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Emulsifier-free emulsion copolymerization of styrene and acrylamide using an amphoteric initiator

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Abstract Emulsifier-free emulsion copolymerization of styrene (St) and acrylamide (AAm) has been investigated in the presence of an amphoteric water-soluble initiator, 2,2′-azobis[*N*-(2-carboxyethyl)-2-2-methylpropionamidine]hydrate (VA057). The kinetics of polymerization and the colloidal properties of the resulting latices were studied and compared with the cases using ionic initiators. When adopting the amphoteric initiator at pHs lower than 10, stable amphoteric poly (St/AAm) latices, evidenced by the electrophoretic mobility, were prepared directly. Meanwhile, almost the same conversion versus time curves appeared and there were no apparent differences in the final particle sizes for those polymerizations, whereas in the polymerization at pH 10, a much lower rate of copolymerization and a larger size of particles were observed. The surface charge density and the growth rate of latex particles produced with VA057 at pH < 10 were comparable to those of the particles with a cationic initiator, 2,2′-azobis(2-amidinopropane)dihydrochloride, but were apparently lower than those with an anionic initiator, potassium persulfate, when the polymerizations were carried out under corresponding conditions. The number of initiator fragments incorporated onto the particle surfaces was independent of polymerization pH, except for pH 10. The abnormal performance of VA057 at pH 10 was attributed to its degradation due to hydrolysis.

Key words Emulsifier-free emulsion polymerization · Amphoteric initiator · Amphoteric latex · Styrene · Acrylamide

Introduction

During recent decades, increasing attention has been focused on emulsifier-free emulsion polymerization by which various colloidal microspheres with high monodispersity and clean surfaces could be easily prepared [1–2]. They have not only been used as model particles in academic research fields [3–4], but have also found widespread, potential applications in numerous industrial areas, especially in biomedical ones [5–7].

One of the most important problems involved in such an emulsifier-free emulsion polymerization system is how to obtain a stable microsphere dispersion in the absence of an emulsifier. As already reported [8], the most convenient approach may be to adopt an ionic-group-containing initiator, which naturally provides ionic radicals or residues which contribute to polymerization and to stabilization of polymer particles. Another route to reach the previously mentioned aim is to add hydrophilic monomer into polymerization recipes. The hydrophilic monomer creates a hydrated layer on the particle surfaces and the sterically repulsive layer enhances the stabilization of the particle [9].

Amphoteric latices are more desirable due to their unique colloidal behavior and properties, depending on pH and ionic strength. They can be prepared by copolymerizing cationic and anionic monomers, or by polymerizing an ionic monomer using its opposite ionic-group-containing initiator [10] or by postmodification of a preformed latex [11–12].

In this work, amphoteric latices were prepared by emulsifier-free emulsion polymerization of nonionic monomers using an amphoteric initiator. The kinetics of polymerization and the properties of the resulting latices were measured and compared with those when using various ionic initiators.

Experimental

Materials

Styrene (St) was distilled under reduced pressure before use. Acrylamide (AAm) and potassium persulfate (KPS) were purified by recrystallization from benzene and water, respectively, and then dried in a vacuum. Two kinds of water-soluble azo initiators, i.e., 2,2′-azobis[*N*-(2-carboxyethyl)-2-2-methylpropionamidine]hydrate (VA057, $[=NC(CH_3)_2C(=NH)NH(CH_2)_2COOH]_2$) and 2,2′-azobis(2-amidinopropane)dihydrochloride (V50) were donated by Wako Pure Chemical Industries, Japan, and were used without purification. The former was an amphoteric compound and the latter a cationic one. Deionized and distilled water was used and HCl or NaOH solution was utilized to adjust the pH in all experiments. Other reagents were all of extra-pure grade and were used without further purification.

Polymerization and purification

Polymerization runs were carried out in a four-necked flask equipped with a stirrer, a reflux condenser, a nitrogen inlet and a feeding and sampling tube. The typical recipes are given in Table 1.

The procedure is described as follows. All reactants except the initiator solution were charged into the flask and were then deoxygenated by bubbling with nitrogen for 30 min under stirring. The temperature was raised to 70 °C and an initiator solution was then injected rapidly into the reaction mixture to start the polymerization. The polymerization proceeded for about 7 h under a nitrogen atmosphere. The latices thus obtained were purified by means of centrifugation (16500 rpm, 1.5 h), decantation and resuspension in order to remove various contaminants in the serum, including water-soluble polymers. This operation was repeated at least three times and those latices were again purified by dialysis for 2 days. The solid content of final lattices was adjusted to about 5 wt% with deionized and distilled water for further characterization.

Table 1 The polymerization recipes. Polymerization temperature 70 °C; speed of stirrer 300 rpm

Ingredients	Amounts (g)	
Styrene	5.8	7.5
Acrylamide	1.7	0
Water	67.5	
Initiator	Variable	

Characterization

The decomposition rate constant of VA057 in water was determined using a UV spectrophotometer at a wavelength of 370 nm. Additionally, the potentiometric titration for VA057 solution was performed according to the method previously reported [13].

Total conversion was measured by precipitating the polymers produced in excess acetone and then drying them at 37 °C. The particle size and its distribution were determined by photon correlation spectroscopy (PCS) using a laser particle analyzer (LPA-3000/3100, Otsuka Electronics, Japan) and transmission electron microscopy (TEM) (JEM-2000, Japan Electronics). The number-average (D_n) and weight-average (D_w) diameters of the particles and the polydispersity were then calculated. Furthermore, the number of polymer particles (N_p) was evaluated by

$$N_p = \frac{6W_{is}}{\rho \pi D_w^3} \ , \qquad (1)$$

where W_{is} is the weight of polymer particles (grams per liter), which excludes the weight of water-soluble polymers and ρ is presumed to be the density of polystyrene (1.045 g/cm^{-3}) due to a very small number of AAm units incorporated into the particles.

The electrophoretic mobility of the latex particles was determined with a ZEECOM zeta potential analyzer (Microtec. Co., Japan) in NaCl solution and an ionic strength of 10^{-2} mol/l. The number of ionogenic groups at the particle surfaces was estimated by conductometric titration of the purified latices using an Auto-3000 Autotitrator (Toa Electronics, Japan).

Results and discussion

Properties of the amphoteric initiator VA057

Dissociation of VA057

The dissociation properties of VA057 initiator containing weakly acidic (—COOH) and basic [—C(=NH)-NHCH$_2$—] groups were examined by potentiometric titration with NaOH and HCl. The difference in the amount of H^+ or OH^- titrated with the initiator solution and water at each pH is plotted as a function of pH in Fig. 1. At a low or high pH region, the amphoteric initiator indicated large net ionization, whereas the net charge was almost zero in a pH range between 5 and 9. These results reflected the chemical structure of the amphoteric initiator, and the p*K* values were determined to be about 4.5 and 9.5 for the acid and base, respectively.

The polymerization behavior and the final colloidal properties in an emulsion polymerization system including a dissociable monomer are inevitably affected by the degree of dissociation of the dissociable monomer [14–15] and, hence, it can be supposed that the degree of dissociation of an amphoteric initiator, depending on the pH for polymerization, would also lead to a similar influence. In this study, polymerizations were carried out at different pHs between 3 and 10.

Decomposition and degradation of VA057

The rate constants of VA057 decomposition (k_d) at 50 and 70 °C were measured as a function of pH. The results are shown in Fig. 2. The rate constants gradually decreased with increasing pH and this was most significant around pH 10. After incubation the products of the aqueous solution of VA057 at pH 10 and 70 °C were examined by NMR and were found to be compounds having $-CONH_2$, $-CONHCH_2CH_2COOH$ and $-COOH$ groups, which resulted from the hydrolysis of $-C(=NH)NH(CH_2)_2COOH$. All azo compounds having these groups have lower k_d than VA057. The small k_d of VA057 at pH 10 was attributed to this degradation in addition to the gradually decreasing trend as shown in Fig. 2.

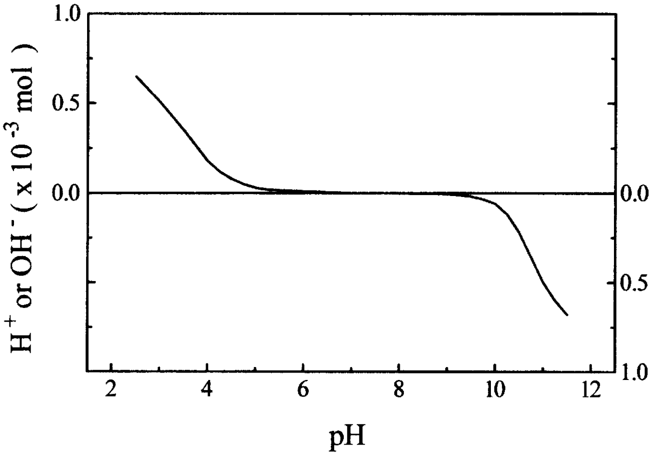

Fig. 1 Dissociation properties of VA057 amphoteric initiator. Titration condition: VA057 3.5×10^{-4} mol in 50 ml H_2O

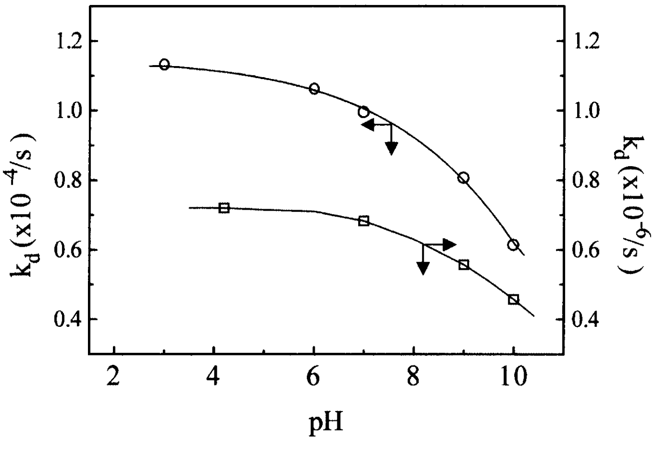

Fig. 2 pH dependence of the rate constant of VA057 decomposition in water. Temperature: 70 °C (○); 50 °C (□)

Kinetics of polymerization

Particle size and its distribution

As is well known, particle nucleation in an emulsifier-free emulsion polymerization is usually considered as a homogeneous or precipitation process, even for a sparingly water soluble monomer system [16–17]. The formation rate and the size of the polymer particles mainly depend upon the concentrations and the nature of the initiator and comonomer, as well as the polymerization temperature. At first, the initiator radicals form amphiphilic or surface-active oligoradicals by polymerizing monomers dissolved in the water phase. Consequently, they either form micellar-like precursor and primary particle or add more monomer units to themselves to become the precipitates, which are another kind of precursor particle. Then, because of high interfacial energy with respect to small particle size, such precursor and primary particles will be colloidally unstable so they have to aggregate to get sufficient surface charges or other forces for stabilization. The adsorption of surface-active oligomers, formed in the aqueous phase, onto the particle surfaces will be helpful in maintaining particle stability at this stage.

A water-soluble monomer added to an emulsifier-free emulsion system, such as AAm in the present case, results in the formation of hydrophilic chains anchored onto particle surfaces, which may enforce the stabilization of the colloids produced due to steric interaction. Thus, the number of particles is really fixed at a very early stage of polymerization. The mature particles continue to grow in the course of polymerization until the monomer droplets disappear.

As ionic initiators are used in the emulsifier-free emulsion copolymerization of St and AAm, the surfaces of the latex particles should be surrounded by hairy, positively or negatively charged chains which contribute to both electrostatic and steric interactions for latex stabilization. In the present case using VA057, the initiator is expected to provide anionic and/or cationic groups towards the particle surfaces, depending on pH, as shown schematically in Fig. 3. The particles thus formed are stabilized with water-hydrated chains and initiator fragments at the surfaces.

The size and the number of polymer particles formed in the polymerization initiated by VA057 and other ionic initiators are indicated in Fig. 4. It is clearly seen that the particles grew progressively and that the number of particles remained constant, regardless of the type of initiators. The number of particles prepared using VA057 or V50 was very similar and was greater than that of the KPS system when the same concentrations were used. This might be caused by the difference in the decomposition rate of the initiators. Much larger decomposition rate constants of the former two initiators led to the faster formation of surface-active oligomers and, hence, to a greater number of polymer particles compared with the KPS system.

The particle diameters determined by PCS and TEM are given in Table 2 for emulsion copolymerization of St and AAm as well as for emulsion homopolymerization of St. The ratio of the PCS diameter to the TEM diameter was less than 1.1 for St homopolymerization, whereas it was larger than 1.1 for St–AAm copolymerization, which reflected the existence of a water-soluble polymer layer for poly(St/AAm) P(St/AAm) latices, no matter which kind of initiator was used. It is worth mentioning that the PSt latex particles were larger than the AAm-containing particles, even those obtained using the amphoteric initiator. This means that the hydrophilic chains on the particle surfaces played a critical role in the colloidal stability, although AAm units might be incorporated mainly into the random copolymers consisting of the latex particles and might not be located exclusively on the surface of the latex particles [8]. Hence, it can be asserted that not only electrostatic interaction but also steric repulsion contributed to the high stability of the P(St/AAm) latices.

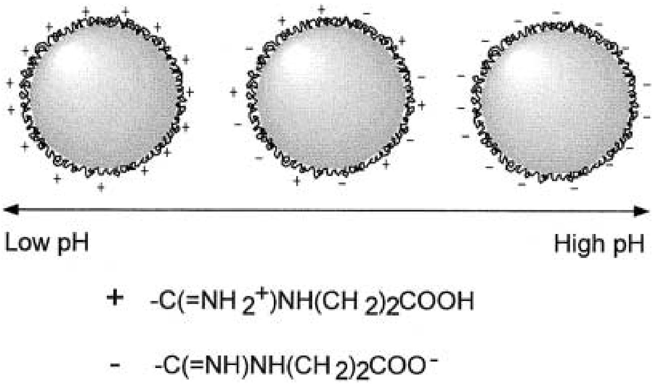

Fig. 3 Schematic diagram of the surface state of latex particles prepared with VA057 amphoteric initiator

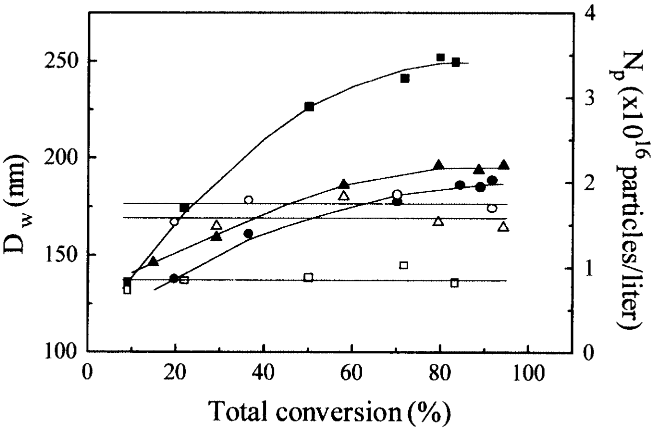

Fig. 4 The size and the number of polymer particles as a function of total conversion in the course of polymerization. Particle size (*filled symbols*) and number (*open symbols*). Initiator concentration 5.2×10^{-3} mol/l, VA057 (▲, △); potassium persulfate (*KPS*) (■, □); V50(●, ○)

The characteristics of the P(St/AAm) latices when varying the initiator concentration and the initial polymerization pH are summarized in Table 3. The pH was found to decrease significantly during the polymerization when the polymerization was started at pH 10. In order to understand the cause, we measured the pH of the initiator solution during the decomposition at 70 °C. A similar pH shift was observed and so this was attributed to the hydrolysis of VA057 in an alkaline solution resulting in the loss of cationic amidino groups.

It can also be seen from Table 3 that a stable latex was obtained at pH 3 even if the concentration of the amphoteric initiator was lowered to 1.7×10^{-3} mol/l, but at pH 10 no stable latex could be obtained and the particle aggregation was observed at the earlier stage of polymerization, with an initiator concentration lower than 3.5×10^{-3} mol/l. The reason for the instability of the latex obtained at pH 10 was assumed to be a low rate of initiator decomposition as well as the degradation of the initiator at high pH, so the incorporation of initiator fragments onto the particle surfaces was slower. The pH dependence of the latex particle sizes shown in Table 3 was explained by the low stability of the particles formed at higher pHs.

Table 2 Characteristics of poly(styrene/acrylamide) [*P*(*St*/*AAm*)] (*SA*) and polystyrene (*PSt*) latices prepared with amphoteric or other ionic initiators. The weight-average diameters (D_w) were determined by transmission electron microscopy (*TEM*) and photon correlation spectroscopy (*PCS*)

Sample	Initiator	Diameter (D_w, nm)			Final conversion (%)	Stability[b]
		TEM	PCS	PCS/TEM		
PSt	VA057	231.2	241.0	1.075	80.3	○
PSt	Potassium persulfate	549.0	553.7	1.010	83.5[a]	○
SA	VA057	172.0	194.0	1.128	93.5	◎
SA	Potassium persulfate	216.5	249.2	1.151	85.8	◎
SA	V50	168.9	189.0	1.119	97.6	◎

[a] Polymerized for 15 h because of the conversion of about 43.5% when polymerized for 7 h
[b] ◎ excellent; ○ good; △ fair; X aggregation

Table 3 Characteristics of P(St/AAm) latices prepared with VA057. The particle size was determined by PCS at 20 °C

No.	$[I_2]_o$ (mol/l)	PH values		Particle size		Final conversion (%)	Stability[a]
		Initial	Final	D_w (nm)	D_w/D_n		
1	3.5	10.0					X
2	5.2	10.0	7.18	232.1	1.011	75.5	○
3	6.9	10.0	7.25	227.5	1.012	70.1	◎
4	3.5	9.0	7.90	233.0	1.010	89.9	○
5	5.2	9.0		203.0	1.012	91.8	○
6	5.2	5.75		202.6	1.016	93.4	○
7	1.7	3.0	3.09	223.7	(193.4[a])	86.1	○
8	3.5	3.0	3.12	203.2	(182.3[a])	89.2	◎
9	5.2	3.0	3.22	194.0	1.010	93.5	◎
10	6.9	3.0	3.45	191.2	(169.3[a])	94.5	◎
11	8.6	3.0	3.54	183.5	(159.7[a])	96.9	◎

[a] Determined by TEM

[b] See Table 2 for meaning of symbols

Polymerization rate

AAm is a highly water soluble monomer and, hence, preferentially polymerizes in the aqueous phase. As is well known, the whole course of copolymerization of St and AAm in an emulsifier-free system with KPS as the initiator is divided into three characteristic stages based on the main reaction loci. The first stage might be an aqueous-phase polymerization of AAm, in preference to St, accompanying the particle nucleation from oligoradicals formed in the same phase. In the second stage only St polymerized exclusively in the particles until St droplets disappeared, whereas the polymerization of AAm was negligible. In the third stage the polymerization of AAm was re-accelerated in the aqueous phase [8, 18].

The total conversion as a function of polymerization time when the polymerizations were carried out at different pHs using the amphoteric initiator VA057 is illustrated in Fig. 5. Two other time–conversion curves, which were obtained from the polymerizations using KPS and V50 as initiators with the same concentration, are also presented in Fig. 5. Regarding various initiators, the polymerization rate increased in the sequence KPS, VA057 and V50 and their copolymerization rates at 20% conversion were approximately 8.0×10^{-5}, 1.9×10^{-4} and 2.3×10^{-4} mol/l/s, respectively, at the same initiator concentration (5.2×10^{-3} mol/l). These results are in accordance with the initiation activities because of their half lifetimes of about 33, 7 and 5.4 h at 60 °C in purified water, respectively. Figure 5 shows a significant difference in the polymerization rate between pH 10 and pH < 10 with the VA057 initiator. This is mainly attributable to the lower number of polymer particles produced at pH 10.

The effects of initiator concentration and polymerization temperature on the rate of VA057-initiated polymerization at 20% conversion are shown in Fig. 6. The rate at 20% conversion was proportional to the power 0.52 of the concentration of the initially charged initiator. Furthermore, an apparent activation energy for the conversion was evaluated to be about 36.7 kJ/mol, close to the propagation activity energy of styrene polymerization [19].

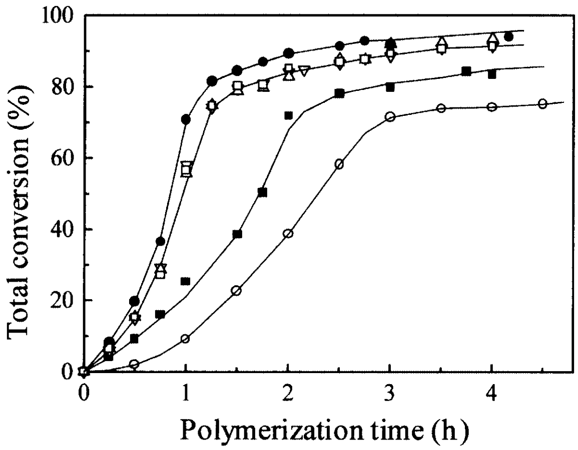

Fig. 5 Total conversion versus polymerization time with various conditions. Initiator concentration 5.2×10^{-3} mol/l, T = 70 °C. VA057: pH 3.0 (△); pH 5.75 (▽); pH 9.0 (□); pH 10.0 (○). KPS (■); V50 (●)

Interfacial electric properties of particles

Electrophoretic mobility

The electrophoretic mobilities of a series of latex particles were determined in order to study the electrodynamic characteristics of latex particles. The pH dependence of the electrophoretic mobilities of latex particles, obtained in the polymerizations with varying pH, at a constant ionic strength (10^{-2} mol/l) are shown in Fig. 7.

As expected, the latex particles prepared using V50 initiator exhibited a positive mobility and the particles prepared using KPS displayed a negative one in a broader pH region, corresponding to the nature of the charged particles. The electrophoretic mobilities of the

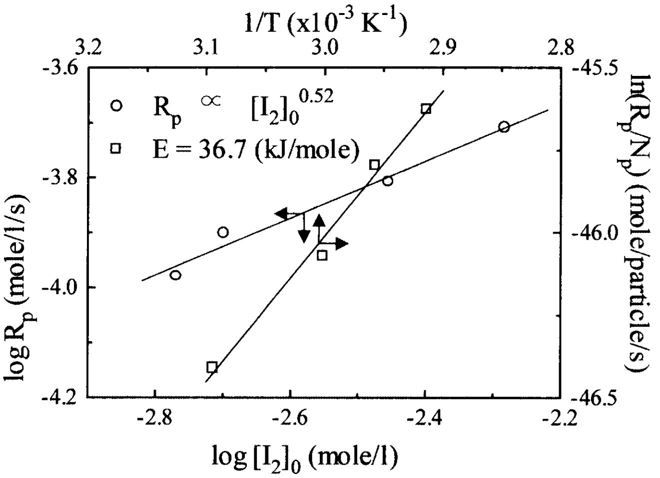

Fig. 6 The effects of polymerization temperature and initiator concentration on the polymerization rates at 20% conversion. Polymerization temperature 70 °C (○); initiator concentration 5.2 x 10^{-3} mol/l (□)

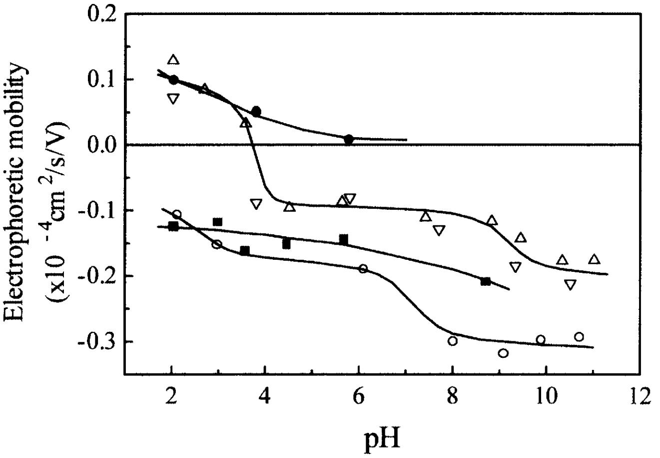

Fig. 7 The pH dependence of electrophoretic mobility of poly(styrene/acrylamide) lattices prepared with various conditions. VA057(5.2 x 10^{-3} mol/l): pH 3.0 (△); pH 5.75 (▽); pH 10.0 (○). KPS(5.2 x 10^{-3} mol/l) (■); V50(5.2 x 10^{-3} mol/l) (●). Ionic strength 10^{-2} M; T = 20 °C

latex particles produced with VA057 initiator at lower polymerization pHs displayed positive values in a strongly acidic region and then changed to negative ones in weakly acidic and totally basic regions. This behavior indicates that the latices were of amphoteric nature. Furthermore, the electrophoretic mobility of the amphoteric latex particles was seriously affected by pH in a strongly acidic or basic region, but remained almost the same between pH 5 and 9. Two inflection points of the mobility versus pH curves for VA057 cases (pH 3.0, 5.75) reflected the dissociation of two groups of the VA057 molecule well. The isoelectric points did not change significantly between two latices prepared at pH 3 and 5.75, respectively; however, the latex particles produced at pH 10 presented exclusively a negative mobility even in a strongly acidic region; thus, no amphoteric latex could be really obtained under this condition. These results indicate that the cationic groups, —C(=NH)NHCH$_2$—, which should originate from the decomposed initiator fragments and then be incorporated onto the particle surfaces, were cleaved or/and degraded during the course of polymerization. This can be explained if the cationic groups at the particle surface are converted to other groups due to their hydrolysis at pH 10. Additionally, the electrophoretic mobility of the particles prepared at pH 10 had much lower negative values at a broader electrophoresis pH compared to those of the latex particles prepared at lower polymerization pHs.

The electrophoretic mobility of amphoteric latex particles is plotted against ionic strength at a constant pH in Fig. 8. Apparently, the electrophoretic mobility showed a very slight increase and then a marked drop with increasing ionic strength and had a maximum value around 10^{-2} M NaCl. As hairy polyelectrolyte chains formed on the particle surfaces, such a variation in the mobility versus ionic strength curve for the present case of an amphoteric latex probably arose from the adsorption of coions onto the particle surface layer and the change in the volume charge density of the charged particles at a high electrolyte concentration. Similar behavior has already been reported in some other investigations [20–22].

Surface charge density

A typical curve of the conductometric titration of the latex particles produced with the amphoteric initiator

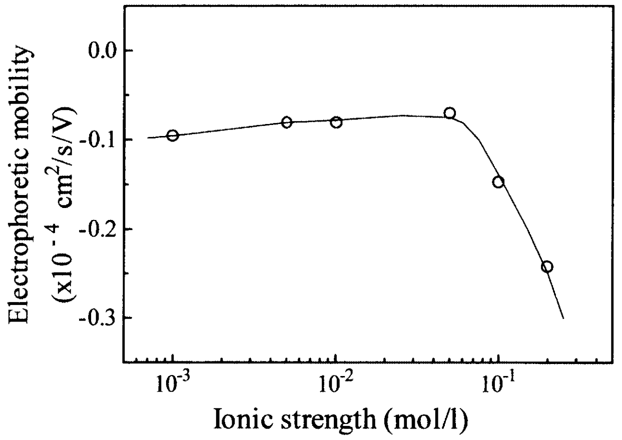

Fig. 8 Effect of ionic strength on electrophoretic mobility of an amphoteric latex prepared with VA057 initiator. pH 5.8

is presented in Fig. 9. Determination of two kinds of ionogens, =NH and —COOH from VA057 fragments, on the particles could not be done from the curve. According to the present experimental conditions, the effect of carboxyl groups possibly formed by hydrolysis of AAm during the polymerization could be safely neglected [8]. Hence, for amphoteric latices the total number of ionogens on the particle surfaces was initially estimated from conductometric titration and then the surface charge density was evaluated by only assuming an equivalence of two kinds of groups. The results are summarized in Table 4 and, as a comparison, the data of the surface charge density of latex particles prepared from two ionic initiators are also included. At first, the surface charge densities of the latex particles obtained from VA057 at low and medium pHs were very close to that of the V50 system but were much lower than that of the KPS one. The ionic group SO_4^- originating from KPS seemed to stay on the particle surfaces comfortably, whereas the ionogenic groups of the azo initiators might be partially pulled into the core of the particles.

Secondly, it can be seen that the surface charge density of the latex particles obtained with VA057 at pH < 10 was independent of polymerization pH; however, the particles obtained at pH 10 had a much larger surface charge density compared with the above cases. For the latter case the amphoteric groups were broken due to hydrolysis and no amphoteric latex could be produced, as indicated at Table 3, so only carboxyl ionic groups were linked to the latex particles. On the other hand, a large number of carboxyl groups incorporated onto the particle surfaces seemed to be necessary for latex particles to gain sufficient stability. High surface charge density would lead to a decrease in radical capture efficiency due to electrostatic repulsions and, hence, to a decrease in the polymerization rate [19]. The behavior was supported by the kinetics results as mentioned previously.

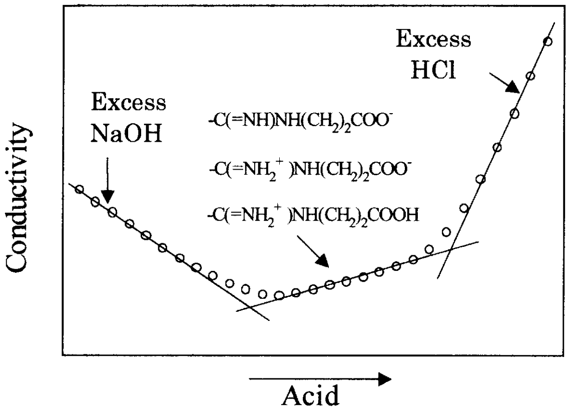

Fig. 9 A typical curve of conductometric titration for amphoteric latex particles

Finally, the surface charge density of the latex particles produced increased slightly with increasing VA057 initiator concentration, as shown in Table 4, although the number of surface groups determined by conductometric titration would, more or less, be underestimated for the P(St/AAm) hairylike latex system. These results can be explained if after the nucleation the oligoradicals produced in the aqueous phase passed through the water–polymer interface and then initiated the polymerization inside the particles. As a consequence, VA057 initiator fragments did not stay at the interface and were actually buried inside the particles.

Conclusions

An amphoteric initiator was successfully used in the emulsifier-free emulsion polymerization of St and AAm and, as a result, stable amphoteric latices were prepared directly. The decomposition rate constant and dissociation of VA057 amphoteric initiator in water were dependent on pH, i.e., the rate constants decreased very apparently around pH 10 and a large net ionization was induced at pHs lower than 4 and higher than 9. Using VA057 amphoteric compound as an initiator in St/AAm emulsion copolymerization, a smaller copolymerization rate and a larger size of the final particles at pH 10 were

Table 4 The surface charge density of P(St/AAm) latex particles prepared with amphoteric or other ionic initiators

Initiator type	VA057				V50				Potassium persulfate
$[I_2]_0$ (mmol/l)	5.2	5.2	5.2	5.2	1.7	3.5	8.6	5.2	5.2
PH[a]	3.0	5.75	9.0	10.0	3.0	3.0	3.0		
SIG[b] (μEq/g polymer)	5.7	4.4	3.9	11.6	4.3	5.4	7.3	7.6	12.6
D_w (nm)	194.0	202.6	203.0	232.1	223.7	203.2	183.5	189.0	249.2
SCD[c] ($\times 10^{-2}$ charge/nm^2)	11.1	9.0	8.0	27.0	9.7	11.0	13.4	13.5	31.6

[a] Indicates the pH for polymerization

[b] The number of surface ionic groups determined by conductometric titration

[c] The surface charge density per surface area of the particles

observed than those at pHs lower than 10. The surface charge density and the size of the latex particles obtained with VA057 at pH < 10 were comparable to those of the particles prepared using the V50 system, but were significantly lower than those prepared using the KPS system at the same molar concentration. In addition, some abnormal behavior appeared in the polymerization with VA057 at pH 10 and the properties of resulting latex due to the hydrolysis of amphoteric groups in a strongly alkali condition.

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