

Copolymerization of Styrene with Acrylamide in an Emulsifier-Free Aqueous Medium

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Synopsis

Copolymerization of styrene with acrylamide was carried out in an emulsifier-free aqueous medium. The resulting latex contained an appreciable amount of acrylamide-rich copolymer in the serum. The copolymerization course was divided into three stages on the basis of the main reaction locus. At first, acrylamide polymerized in preference to styrene in the aqueous phase. Water-soluble growing radicals lost hydrophilicity rapidly and nucleated the particles. After particle formation, styrene polymerized exclusively in the particles until styrene droplets disappeared. The decrease in the concentration of residual styrene monomer caused growing radicals to keep the hydrophilicity for a long time, and polymerization of acrylamide was accelerated in the aqueous phase. Polymerizations at higher temperature and lower pH resulted in prolongation of the first stage of the polymerization, that is, preferential polymerization of acrylamide in the aqueous phase. An increase in the acrylamide fraction in monomer feed caused some decreases in the particle size and its uniformity.

INTRODUCTION

Emulsifier-free polymer latices are put to practical use because of improved properties of the resulting film. They are also capable of serving colloidal studies because of the well-characterized and stable properties, and being used for some medical and biochemical purposes because of cleanness of the disperse medium and functionality due to the on-surface groups.

The following methods have been adopted to obtain such emulsifier-free polymer latices from the dispersions of hydrophobic monomers: (1) polymerization by use of ionic group-containing initiators, for example, potassium persulfate,¹⁻³ azobis(alkylamidine hydrochloride),⁴⁻⁶ potassium peroxydiphosphate,⁷ etc.; (2) polymerization in the presence of amphiphilic polymer or oligomer^{8,9}; and (3) copolymerization with hydrophilic monomers. The hydrophilic comonomers used so far are carboxylic monomers,^{10,11} sodium styrenesulfonate,¹² sodium *p*-vinylbenzyl sulfonate,⁴ 2-acrylamido-2-methylpropane sulfonic acid,¹³ vinylpyridine (VP)¹⁴ and its derivatives,⁴ and others. They are all dissociable. The degree of dissociation of weakly acidic or weakly basic monomers is dependent on pH at which polymerization is carried out.

The effect of the degree of dissociation on the polymerization mode was discussed for some comonomer systems.^{11,14} It was found that in the copolymerization of styrene (St) with VP under acidic condition, VP polymerized in preference to St and was localized on the particle surface, whereas under basic condition it polymerized with St at a comparable rate and distributed statistically in the latex particles. These phenomena were explained by the difference in

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the hydrophilicity of VP dependent on the degree of dissociation. Reduction of the hydrophilicity of comonomer accompanied with undissociation is depressed by hydrogen bonding between the comonomer and water to some extent.

In the present work, acrylamide (AA), a monomer capable of strongly hydrogen bonding but not capable of ionizing, is used as the comonomer in the polymerization of St in an emulsifier-free aqueous medium.

AA is expected to serve as stabilizer of the resulting latex and make it possible to utilize the latex for various purposes owing to a large number of amide groups on the particle surface.

EXPERIMENTAL

Materials

Ion-exchanged and distilled water was used in all the polymerizations. Styrene (St, Kashima Kagaku Yakuhin Co.) was distilled under reduced pressure. Acrylamide (AA, Wako Chemicals Co.) and potassium persulfate (KPS, Taisei Kagaku Co.) were recrystallized from benzene and water, respectively. *N,N'*-Methylenebisacrylamide (specially prepared reagent, Nakarai Chemicals Co.) and *N*-allylacrylamide (Polysciences, Inc.) were used without further purification. Divinylbenzene (Tokyo Kasei Co.) was treated with 10% sodium hydroxide to remove inhibitor and dried before use.

Latex Preparation and Characterization

A standard recipe for emulsifier-free emulsion copolymerization is shown in Table I. Polymerizations were carried out in a 300-ml flask fitted with a stirrer. Ingredients, except the aqueous solution of the initiator, were placed in the flask. Nitrogen was bubbled through the reaction mixture for about 1 hr, and then the initiator was added to the flask. Small amounts of the samples were withdrawn from the flask at various time intervals for determination of the conversion, polymer composition, and particle size. The conversion was determined by precipitating the polymer with an excess of acetone and filtrating and drying the precipitate. The polymer composition was determined from the ratio of C and N contents. The AA fraction in instantaneously formed polymer (F_i) was calculated:

$$F_i = F_c + c(dF_c/dc) \quad (1)$$

where F_c is the AA fraction in accumulated polymer at conversion c .

TABLE I
Recipe for Copolymer Latex of Styrene and Acrylamide^a

Ingredients	Quantity
Styrene + acrylamide	20 g
Weight fraction of acrylamide in monomer feed	0.1–0.5
Water (+ buffer)	150 ml
KPS solution (5 mmole/l.)	10 ml

^a Temperature: 55 or 70°C; pH: 3.0 or 9.0.

Transmission electron micrographs of the latex particles were obtained by using a Hitachi electron microscope HU-12AF. The particle size and its distribution were determined by sizing more than 100 particles. The uniformity ratio of particle size (U) was calculated:

$$U = D_w/D_n \quad (2)$$

where $D_w = \sum N_i D_i^4 / \sum N_i D_i^3$, $D_n = \sum N_i D_i / \sum N_i$, and N_i is the number of particles with diameter D_i .

In some cases precipitated polymers were fractionated by using a Soxhlet extractor with water and benzene.

The partition of AA between St and water was determined as mentioned below. Three grams AA was dissolved in 30 g water in a test tube and 30 g St was added. The test tube was shaken at 70°C for 1 hr. The concentration of AA in each phase was measured from the absorbance of the solution at 201 nm.

RESULTS AND DISCUSSION

Polymerization Mechanism

Results for the copolymerization of St with AA in an emulsifier-free aqueous medium at 70°C and pH 9.0 are shown in Figure 1 [the weight fraction of AA in monomer feed (f) is 0.4]. It is found from the shape of AA fraction in instantaneously formed polymer (F_i)-versus-time curve that polymerization of AA proceeded at first in preference to that of St, gradually lost its preference (0–1 hr), then exclusive polymerization of St took place (1–1.5 hr), and at last polymerization of AA reaccelerated. The duration over which the slope of the time-conversion curve increased (~1.5 hr) coincided with that of reacceleration of AA polymerization.

The change in the polymer composition with time is shown in Figure 2. The values presented by solid marks (AA conversion $\times f$) are proportional to the amount of polymerized AA and the difference between the total conversion and (AA conversion $\times f$) are proportional to the amount of polymerized St. In Figure 2, first the AA conversion increased, leveled off, and then reaccelerated for the polymerization at $f = 0.4$. For the reaction at $f = 0.2$, the (AA conversion $\times f$) curve was apart from the total conversion curve even just after the initiation of polymerization. This result implies that the duration of preferential polymerization of AA shortens with decreasing f .

Juang and Krieger¹² studied the emulsion copolymerization of St with sodium styrenesulfonate (SS) and divided the polymerization course into four stages, as shown below. Homogeneous polymerization took place in the aqueous phase at a low rate up to 0.2% conversion (first stage); then the reaction locus changed from the aqueous phase to the polymer particles (second stage). The alteration was indicated by a change in the polymerization rate. After 60% conversion was attained, an acceleration attributed to the gel effect was observed (third stage), and finally the polymerization slowed down above 90% conversion (fourth stage). Their conductivity studies confirmed the mechanism deduced from the kinetic measurements. The copolymerization mode of the St-AA system seems to resemble that of the St-SS system, except for two points: in the present case (1) polymerization at the first stage was faster than those at other stages; and (2)

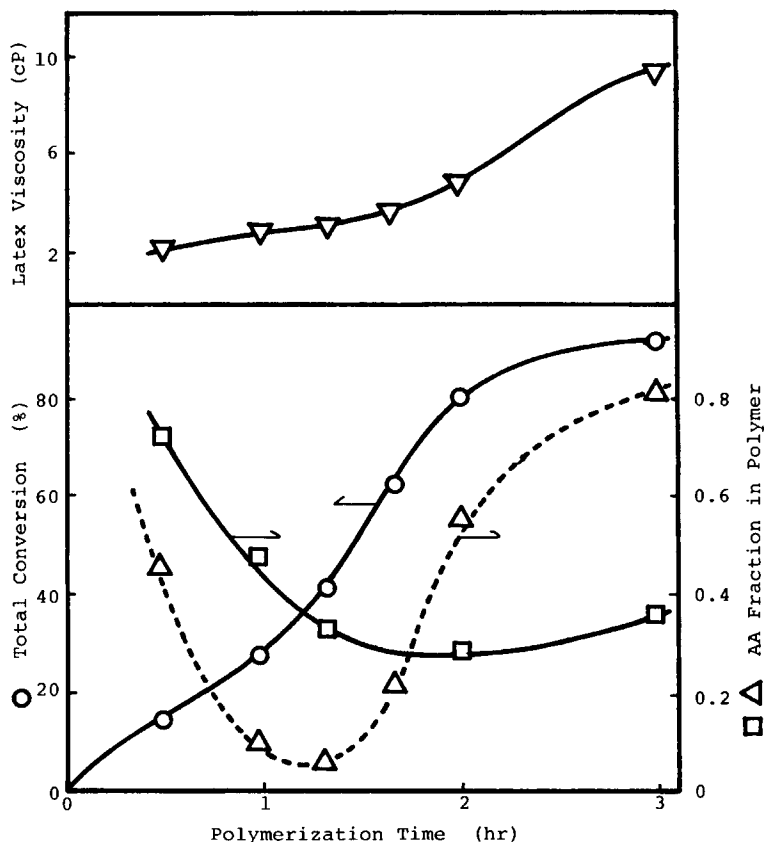


Fig. 1. Dependence of conversion, polymer composition, and latex viscosity on polymerization time: (○) conversion; (□) AA fraction in accumulated polymer; (△) AA fraction in instantaneously formed polymer; (▽) viscosity of reaction system. Polymerization conditions: $f = 0.4$, $\text{pH} = 9.0$, $T = 70^\circ\text{C}$.

reacceleration of polymerization of residual hydrophilic monomer took place at a later stage. The former would be attributed to the difference in the reactivity between SS and AA. The latter would be concerned with the reactivity and monomer feed ratio. Juang and Krieger carried out the polymerization at $\text{SS}/\text{St} < 0.006$ (molar ratio), whereas St-AA copolymerization shown in Figure 1 was carried out at $\text{AA}/\text{St} = 0.67$.

Judging from the dependence of the conversion and polymer composition on the reaction time, the St-AA copolymerization course consists of three stages, which are discussed in the following sections.

First Stage of Polymerization

AA polymerized preferentially in the aqueous phase. This stage resembles Juang and Krieger's first stage. The AA polymerization slowed down, but the rate of slowdown was much larger than the one estimated from the residual amount of AA in the aqueous phase. The rate of AA polymerization decreased at least one order of magnitude during only 35% AA conversion, that is, despite of about 35% decrease in the AA concentration in the aqueous phase. (The

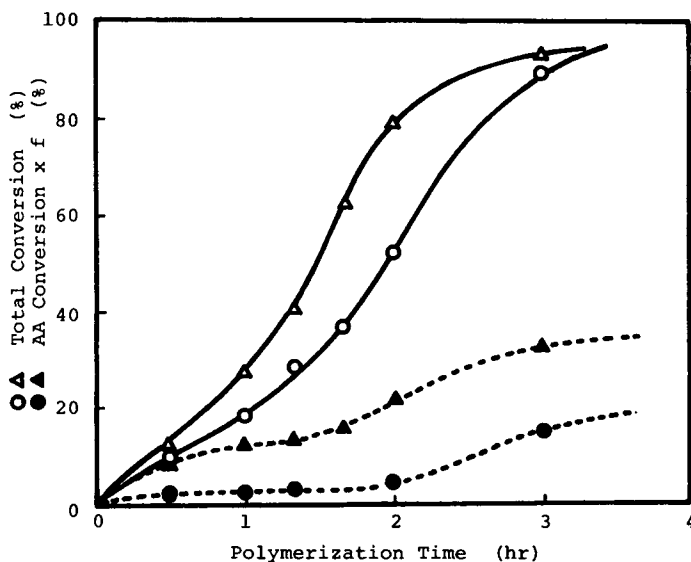


Fig. 2. Time-conversion curves at different f values: (Δ , \blacktriangle) $f = 0.4$; (\circ , \bullet) $f = 0.2$. Open marks, total conversion; solid marks, AA conversion $\times f$.

partition coefficient of AA between St and water was determined to be 0.093 from the partition measurement and in the present copolymerization system (St/water = 12/160 by weight) more than 99% AA should dissolve in the aqueous phase. Therefore, the increase in the AA conversion corresponds directly to the decrease in the AA concentration in the aqueous phase.) The above-mentioned situation might be reasonable, even if in homogeneous reaction, in the case that the monomer reactivity ratio was somewhat unusual. There have been no reports on the reactivity ratios r_1 and r_2 for St (M_1)-AA (M_2) copolymerization in the aqueous phase because of the extremely low solubility of St in water.

Minsk and his co-workers¹⁵ determined r_1 and r_2 for the same monomer combination in a variety of solvents and concluded that the more polar and the more capable of hydrogen bonding the solvent, the richer in St the resulting polymer was. Among the solvents examined, the one that could form the St-richest polymer was dimethyl sulfoxide, in which $r_1 = 2.01$ and $r_2 = 0.16$. With respect to the polarity of solvents, the same tendency was reported by Saini and his co-workers.¹⁶ These results imply the possibility that r_1 might be much larger than unity and r_2 might be close to zero in water. If this is the case, St would polymerize at a much higher ratio than the concentration ratio of St and AA in water. We attempted to explain the change in F_i with residual amount of monomers by supposing large r_1 and small r_2 values, but in vain. The changes were too complicated to consider the reaction homogeneous even just after the beginning of the polymerization. Consequently, it was concluded that the first stage should be regarded as a transitional period during which the main reaction locus transferred from the aqueous phase to the particles, and the particles were inferred to be formed by the mechanism envisaged in Figure 3. The radicals dissolved in water decrease the hydrophilicity gradually as they grow, and they begin to offer loci for St to be concentrated. Concentration of St around the growing radicals would accelerate polymerization of St and the composition would shift to a St-rich one rapidly. When the St fraction in growing radicals

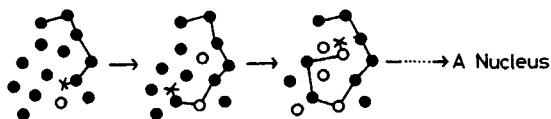


Fig. 3. Mechanism of particle nucleation: (●) AA; (Δ) St; (X) Radical.

exceeds a critical level, growing radicals precipitate to nucleate latex particles. Actually, latex particles appeared first on the electron micrographs when the AA fraction in accumulated copolymer decreased to less than 60%, which was midway of the first stage.

Second Stage of Polymerization

A leveling-off in AA conversion was observed in the course of the reaction despite the fact that much AA still remained unreacted. This period was defined as the second stage. The polymerization at the second stage is considered to take place in the particles exclusively. Newly formed initiator radicals should become hydrophobic in the manner similar to that shown in Figure 3, but at a much higher rate because of the change in the ratio of the dissolved amount of the two monomers in water. Consequently, the radicals diffuse into the particles before reacting with an appreciable amount of AA in the aqueous phase. Using the data on the reactivity of AA and St in benzene determined by Minsk¹⁵ and on the partition of AA between St and water, the polymerization rate of both monomers in the particles was estimated as shown below.

About 0.073 [= $8 \times (1 - 0.35)/71$] mole AA (MW = 71) remained at the end of the first stage (35% conversion) for the copolymerization at $f = 0.4$ (St/AA/water = 12 g(13.3 ml)/8 g/160 g). Assuming that the partition coefficient (0.093) of AA between St and water is not influenced by the feed amount of AA, coexistence of polystyrene in St monomer and of KPS in water, etc., the AA concentration in the particles was estimated to be 0.042 [= $0.073/(0.0133 + 0.160/0.093)$] mole/l. The r_1 and r_2 in benzene reported by Minsk are 0.25 and 12.5, respectively. These values were substituted in the copolymer equation:

$$\frac{1}{F_{i_p}} = 1 + \frac{[\text{St}]_p r_1 [\text{St}]_p + [\text{AA}]_p}{[\text{AA}]_p [\text{St}]_p + r_2 [\text{AA}]_p} \quad (3)$$

where the subscript p refers to the values in the particles. The F_{i_p} was calculated to be 0.033, which was consistent with the result shown in Figure 2. This consistency implies that the polymerization at the second stage takes place not in the aqueous phase but exclusively in the particles.

The polymerization data were discussed from the viewpoint of kinetics. According to the Harkins-Smith-Ewart theory, the polymerization rate per particle should be equal to $k_p [\text{St}]_p / 2$ at the steady state of the typical emulsion polymerization of St, which was estimated to be about 1010 molecule/sec at 70°C.¹⁷ In the present system, the particle number (N) was calculated from eq. (4), supposing that the weight of particle-composing polymer corresponded to $(P_t - P_w)$ (where P_t and P_w are the weight of total polymer and water-soluble polymer, respectively):

$$N = \frac{P_t - P_w}{d_{\text{St}}} \frac{6}{\pi D_w^3} = \frac{20(1 - P_w/P_t)c}{100 d_{\text{St}}} \frac{6}{\pi D_w^3} \quad (4)$$

where d_{St} is the density of poly-St (1.05 g/cm^3), D_w is the weight-average particle diameter, and c is the total conversion. As there was no clearly linear part on the time–St conversion curve, the polymerization of St at 40% St conversion ($R_{St,40}$) was regarded as the rate in the particle. The polymerization rate per particle ($R_{St,40}/N$) decreased with increasing f (Table II). It would be attributed mainly to characteristic copolymerization kinetics dependent on the monomer composition and reactivity ratio and maybe additionally to some other factors, e.g., the particle size effect suggested by Vanderhoff¹⁸ and van der Hoff.¹⁹

The second stage continued until about 50% St conversion was attained. This critical St conversion was constant regardless of f and corresponded to the equilibrium concentration of poly-St in St solution. Consequently, it is concluded that the second stage comes to end when all of the St droplets disappear.

Third Stage of Polymerization

The beginning of the third stage is characterized by gradual slowdown of St polymerization and reacceleration of AA polymerization, accompanied by an increase in the latex viscosity. These phenomena show that the main reaction locus returns to the aqueous phase. The alteration of the main reaction locus would be concerned with disappearance of St droplets. The droplets have supplied St to the particles through the aqueous phase. Their disappearance causes a decrease in the concentration of St not only in the particles but also in the aqueous phase. The decrease in the latter retards the change of the hydrophilicity of growing radicals, which consequently stay longer in the aqueous phase and facilitate the reaction with AA in the aqueous phase. In contrast to this, the decrease in the concentration of both radicals and St in the particles causes St polymerization to slow down although the slowdown might be canceled out by the gel effect at the beginning of the third stage.

Judging from the dependence of the latex viscosity on the reaction time (Fig. 1), most of the water-soluble polymer is considered to be formed at the third stage although the possibility cannot be ignored that a part is formed just at the beginning of the first stage. To suppress the increase in the latex viscosity at the third stage, that is, to reduce formation of water-soluble polymer, a few cross-linking reagents were added to the copolymerization system. Addition of *N,N'*-methylenebisacrylamide or *N*-allylacrylamide (2% to total monomer) caused gelation during the polymerization and addition of divinylbenzene was not effective for suppression of the increase in the latex viscosity and resulted in formation of a latex similar to the one prepared without a crosslinking reagent.

TABLE II
Kinetic Data for Copolymerization of Styrene with Acrylamide at 70°C and pH 9.0

f	$R_{St,40} \times 10^2$, mole/sec	$N \times 10^{-14}$, particles	$R_{St,40}/N$, molecules/sec	$[AA]_p/[St]_p^a$
0.2	1.75	9.5	10850	0.0010
0.3	2.77	35.2	4750	0.0015
0.4	2.92	62.0	2840	0.0033

^a $[AA]_p/[St]_p$: Monomer concentration ratio in latex particles.

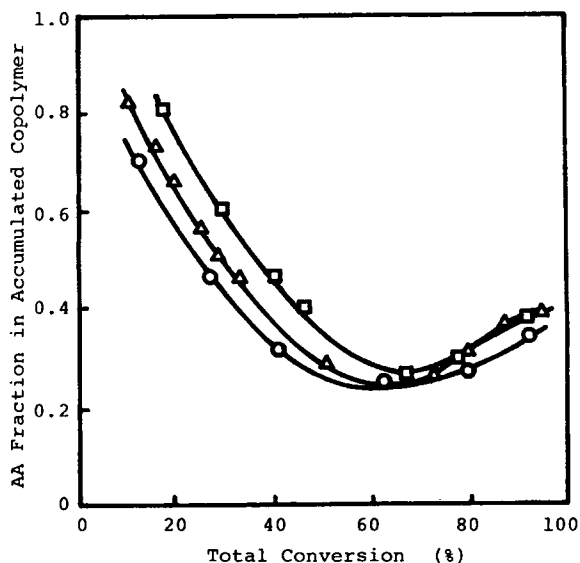


Fig. 4. Change of polymer composition with conversion at $f = 0.4$: (Δ) 55°C, pH 2.5; (\square) 70°C, pH 2.5; (\circ) 70°C, pH 9.0.

Effect of Temperature and pH on Polymerization Mode

Polymerizations were carried out at 55 and 70°C. Elevation of the reaction temperature promoted preferential polymerization of AA at the first stage (Fig. 4). At higher temperatures, growing radicals would stay longer in the aqueous phase and precipitate after more propagation, or the critical composition for radical precipitation would shift to the St-rich side. Elevation of the reaction temperature also caused a decrease in the particle size, that is, an increase in the number of particles (Table III). The increase in radical formation might overcome the increase in coalescence between a radical and a particle or between radicals themselves at higher temperature.

As shown in Figure 4, pH also affected the polymerization mode. Under acidic conditions, AA behaves as a weak base and AA-rich growing chains take a more extended conformation which reduced the number of loci for St to be localized

TABLE III
Characteristics of Copolymer Latices of Styrene with Acrylamide^a

f	T , °C	pH	D_n , nm	U	Extraction			
					P_w/P_t	P_{aw}/P_w	P_b/P_t	P_{ab}/P_b
0.2	55	3.0	434	1.016				
0.3			239	1.024				
0.4			204	1.039				
0.5			187	1.101				
0.4			159	1.035				
0.2	70	9.0	312	1.011	0.18	0.76	0.055	0.015
0.3			189	1.060	0.26	0.83	0.093	0.014
0.4			147	1.055	0.39	0.82	0.057	0.00

^a P_w , P_b , and P_t are the amount of water-soluble, benzene-soluble, and total polymer, respectively; P_{aw}/P_w and P_{ab}/P_b are the weight fraction of AA in the water-soluble and benzene-soluble polymers, respectively.

in concentrated state. Less affinity between growing radicals and St at low pH results in prolongation of the first stage.

Effect of AA Fraction in Monomer Feed on Resulting Latices

The particle size and its uniformity decreased with increasing f in the range $f = 0.2$ to 0.5 . At f above 0.5 , no stable latices were obtained. Latex polymers prepared at 70°C and pH 9.0 were precipitated and extracted (Table III). It is assumed that AA units in the particle-composing polymer are relatively localized on the particle surface but the localization is not so distinct because the fraction extracted with benzene is fairly small, that is, the particles mainly consist of random copolymer which could not be extracted with benzene.

It is worth discussing the role of AA for stabilization of latex particles. In Table IV, the total surface area of the particles (S) and the amount of particle-composing AA units (Z) are presented. If particle-composing AA units are localized exclusively on the particle surface, it is expected that S would have a reasonable relation to Z . S increases with Z , but the intercept of the S -vs.- Z plots is negative. This might suggest no exclusive localization of AA units on the particle surface. Supposing a monomer unit with volume v to occupy the area $\pi \times (6v/\pi)^{2/3}$ on the particle surface, the ratio of on-surface monomer units/total monomer units in a particle with diameter D should be $(6v/\pi)^{1/3}/D$ (calculated from the number of on-surface units, $\pi D^2/[\pi(6v/\pi)^{2/3}]$, and the number of total units in a particle, $\pi D^3/6v$). The amount of on-surface AA is assumed to be a function of $k(6v/\pi)^{1/3}Z/D$, where k is a priority coefficient of AA for localization on the surface. The values Z/D are also presented in Table IV and the following equation is obtained:

$$S = 35 Z/D + 2.1 \times 10^6 \text{ (cm}^2 \text{ in whole system)}$$

The equation is considered to express the contribution of AA units and some other units to the stabilization of the particles. The intercept (2.1×10^6) might be concerned with the amount of on-surface ionic groups, because it was reported that in some emulsifier-free emulsion copolymerizations, the amount of ionic groups originated in the initiator was a determinant in regulation of the particle size.¹

In the present system, SO_4^- end groups would serve as stabilizers of the particles. In addition, it is possible that carboxyl groups, which are formed by hydrolysis of AA during the polymerization, stabilize the particles. To check this point, 2.5% aqueous solution of AA was treated at 70°C in the presence or absence of KPS, and the amount of carboxyl groups formed was determined by conductometric titration (Table V). Judging from the results shown in the table, the

TABLE IV
Relation Between Surface Area of Particles and Amount of Particle-Composing Acrylamide

f	D , nm	$\pi D^2 N(S) \times 10^{-6}$, cm ²	$20fc'/100 - P_{aw}$ (Z) g	$Z/D \times 10^{-4}$, g/cm
0.2	312	2.91	0.784	2.51
0.3	189	3.95	0.844	4.47
0.4	147	4.21	0.884	6.01

^a c' : AA conversion (%).

TABLE V
 Hydrolysis of Acrylamide^a

pH	KPS, mole/l.	Reaction time, hr	% Hydrolyzed
9	0	3	0.11
	0	6	0.21
	5	6	0.26
3	0	3	0.96
	0	6	2.89
	5	6	3.88

^a The 2.5% aqueous solutions of acrylamide were treated at 70°C.

contribution of carboxyl groups to stabilization of St-AA copolymer latex is not significant.

Effect of Initiator Concentration on Properties of Resulting Latices

It is expected that an increase in the initiator concentration causes (1) an increase in stability of the particles because of increasing electrostatic repulsion by more sulfate end groups on the surface, or (2) a decrease in stability of the particles owing to disturbance of hydration of acrylamide units on the surface by more electrolytes. At [KPS] > 10 mmole/l., the viscosity of St-AA copolymer latices increased, although the number of particles did not increase and the latices became less stable. These results indicate that the latter effect predominates in the copolymerization at [KPS] > 10 mmole/l.

CONCLUSIONS

Copolymerization of styrene with acrylamide was carried out under various conditions in an emulsifier-free aqueous medium. The polymerization course was divided into three stages with respect to the main reaction locus. At the beginning, acrylamide polymerized preferentially in the aqueous phase. After the particle formation, styrene polymerized exclusively in the particles, even if a significant amount of acrylamide remained in the aqueous phase. Disappearance of styrene droplets, the source of styrene supply to the particles, resulted in transfer of the main reaction locus from the particles to the aqueous phase. Elevating the reaction temperature and lowering the pH caused prolongation of the polymerization in the aqueous phase. The particle size and its uniformity decreased with increasing acrylamide fraction in the monomer feed.

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