

## Determination of Surface Basic Groups in Cationic Polystyrene Latexes

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### Synopsis

Basic groups chemically bound to the surface of particles (surface basic groups) in cationic polystyrene latexes prepared by using 2,2'-azobis(2-amidinopropane) hydrochloride as initiator (initiator process) or by copolymerizing dialky aminoethyl methacrylates (copolymerization process) have been determined. It is clarified that in the initiator process amidino endgroups of polymers are effectively localized on the surface of particles and the latex is sufficiently stabilized with surface amidino groups. In the copolymerization process, the neutralized form of dialkylaminoethyl methacrylates is preferably localized on the surface of particles and the latex is sufficiently stabilized with surface amino groups. A particle formation process in both cases has been proposed.

### INTRODUCTION

The authors have recently investigated the preparation of cationic polystyrene latexes and clarified that stable latexes can be obtained in the absence of emulsifiers by using 2,2'-azobis(2-amidinopropane) hydrochloride (AAP) as initiator (initiator process) or by copolymerizing dialkylaminoethyl methacrylates as cationic monomer (copolymerization process).<sup>1</sup> Further, the authors have established the method for the determination of basic groups chemically bound to the surface of particles (surface basic groups) such as amidino groups resulting from AAP and amino groups resulting from dimethylaminoethyl methacrylate with which these latexes are stabilized.<sup>2</sup> Although some investigators have investigated emulsion polymerization of styrene initiated by AAP<sup>3</sup> and preparation of cationic latexes by copolymerizing cationic monomers,<sup>4</sup> the determination of surface basic groups has not been referred to.

In this paper, surface basic groups in cationic polystyrene latexes obtained by the initiator process and the copolymerization process were determined by the previously established method. Further, the authors attempted to elucidate the particle formation process in both cases.

### EXPERIMENTAL

**Materials.** All reagents and latexes have been described in the previous papers.<sup>1,2</sup>

**Procedures.** The determination of surface basic groups was carried out by the following procedure as has been described in detail in the previous paper.<sup>2</sup> First, the latexes were cleaned and surface basic groups were converted to the unneutralized form with ion exchange, and then were titrated conductometrically with strong acid. The surface area occupied by a surface basic group was calculated assuming a polymer density<sup>5</sup> of 1.05 g/cm<sup>3</sup>.

## RESULTS AND DISCUSSION

### Initiator Process Latexes

The results of the determination of surface amidino groups in cationic polystyrene latexes prepared by the initiator process are shown in Table I, where St and DPC represent styrene and dodecylpyridinium chloride, respectively. It is apparent from Table I that in the latex prepared in the absence of DPC the concentration of surface amidino groups is remarkably high. The amount of primary radicals formed in the aqueous phase by the decomposition of AAP during the period of polymerization (approximately 3 hr)<sup>1</sup> is calculated to be 1.584 mmole per 1 g polymer from the first-order rate constant of AAP<sup>3</sup> at 80°C on the assumption that the radical efficiency for polymerization initiation is 1. This means that the theoretical maximum concentration of total amidino endgroups of the polymers is 1.584 meq per 1 g polymer.

Consequently, the above-described high concentration of surface amidino groups seems to be probable, because it is believed that amidino endgroups of polymers are preferably localized on the surface of particles because of their hydrophilic nature. In this case, however, the number-average molecular weight of the polymers is calculated to be approximately  $1.5 \times 10^3$  on the assumption that each polymer chain has two amidino endgroups<sup>6,7</sup> and all the amidino endgroups are localized on the surface of the particles. This is extraordinarily small compared with that observed in the usual emulsion polymerization of St.<sup>6,7</sup> A detailed investigation concerning the determination of the number-average molecular weight of polymers as well as the determination of the concentration of total amidino endgroups of polymers seems to be necessary to settle this difficulty. The surface area occupied by a surface amidino group is only about 4 Å<sup>2</sup>, which is much smaller than the molecular

TABLE I  
Results of Determination of Surface Amidino Groups in the Initiator Process Latexes

Latex	Polymerization recipe, <sup>a</sup> g		Polymerization temperature, °C	Particle diameter, μ	Concentration of surface amidino groups, <sup>b</sup> meq/g	Surface area, <sup>c</sup> Å <sup>2</sup>
	St	DPC				
S-1586	4.55	0.00	80	0.181	1.294	4.1
S-1482	27.27	0.50	60	0.078	0.039	312
S-1481	27.27	1.00	60	0.051	0.037	503
S-1483	27.27	2.00	60	0.037	0.023	1112

<sup>a</sup> Polymerization recipe, g: water/St/DPC/AAP = 100/variable/variable/1.00.

<sup>b</sup> The milliequivalents of surface amidino groups found per 1 g polymers.

<sup>c</sup> Surface area occupied by one surface amidino group.

area of  $46.0 \text{ \AA}^2$  reported by Orr et al.<sup>8</sup> for hexadecylpyridinium chloride on the surface of particles in a butadiene/styrene copolymer latex. This indicates that, in spite of the absence of emulsifiers, the latex is sufficiently stabilized with surface amidino groups.

In the latexes prepared in the presence of DPC, the concentration of surface amidino groups is fairly low, and the surface area occupied by a surface amidino group reaches about  $300\text{--}1100 \text{ \AA}^2$ , which is much larger than the above-mentioned molecular area of a cationic emulsifier. In this case, however, DPC may be at least partially adsorbed on the surface of particles to stabilize them. The surface area occupied by a surface basic group was calculated regarding both surface amidino groups and DPC as surface basic groups. The results are shown in Table II, where it is assumed that DPC is completely adsorbed on the surface of particles. It is apparent from Table II that the surface area occupied by a surface basic group reaches about  $100 \text{ \AA}^2$ , which is about two times the above-mentioned molecular area of a cationic emulsifier. This indicates that these latexes are not sufficiently stabilized with surface basic groups, which may reasonably explain the reversible coagulation of these latexes.<sup>1</sup>

Based on these considerations, it may be concluded that in the initiator process, amidino endgroups of the polymers are effectively localized on the surface of particles and the latex is sufficiently stabilized with surface amidino groups. The particle formation process in the initiator process will be somewhat similar to that proposed by Ottewill et al.<sup>9</sup> for the polymerization of St initiated by potassium persulfate and may be represented as follows. The thermal decomposition of AAP gives primary radicals,<sup>10</sup> which will add to St slightly dissolved in water to form growing radicals. Since growing radicals propagate and become increasingly hydrophobic, they will precipitate out to form primary particles at a critical degree of polymerization. Primary particles are unstable, and coagulation will occur until the particles are sufficiently stabilized by the localization of amidino endgroups of polymers on the surface of the particles. Growing radicals newly formed in water will precipitate out to form new primary particles or be captured by preformed primary particles. Finally, both the increase in the number of particles by precipitation and the decrease by coagulation will become almost negligibly small and the number of particles in the polymerization system will become constant.

TABLE II  
Calculation Results of the Surface Area Occupied by  
a Surface Basic Group in the Initiator Process Latexes

Latex	Concentration of DPC, <sup>a</sup> meq/g	Concentration of surface basic groups, <sup>b</sup> meq/g	Surface area, <sup>c</sup> $\text{\AA}^2$
S-1482	0.065	0.104	117
S-1481	0.130	0.167	111
S-1483	0.259	0.282	91

<sup>a</sup> The milliequivalents of DPC added per 1 g polymers.

<sup>b</sup> The milliequivalents of surface basic groups including surface amidino groups and DPC per 1 g polymers.

<sup>c</sup> Surface area occupied by one surface basic group.

### Copolymerization Process Latexes

Surface basic groups in the copolymerization process latexes are composed of amino groups and amidino groups, which cannot be determined separately by the method previously described.<sup>2</sup> However, since the concentration of the latter seems to be much lower than that of the former, in the following discussion it was assumed that surface basic groups are composed of amino groups only.

In Table III are shown the results of the determination of surface amino groups in cationic polystyrene latexes prepared by the copolymerization process using dimethylaminoethyl methacrylate (DM) as cationic monomer. It is apparent from Table III that, irrespective of the amount of DPC or AAP, only about 8% of amino groups are localized on the surface of particles when DM is unneutralized, whereas about 80% of amino groups are localized on the surface of particles when DM is neutralized. This indicates that the neutralized form of DM is preferably localized on the surface of particles because of its hydrophilic nature. In Table III are shown also the calculation results of the surface area occupied by a surface amino group. It is apparent from Table III that in the latexes prepared by using the neutralized form of DM, the surface area occupied by a surface amino group is much smaller than the above-mentioned molecular area of a cationic emulsifier, which indicates that these latexes are sufficiently stabilized with surface amino groups.

The effect of the degree of neutralization of the cationic monomer on the distribution of amino groups was investigated more precisely. In Tables IV and V are shown the results of the determination of surface amino groups in cationic polystyrene latexes prepared by the copolymerization process using DM and diethylaminoethyl methacrylate (DE) as cationic monomer at various degrees of neutralization. It is apparent from the tables that the particle diameter is particularly large at a degree of neutralization of 0.00 and almost constant in the range of 0.25–1.00, that is, the presence of a small amount of the neutralized form of the cationic monomer considerably increases the

TABLE III  
Results of Determination of Surface Amino Groups  
in the Copolymerization Process Latexes

Latex	Polymerization recipe <sup>a</sup>			Particle diameter, $\mu$	Concentration of surface amino groups, <sup>c</sup> meq/g	Distri- bution of amino groups <sup>d</sup>	Surface area, <sup>e</sup> $\text{Å}^2$
	DN <sup>b</sup>	DPC, g	AAP, g				
S-1484	0.00	1.00	1.00	0.070	0.050	0.076	271
S-1486	1.00	1.00	1.00	0.096	0.533	0.815	18.5
S-1507	1.00	0.00	0.20	0.113	0.515	0.787	16.3
S-1491	1.00	0.00	1.00	0.134	0.534	0.817	13.3

<sup>a</sup> Polymerization recipe, g: water/St/DM/DPC/AAP = 100/24.47/2.80/variable/variable. DM was neutralized with hydrogen chloride; polymerization temperature: 60°C.

<sup>b</sup> Degree of neutralization of DM.

<sup>c</sup> The milliequivalents of surface amino groups found per 1 g polymers.

<sup>d</sup> Ratio of the concentration of surface amino groups to that of total amino groups.

<sup>e</sup> Surface area occupied by one surface amino group.

number of particles. This indicates that the neutralized form of the cationic monomer plays an important role in the formation of particles.

The relationship between the percentage of amino groups localized on the surface of particles and the degree of neutralization of the cationic monomer can be represented by Figure 1. It is apparent from the figure that the percentage of amino groups localized on the surface of particles increases significantly with increase in the degree of neutralization of the cationic monomer, which indicates that the neutralized form of the cationic monomer is preferably localized on the surface of particles because of its hydrophilic nature. A distinct difference between the distribution behavior of DM and DE, however, can be observed at a degree of neutralization of 0.00–0.25; that is, in the case of DM, the percentage of amino groups localized on the surface of particles increases gradually from 12% to 19% with increase in the degree of neutralization from 0.00 to 0.25, whereas in the case of DE this percentage increases considerably from 2% to 29%. Such a difference between the distri-

TABLE IV  
Effect of Degree of Neutralization of DM on the Distribution of Amino Groups

Latex	Degree of neutralization of DM <sup>a</sup>	Particle diameter, $\mu$	Concentration of surface amino groups, <sup>b</sup> meq/g	Distribution of amino groups <sup>c</sup>	Surface area, <sup>d</sup> $\text{\AA}^2$
S-1493	0.00	0.122	0.237	0.121	32.8
S-1494	0.25	0.081	0.374	0.191	31.3
S-1496	0.50	0.072	0.904	0.461	14.6
S-1495	0.75	0.073	1.328	0.677	9.8
S-1492	1.00	0.078	1.643	0.837	7.4

<sup>a</sup> Polymerization recipe, g: water/St/DM/AAP = 100/6.29/2.80/1.00; DM was neutralized with hydrogen chloride; polymerization temperature: 60°C.

<sup>b</sup> The milliequivalents of surface amino groups found per 1 g polymers.

<sup>c</sup> Ratio of the concentration of surface amino groups to that of total amino groups.

<sup>d</sup> Surface area occupied by one surface amino group.

TABLE V  
Effect of Degree of Neutralization of DE on the Distribution of Amino Groups

Latex	Degree of neutralization of DE <sup>a</sup>	Particle diameter, $\mu$	Concentration of surface amino groups, <sup>b</sup> meq/g	Distribution of amino groups <sup>c</sup>	Surface area, <sup>d</sup> $\text{\AA}^2$
S-1580	0.00	0.242	0.028	0.015	140
S-1581	0.25	0.094	0.546	0.294	18.5
S-1582	0.50	0.094	0.718	0.386	14.1
S-1583	0.75	0.077	0.811	0.436	15.2
S-1584	1.00	0.088	1.574	0.846	6.9

<sup>a</sup> Polymerization recipe, g: water/St/DE/AAP = 100/6.29/3.30/1.00; DE was neutralized with hydrogen chloride; polymerization temperature: 60°C.

<sup>b</sup> The milliequivalents of surface amino groups found per 1 g polymers.

<sup>c</sup> Ratio of the concentration of surface amino groups to that of total amino groups.

<sup>d</sup> Surface area occupied by one surface amino group.

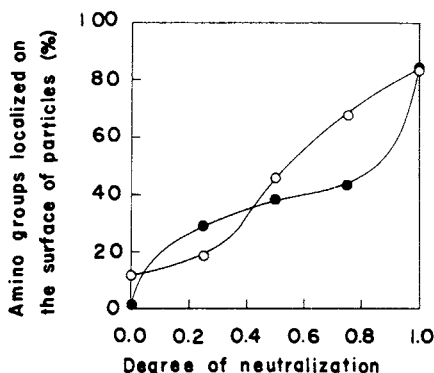


Fig. 1. Relationship between percentage of amino groups localized on the surface of particles and degree of neutralization of cationic monomers: (○) DM; (●) DE.

bution behavior of DM and DE may be attributed to the difference in the monomer reactivity ratio with St or the solubility in water between these monomers as was described in the previous paper.<sup>1</sup>

Based on these considerations, the formation of particles in the copolymerization process seems to be somewhat similar to that in the initiator process. In this process, however, growing radicals formed in water will be composed of St, the cationic monomer, and the neutralized form of the cationic monomer, of which the hydrophilic nature will be strongly affected by the degree of neutralization. Therefore, the number of particles and the percentage of amino groups localized on the surface of particles will be strongly dependent on the degree of neutralization of cationic monomers.

### Copolymerization Process Latexes with High Solids Content

Cationic polystyrene latexes with high solids content can be obtained by two-step polymerization.<sup>1</sup> First, particles are prepared by the copolymerization process (step 1), then St is polymerized in the particles (step 2). In Table VI are shown the results of the determination of surface amino groups in the latexes prepared at various degrees of neutralization of DM in step 1. It is apparent from Table VI that the relationship between the percentage of amino groups localized on the surface of particles and the degree of neutralization of DM is almost consistent with that in Table IV, where all runs correspond to step 1 in Table VI. This indicates that the distribution of amino groups is predominantly determined in step 1 and St polymerizes in the interior of particles in step 2. In step 2, the outer layer of particles containing surface amino groups will be expanded without being buried in the interior of particles, and the number of surface amino groups per one particle will not change. It is apparent from Table VI that the surface area occupied by a surface amino group is in the range of 15–43 Å<sup>2</sup>, which is smaller than the above-mentioned surface area of a cationic emulsifier. This indicates that these cationic polystyrene latexes with high solids content are sufficiently stabilized with surface amino groups in spite of the absence of emulsifiers.

TABLE VI  
Results of Determination of Surface Amino Groups in the  
Copolymerization Process Latexes with High Solids Content

Latex	Degree of neutralization of DM <sup>a</sup>	Particle diameter, $\mu$	Concentration of surface amino groups, <sup>b</sup> meq/g	Distribution of amino groups <sup>c</sup>	Surface area, <sup>d</sup> $\text{\AA}^2$
S-1499	0.50	0.482	0.058	0.296	34.1
S-1498	0.75	0.430	0.144	0.735	15.3
S-1497	1.00	0.182	0.175	0.893	29.8

<sup>a</sup> Polymerization recipe, g: step 1, water/St/DM/AAP = 100/6.29/2.80/1.00; step 2, St = 81.81; DM was neutralized with hydrogen chloride; polymerization temperature: 60°C.

<sup>b</sup> The milliequivalents of surface amino groups found per 1 g polymers.

<sup>c</sup> Ratio of the concentration of surface amino groups to that of total amino groups.

<sup>d</sup> Surface area occupied by one surface amino group.

## CONCLUSIONS

Surface amidino groups in the initiator process cationic polystyrene latexes were determined. In the latex prepared in the absence of DPC, the concentration of surface amidino groups is considerably high and the latex is sufficiently stabilized with surface amidino groups, whereas in the latexes prepared in the presence of DPC, the concentration of surface amidino groups is fairly low and the latex is not sufficiently stabilized with surface amidino groups. The formation of particles in the initiator process can be explained by the precipitation of growing radicals formed in water.

Surface amino groups in the copolymerization process cationic polystyrene latexes were determined. The percentage of amino groups localized on the surface of particles increases remarkably with the increase in the degree of neutralization of cationic monomers. The number of particles also increases significantly by the neutralization of cationic monomers. The formation of particles in the copolymerization process can be explained by the precipitation of growing radicals composed of St, the cationic monomer, and the neutralized form of the cationic monomer. Further, in the preparation of the copolymerization process latexes with high solids content by two-step polymerization, the distribution of amino groups is predominantly determined in step 1 and St polymerizes in the interior of particles in step 2, that is, the outer layer of particles containing surface amino groups is expanded without being buried in the interior of the particles.

## References

1. K. Sakota and T. Okaya, to be published.
2. K. Sakota and T. Okaya, to be published.
3. J. W. Breitenbach, K. Kuchner, H. Fritze, and H. Tarnowiecki, *Brit. Polym. J.*, **2**, 13 (1970).
4. W. J. Le Herve and D. P. Sheetz (to Dow Chemical Co.), Jap. Pat. 68-28, 110.

5. O. G. Lewis, *Physical Constants of Linear Homopolymers*, Springer-Verlag, New York, 1968, pp. 134-135.
6. J. Hearn, R. H. Ottewill, and J. N. Shaw, *Brit. Polym. J.*, **2**, 116 (1970).
7. H. J. van den Hul and J. W. Vanderhoff, *Brit. Polym. J.*, **2**, 121 (1970).
8. R. J. Orr and L. Breitman, *Can. J. Chem.*, **38**, 668 (1960).
9. J. W. Goodwin, J. Hearn, C. C. Ho, and R. H. Ottewill, *Brit. Polym. J.*, **5**, 347 (1973).
10. G. S. Hammond and R. C. Newman, Jr., *J. Amer. Chem. Soc.*, **85**, 1501 (1963).

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