Preparation of Cationic Polystyrene Latexes in the Absence of Emulsifiers

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Synopsis

Preparation of cationic polystyrene latexes has been investigated in the absence of emulsifiers. It is clarified that a stable latex can be obtained by using 2,2'-azobis(2-amidinopropane) hydrochloride as initiator (initiator process). The latex seems to be stabilized with the fragments of the initiator chemically bound to the surface of particles. More stable latexes can be obtained by copolymerizing cationic monomers such as dialkyl aminoethyl methacrylates (copolymerization process). The stability of these latexes may predominantly be attributed to cationic monomers chemically bound to the surface of particles. Stable latexes with high solids content can be obtained by using the two-step polymerization technique in the copolymerization process. The particle formation process in the initiator process and the copolymerization process is discussed.

INTRODUCTION

It has been demonstrated that cationic latexes can be obtained by using cationic emulsifiers,[1] by using cationic polymers as emulsifier,[2] or by copolymerizing cationic monomers.[3,4] Among these processes, the last one gives cationic latexes having the advantage of enhanced stability,[4] excellent water resistance,[4] and presumably low toxicity because of the absence of emulsifiers.[5] It seems, however, that there have been no earlier published studies on the *locus* of polymerization of these monomers.

Some investigators have obtained anionic latexes in the absence of emulsifiers by using potassium persulfate as initiator and clarified that these latexes are stabilized with the fragments of the initiator chemically bound to the surface of particles.[6–9] This process seems to be applicable also to preparation of cationic latexes.

Based on the above-described considerations, the authors intended to obtain stable emulsifier-free cationic latexes. First, typical cationic emulsifier was used as reference, then the emulsifier was excluded. In this paper, preparation of emulsifier-free cationic polystyrene latexes by two processes, that is, by using 2,2'-azobis(2-amidinopropane) hydrochloride (AAP) as initiator (initiator process) or by copolymerizing dialkyl aminoethyl methacrylates (copolymerization process), in the manner mentioned above will be dealt with.

EXPERIMENTAL

Materials

Deionized water was used. Styrene (St) of extrapure grade and dimethyl aminoethyl methacrylate (DM) and diethyl aminoethyl methacrylate (DE) of chemically pure grade were used after distillation under reduced pressure. Dodecylpyridinium chloride (DPC) (Wako Pure Chemicals Co., Ltd.), poly (oxyethylene nonylphenyl ether) (PNE) (average number of moles of ethylene oxide per one molecule, 10; Kao-Atlas Co., Ltd.), and AAP (Wako Pure Chemicals Co., Ltd.) were used without further purification.

Procedures

Preparation of latexes was carried out at 60°C unless otherwise stated. The prescribed amounts of water, DPC, hydrogen chloride, St, and DM (or DE) were placed in a 500-ml flask equipped with a stirrer and heated to and kept at the polymerization temperature. After the completion of dissolution and emulsification, the prescribed amount of AAP dissolved in water was introduced. The polymerization was continued till it was substantially completed. Conversions were determined gravimetrically.

Characterization of latexes was carried out as follows. The type of emulsion was judged by staining the continuous phase of emulsion with water-soluble dye dissolved in water or oil-soluble dye dissolved in toluene.[10] The pH was observed at 25°C. The particle diameter was determined as number average by electron microscopy. The stability was judged by the mechanical stability determined qualitatively by rubbing a small amount of latex with fingers.

RESULTS AND DISCUSSION

Preparation of Latexes by Initiator Process

Preparation of cationic polystyrene latexes by the initiator process was investigated. Using AAP as initiator, the effect of the amount of cationic emulsifier DPC on the polymerization of St was examined, and the results are

TABLE I
Effect of Amount of DPC on the Polymerization of St[a]

Run no.	Amount of DPC, g	Properties of latex		
		Stability	pH	Particle diameter, μ
S-1479	0.0	poor (coagulated)	—	—
S-1480	0.1	poor (coagulated)	—	—
S-1482	0.5	poor (reversible coagulation)	4.61	0.078
S-1481	1.0	poor (reversible coagulation)	4.70	0.051
S-1483	2.0	good	3.99	0.037

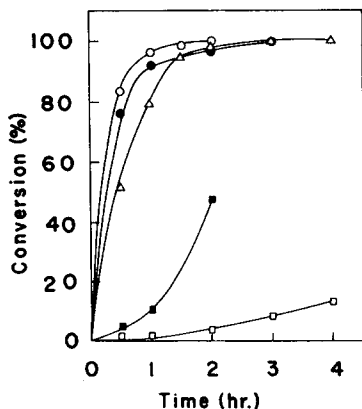[a] Polymerization recipe, g: water/St/DPC/AAP = 100/27.27/variable/1.00.

Fig. 1. Effect of amount of DPC on the polymerization of St: (□) S-1479; (■) S-1480; (△) S-1482; (●) S-1481; (○) S-1483. All runs correspond to those in Table I.

shown in Table I and Figure 1. It is apparent that the rate of polymerization increases remarkably with increase in the amount of DPC, which corresponds to the increase in the number of particles as is generally recognized in emulsion polymerization.[11] In the absence of DPC, although the formation of particles was confirmed by the increase in the turbidity of polymerization system, the latex coagulated through the phase inversion from O/W emulsion to O/W/O emulsion.[10] The latexes obtained with 0.5 g or 1.0 g DPC show reversible coagulation, that is, these latexes form coagulum on standing which disperse into separate particles with mechanical stirring. By the introduction of about 1.7–1.9 wt-% nonionic emulsifier PNE, these latexes become sufficiently stable and do not show any coagulation.

In the absence of DPC, the effect of the polymerization temperature was examined using a reduced amount of St to avoid coagulation through phase inversion. The results are shown in Table II and Figure 2. It is apparent that at the polymerization temperature of 60°C, the rate of polymerization is extremely low and the latex coagulates through phase inversion, whereas at a polymerization temperature of 80°C, the polymerization is substantially completed within a few hours and a stable latex is obtained. Such a remarkable effect of the increase in polymerization temperature may be attributed to an increase in the thermal decomposition rate of AAP which increases the number of particles and enhances the stability of particles.

TABLE II
Effect of Polymerization Temperature on the Initiator Process[a]

Run no.	Polymerization temperature, °C	Properties of latex		
		Stability	pH	Particle diameter, μ
S-1585	60	poor (coagulated)	—	—
S-1586	80	good	6.84	0.181

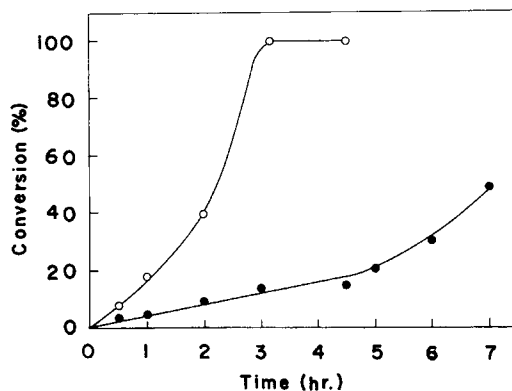[a] Polymerization recipe, g: water/St/AAP = 100/4.55/1.00.

Fig. 2. Effect of polymerization temperature on the initiator process: (●) S-1585; (○) S-1586. All runs correspond to those in Table II.

Based on the above-described considerations, it may be concluded that a stable cationic polystyrene latex can be obtained in the absence of emulsifiers by the initiator process. The particle formation process in the initiator process seems to be somewhat similar to that proposed by Ottewill et al.[9] and Fitch et al.[12] for anionic latexes and may be represented as follows. Thermal decomposition of AAP gives primary radicals[13] which add to St slightly dissolved in water[14] to form growing radicals. Since growing radicals propagate and become increasingly hydrophobic, they precipitate out to form particles.

Some investigators[15,16] have demonstrated that, in emulsion polymerization of St initiated by potassium persulfate, each polymer chain has two endgroups resulting from the fragments of the initiator. It seems that this is also the case for the initiator process, and each polymer chain has two endgroups resulting from the fragments of AAP. These endgroups may be at least partially localized on the surface of particles because of their hydrophilic nature and dissociate to form cations represented by the following formula[13]:

$$
\begin{array}{c}
\quad\quad CH_3 \quad NH_2 \\
\quad\quad | \quad\quad \diagup\!\!\!\!= \\
R_1 - C - C^+ \quad\quad Cl^- \\
\quad\quad | \quad\quad \diagdown\!\!\!= \\
\quad\quad CH_3 \quad NH_2
\end{array}
\tag{1}
$$

where R_1 is a polymer chain. Therefore, the initiator process latex may be stabilized with these cations chemically bound to the surface of particles.

Preparation of Latexes by Copolymerization Process

Preparation of more stable cationic polystyrene latexes by the copolymerization process was investigated. In the presence of cationic emulsifier DPC, St was copolymerized with cationic monomer DM using AAP as initiator. The effect of the amount of DM and the degree of neutralization of DM with hydrogen chloride was examined, and the results are shown in Table III. The amount and degree of neutralization of DM had little effect on the rate of polymerization, which indicates that the number of particles is predomi-

TABLE III
Effect of Amount and Degree of Neutralization of DM on the Copolymerization
of St with DM[a]

Run no.	Amount of DM, g	Degree of neutralization of DM	Properties of latex		
			Stability	pH	Particle diameter, μ
S-1481[b]	0.00	0.00	poor (reversible coagulation)	4.70	0.051
S-1485	0.93	0.00	good	—	—
S-1484	2.80	0.00	good	7.20	0.070
S-1486	2.80	1.00	excellent	3.09	0.096

[a] Polymerization recipe, g: water/St/DM/DPC/AAP = 100/(27.27-variable)/variable/1.00/1.00.
[b] See also Table I.

nantly determined by emulsifiers, as is generally recognized in emulsion polymerization.[11] On the other hand, Table III shows that the stability of latex is much enhanced by the introduction of DM, especially when neutralized.

In the absence of DPC, St was copolymerized with DM using AAP as initiator. The effect of the degree of neutralization of DM with hydrogen chloride and the amount of AAP was examined, and the results are shown in Table IV. In the run in which DM was not neutralized, the rate of polymerization was low and the latex coagulated through phase inversion, whereas in the runs in which DM was neutralized, the rate of polymerization was sufficiently high and stable latexes were obtained. In the latter runs, the amount of AAP had little effect on the rate of polymerization or the stability of latex. These results indicate that in the copolymerization process, the neutralized form of DM plays an important role in the formation and stabilization of particles.

To confirm this, the effect of the degree of neutralization of cationic monomers with hydrogen chloride on the copolymerization process was examined more precisely, using a reduced amount of St to avoid coagulation through

TABLE IV
Effect of Degree of Neutralization of DM and Amount of AAP
on the Copolymerization Process[a]

Run no.	Degree of neutralization of DM	Amount of AAP, g	Properties of latex		
			Stability	pH	Particle diameter, μ
S-1490	0.00	1.00	poor (coagulated)	—	—
S-1507	1.00	0.20	good	2.30	0.113
S-1506	1.00	0.50	good	2.24	0.118
S-1491	1.00	1.00	good	3.20	0.134

[a] Polymerization recipe, g: water/St/DM/AAP = 100/24.47/2.80/variable.

TABLE V
Effect of Degree of Neutralization of DM on the Copolymerization Process[a]

Run no.	Degree of neutralization of DM	Properties of latex		
		Stability	pH	Particle diameter, μ
S-1493	0.00	good	8.37	0.122
S-1494	0.25	good	7.41	0.081
S-1496	0.50	good	6.75	0.072
S-1495	0.75	good	6.06	0.073
S-1492	1.00	excellent	2.24	0.078

[a] Polymerization recipe, g: water/St/DM/AAP = 100/6.29/2.80/1.00.

phase inversion.   Using DM or DE as cationic monomer, St was polymerized by the copolymerization process at various degrees of neutralization.   The results for DM are shown in Table V and Figure 3 and the results for DE are shown in Table VI and Figure 4.   It is apparent from Table V and Figure 3 that the rate of polymerization increases with increase in the degree of neutralization of DM, which corresponds to the increase in the number of particles.   Table V shows that the stability of latex is excellent when DM is completely neutralized.   As can be expected from the decrease in dispersed-phase concentration, the stability of latexes in Table V is better than that of corresponding latexes in Table IV.

It is apparent from Table VI and Figure 4 that this trend is also the case for DE.   The substitution of DE for DM, however, brings about a lowering of the rate of polymerization and a decrease in the number of particles, which may be attributed to the difference in the monomer reactivity ratio or solubility in water between these monomers.   That is to say, the monomer reactivity ratios r_1 and r_2 between St (M_1) and these monomers (M_2) are reported[17] to be 0.51 and 0.38, respectively, for DM, whereas they were calculated[18] to be 0.18 and 1.25, respectively, for DE.   Further, DM is freely soluble in water, whereas DE is sparingly soluble in water.[19]
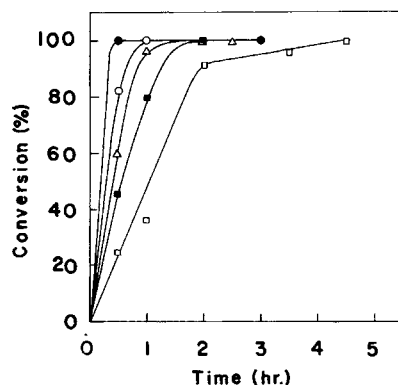

Fig. 3. Effect of degree of neutralization of DM on the copolymerization process: (□) S-1493; (■) S-1494; (▲) S-1496; (●) S-1495; (○) S-1492. All runs correspond to those in Table V.

TABLE VI
Effect of Degree of Neutralization of DE on the Copolymerization Process[a]

Run no.	Degree of neutraliza- tion of DE	Properties of latex		
		Stability	pH	Particle diameter, μ
S-1580	0.00	good	9.20	0.242
S-1581	0.25	good	7.74	0.094
S-1582	0.50	good	7.38	0.094
S-1583	0.75	good	6.89	0.077
S-1584	1.00	excellent	2.10	0.088

[a] Polymerization recipe, g: water/St/DE/AAP = 100/6.29/3.30/1.00.

The above-described considerations lead us to the conclusion that stable cationic polystyrene latexes can be obtained in the absence of emulsifiers by the copolymerization process. The particle formation process in the copolymerization process seems to be somewhat similar to that in the initiator process. In the copolymerization process, however, growing radicals formed in water may be comprised of St, the cationic monomer, and the neutralized form of the cationic monomer, of which the hydrophilic nature is strongly affected by the degree of neutralization of the cationic monomer. This particle formation process may reasonably explain the great dependence of the number of particles on the degree of neutralization of the cationic monomer. The stability of the copolymerization process latex may be attributed to cationic monomers, especially their neutralized form, chemically bound to the surface of particles which dissociate to form cations represented by the following formula:
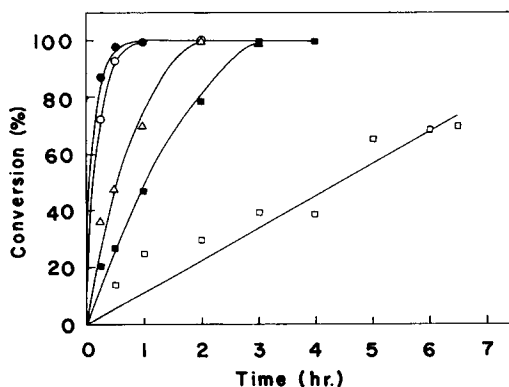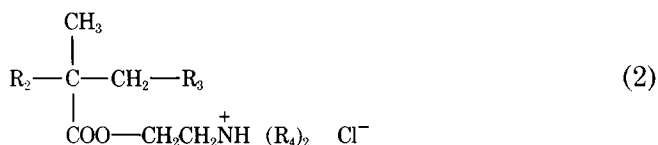
$$
\begin{array}{c}
CH_3 \\
| \\
R_2-C-CH_2-R_3 \\
| \\
COO-CH_2CH_2\overset{+}{N}H \ (R_4)_2 \quad Cl^-
\end{array} \qquad (2)
$$

Fig. 4. Effect of degree of neutralization of DE on the copolymerization process: (□) S-1580; (■) S-1581; (△) S-1582; (●) S-1583; (○) S-1584. All runs correspond to those in Table VI.

TABLE VII
Results of Two-Step Polymerization[a]

| Run no. | Degree of neutraliza-tion of DM | Properties of latex | | | |
		Stability	Solids content, %	pH	Particle diameter, μ
S-1499	0.50	good	48.8	6.79	0.482
S-1498	0.75	good	49.4	6.30	0.430
S-1497	1.00	excellent	48.8	2.90	0.182

[a] Polymerization recipe, g: step 1, water/St/DM/AAP = 100/6.29/2.80/1.00; step 2, St = 81.81.

where R_2 and R_3 are polymer chains and R_4 is methyl or ethyl. It is apparent that the fragments of AAP chemically bound to the surface of particles also contribute to the stability of latex as has already been represented by formula (1).

Further studies on these basic groups localized on the surface of particles will be described elsewhere.

Preparation of Latexes with High Solids Content

It is preferable to prepare latexes with high solids content from a practical point of view. Cationic polystyrene latexes with high solids content were prepared by using the two-step polymerization technique in the copolymerization process; that is, in step 1, the seed latex was prepared at a degree of neutralization of 0.50–1.00, which gives a sufficient number of particles and good stability of latex as has already been shown in Table V, and in step 2, the additional St was introduced and polymerized. The results are shown in Table VII. All latexes in Table VII have good stability and a solids content of about 49%. The number of particles, however, in these runs is not precisely consistent with that of corresponding runs in Table V, which may be ascribed to poor reproducibility in the particle formation process, as is generally recognized in this type of polymerization.[12]

CONCLUSIONS

A stable cationic polystyrene latex can be obtained in the absence of emulsifiers by the initiator process. The formation of particles in this process may be attributed to the precipitation of growing radicals formed in water. The latex seems to be stabilized with the fragments of AAP chemically bound to the surface of particles which will dissociate to form cations.

More stable cationic polystyrene latexes can be obtained in the absence of emulsifiers by the copolymerization process. The formation of particles in this process may also be attributed to the precipitation of growing radicals formed in water. The number of particles is strongly dependent on the degree of neutralization of the cationic monomer which may affect the hydrophilic nature of growing radicals. The stability of these latexes may predom-

inantly be attributed to cationic monomers chemically bound to the surface of particles which will dissociate to form cations.

Stable cationic polystyrene latexes with solids content of about 49% can be obtained by using the two-step polymerization technique in the copolymerization process.

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