

Copolymerization of Styrene With Acrylamide Derivatives in an Emulsifier-Free Aqueous Medium

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Synopsis

Acrylamide derivatives were copolymerized with styrene in an emulsifier-free aqueous medium, and the copolymerization mode and the characteristics of the resulting latices were compared with those of a styrene-acrylamide copolymerization system. In their copolymerization mode, *N*-(hydroxymethyl)acrylamide and *N,N*-dimethylacrylamide resembled acrylamide, and their heterogeneous copolymerization course was divided into three stages on the basis of the main reaction locus. Copolymerization of styrene-methacrylamide did not resemble that of the others. The interfacial property and reactivity of acrylamides affected not only the polymerization mechanism but also the latex properties, e.g., particle size, distribution of acrylamides units in the latex, etc. The narrowest distribution of particle size was obtained in styrene-*N*-(hydroxymethyl)acrylamide copolymerization at a monomer ratio of 10:1. Delayed addition of styrene into the aqueous solution of *N*-(hydroxymethyl)acrylamide prepolymerized to some extent was found to be effective in preparing a latex with nearly monodisperse and large particles.

INTRODUCTION

It was previously reported¹ that copolymerization of styrene (St) with acrylamide (AA) in an emulsifier-free aqueous medium resulted in formation of a stable latex, and the polymerization course was divided into three stages in terms of the main reaction locus: first stage, preferential polymerization of AA in the aqueous phase; second stage, preferential polymerization of St in the particles; and third stage, polymerization of residual AA in the aqueous phase. The composition of the polymer formed at each stage depended on the affinity and reactivity of the monomers. The strong hydrophilicity of AA led to formation of a large amount of water-soluble polymer containing about 75% AA. Addition of some crosslinking reagents into the copolymerization system had little effect on the reduction in the formation of water-soluble polymer.

The distribution of carboxylic monomer units in St-carboxylic monomer copolymer latex was shown to be dependent on the pH at which the polymerization was carried out.^{2,3} Undissociated carboxylic monomer shows less hydrophilicity than dissociated carboxylic monomer and tends to be localized on the surface of latex particles rather than in the serum. Some acrylamide derivatives with less hydrophilicity are expected to reduce the formation of water-soluble polymer in the aqueous copolymerization with St.

Another interest is to prepare monodisperse latices. In St-AA polymerization, the uniformity in the particle size was dependent on the monomer feed ratio and no satisfactory monodisperse latices were obtained under the conditions carried

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out. Use of some acrylamide derivatives might make it possible to prepare monodisperse latices.

In the present work, three kinds of acrylamide derivatives were used for the copolymerization with St in an emulsifier-free aqueous medium, and the influence of the properties of acrylamides on the polymerization mechanism and the characteristics of the resulting latices were studied.

EXPERIMENTAL

Materials. Distilled water was used in all polymerizations. Styrene (St, Kashima Kagaku Yakuhin Co.) was distilled at 40°C and 14.5 torr. The following acrylamide derivatives were used as comonomers: *N*-(hydroxymethyl)acrylamide (HMA); *N,N*-dimethylacrylamide (DMA); and methacrylamide (MA). All acrylamides were from Tokyo Kasei Co. HMA was recrystallized from ethyl acetate. DMA was distilled at 54°C and 3.5 torr. MA was recrystallized from benzene. Potassium persulfate (KPS, Taisei Kagaku Co.) was recrystallized from water. Another initiator, 2,2'-azobis(2-amidinopropane) hydrochloride (AAP, Wako Chemicals Co.), was used without further purification.

Procedures. Polymerizations were carried out at 70°C under nitrogen. A typical recipe was as follows: 160 g water with buffer, 20 g monomer in which acrylamides/St (w/w) = 0.1/20–8/12 and the initiator concentration = 5 mmole/l. The conversion and polymer composition were determined from the weight and nitrogen content of precipitated samples, respectively. The diameter of the resulting latex particles was measured on electron micrographs. The uniformity ratio was defined as the ratio of the weight-average to number-average diameter. Some precipitated polymers were extracted with benzene and water for 25 hr and the extracts were subjected to elemental analysis. Another method of fractionation—centrifugation—was done for some latices. Samples were centrifuged with a Kokusan H-502 centrifuge at 25,000 g for 1 hr. The concentrations and compositions of the polymer dissolved in the supernatant and the precipitate were determined. The partition coefficient, the ratio of the acrylamides concentration in St to that in water, was determined from the absorbance (at 200 nm) for DMA, 203 nm for HMA, and 205 nm for MA) of each phase equilibrated at 70°C.

RESULTS AND DISCUSSION

Analysis of Polymerization Course

HMA, DMA, and MA were polymerized with St in an emulsifier-free aqueous medium at an acrylamides fraction in monomer feed (f) of 0.40, at pH 8.0, and at 70°C. Aqueous copolymerization of St with HMA under acidic conditions resulted in gelation, supposedly because of the crosslinking catalyzed by persulfate.⁴ But the copolymerization at pH 9.0 led to the formation of stable latices as well as copolymerizations of St-AA and St-DMA. On the other hand, a stable St-MA copolymer latex was obtained from aqueous polymerization under acidic condition but not at pH 9.0. The reason is unknown at the present time.

The copolymerization data at pH 9.0 for HMA and DMA and those at pH 3.8

for MA are shown in Figure 1. For AA the data at pH 9.0 alone are presented in Figure 1, as in the St-AA polymerization pH did not affect the reaction mechanism significantly.¹ The polymer composition-conversion curves for St-HMA and St-DMA polymerization resemble that for St-AA polymerization. They obviously indicate the specific reaction pathway mentioned previously,¹ that is, acrylamides preferentially polymerize in the aqueous phase at first (first stage), St polymerizes exclusively after formation of the particles (second stage), and acrylamides remaining in the aqueous phase polymerize progressively (third stage) as the St concentration in the aqueous phase decreases.

On the other hand, the course of St-MA polymerization is much different from that of the others. The division of the reaction course for St-MA system is obscure or there is no distinct alteration of the main reaction locus during the polymerization.

Although the polymerization mode for the former three systems is similar, some differences should be pointed out. For example, the initial slope of the composition-conversion curves changes in the following order: DMA > HMA > AA. The slope is a measure of the preferential polymerizability of acrylamides, and the above-mentioned results manifest that first-stage polymerization is more pronounced for the St-AA system and less for the St-DMA system. The conversion range during which acrylamides polymerization is suppressed is also different among three copolymerization systems. The details of each stage of polymerization for each comonomer system are compared and discussed.

First Stage of Polymerization

The differences in polymerization mode in some copolymerization systems can be explained by the differences in the hydrophilic-hydrophobic property of comonomers and the reactivity of comonomers with St. The partition coef-

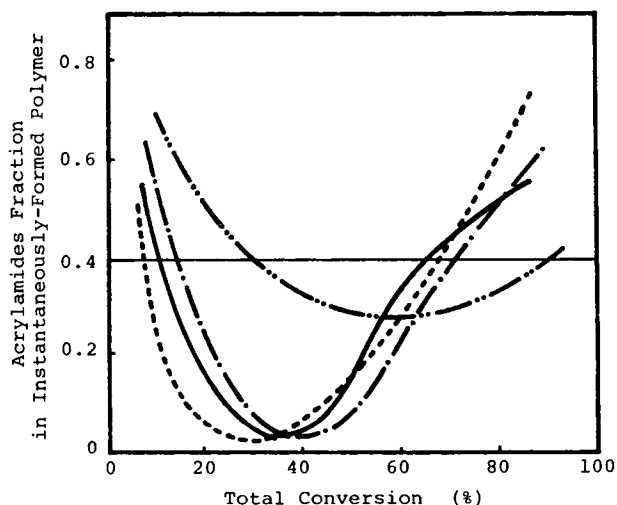


Fig. 1. Polymer composition vs. conversion curves for aqueous copolymerization of styrene with acrylamides: (---) acrylamide (9.0); (—) *N*-(hydroxymethyl)acrylamide (9.0); (···) *N,N*-dimethylacrylamide (9.0); (- · - ·) methacrylamide (3.8). The values in parentheses are the pH's at which polymerizations were carried out.

ficient, which was defined as the ratio of the acrylamide concentration in St to that in water, is shown in Table I. A small partition coefficient should cause prolongation of the first stage because it means that more acrylamides dissolve in the aqueous phase. The partition coefficient is closely related to the hydrophilicity and consequently would be a measure of the ability of acrylamide-rich growing radicals to maintain themselves in water. In this sense a small partition coefficient might also cause prolongation of the first stage. The short duration of the first stage for the St-DMA system is attributed to DMA's large partition coefficient. Namely, a growing radical composed of DMA and St would easily precipitate to a nucleus, even though the DMA fraction in the radical is relatively high, and it would enhance alteration of the reaction stage to the second stage. The average diameter of particles in the resulting latices is shown in Table II. St-DMA particles are much bigger than St-AA or St-HMA particles. The reason why the rapid nucleation does not lead to formation of the latex with a large number of small particles in the St-DMA system would be the instability of St-DMA nuclei.

The difference in the polymerization mode between the St-AA and St-HMA systems is interesting because the partition coefficients of AA and HMA are almost the same; and if the difference in the coefficients (0.093 to 0.089) is significant, it is rather reasonable that the first stage continues longer in the St-HMA system than in the St-AA system. But this is not the case, as shown in Figure 1 and as mentioned in the preceding section. Comparison of extraction data presented in Table III explains the results in Figure 1. According to the data

TABLE I
Partition Coefficient of Acrylamides between Styrene and Water at 70°C

Acrylamides	Partition coefficient
Acrylamide	0.093
<i>N</i> -(Hydroxymethyl)acrylamide	0.089
Methacrylamide	0.159
<i>N,N</i> -Dimethylacrylamide	0.293

TABLE II
Particle Size and Its Distribution^a

Acrylamides	pH	<i>f</i>	<i>D_n</i> , nm	<i>U</i> ^b
Acrylamide	9.0	0.2	312	1.011
		0.3	189	1.060
		0.4	147	1.055
<i>N</i> -(Hydroxymethyl)acrylamide	9.0	0.2	300	1.004
		0.3	178	1.012
		0.4	144	1.034
<i>N,N</i> -Dimethylacrylamide	9.0	0.4	329	1.010
Methacrylamide	9.0	0.3	coagulated	
	3.8	0.3	294	
		0.4	214	

^a *D_n*, number-average diameter.

^b *U*, uniformity ratio (weight-average diameter/number-average diameter).

TABLE III
Extraction of Precipitated Polymer with Water and Benzene and Analysis of Extracted Polymer^a

Acrylamides	<i>f</i>	P_w/P_t	P_a/P_w	P_b/P_t	P_a/P_b
Acrylamide	0.2	0.18	0.76	0.055	0.015
	0.3	0.26	0.83	0.093	0.014
	0.4	0.39	0.82	0.057	0
<i>N</i> -(Hydroxymethyl)acrylamide	0.2	0.16	0.85		
	0.3	0.13	0.97	0.073	0.03
	0.4	0.22	0.93	0.055	0

^a P_w , Weight of water-soluble polymer; P_t , weight of total polymer, P_a , weight of polymerized acrylamides, P_b , weight of benzene-soluble polymer.

in Table III, the HMA fraction in the water-soluble HMA–St copolymer is larger than the AA fraction in the water-soluble HMA–St copolymer. HMA–St copolymer must lose its water solubility by containing a relatively small fraction of St, and as a result the amount of water-soluble HMA–St copolymer is less than that of the water-soluble AA–St copolymer (third column in Table III). This is regarded as one of the reasons for the short duration of the first stage in St–HMA polymerization.

The St–HMA copolymer latex particles were centrifuged a little more easily than the St–AA particles, although St–butadiene–HMA particles were reported to be more stable against electrolytes than St–butadiene–AA particles.⁵ It might be worth studying the difference in the stability of these latices, but no more data are available at the present time.

Second Stage of Polymerization

The AA fraction in the polymer formed at the second stage was calculated previously¹ by using the partition coefficient and monomer reactivity ratio measured by Minsk and his co-workers.⁶ The calculation led to the conclusion that the main reaction locus at the second stage should be in the particles. In the case of St–DMA copolymerization, it is expected that the DMA fraction in the polymer formed during the second stage would be relatively high because of the large partition coefficient. But it was not. The fact that the DMA fraction in the instantaneously formed polymer remained about 0.05 in the total conversion range between 15 and 35% indicates not only that the polymerization in the aqueous phase is negligible at this stage but also that the copolymerizability of DMA with St is small. Saini and his co-workers measured the reactivity ratio of acrylamide–St in dioxane and ethanol.⁷ Judging from their data shown in Table IV, St polymerizes preferentially in a DMA–St system than in other systems. This would be the cause for the low DMA fraction in the polymer formed at the second stage, that is, in the particles.

In ordinary emulsion polymerization, the reaction rate is proportional to the number of particles. The small number of particles in the St–DMA system resulted in slow conversion of St and consequently in long duration of the second stage which was evidenced by the length of the flat part of DMA conversion curve in Figure 2.

According to the data in Tables I and IV, the MA fraction in the polymer

TABLE IV
Monomer Reactivity Ratio for Acrylamides (M1)–Styrene (M2) Copolymerization^a

Acrylamides	Reactivity ratio	Solvent	
		Dioxane	Ethanol
Acrylamide	r_1	1.38	0.30
	r_2	1.27	1.44
<i>N,N</i> -Dimethylacrylamide	r_1	0.44	0.23
	r_2	1.28	1.23
Methacrylamide	r_1	1.29	0.54
	r_2	1.46	1.44

^a Reported by Saini and Co-workers.⁷

formed at the second stage should be 3.5 times higher than the corresponding AA fraction if the same polymerization mechanism can be assumed. But as shown in Figure 1, the former is about ten times higher than the latter. This would result from the competitive polymerization in the aqueous phase and in the particles of the St–MA system.

Only few kinetic data were found on St–HMA copolymerization, and there are considerable differences between them.^{8,9} Judging from our results, the reactivity of HMA with St would be similar to that of AA in the particles.

Third Stage of Polymerization

The main reaction locus at the third stage was concluded to be the aqueous phase because the polymerization rate of acrylamides at this stage drastically increased and the slope of the third-stage part of each time–conversion curve seemed to be identical with that of the respective first-stage part (Fig. 2). The

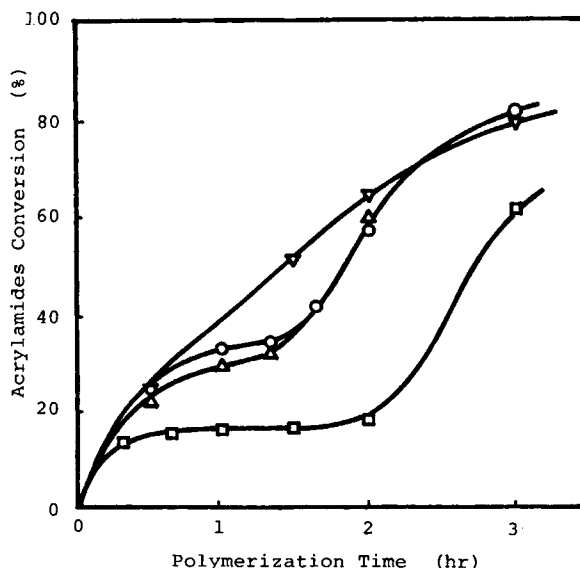


Fig. 2. Acrylamide conversion as function of reaction time: (O) acrylamide; (Δ) *N*-(hydroxymethyl)acrylamide; (□) *N,N*-dimethylacrylamide; (∇) methacrylamide.

rate was too large to consider it as the rate in the particle in which the acrylamides concentration should be very low.

The third-stage polymerization begins when all of the St droplets are depleted. Disappearance of St droplets causes a gradual decrease in the St concentration not only in the particles but also in the aqueous phase. A decrease in the St concentration in the aqueous phase leads to reacceleration of aqueous polymerization of acrylamides because the St fraction in growing radicals increases only at a low rate; consequently, growing radicals react with more acrylamides before they diffuse into the particles. Some polymeric molecules maintain the water solubility until the end of the polymerization.

In the St-AA copolymerization, a fair amount of the polymer formed at the third stage stayed in the latex serum.¹ The conversion at which the third stage begins shifts to the lower one in the order of AA, HMA, and DMA, but this shift does not mean that the amount of water-soluble polymer increases in this order because the acrylamides fraction in water-soluble polymer is different for the three acrylamides. In practice, the amount of water-soluble polymer was more in the St-AA system than in the St-HMA system, as judged from the data shown in Table III.

Particle Size and Particle Size Distribution

The determining factors of particle size would be the rate of nucleation at the first stage, the surface density of acrylamides on the particles, and the capability of acrylamides to stabilize the particles. As mentioned by Yeliseyeva and his co-workers in the study on emulsion copolymerization of alkyl acrylate with water-soluble monomers,¹⁰ such factors play a role in a complicated manner. Moreover, the determination of the surface density of acrylamides has not been attempted. Therefore, it is difficult to discuss the number of particles quantitatively from the available data.

St-HMA copolymerization resulted in formation of particles with more amido-monomer fraction than St-AA copolymerization did. Nevertheless, the number of particles in St-HMA latex is almost the same as that in St-AA latex. This might result from a poorer stabilizing ability of HMA.

It is worth noting that the uniformity ratio of particle size becomes close to unity with decreasing f , as shown in Table II. Some copolymerizations by use of less HMA were carried out to prepare monodisperse latices. Using a reduced amount of HMA is also favorable to obtain clean latices whose serum contains no or negligible contaminants. In the polymerization, 20 g St and 0.2 to 2.0 g HMA were charged. The particle size decreased and the uniformity ratio approached unity with increasing HMA in the above-mentioned charge amount range (Fig. 3). More charge of HMA caused a departure of the uniformity ratio from unity. It was concluded that some clean and monodisperse latices could be prepared from the copolymerization of St with HMA at $f = 0.09$.

The mode of monomer charge was found to affect the particle size. The aqueous prepolymerization of HMA followed by addition of St resulted in formation of latices with large particles and without significant broadening of the particle size distribution (Fig. 3). The conversion of HMA after 1 hr of polymerization was about 60%.

Some other alterations in the reaction conditions were attempted for St-HMA

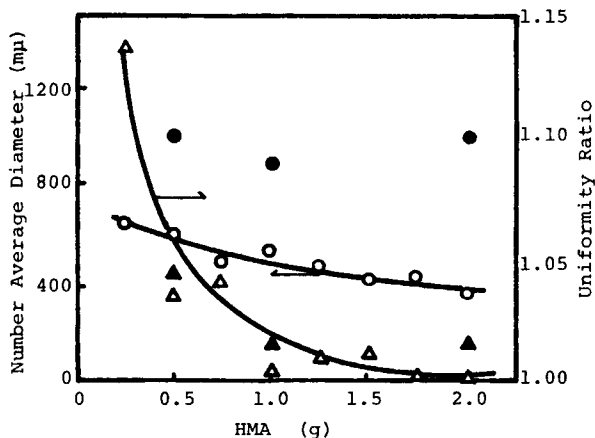


Fig. 3. Particle size and its uniformity for styrene-HMA copolymer latexes: (O, ●) number-average diameter; (Δ , \blacktriangle) uniformity ratio. Solid marks: St was added after 1 hr of prepolymerization of HMA.

copolymerization. Initiator was changed from KPS to 2,2'-azobis(2-amidino-propane) hydrochloride (AAP). The particle size and the amount of the polymer dissolving in water decreased in the AAP-initiating system (Table V). The effect of the initiator on the particle size should be discussed on the basis of the rate of radical formation and the ability of initiator residues on the particle surface to stabilize the particles. The particles formed in the AAP-initiating system did not show appreciable cationic property in electrophoretic measurements, although it was reported that homopolystyrene latex containing AAP residues was cationic.¹¹ The electrostatic repulsion force due to AAP residues on the particle surface would not contribute significantly to stabilization of the particles in St-HMA latex. Inversely, weak electrostatic force might enhance precipitation of growing radicals and consequently increase the number of particles.

The effect of salt addition on the particle size and on the distribution of HMA in the resulting latex was also examined (Table VI). Generally, addition of some salt into an oil-in-water emulsion which contains a solute participated between two phases results in the following changes. One of the changes is transfer of the solute from the aqueous phase to the oil phase, and the other change is some coalescence of particles due to instabilization. The addition of sodium chloride into the St-HMA copolymerization system resulted in the former change, that is, the amount of HMA in the serum decreased. But the latter change, that is,

TABLE V
Particle Size and Amount of Polymer Dissolving in Latex Serum Prepared from AAP-Initiating System^a

Initiator	f	D_n , m μ	P_w/P_t	P_{ap}/P_{at}
KPS	0.3	178	0.33	0.21
AAP	0.3	125	0.28	0.22
	0.2	169	0.18	0.28
	0.1	187	0.10	0.36

^a P_{ap}/P_{at} , fraction on HMA in the particles to total HMA.

TABLE VI
Effect of NaCl Addition to St-HMA Copolymerization System

[NaCl], mole/l.	$D_n, m\mu$	P_w/P_t	P_{ap}/P_{at}
0.0	125	0.28	0.22
0.1	119	0.21	0.28
0.2	119	0.22	0.25
0.4	120	0.22	0.36

any decrease in the number of particles caused by coalescence, was not observed in the sodium chloride concentration range from 0.1 to 0.4 mole/l.

CONCLUSIONS

In the copolymerization of styrene (St) with *N*-(hydroxymethyl)acrylamide (HMA) and *N,N*-dimethylacrylamide in an emulsifier-free aqueous medium, the reaction course was divided into three stages: first stage, polymerization of acrylamides in the aqueous phase; second stage, polymerization of St in the particles; and third stage, polymerization of residual acrylamides in the aqueous phase. The copolymerization of St with methacrylamide proceeded in a different mode. Some differences in the polymerization mode could be explained by the differences in the hydrophilic-hydrophobic property of acrylamides and reactivity of acrylamides with St. Copolymerization of St with HMA resulted in latices whose serum contained less water-soluble polymer than that of acrylamide-St copolymer latex. Some clean and monodisperse latices were prepared from the copolymerization of St-HMA with HMA/St = 0.09. Delayed addition of St in the aqueous solution of HMA prepolymerized to some extent led to formation of latices with larger particles and without significant broadening of the particle size distribution.

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