

Preparation of Amphoteric Latex by Modification of Styrene–Acrylamide Copolymer Latex

HARUMA KAWAGUCHI, HIROTOMO HOSHINO, and YASUJI OHTSUKA, *Department of Applied Chemistry, Keio University, 3-14-1, Hiyoshi, Yokohama 223, Japan*

Synopsis

Styrene–acrylamide copolymer latex prepared from the polymerization in an emulsifier-free aqueous medium was treated with hypochlorite and sodium hydroxide. The resulting latex indicated amphoteric property due to amino and carboxyl groups formed by the Hofmann reaction and competitive hydrolysis of amide groups, respectively. Amphoteric latices with the same particle size but different charge density (1.0–3.0 ionic groups/100 Å²) and different isoelectric points (6.4–9.2) have been prepared by changing the reaction conditions.

INTRODUCTION

Amphoteric latices are of interest because of their various uses. They can be used as specific absorbents, protein models, thermally regenerable ion exchanger, etc. They can also serve colloidal studies in which unstable and less-characterizable natural dispersants have been used so far.

Some methods have been tried to prepare amphoteric latices. Homola and James¹ copolymerized styrene, *N,N*-dimethylaminoethyl-methacrylate and methacrylic acid in emulsifier-free aqueous media at various monomer feed ratio and obtained amphoteric latices with isoelectric points from 4 to 8. Amphoteric latices also could be obtained from aqueous polymerization of core-composing monomer with an ionic monomer by use of an initiator capable of giving the opposite charge against the ionic monomer. For example, Ohtsuka et al.² obtained amphoteric latices from a styrene–vinylpyridine–persulfate system.

In addition to these preparative methods, it is expected that some existing latices can be modified to have an amphoteric property. The latter, modification methods, make it possible to obtain a series of amphoteric latices with the same size and the same size-distribution but different charge balance.

It was mentioned in our previous papers^{3,4} that copolymerization of styrene with acrylamides in emulsifier-free aqueous media resulted in the formation of stable copolymer latices. In this paper modification of styrene–acrylamide (ST–AA) copolymer latex to amphoteric one was attempted via the Hofmann reaction.

The Hofmann reaction changes amide groups to amine groups. A method to convert polyacrylamide to polyvinylamine effectively via the Hofmann reaction was developed by Tanaka and Senju^{5,6} and it was found that the suitable reaction condition for the polymer should be somewhat different from that for low-molecular-weight compounds. They obtained almost pure polyvinylamine by the Hofmann reaction in the aqueous solution under the following conditions: (1) The molar ratio of sodium hypochlorite to amide unit close to but less than

unity; (2) the reaction temperature lower than 0°C; and (3) the concentration of sodium hydroxide higher than 4 mole/liter.

On the contrary, the application of these conditions to the reaction for St-AA copolymer latex led to the formation of appreciable amounts of carboxyl groups due to the competitive hydrolysis reaction. Recently Eldridge⁷ obtained a similar result in the Hofmann reaction of polyacrylamide grafted on magnetic PVA beads although the conditions used by him were slightly different from Tanaka's with respect to the mode of reagents charge and the hypochlorite concentration. Judging from these results a low yield of amine groups might be unavoidable in the heterogeneous Hofmann reaction.

Competitive hydrolysis accompanied by the Hofmann reaction is rather advantageous for the preparation of an amphoteric latex with amide, amine, and carboxyl groups on its particle surface. Some variation in the reaction conditions was tried in order to change the balance of the amount of amine and carboxyl groups. The resulting amphoteric latices were characterized with conductometric and turbidimetric titration and electrophoresis.

EXPERIMENTAL

Materials

The St-AA copolymer latex to be modified was prepared in the manner described in the preceding papers.^{3,4} The latex resulting from copolymerization of 36 g of St with 4 g of AA in 160 g of distilled water with 2,2'-azobis(2-amidinopropane)hydrochloride as initiator at 70°C was centrifuged and the supernatant was decanted to remove the water-soluble polymer and other contaminants. The process of centrifugation-decantation-redispersion was repeated three times. The surface average diameter ($= \sum D_i^3 N_i / \sum D_i^2 N_i$, where N_i refers to the number of particles with diameter D_i) of latex particles was 250 nm and the ratio of the weight average diameter to surface average diameter was 1.010 according to electron microscopy. The amide fraction in particle-composing polymer was determined by elemental analysis and found to be 2.9%.

Sodium hypochlorite (NaOCl, Wako Chemicals Co., 7.4% aqueous solution, the concentration was determined by iodometry) and sodium hydroxide (Wako Chemicals Co.) was used as received. Cellulose tubing 32/36 (Visking Co.) and a mixture of Amberlite IR-120B and IRA 410 (Rohm & Haas Co.) were used for dialysis and ion exchange of latex, respectively, after the Hofmann reaction.

Modification of Copolymer Latex

NaOCl was added to the latex (containing 30% solid) by a molar ratio, $[\text{NaOCl}]/[\text{amide unit}]$, between 0.2 and 1.0 with stirring and cooling at 4°C. After 5 min NaOH (20 times of amide units in molar quantity) was added and the reaction temperature was changed to a specified one between 4 and 70°C. The reaction time was fixed to be 6 hr because leveling-off of the reaction was observed at more than 6 hr. The latex was stirred for the duration. Then the latex was purified by centrifugation, dialysis or, in some cases, ion exchange.

Characterization

All of the following measurements were carried out at 20°C. Almost all of the latices treated by NaOCl and NaOH indicated reversible coagulation-dispersion with changing pH and had their specific pH ranges of coagulation. Intensity of He-Ne laser (6328 Å) passing through the latices containing 0.05% solid was measured by a Hamamatsu TV 931-A photomultiplier as a function of pH. Intensity of the incident beam was monitored using a half mirror and another photomultiplier to eliminate the influence of periodical variation in the laser intensity. The isoelectric point of latex particles was determined from this measurement by reference to the Healy's method.⁸

The electrophoretic mobility of amphoteric particles was measured by use of a modified Tiselius-type apparatus at 0.02 ionic strength.

The amount of the ionic groups formed was determined by conductometric titration using a Metrohm Herisau Multi-Dosimat E 415 and a Toa Conductometer CM-2. The carboxyl and amine titration range was distinguished by the inflection point on the titration curve.

RESULTS AND DISCUSSION

Reversible Dispersion

One of the characteristic properties of amphoteric latex is reversible dispersion, that is, the latex coagulates in a specific pH range and redisperses in other pH range. Coagulation-titration curves for a series of St-AA copolymer latices treated by NaOCl and NaOH are shown in Figure 1. All of the latices showed coagulation-redispersion behavior but the transmittance at the end point of ti-

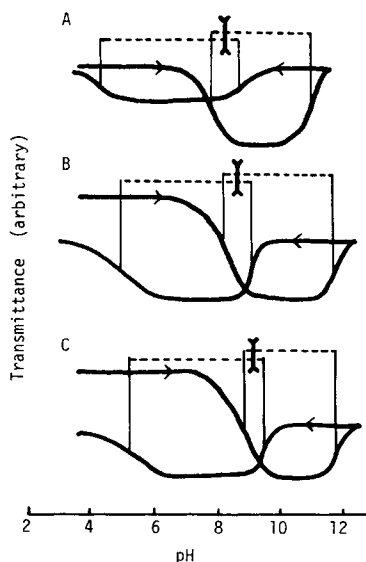


Fig. 1. Coagulation-titration curves for styrene-acrylamide copolymer latices treated with NaOCl and NaOH at 4°C. $[\text{NaOCl}]/[\text{Amide Unit}]$: (A) 0.19; (B) 0.38; (C) 0.74. Each latex was first titrated with NaOH and then back-titrated with HCl. The coagulation pH range (---) was defined as the range interposed by the half-value points of the difference in transmittance. The isoelectric point (|) was defined as the midpoint of the overlapped coagulation pH range.

tration was slightly lower than the original transmittance. This was attributed to the partial unredispersible coagulates resulting from a significant increase in the amount of ions added during the titration.

It was reported that the coagulation pH ranges in the forward titration (with base) and backward titration (with acid) for the amphoteric latex overlapped partially and the middle point of the overlapped pH range coincided with the isoelectric point measured by electrophoresis.⁸ The isoelectric point determined according to this method was presented in Figure 1 and Table I. The results indicate that the latex treated with more NaOCl has a higher isoelectric point. Namely, use of more NaOCl causes an increase in the ratio of amine formed by the Hofmann reaction to carboxyl groups formed by hydrolysis.

Electrophoresis

The relative amounts of cationic and anionic groups in some proteins and amphoteric particles were roughly estimated by electrophoretic method by some investigators.^{1,9} To estimate them the electrophoretic mobility (\bar{v}) of NaOCl-treated St-AA copolymer was measured at pH 3 and 11 and the zeta potential (ζ) and the charge density in the diffuse part of double layer (σ_D) were calculated from eqs. (1) and (2).

$$\zeta = \frac{6\pi\eta\bar{v}}{\epsilon f(\kappa a)} \quad (1)$$

$$\sigma_D = \left(\frac{2\epsilon RT}{\pi}\right)^{0.5} c^{0.5} \sinh \frac{zF\zeta}{2RT} \quad (2)$$

where η is the dynamic viscosity, ϵ the permittivity, $f(\kappa a)$ is the Henry's function,¹⁰ R is the gas constant, T is the temperature, c and z are the concentration and valence of electrolytes, and F is the Faraday constant.

σ_D at pH 3 and 11 was considered to be a measure of the amount of amine and carboxyl groups, respectively, although the real surface charge density of each ion cannot be known because it should be the sum of σ_D and the charge density in the Stern layer, the latter hardly being estimated.¹¹ As shown in Table II, the amount of amine formed increased by use of more NaOCl but that of carboxyl groups was not affected by the amount of NaOCl significantly.

TABLE I
Isoelectric Point of Amphoteric Latex Prepared via the Hofmann Reaction of
Styrene-Acrylamide Copolymer Latex

Reaction temperature (°C)	$\frac{[\text{NaOCl}]}{[\text{Amide unit}]}$ (mole/mole)	Isoelectric point
4	0.19	8.1
	0.38	8.6
	0.74	9.2
35	0.19	6.4
	0.74	8.7
70	0.99	Unmeasurable ^a

^a The latex did not redisperse.

TABLE II
Electrodynamic Property of Amphoteric latex Particles Prepared via the Hofmann Reaction of Styrene-Acrylamide Copolymer Latex

Reaction temperature (°C)	$\frac{[\text{NaOC}]}{[\text{Amide unit}]}$ (mole/mole)	pH	Electrophoretic Mobility $\times 10^4$ (cm ² /V sec)	$\sigma_D^a \times 10^{-3}$ (esu/cm ²)	$\frac{\sigma_{D3}^b}{\sigma_{D3} + \sigma_{D11}}$
4	0.19	3	2.5	3.3	0.47
		11	-2.8	3.8	
	0.38	3	3.0	4.2	0.53
		11	-2.7	3.7	
	0.74	3	4.0	5.8	0.58
		11	-3.0	4.2	
35	0.19	3	2.9	3.9	0.47
		11	-3.2	4.4	
	0.38	3	5.2	8.3	0.71
		11	-2.5	3.3	
70	0.99	3	2.3	3.0	0.40
		11	-3.3	4.5	

^a σ_D : The charge density in the diffuse part of double layer.

^b σ_{Di} ($i = 3$ or 11): σ_D measured at pH i .

Determination of Ionic Groups on Particle Surface

After the Hofmann reaction the latex was centrifuged to separate the particles from the serum. The amount of amine and carboxyl groups formed by the reaction was determined by conductometric titrations for the serum and the redispersed particles separately. The conductometric titration curves for the amphoteric particles are shown in Figure 2.

Ionic groups on the particle surface hardly affect the conductivity of the latex directly because of much less mobility of the particles, but they indirectly play an important role in deciding the conductivity because they restrict the corresponding amount of the counter-ions inside the slipping plane. The amount of ionized groups on the particle surface, Y , is changed by alteration in pH. A decrease in Y during titration causes release of the counter-ions out of the slipping plane and increases the conductivity of the latex. An increase in Y leads to the restriction of more counter-ions inside the slipping plane and suppress the elevation of conductivity. On the basis of this concept Ozaki and his co-workers, who reinvestigated the Homola's work,¹ regarded the intersection P in Figure 3 (a simplified conductometric titration curve) as the point of zero charge by checking the shape of potentiometric titration curve of the amphoteric latex simultaneously.¹² Because at the point of zero charge the amount of protonated amine groups should be equal to that of carboxylic ions, the range OP is referred to as the amount of carboxyl groups. Consequently PR is referred to as the total amount of amine groups since it corresponds to the sum of amine groups which remain still unprotonated at the point P but are protonated in the range PQ and carboxyl groups that are protonated in the range QR that is equal to OP in length. The slope of the range PQ may not be necessarily equal to that of QR but no difference in the slope was observed on the titration curves by Ozaki et al.¹²

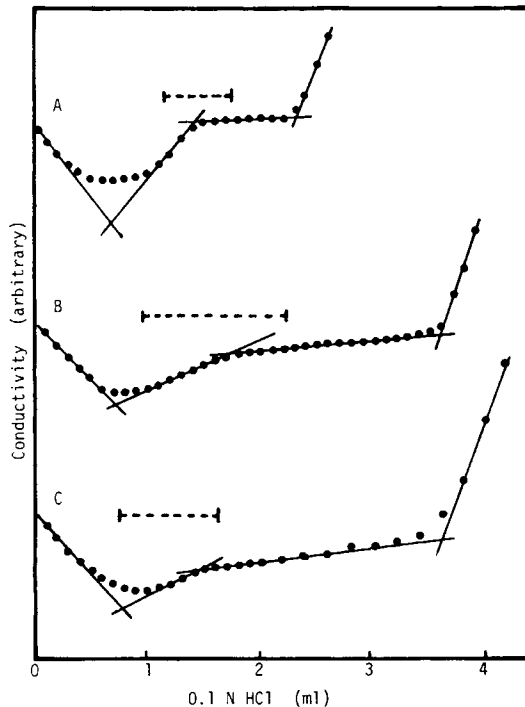


Fig. 2. Conductometric titration curves for styrene-acrylamide copolymer latices treated with NaOCl and NaOH at 4°C. $[\text{NaOCl}]/[\text{Amide Unit}]$: (A) 0.19; (B) 0.38; (C) 0.74. Solid content in each titrated latex (g): (A) 4.04; (B) 3.50; (C) 2.48. ---: Coagulation range which was observed during titration.

Each conductometric titration curve in Figure 2 had one inflection point between OR and it was provisionally regarded as *P*. The meaning of the relative length of *OP* and *PR* was considered by reference to the results from other measurements. According to Tables I and III the lower the isoelectric point is, the larger the value *OP/PR* is and an increase in $\sigma_{D3}/(\sigma_{D3} + \sigma_{D11})$ in Table II seems to be correlated to a decrease in *OP/OR* although the relation between them is not linear because σ_D is not necessarily a linear function of the surface charge density as mentioned previously. Judging from these relations the Ozaki's method is acceptable for determination of the amount of carboxyl and amine groups on the particle surface. The results are summarized in Table III. The end point for protonation of amine groups (corresponding to *Q* in Fig. 3) also could not be detected on the titration curves.

The amount of ions formed by the Hofmann reaction and hydrolysis on the particle surface but diffusing from the particle into the serum increased with elevating reaction temperature. Use of some cross-linking reagents might be effective to reduce the amount of diffusable ions. The amount of amine groups on the particles increased significantly by use of more NaOCl whereas that of carboxyl groups hardly was affected by $[\text{NaOCl}]$. The dependence of the amount of amine groups on $[\text{NaOCl}]$ decreased with elevating temperature and reaction at lower temperature was more advisable to form more amine groups on the particle surface. This temperature effect on the Hofmann reaction of acrylamide

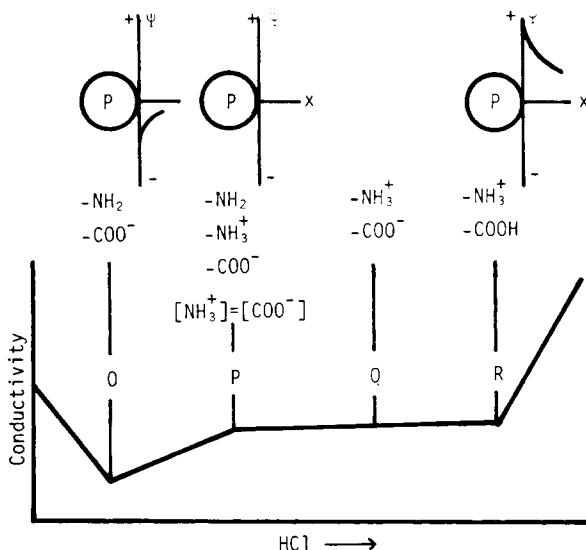


Fig. 3. Relation between surface charge of amphoteric latex particle (*P*) and shape of conductometric titration curve. Ψ : Potential, x : distance from particle surface.

units on the latex particles resembles that of the proacrylamide in the aqueous solution.⁵

More quantitative analyses of the reaction and investigation of the structure of modified polymer chain on the particle surface are now in progress.

CONCLUSIONS

The Hofmann reaction of acrylamide units on the particle surface of styrene-acrylamide copolymer latex was accompanied by hydrolysis of amide units. These competitive reactions were used for the preparation of amphoteric latices whose particle surface was occupied by amino, carboxyl, and unreacted amido groups. The amount of amine groups formed increased with lowering reaction temperature and increasing amount of sodium hypochlorite whereas the amount of carboxyl groups formed was not affected significantly by these conditions. The resulting latices showed reversible coagulation-dispersion with changing

TABLE III
Amount of Ionic Groups Formed by the Hofmann Reaction and Competitive Hydrolysis of Styrene-Acrylamide Copolymer Latex

Reaction temperature (°C)	$\frac{[\text{NaOCl}]}{[\text{Amide unit}]}$ (mole/mole)	Fraction of ions diffusing into the serum	$\frac{OP}{OR}$	On-surface ionic groups (units/100 Å ²)	
				Amine	Carboxyl
4	0.19	0.07	0.45	0.56	0.47
	0.38	0.08	0.30	1.48	0.63
	0.74	0.08	0.23	2.27	0.66
35	0.19	0.16	0.55	0.58	0.71
	0.74	0.24	0.35	1.42	0.76
70	0.99	0.41	0.36	0.90	0.50

pH and the isoelectric point of the particles ranged from 6.4 to 9.2 depending on the reaction conditions.

References

1. A. Homola and R. O. James, *J. Colloid Interface Sci.*, **59**, 123 (1977).
2. Y. Ohtsuka, H. Kawaguchi, and S. Hayashi, *Polymer*, **22**, (3) (1981) (to appear).
3. Y. Ohtsuka, H. Kawaguchi, and Y. Sugi, *J. Appl. Polym. Sci.*, **25**, 1637 (1981).
4. H. Kawaguchi, Y. Ohtsuka, and Y. Sugi, *J. Appl. Polym. Sci.*, **25**, 1649 (1981).
5. H. Tanaka and R. Senju, *Kobunshi Ronbunshu*, **33**, 309 (1976).
6. H. Tanaka, *J. Polym. Sci., Polym. Chem. Ed.*, **17**, 1239 (1979).
7. R. J. Eldridge, *Org. Coatings Plast. Chem.*, **40**, 157 (1979).
8. T. W. Healy, A. Homola, and R. O. James, *Faraday Dis. Chem. Soc.*, **65**, 156 (1978).
9. M. J. Hill, A. M. James, and W. R. Maxted, *Biochim. Biophys. Acta*, **75**, 402 (1963).
10. D. C. Henry, *Proc. Roy. Soc. A*, **133**, 106 (1931).
11. A. M. James, *Surface and Colloid Science II*, R. J. Good and R. R. Stromberg, Eds., Plenum, New York, 1979, p. 129.
12. M. Ozaki, K. Kurita, and Y. Kohata, *Preprints Symp. Colloid Interface Chem. Jpn.*, **32**, 314 (1979).

Received November 24, 1980

Accepted December 19, 1980