAL

Materials and Apparatus

The monomers 4VP and nBA; the water-soluble crosslinker ethylene glycol dimethacrylate (EGDMA); and the solvents ethyl acetate (EA), diethyl ether (DE), isopropanol, acetone, and acetonitrile were purchased from Kishida Chemical Industries Co. Ltd. The water-soluble initiator 2,2'-azobis(2-amidinopropane) · 2HCl (V50) was

Table I Typical Recipe of P4VP/nBA Soap-Free Emulsion Polymerization

Monomer (wt %)		Continuous Phase (wt %)		V50 Initiator ^a (wt %)	EGDMA Crosslinker ^a (wt %)
4VP	nBA	Water	Solvent		
80	20	90	10	3	Variable
10			90		

V50, 2,2'-azobis(2-amidinopropane) · 2HCl; EGDMA, ethylene glycol dimethacrylate.

^a Based on the amount of monomer.

offered by Wako Chemical Industry Co. Ltd. The solvents were distilled. The monomers and water-soluble crosslinker were distilled under reduced pressure. The initiator was used without further purification. The water was purified by ion-exchange resin and then distilled.

A scanning electron microscope (Jeol JSM-5310), transmission electron microscope (Hitachi H-700H), differential scanning calorimeter (Mac Science DSC-3100), and ζ potential analyzer (Sony Zeecom) were used.

Preparation of P4VP/nBA Seed Latex

The P4VP/nBA latex was synthesized by radical soap-free emulsion polymerization. A standard recipe for polymerization is shown in Table I. Two kinds of methods were applied to the polymerization: using a vacuum sealed ampoule to find the best experimental conditions and then using a separator glass flask to prepare the seed latex for the following experiments according to the best conditions.

A 15-g mixture of ingredients was charged in a 30-mL ampoule and deoxidized by the freeze-thaw method with liquid nitrogen. Then the ampoule was fastened to a tumbling device set in a thermostated water bath. The water bath was heated to the required temperature before the tumbling device was placed.

The polymerization 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 thermostated water bath. For the batch polymerization, 270 g of a mixture of water and solvent was first charged and fully mixed by stirring and then heated to the required temperature before a 30 g mixture of monomers was charged. The initiator, dissolved in 30 mL of water, was charged finally. For the semicontinuous polymerization, the monomer

mixture was added dropwise into the preheated reaction mixture at a rate of 0.25 g/min. Three operational approaches were employed. The first (SP1) was that all the monomers were mixed before dripping. The second (SP2) was that a mixture of 6 g of 4VP and 6 g of nBA was first mixed and then dripped, and the remaining 4VP monomer was charged to the monomer mixture at a rate 3 g/15 min. The third method (SP3) was that EA was charged in portions (i.e., half at 30 min and another half at 60 min) after all the monomers were mixed and dropwise addition was started.

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 10 h.

Characterization of Microspheres

The conversion of the monomer was determined by gravimetry: a known amount of latex was dried and weighed. The size and shape of the dry microspheres were observed by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The SEM sample was prepared as follows: one drop of dilute latex (1×10^{-4} g/mL) was cast on a stage covered with an aluminum film; after being dried at room temperature, it was coated with a thin gold film. The particle size was determined by direct measurement of 200 particles/sample on an SEM photo. The ultra-thin cross section of a TEM specimen was prepared as follows: the vacuum dried latex was embedded in epoxy resin and sliced after the epoxy resin solidified. The thin chips were put on thin carbon film covered copper mesh and then, after drying, they were stained with CH_3I vapor in a closed bottle for 3 or 4 days at room temperature. The latex was diluted to 1×10^{-4} g/mL by pH

Table II Effects of Second Solvents and Crosslinker

Run	Solvent and Amount (wt %)	EGDMA (wt %)	Solid Content (wt %)	Results
1102	Water		5	Precipitate
1104	Isopropanol, 10		5	Solution
1105	Ethyl acetate, 10		5	Latex
1106	Acetone, 10		5	Unstable latex
1107	Acetonitrile, 10		5	Unstable latex
1112	Diethyl ether, 5		5	Latex
1109	Ethyl acetate, 10		10	Latex
1114	Ethyl acetate, 20		15	Unstable latex
1115	Diethyl ether, 10		10	Coagulation
1118	EA + DE, 5 + 5		10	Latex
1120	EA + DE, 10 + 10		15	Unstable latex
1108	Ethyl acetate, 10	0.5	5	Latex
1110	Ethyl acetate, 10	0.5	10	Coagulation
1113	Ethyl acetate, 20	0.5	10	Unstable latex
1130	Ethyl acetate, 10, pH 3.65 ^a	0.5	10	Latex
1116	Diethyl ether, 10	0.5	10	Coagulation
1119	EA + DE, 5 + 5	0.5	10	Coagulation

EA + DE, ethyl acetate and diethyl ether; EGDMA, ethylene glycol dimethacrylate.

^aThe pH of the continuous phase prior to the polymerization.

6.69 deionized water for measurement of the ζ potential. The ζ 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.

RESULTS AND DISCUSSIONS

Selection of Solvents

Soap-free emulsion polymerization of uncrosslinked P4VP/nBA was carried out in an ampoule to select the solvent. The results are shown in Table II. As was done for the conventional soap-free emulsion polymerization, run 1102 employed water as the continuous phase to prepare a latex with 5 wt % solid content. The polymer precipitated during the polymerization. We therefore attempted to charge solvents with weaker polarities to the water to lower the polarity of the continuous phase and enhance the stability of the P4VP microspheres. Hence, based on water, 10 wt % of isopropanol, acetonitrile, acetone, and EA and 5 wt % of DE were charged to the continuous phase. Isopropanol was selected in this study, rather than methanol and ethanol, because its polarity was weaker than the others and 5 wt % of DE was selected because its solubility in water is

6.05 wt % at 25°C and less at a higher temperature. As a result, no latex was formed in the mixture of water–isopropanol. When mixing acetone and acetonitrile, a stable latex with 5 wt % solid content could not be prepared, probably because of their strong polarities. The stable latex was prepared by charging 10 wt % of EA and 5 wt % of DE, respectively.

Preparation of Uncrosslinked Latex with 10 wt % Solid Content

According to the results of the preparation of a 5 wt % solid content latex, we tried to prepare a higher solid content by charging EA and DE to the continuous phase in ampoules. As shown in Table II, the stable latex of 10 wt % solid content was also prepared by charging 10 wt % EA or the mixture of 5 wt % EA and 5 wt % DE, but it was impossible to obtain by charging 10 wt % DE. However, a stable latex with 15 wt % solid content was not prepared by charging 10 wt % of EA or DE. Moreover, 20 wt % of EA and the mixture of EA and DE were also charged in order to obtain a 15 wt % solid content. Unfortunately, coagulation occurred. This result implied that 15 wt % or more solid content of stable latex was hardly achievable by this method.

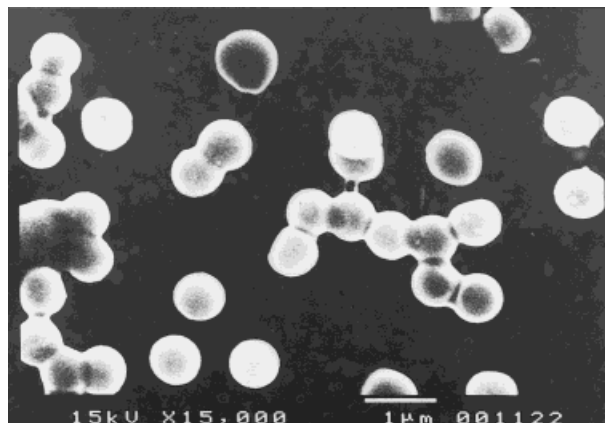


Figure 2 A scanning electron micrograph of the un-crosslinked seed latex run 1122 with a 10 wt % solid content and 10 wt % ethyl acetate.

According to the recipe of run 1109, the un-crosslinked seed latex was prepared by using a separator glass flask. The SEM photograph of seed particles is shown in Figure 2.

Effects of EA on Characteristics of Latex

The polymerization was performed by charging 0, 3, 5, 8, and 10 wt % of EA while the monomer concentration was 10 wt %. The changes of the mass of coagulum, particle size, and ζ potential versus the percentage of EA in the continuous phase are shown in Figure 3. It clearly shows that the mass of coagulum decreased rapidly as the percentage of EA increased. From 0 to 3 wt % of EA, the coagulum decreased from 100 to 29.7 wt %. This implies that the stability of these microspheres was greatly improved by the addition of EA. At 8 wt % of EA, the coagulum disappeared and a stable latex was obtained. The reasons for these phenomena are thought to be that with more EA charged, the weaker the polarity of the continuous phase is and, in turn, the more stable the microspheres are, although they are limited by the solubility of EA in water. The azeotropic mixture of EA and water is 7.8% (w/w) with a boiling point of 70.3°C. This implies that only 7.8 wt % of EA can effectively mix with water at the polymerization temperature. Hence, if the charged EA were higher than its solubility in water, the excess would phase separate from water rather than lower the polarity of the continuous phase. For the DE, its solubility in water at the polymerization temperature would be less than 6.05 wt % (25°C). This is probably the reason why 10 wt % of latex was not prepared by charg-

ing 10 wt % of DE, and furthermore, a 15 wt % solid content was not achieved by charging more than 10 wt % EA or the mixture of EA and DE. In light of the above discussions, we can conclude that the maximum solid content of the P4VP/nBA latex was about 10 wt % and the maximum charged EA was about 10 wt % based on water by using this method.

In addition, the ζ potential of microspheres increased from -100 to $+45.7$ mV as charged EA increased from 0 to 10 wt %. Because the initiator used in these experiments was V50, the decomposition fragments were hydrophilic and positively charged. According to the fact that the ζ potential of the microspheres mainly originated from the hydrophilic fragments of the initiator that anchored on the surface of microspheres, the resulting microspheres should have been positively charged. However, the ζ potential was negative when the charged EA was less than 8 wt %.

These phenomena reflect the changes of configuration of the particle surface with the addition of EA and verify our assumption as well. In the case of the lower percentage of EA, the hydrophilic hairy layer arising from the high solubility of P4VP moved the "slipping plane" of the electrical double layer far out of the particle surface where the counterions, such as Cl^- and OH^- , dominate. As the charged EA increased, the thickness of the hairy layer decreased due to the decrease of P4VP

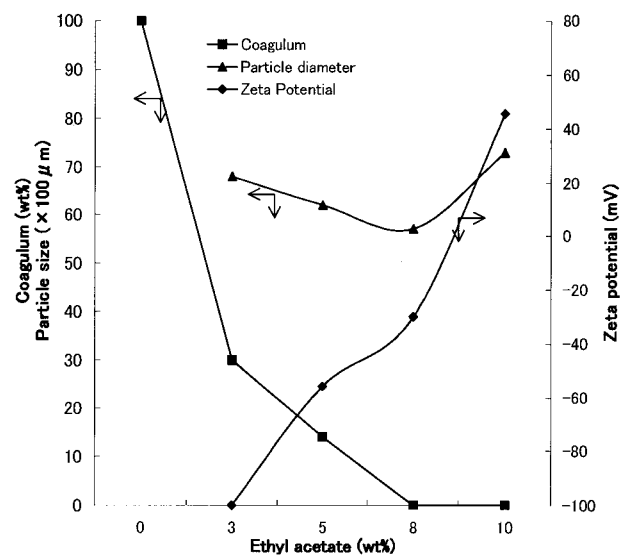


Figure 3 The coagulum, ζ potential, and particle size vs. charged ethyl acetate to the continuous phase with a 10 wt % concentration of the monomers and un-crosslinked.

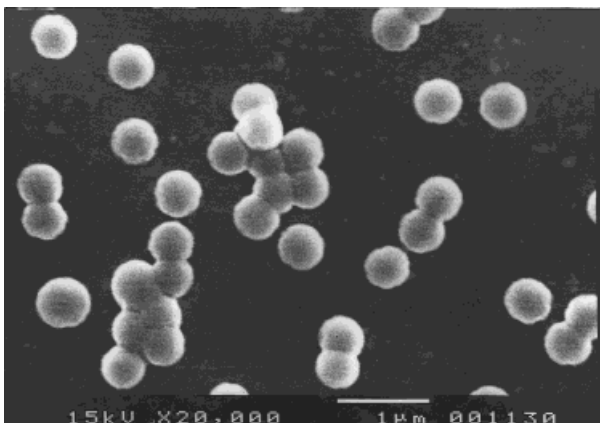


Figure 4 A scanning electron micrograph of the crosslinked seed latex run 1130 with 0.5 wt % EGDMA crosslinker, 10 wt % solid content, and 10 wt % ethyl acetate at pH 3.65 prior to polymerization.

solubility. When adding EA up to 10 wt %, the slipping plane was very near the “real” surface of the particle where the fixed charge arising from initiator fragments dominates.

The particle diameters ranged from 0.57 to 0.73 μm and decreased as EA increased, except for that of 10 wt %. This agrees well with our assumption that the particles would become smaller as a result of the solubility of P4VP decreasing as the polarity of the continuous phase was getting lower. The exception in the case of 10 wt % may have resulted from the slight excess of EA.

Preparation of Crosslinked Latex and Effects of pH

As shown in Table II, stable latex with a 5 wt % solid content and 0.5 wt % EGDMA was obtained by charging 10 wt % of EA. However, the stable crosslinked latex with 10 wt % solid content was not obtained by charging 10 wt % of EA or DE. As

expected from the above discussion, 20 wt % of EA was no help. It was prepared by adjusting the pH of the continuous phase down to 3.65 prior to the polymerization. The SEM photograph of crosslinked seed particles is shown in Figure 4.

However, the stable latex with 1 wt % EGDMA could not be obtained even by decreasing the pH of the continuous phase to 2.

The effects of the crosslinker and pH of the continuous phase on the properties of the resulting latex are shown in Table III. It was observed that the particle size, the particle size distribution and the ζ potential of the particles were greatly affected by the adjustment of the pH. In the absence of EGDMA the particle size and its distribution decreased but the ζ potential increased as the pH decreased. In the presence of EGDMA, it was more complicated, because of the two effects of EGDMA and pH. Nevertheless, in considering the overall effects of EGDMA and pH, we can conclude that the decrease of the particle size distribution was due to the increase of EGDMA and the increase of the ζ potential resulted from the decrease of the pH. The particle size seemed unchanged when EGDMA was more than 0.2 wt %. A large difference in the ζ potential between runs 1135 and 1139 was also found. It probably resulted from the addition of EGDMA.

It is easy to understand why the ζ potential increased as the pH decreased, because the higher the $[\text{H}^+]$ was, the more H^+ would be bonded to the pyridine groups on the surface of the microspheres. The decrease of the particle diameter was because of the quaternization of pyridine groups in the polymer chains. The ionization of pyridine groups stabilized the P4VP nucleus at an earlier stage and consequently prevented the nuclei from further growth by coagulation.

Table III Effects of Crosslinker and pH on Properties of Latex

Run	pH of Continuous Phase	EGDMA (wt %)	Diameter (μm)	CV (%)	ζ Potential (mV)
1122	6.69	0	0.77	9.50	95.7
1135	3.30	0	0.58	8.93	>100
1139	3.50	0.05	0.58	12.3	40.6
1140	3.78	0.2	0.53	11.2	19.8
1130	3.65	0.5	0.53	6.52	36

EGDMA, ethylene glycol dimethacrylate; CV, distribution of particle size.

Table IV Comparison of Uncrosslinked Latex Properties Prepared by Batch and Semicontinuous Polymerization

Run	Operation Method	EA (wt %)	Solid Content (wt %)	Latex	Diameter (μm)	T_g ($^{\circ}\text{C}$)
1122	BP	10	10	Stable	0.77	22.1–41.4
1141	SP1	10	10	Stable	1.16	18.3–40.5
1142	SP2	10	10	Stable	1.08	12.8–40.7
1144	SP3	10	10	Stable	1.14	28.1–37.2
1147	SP1	0	5	Coagulation		

EA, ethyl acetate; BP, batch polymerization; SP, semicontinuous polymerization.

Effects of Batch Polymerization and Semicontinuous Polymerization

El-Aasser and coworkers^{21,22} investigated the effects of batch and semicontinuous operations on the morphology of microspheres. They reported that batch polymerization could lead to a core-shell structure by using a monomer mixture with disparate copolymerization reactivity ratios, such as a vinyl acetate (1)-nBA (2) copolymerization system where $r_1 = 0.00-0.04$ and $r_2 = 3-8$. The semicontinuous polymerization could yield a relatively uniform composition and minimum coagulum. These results are important to our further preparation of dipole-like microspheres because the subsequent preparations of dumbbell-like microspheres are closely related to the morphology of seed particles and, moreover, in this study the copolymerization reactivity ratios of a 4VP (1)-nBA (2) mixture (i.e., $r_1 = 4.3$ and $r_2 = 0.23$) are disparate, too. For this reason semicontinuous and batch copolymerizations were carried out in the presence of EA to verify whether the same results would be found as their results implied. The results are shown in Table IV.

Unfortunately, in the absence of EA a large amount of coagulum occurred during the polymerization with only 5 wt % solid content, even when using semicontinuous copolymerization. A stable latex with 10 wt % solid content was obtained by all methods in the presence of 10 wt % EA. Apparently, the advantage of minimum coagulum using semicontinuous copolymerization was not reflected in run 1147 without EA.

The sizes of the microspheres prepared by semicontinuous copolymerization were generally bigger than those by batch polymerization.

The DSC curves of the samples prepared by batch and semicontinuous copolymerizations are shown in Figure 5. The DSC showed that the T_g of

copolymers prepared by different methods were mainly distributed in the range of about 20–40 $^{\circ}\text{C}$, although the T_g of homopolymers of P4VP and PnBA were 142 and -54°C , respectively. No glass transition was found in the vicinity of -54 and 142°C . This implies that no domains, which predominantly comprised P4VP or PnBA segments, existed in any of the microspheres, even though monomer mixtures with disparate reactivity ratios and different operation methods were applied to the copolymerization. This is probably due to the presence of EA in the continuous phase. Because the solubility of nBA in the continuous phase was increased by the addition of EA, the particles would not be “flooded” by nBA as the batch polymerization progressed.

Figure 6 shows the TEM photo of an ultrathin cross section, stained by CH_3I vapor, of a sample prepared by batch copolymerization. The black parts are the domains of quaternized P4VP phases. Because the particles were soft, because of the lower T_g shown in Figure 5, we found that the particles distorted during the preparation of the TEM specimen. The core-shell morphology was not found in the sample.

CONCLUSIONS

EA and DE were effective solvents for increasing the solid content of P(4VP-nBA) (4:1) by soap-free emulsion polymerization. A stable latex with a 10 wt % solid content was prepared by charging 10 wt % EA or a EA/DE mixture (5 + 5 wt %), but more than 10 wt % solid content of the stable latex was not obtained by charging more than 10 wt % EA or a EA/DE mixture. The mass of coagulum decreased as EA increased. At about 8 wt %

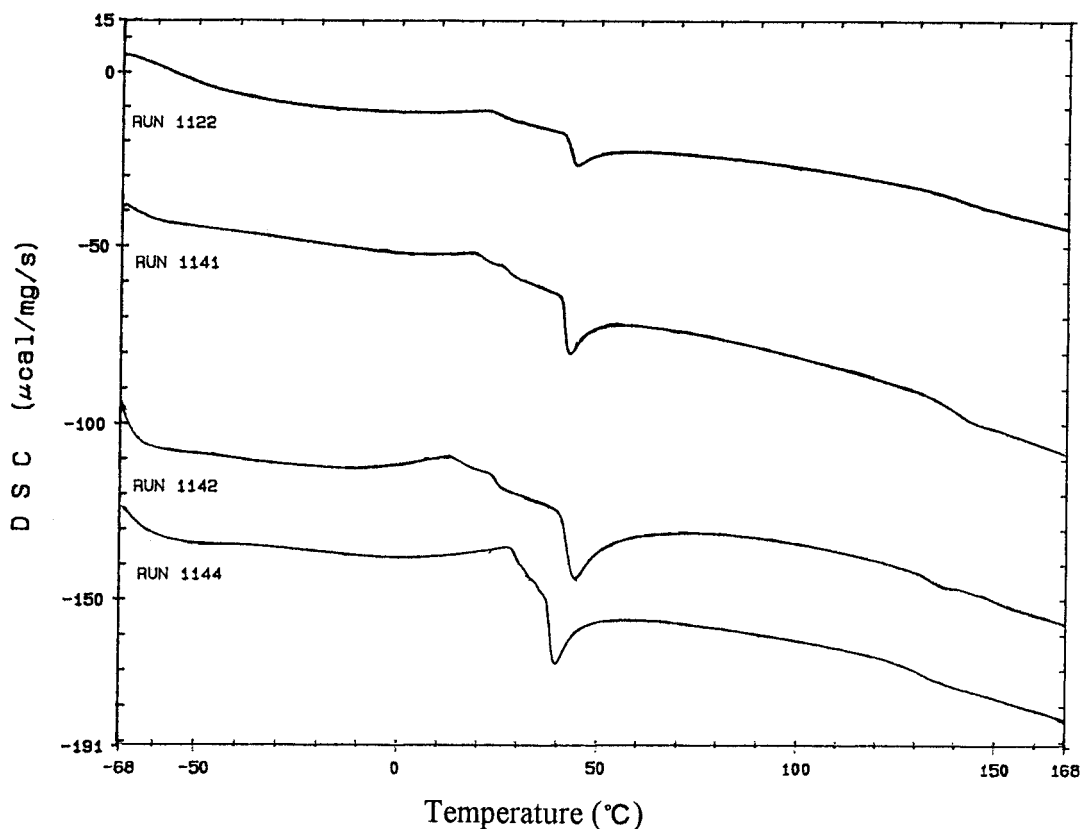


Figure 5 The DSC of uncrosslinked specimens prepared by batch and semicontinuous polymerization. The solid content of the latex is 10 wt %, and the charged ethyl acetate is 10 wt %; run 1122, batch; run 1141, SP1; run 1142, SP2; run 1144, SP3.

of EA a stable latex of 10 wt % solid content without coagulum was obtained. The ζ potential of uncrosslinked particles increased from -100

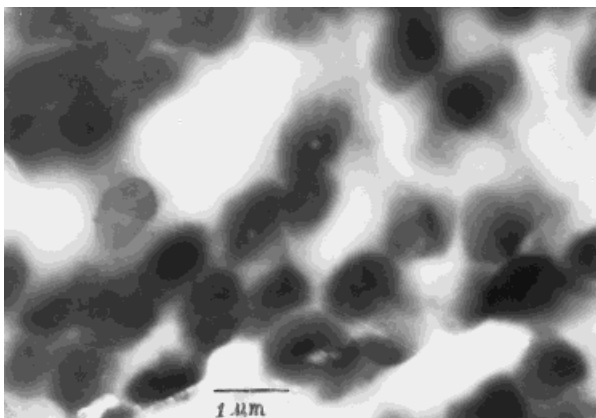


Figure 6 A transmission electron micrograph of an ultrathin cross section of the uncrosslinked seed latex run 1122 prepared by batch polymerization with 10 wt % solid content and 10 wt % charged ethyl acetate and stained by CH_3I vapor at room temperature for 4 days.

up to 45.7 mV as the EA increased from 0 to 10 wt %. A stable latex with 10 wt % solid content, crosslinked with less than 0.5 wt % (based on monomer) of EGDMA, was prepared by charging 10 wt % of EA. In this case, however, the pH of the continuous phase had to be adjusted to lower than 4. Batch and semicontinuous copolymerizations were employed for the preparation with 10 wt % solid content. The size of the microspheres by semicontinuous operations was bigger than that by batch operations. But the core-shell structure was not found from the DSC curves and the ultrathin cross section TEM photo, despite the use of batch copolymerization of 4VP (1)/nBA (2) ($r_1 = 4.3$, $r_2 = 0.23$) with disparate reactivity ratios.

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