

N-Substituted Acrylamide–Styrene Copolymer Latices[†] II. Polymerization Behavior and Thermosensitive Stability of Latices

Futoshi HOSHINO, Takeshi FUJIMOTO, Haruma KAWAGUCHI,
and Yasuji OHTSUKA

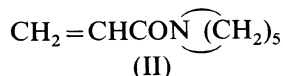
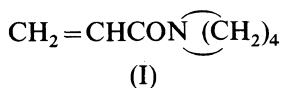
*Department of Applied Chemistry, Faculty of Science & Technology,
Keio University, 3–14–1 Hiyoshi, Kohoku-ku, Yokohama 223, Japan*

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ABSTRACT: Two kinds of *N*-substituted acrylamides having different hydrophilicity were copolymerized with styrene in soap-free aqueous media. The polymerization behavior of acrylamides depended on their hydrophilicity. The resulting latices were stable at low temperature and low electrolyte concentration but they flocculated above a critical temperature and a critical electrolyte concentration. The critical conditions were decided by the components on particle surface and a series of latices having the critical temperature between 5 and 50°C could be prepared. Reversible transition between dispersion and flocculation by changing temperature was observed in some latices.

KEY WORDS Soap-Free Emulsion Polymerization / Latex / Polymer Particle / Acryloyl Pyrrolidine / Acryloyl Piperidine / Hydrophilic Polymer / Flocculation / Hydration-Dehydration /

In aqueous solutions of acrylamides having bulky *N*-substituent(s) and their polymers the extent of hydration is sensitive to the electrolyte concentration in the medium and temperature.^{1,2} Therefore, copolymerization of such *N*-substituted acrylamides with styrene in an aqueous medium is expected to result in the formation of latices whose stability depends on the electrolyte concentration and temperature.³ In this study two kinds of *N*-substituted acrylamides having different hydrophilicity were employed in the preparation of latices. They are acryloyl pyrrolidine (I, APr) and acryloyl piperidine (II, APp).



These two acrylamides with cyclic substituents are especially interesting because the difference of only one methylene group between them introduces a significant difference in the hydrophilicity of the two polymers and the cloud points of poly-APr and poly-APp are 50 and 5°C, respectively. It should be mentioned that poly(*N*-butyl acrylamide) whose substituent is composed of the same number of carbon atoms with APr's is insoluble in water.

In this paper the dependence of polymerization behavior and characteristics of resulting latices on the kind of acrylamides was investigated and a series of latices was designed showing reversible transition between stable dispersion and flocculation at any desired temperature.

[†] I. *Makromol. Chem., Rapid Commun.*, 7, 109 (1986).

EXPERIMENTAL

Materials

Styrene (St) was distilled at 46°C/21.5 mmHg. APr and APp were given by Mitsui Toatsu Chemicals Inc. and distilled at 89°C/0.5 mmHg and 85°C/0.05 mmHg, respectively. *N,N'*-Azobis-amidinopropane hydrochloride (V50, Wako Chemicals Co.) was used as an initiator which is suitable for the polymerization in the temperature range from 40 to 70°C. Potassium persulfate was not used because it was apt to form less stable latices.

Polymerization

Soap-free copolymerization was carried out in a 300 ml four-neck round-bottom flask equipped with stirrer, nitrogen inlet, condenser, and serum rubber cap. The standard recipe for the copolymerization is as follows: (St+APr or APp) 30 g, distilled water 180 g, V50 0.50 g. The weight fraction of acrylamide derivatives in monomer feed (*f*) was varied from 0.1 to 0.4.

Water-soluble copolymers of APr and APp with different compositions were prepared to determine their cloud points. The polymerization was carried out in the system containing (APr+APp) 2 g, water 18 g, ferrous ammonium sulfate 0.02 g, and ammonium persulfate 0.02 g at 0°C for 1 h.

Characterization

Conversion and polymer composition were measured by a gravimetric method and elemental analysis, respectively. Latex particles were observed by transmittance and scanning electron microscopes.

Critical flocculation concentration (CFC) was determined by the following method: Fixed amounts of NaCl aqueous solutions of different concentrations were added to diluted latices in test tubes and the samples were kept standing for 2 h at the constant temperature. The minimum concentration of NaCl solution for flocculation was defined

as the CFC at the temperature. The measurement was carried out at every ten degrees from 10 to 70°C. Electrophoretic mobility of particles was measured by using an electrophoresis microscope system of Sugiura Lab. Co. The hydrodynamic size of latex particles was determined by a quasi-elastic light scattering method using a sub-micron particle analyzer Coulter N4 as a function of temperature. Partition of acrylamide derivatives between St and water phase was measured by gas chromatography.

The cloud point of the APr-APp copolymers was determined by observing the transparency of aqueous solution of 0.5 g polymer dl⁻¹ at each temperature.

RESULTS AND DISCUSSION

Soap-Free Emulsion Copolymerization

Typical time-conversion curves of soap-free emulsion copolymerization of St with acrylamide derivatives are shown in Figure 1. Copolymerization of St with APr resulted in time-conversion curves having shoulders, the tendency of which was more pronounced with lowering polymerization temperature. On the other hand, the time-conversion curves of St-APp systems had no apparent shoulders regardless of polymerization temperature. In each figure, polymer composition is shown by the curve dividing the whole amount of polymer into the fractions of St and acrylamide derivatives. The results on polymer composition as a function of polymerization time indicated that APr polymerizes preferentially at the initial stage of polymerization whereas APp polymerizes more steadily. The behavior of APr is similar to that of acrylamide and some acrylamide derivatives in this respect.^{4,5}

The difference in polymerization behavior between APr and APp was explained as follows: The partition of acrylamide derivatives between St and water phases was determined by gas chromatography for the systems

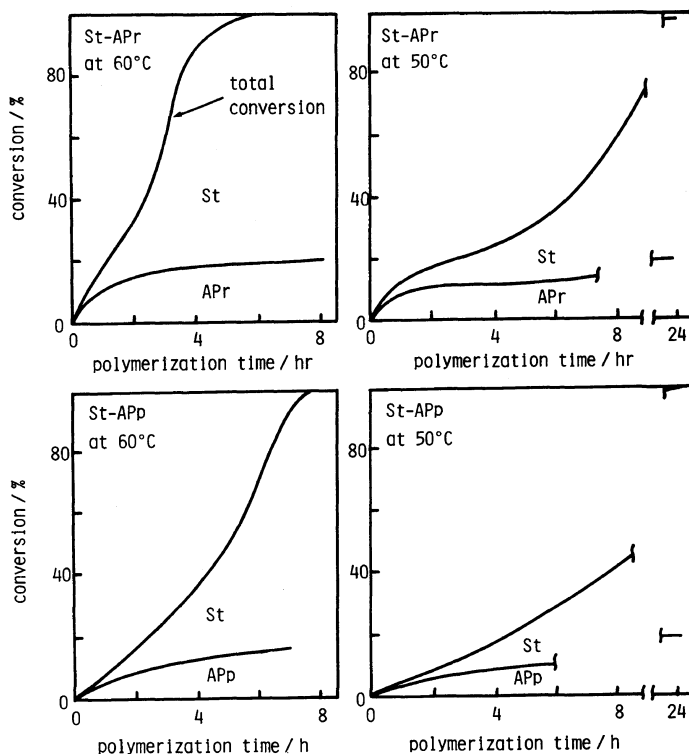


Figure 1. Time-conversion curves for the soap-free emulsion copolymerization of styrene with *N*-substituted acrylamides at $f=0.2$.

	APr		APp	
	St phase	water phase	St phase	water phase
partition at 40 °C				
partition at 60 °C				
r_1^b	0.68		0.31	
r_2^b	1.24		2.17	
F_1^c	0.97		0.88	

Figure 2. Partition of acrylamides between styrene and water phases^a and composition of copolymers formed just after the start of polymerization.

^a APr or APp 6 g, St 24 g, water 180 g.

^b Reference 6, $M_1 = \text{APr or APp}$ and $M_2 = \text{St}$.

^c Calculated fraction of acrylamides in copolymer formed just after the start of polymerization.

based on the polymerization recipe. The results are shown in Figure 2. The solubility of St in water phase was very small (about 4 mmol l^{-1}) and mostly independent of temperature. The fraction of APr dissolving in water phase is much larger than that of APp.

A higher concentration of APr in water and larger r_1 value⁶ must cause a higher fraction of APr in the polymer which formed in the aqueous phase just at the beginning of polymerization. The calculated compositions of initially-formed polymers are also presented in Figure 2. Soon after starting the polymerization, particle nuclei formed and the main polymerization site gradually shifted from the aqueous phase to growing particles. The contribution of two reaction sites to the polymerization at each step cannot be determined and thus no further discussion is made. But it is apparent that the oligomer or polymer molecules initially-formed in APr-St systems keep their solubility for longer time and form particle nuclei more slowly, compared with those in the APp-St system, because of the difference in the fraction of hydrophilic com-

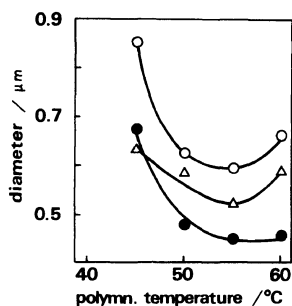


Figure 3. Effects of polymerization temperature on the diameter of latex particles: ○, APr, $f=0.1$; △, APr, $f=0.2$; ●, APp, $f=0.1$.

ponents between two systems and the difference in the hydrophilicity between APr and APp. In conclusion, the preferential polymerization of APr and slow formation of particle nuclei brings about the unusual shape of the time-conversion curves of APr–St systems.

Dependence of the size of resulting latex particles on the kind of comonomers and polymerization temperature is shown in Figure 3. As mentioned above, slow nucleation in APr–St systems is considered to give rise to the formation of a small number of large particles. Higher polymerization temperature generates larger number of initiator radicals and this will be a cause for the decrease in particle size with elevating polymerization temperature. Calculation of the rate of radical formation supports this speculation. Figure 3 shows that the temperature-dependence of particle size changes at about 55°C for APr–St system and a similar phenomenon is observed for APp–St system although the turning temperature is not necessarily the same. These results would be attributed to instabilization of particles at higher temperature. The coincidence between the turning point in particle size-temperature curve and the cloud point (CP) of poly-APr ($=51^{\circ}\text{C}$) may be incidental. In the case of the APp–St system, the turning point is rather higher than that for APr–St system and quite different from the CP of poly-APp ($=5^{\circ}\text{C}$).

It was expected that the ratio of particle-

composing APr to charged APr would increase discontinuously at the CP of poly-APr because poly-APr would lose its hydrogen-bonding ability at the CP. The ratio was determined as a function of polymerization temperature at two different f values. The ratios scarcely depended on the temperature unexpectedly and they were about 0.82 at $f=0.1$ and about 0.70 at $f=0.2$. This result would mean that dehydration proceeds gradually from a temperature much lower than the CP of poly-APr. In the APp–St system, due to the hydrophobicity of APp, most of the charged APp units existed in or on the particles and did not remain in the aqueous phase.

Stability of St–APr Latices

The critical flocculation concentration at different temperatures is plotted in Figure 4. Each curve in the figure indicates the boundary between stable dispersion and flocculation for the respective latices. Namely, latices are stable dispersions at the left and lower side of the curve whereas they flocculate at the right and upper side of the curve. Three curves in Figure 4 were obtained for three latices prepared from St–APr copolymerization at different f values. Two latices of higher f values showed reversible transition between stable dispersion and flocculation although the latex prepared with $f=0.1$ had a CFC-temperature curve relatively insensitive to temperature and the transition was irreversible. The curves had inflection points or critical temperatures above which the latex flocculates at the same salt concentration. Such a temperature is referred to as the critical flocculation temperature (CFT). The definition is presented in Figure 4. All of the CFTs for three latices in the figure were about 45°C and close to the cloud point of poly-APr. This fact implies that the particles of these latices have surface layers composed mainly of poly-APr and most of St units are buried inside the particles.

Sterically stabilizing effects due to hydration

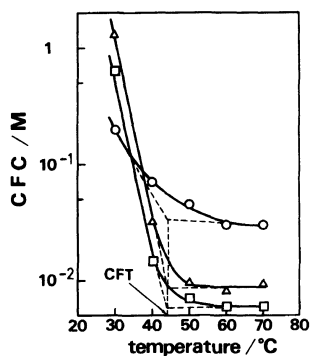


Figure 4. Dependence of stability of St-APr latices on temperature and NaCl concentration: \circ , $f=0.1$; \triangle , $f=0.2$; \square , $f=0.3$.

of on-surface APr units seem to disappear at the CFT and the stability of latex is decided by electrostatic and van der Waals interactions above the CFT.

Elevation of the temperature from room temperature up to CFT causes gradual dehydration of surface layers of the particles. The contraction or shrinkage of hydrated layer is expected to give rise to an increase in the effective electric charge of particles. Under a certain condition, it is said that the effective surface charge is proportional to the product of electrophoretic mobility (u) and viscosity (η) of the medium. Actually the $u\eta$ values for St-APr latex particles started to increase from about 30°C although the value for homo-poly-St particles was unchanged in the temperature range examined.³

Dehydration behavior can be determined more directly from the measurement of hydrodynamic size of particles. This measurement was carried out by using a quasielastic light scattering method and the results are shown in Figure 5. It is indicated that the hydrated layer of APr-containing particles shrinks gradually below the CFT and the hydrodynamic size of particles does not change anymore above the CFT. In the case of St-APr particles prepared at $f=0.1$ the hydrodynamic size above CFT coincides with the size measured by electron microscopy.

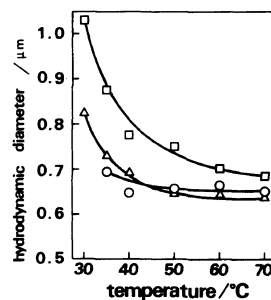


Figure 5. Dependence of hydrodynamic size of St-APr latex particles: \circ , $f=0.1$; \triangle , $f=0.2$; \square , $f=0.3$.

On the other hand, the hydrodynamic size of latex particles prepared at higher f s is slightly larger than that on electron micrographs. Therefore, it is probable that the particles having thick APr-rich surface-layer do not necessarily lose all their hydrating water but keep a part of it even above the CFT. The higher stability of latices prepared from lower f above CFT and their higher $u\eta$ values imply that they have thinner hydrated layers and the more exposed ionic groups on the particles contribute to electrorepulsive stabilization.

Preparation of Latices Showing Reversible Transition of Dispersion-Flocculation at Desired Temperature

It was expected that the latices containing both of APr and APp would have their specific CFTs dependent on the composition of APr and APp because the CPs of APr-APp copolymers, which were prepared in aqueous solution polymerization, had a linear relation with the composition as shown by solid circles in Figure 6.

By changing the monomer composition in the feed, terpolymerizations were carried out in soap-free media. The terpolymerization from the standard recipe resulted in polydispersed latex particles. Therefore, the recipe was changed as follows: St 16 g, (APr and/or APp) 4 g, water 190 g, V50 0.157 g. The polymerization was carried out at 60°C. The concentration of three monomers in the aqueous phase under the above mentioned

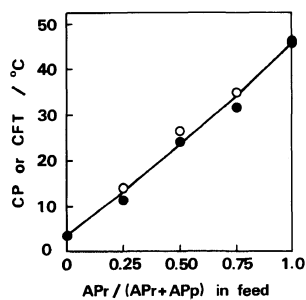


Figure 6. Influence of APr/(APr+APp) weight ratio in feed on cloud point (CP) of APr-APp copolymers and critical flocculation temperature (CFT) of St-APr-APp latices: ●, CP; ○, CFT.

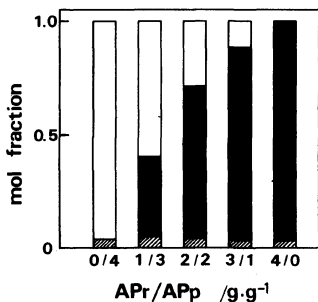


Figure 7. Composition of monomers dissolving in water phase at different APr/APp feed ratios: St 16 g, (APr+APp) 4 g, water 120 g, 60°C. ▨, St; ■, APr; □, APp.

conditions was determined by gas chromatography and the results are shown in Figure 7. The partition coefficients of APr and APp between water and St were 66 and 38, respectively, although the values decreased gradually with the coexistence of the other acrylamide derivative. The ratio APr/APp in aqueous phase is higher than the ratio of charged monomers. According to the calculation of copolymer composition by using the APr/APp in the aqueous phase and the monomer reactivity ratio, the copolymers would have formed having APr molar fractions of 0.53, 0.82, and 0.93 at the initial stage of polymerization in the aqueous phase from the recipes in which APr/APp were 8/22, 16/14, and 24/7 (mmol/mmol), respectively. It was investigated how such difference in po-

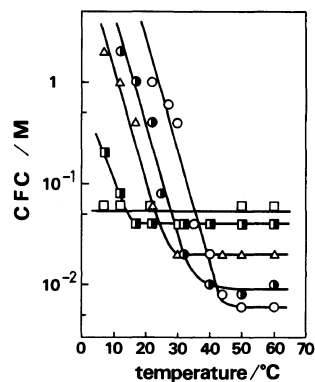


Figure 8. Dependence of stability of St-APr-APp latices on temperature and NaCl concentration. APr (g)/APp (g): □, 0/4; ■, 1/3; △, 2/2; ●, 3/1; ○, 4/0.

lymerization timing, as well as the composition of charged acrylamides, would affect the characteristics of resulting latices, especially their CFC and CFT.

Latices prepared from the above-mentioned recipe had excellent monodispersity; the coefficient of variation (CV, = (standard deviation/average diameter) × 100) was less than 5% for all the latices. The particle size changed with the composition of acrylamide derivatives and ranged from 0.285 μm at APr = 4 g (APp = 0 g) to 0.362 μm at APr = 0 g (APp = 4 g). CFC-temperature curves of a series of latices are shown in Figure 8. The lower-temperature range of CFC curves shifts to the up-side with increasing the fraction of APr, as expected. Namely, around an ambient temperature, latices containing more APr keep their stability up to a higher salt concentration.

CFT versus APr/(APr+APp) in monomer feed is plotted in Figure 6. According to the figure, the CFTs were mostly proportional to the composition of charged acrylamides even in the case of soap-free emulsion polymerization. This would imply that the surface layer of particles would be composed of APr and APp units of almost the same composition with the feed, perhaps, due to the compensation between the fraction of APr units remaining the

aqueous medium and that of APp units buried inside the particles. It is quite likely that St units are buried under the hydrophilic surface layer.

The CFC level of horizontal part of each curve above CFT in Figure 8 is in the reverse order with that at lower temperature; that is, the above CFT APp-rich particles have higher stability than APr-rich particles. This is attributed to the higher effective surface charge of APp-rich particles. The electrophoretic mobility was $2.3 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}$ for St-APp particles and increased with increasing APp/APr ratio in particles up to $5.3 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}$ for St-APp particles at 50°C and an ionic strength of 0.01.

CONCLUSIONS

The highly hydrophilic monomer, acryloyl pyrrolidine, polymerizes preferentially in the initial stage of soap-free emulsion copolymerization whereas the less hydrophilic mono-

mer, acryloyl piperidine does not do so remarkably.

The stability of resulting latices depends on the extent of hydration in the temperature range lower than a critical flocculation temperature, which is decided by the hydrophilicity of monomer units composing the particle surface. Above the critical temperature, the latex stability depends mainly on the electrorepulsive force between particles.

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