

Synthesis of High Molecular Weight Polyacrylamide Flocculant by Radiation Polymerization

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Synopsis

The radiation-induced polymerization of acrylamide was studied to prepare a high molecular weight and highly effective polyacrylamide flocculant. Among various solvents, mixtures of water-*tert*-butyl alcohol and water-acetone were found to be suitable for the synthesis of the high molecular weight polyacrylamide. For polymerization in acetone-water mixtures, the molecular weight of polymer increases with monomer concentration; but at the high concentration, intermolecular imidation of amide groups tends to take place during the polymerization to form crosslinked and water-insoluble polymer. The water-soluble polymer with the largest molecular weight of 6.7×10^6 is produced in the polymerization with monomer concentration of 2.91 moles/l. at 0°C at a dose rate of 6.2×10^2 rad/hr in acetone-water mixture containing 60 vol-% water. The crosslinking of polymer or the formation of water-insoluble polymer could be avoided by the addition of K_2CO_3 or NaOH to raise the pH of the reaction mixture above 6.5. The flocculation effects were evaluated from sedimentation speed of kaolin suspension and transparency of the separated water. The sedimentation speed is proportional to the intrinsic viscosity of the polymer in the range of 4 to 23 dl/g. The polymers prepared in this study show much higher sedimentation speed than commercial polyacrylamide flocculants. The transparency of the separated water is higher than 93%, similar to the results with commercial flocculants.

INTRODUCTION

Polyacrylamide has been used as an effective flocculant for various types of liquid-solid separation. It was found that the flocculation effect increases with increase in the molecular weight of polyacrylamide.^{1,2} Therefore, it is useful industrially to find the polymerization condition where high molecular weight polyacrylamide is obtained. Since high molecular weight polymer tends to be formed at low temperature in the radical polymerization, some redox catalyst which can initiate the polymerization at relatively low temperature has been used industrially. Radiation initiation is also favorable for the polymerization at low temperature, because the activation energy for initiation reaction is almost zero. In addition, from the viewpoint of process engineering, the heterogeneous polymerization in which the polymer precipitates as forms is convenient for obtaining the powdery polyacrylamide.

In our previous paper,³ a kinetic study was reported on the radiation-induced polymerization of acrylamide in a heterogeneous system using acetone and acetone-water solvents. It was found that the polymer molecular weight increases with decrease in both temperature and dose rate and with increase in monomer

concentration. However, polyacrylamide sometimes crosslinks during polymerization at high monomer concentration and at high conversion to form insoluble polymer which cannot be used as flocculant.

The purpose of this study is to find the conditions for synthesizing soluble polyacrylamide with molecular weight as high as possible in precipitating media.

EXPERIMENTAL

EP-grade acrylamide of purity higher than 95% was used as obtained, since further purification did not give any marked change in polymerization rate and polymer molecular weight. All organic solvents shown in Table I and inorganic salt in Table III were GR-grade and used as obtained. Water was ion-exchanged and redistilled before use.

Monomer solution in a glass ampoule was degassed five times by freezing-thawing cycles and sealed under vacuum. The ampoule was then irradiated in a temperature-controlled bath by γ -rays from a ^{137}Cs source. After definite time of irradiation, the reaction mixture was poured into an excess of acetone. The polymer was powdered in excess acetone by a homogenizer of Tokyo Nihonseiki Seisakusho Co., Ltd., at about 1700 rpm, then filtered, washed with acetone, and dried at room temperature under vacuum.

Intrinsic viscosity of polymer was measured in 1N NaNO_3 aqueous solution at 30°C by a Fica VISCOMATIC autoviscometer. The number-average molecular weight of polymer was determined by the following equation:⁴

$$[\eta] = 6.8 \times 10^{-4} \bar{M}_n^{0.66}$$

TABLE I
Radiation-Induced Polymerization of Acrylamide in Various Solvents^a

Solvent	Temperature, °C	Dose rate, $\times 10^{-3}$, rad/hr	Time, hr	Conversion, %	Polymer intrinsic viscosity $[\eta]$, dl/g	Polymer molecular weight $\bar{M}_n \times 10^{-4}$
AcN ^b	35	4.7	2	14.1	0.94	5.6
MeOH	35	4.7	2	56.0	0.76	4.1
<i>t</i> -BuOH	35	4.7	2	40.0	2.2	20.8
Acetone	35	4.7	2	9.0	1.1	6.8
Mixed solvents						
EA ^b -water (95/5) ^c	35	4.7	2	100	insoluble	
AcN-water (90/10)	0	0.62	6	82.5	insoluble	
DMA ^b -water (90/10)	0	0.62	6	76.2	0.98	6.1
MeOH-water (90/10)	0	0.62	6	11.4	1.5	11.7
<i>t</i> -BuOH-water (90/10)	0	0.62	6	38.0	4.8	68.0
Acetone-water (90/10)	0	0.62	6	5.0	4.0	52.0
DMA-water (50/50)	0	0.62	6	91.4	4.0	52.0
MeOH-water (50/50)	0	0.62	6	63.5	3.6	46.0
<i>t</i> -BuOH-water (50/50)	0	4.7	0.5	67.7	9.3	185
Acetone-water (50/50)	0	0.62	6	84.5	9.5	191

^a Polymerization condition: monomer concentration, 1.3 mole/l.

^b AcN, acetonitrile; EA, ethyl acetate; DMA, dimethylacetamide.

^c Volume per cent ratio.

The limit of applicability of the equation to high molecular weight is 3.03×10^5 , which is lower than the molecular weight of polymer formed in this study. Since other suitable relationship have not been reported, the above equation was applied as a matter of convenience.

To evaluate the flocculation effect, sedimentation speed of a kaolin suspension in water was measured as follows: in a 25-ml graduated cylinder 12 mm in diameter, 1.25 g kaolin powder was put, and water was added to make 23.75 ml, and then shaken well. After 5 min, 1.25 ml 0.01% polyacrylamide aqueous solution was added. Then the mixture was agitated by turning the cylinder upside down 10 times for 40 sec. Soon after the agitation, the average speed of interface falling between the graduations of 23 ml and 13 ml was measured as sedimentation speed.

Transparency of water was measured by a turbidimeter Model ANA-145 of Tokyo Kodon Co., Ltd., 2 hr after the addition of polyacrylamide solution.

RESULTS AND DISCUSSION

Effects of Solvents

Various polar solvents which dissolve acrylamide but not polyacrylamide are used to obtain the precipitated polymer. In addition, the solvents not containing hydrogen bonded with secondary and tertiary carbon are preferably used to minimize chain-transfer reaction which decreases the molecular weight of polymer.

The results are summarized in Table I. Among the pure solvents, *tert*-butyl alcohol gives the polymer with highest molecular weight. Acetone gives comparatively high molecular weight polymer. By adding 10% to 50% water to the

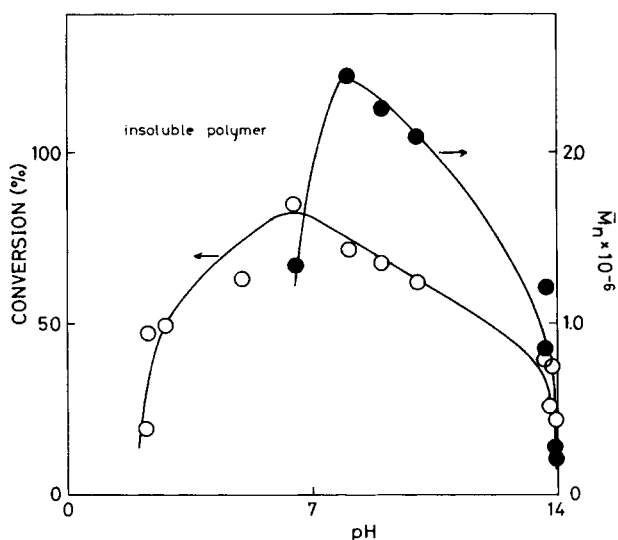


Fig. 1. Effects of pH of reaction mixture on polymerization rate and polymer molecular weight. Reaction conditions: temperature, 0°C ; dose rate, 6.2×10^2 rad/hr; time, 6.0 hr; monomer concentration, 1.3 mole/l.; acetone-water volume ratio, 60/40.

solvents, the molecular weight of polymer significantly increases, mainly because of a decrease in chain-transfer reaction. Mixtures of both *tert*-butyl alcohol and acetone with 50% water give particularly high molecular weight polymer.

Acetone is more convenient for carrying the polymerization at lower temperatures than *tert*-butyl because of its lower melting temperature. Because of smaller latent heat of acetone than *tert*-butyl alcohol, heat requirement for the recovery by distillation is smaller. In addition, acetone is less expensive than *tert*-butyl alcohol. For these reasons, a mixture of acetone and water was chosen as the solvent in the following experiments.

Conditions for Preparing High Molecular Weight Polyacrylamide in Acetone-Water Mixtures

In acetone-water mixtures, as reported in the previous paper,³ the molecular weight of polymer increases with decreasing dose rate and reaction temperature

TABLE II
Radiation-Induced Heterogeneous Polymerization of Acrylamide in Acetone-Water Mixtures at Low Temperature and Low Dose Rate^a

Acetone-water, vol-%	Monomer concn., moles/l.	Time, hr	Con- version, %	Polymer intrinsic viscosity [η], dl/g	Polymer molecular weight $\bar{M}_n \times 10^{-4}$
60/40	1.30	1	3.2	6.5	108
60/40	1.30	2	18.2	9.5	178
60/40	1.30	4	72.0	7.0	120
60/40	1.30	6	84.7	7.5	133
90/10	1.30	4	5.0	4.0	52
80/20	1.30	4	25.4	insoluble	
70/30	1.30	4	48.4	insoluble	
60/40	1.30	4	72.0	7.0	120
50/50	1.30	4	56.5	12.0	275
60/40	0.33	6	60.0	4.8	68
60/40	0.68	6	59.4	5.2	77
60/40	1.30	6	84.7	7.5	133
60/40	1.90	3	56.8	insoluble	
60/40	1.90	6	100	insoluble	
60/40	2.42	3	52.6	insoluble	
60/40	2.42	6	100	insoluble	
60/40	1.90	3	56.8	insoluble	
50/50	1.90	3	68.8	17.0	465
40/60	1.90	3	76.9	19.2	560
40/60	1.90	5	100	17.8	500
30/70	1.90	3	77.5	15.8	420
40/60	1.90	3	76.9	19.2	560
40/60	1.90	5	100	17.8	500
40/60	2.42	3	50.2	15.5	400
40/60	2.42	5	91.0	19.0	550
40/60	2.91	3	41.5	23.0	670
35/65	3.34	5	99.9	insoluble	

^a Polymerization conditions: temperature, 0°C; dose rate, 6.2×10^2 rad/hr.

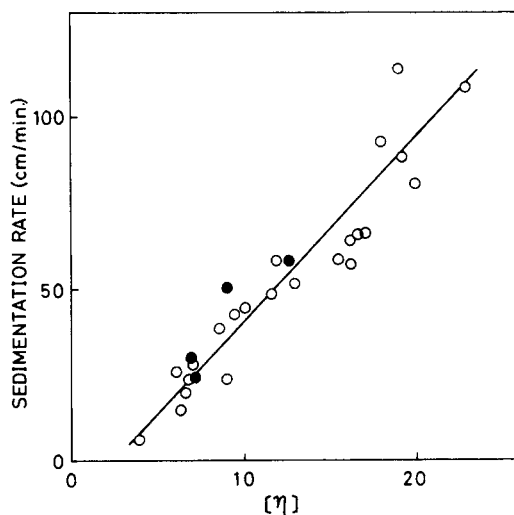


Fig. 2. Relation between sedimentation rate of kaolin suspension and intrinsic viscosity of polyacrylamide. Sample: (O) prepared in this work by radiation; (●) commercial polyacrylamide flocculants.

up to 0°C, and with increasing monomer concentration. Accordingly, in this study the polymerizations were carried out at a low temperature of 0°C and a low dose rate of 6.2×10^2 rad/hr to find the conditions for producing water-soluble polyacrylamide with the highest molecular weight. The results are summarized in Table II. The results of the first series of experiments indicate that the polymer molecular weight is hardly affected at all by reaction time or monomer conversion. The second series of results shows the effect of water content. The molecular weight increases with increasing water content. But in the mixtures containing 20% to 30% water, the polymer formed is insoluble in water because of the crosslinked structure; and in mixtures containing water above 70%, the polymer does not precipitate during polymerization.

In the third series of experiments, carried out in a mixture containing 40% water, it is shown that the polymer molecular weight increases with monomer concentration and that the polymer formed above 1.90 mole/l. is insoluble in water. However, even at 1.90 mole/l. of monomer concentration, as shown in the fourth series of results, in mixtures containing water of more than 50%, the

TABLE III
Effects of K_2CO_3 on the Formation of Water-Insoluble Polyacrylamide^a

K_2CO_3 , moles/l.	Monomer concn., moles/l.	Acetone-water, vol-%	Time, hr	Conversion, %	Polymer intrinsic viscosity $[\eta]$, dl/g	Polymer molecular weight $\bar{M}_n \times 10^{-4}$
0	2.42	60/40	3	52.6	insoluble	
0.005	2.42	60/40	3	56.3	16.7	450
0.02	2.42	60/40	3	50.8	13.0	310
0	4.0	40/60	6	90.4	insoluble	
0.08	4.0	40/60	6	93.0	19.8	550

^a Polymerization conditions: temperature, 0°C; dose rate, 6.2×10^2 rad/hr.

polymer is water soluble and has very high molecular weight which increases with water content.

In the last series of experiments, in the mixture containing 60% of water, the monomer concentration is further increased to raise the polymer molecular weight. Polyacrylamide with the highest molecular weight, 6.7×10^6 , is formed at monomer concentration of 2.91 moles/l., which is much higher than that of commercial polyacrylamide flocculant. However, at 3.34 moles/l. of monomer concentration, the formed polymer is insoluble in water.

In conclusion, it was found that water-soluble polymers with molecular weight higher than 4 million are obtained via polymerization under the following conditions: monomer concentration, 1.9 to 2.9 moles/l.; solvent, acetone-water mixtures containing 50% to 60% water; temperature, 0°C; dose rate, lower than 10^3 rad/hr. It is noteworthy that the rate of polymerization is very high (G -value of monomer consumption is 10^5 – 10^6) and even at a dose rate lower than 10^3 rad/hr, the polymer yield reaches 100% after a reaction time of 5 hr. However, in acetone-water mixtures containing water less than 40%, the polymer formed

TABLE IV
Flocculation Test of Various Polyacrylamides with Kaolin Suspension^a

Intrinsic viscosity [η] of polyacrylamide, dl/g	Sedimentation speed, cm/min	Transparency of water, % transmittance
Radiation-Polymerized Polymers		
4.0	5.6	—
6.1	26.2	94
6.4	14.0	—
6.7	19.7	—
7.0	23.2	—
7.1	27.9	—
8.5	38.4	—
9.0	23.7	—
9.5	42.1	—
10.0	44.0	—
11.6	48.0	—
12.0	53.4	—
12.0	57.2	—
15.8	58.5	95
16.5	65.6	96
16.7	67.6	—
17.0	65.6	96
17.8	92.4	96
19.2	87.3	—
20.0	80.0	94
23.0	107	93
19.0	114	—
Commercial Nonionic Flocculants		
7.0	29.3	89
7.2	24.4	—
9.0	50.5	—
12.4	58.5	96

^a Measurement was carried out in a standard 25-ml graduated cylinder at kaolin concentration of 5% and polyacrylamide concentration of 5 ppm.

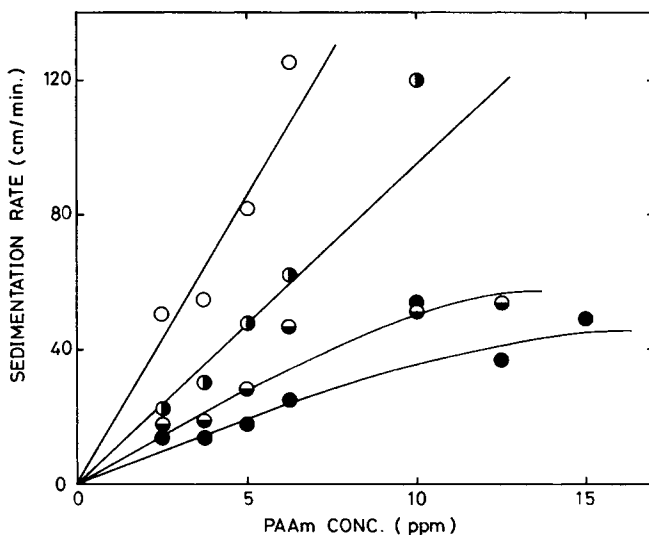
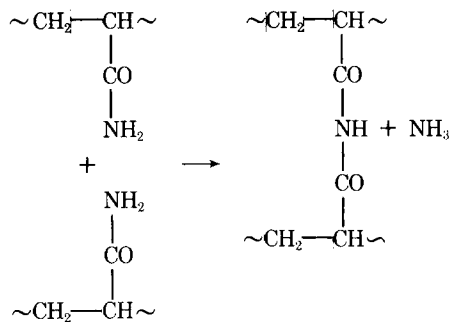


Fig. 3. Relation between sedimentation rate of kaolin suspension and concentration of polyacrylamide for various samples with different intrinsic viscosities. Sample: (O) radiation polymerized, $[\eta] = 15.0$ dl/g; (●) commercial, $[\eta] = 12.5$ dl/g; (◐) radiation polymerized, $[\eta] = 10.0$ dl/g; (●) commercial, $[\eta] = 7.0$ dl/g.

at high monomer concentration and at high conversion tends to be water insoluble. The reason for the water-insoluble polymer formation is intermolecular crosslinking during polymerization due to the imidation of two amide groups:



Effects of pH and Addition of Salts to Reaction Mixture

Since the imidation of two amide groups proceeds in the presence of protons, the pH of the reaction medium is assumed to influence the formation of the water-insoluble polymer. As shown in Figure 1, where pH was changed by adding HCl or NaOH, the polymer formed at pH less than 5 is water insoluble, while the polymer formed at pH higher than 6.5 is water soluble. The polymerization rate and molecular weight are maximal at pH 6.5 and 8.0, respectively.

As shown in Table III, by adding alkaline salt, K_2CO_3 , instead of NaOH to the reaction mixture, the imidation and hence the formation of water-insoluble polymer is retarded. Namely, the addition of K_2CO_3 is effective in producing soluble polymer with increased molecular weight.

Flocculation Effects of Produced Polyacrylamide

The sedimentation speed of kaolin-water suspension by adding polyacrylamide of various molecular weights, including commercial products, and the transparency of the separated water are summarized in Table IV. The transparency of the water in the case of polyacrylamide prepared in the experiment is above 93%, similar to that for commercial flocculants.

The sedimentation speeds shown in Table IV are plotted against the intrinsic viscosities of the polymers in Figure 2. It can be seen that the sedimentation speed increases linearly with the intrinsic viscosity in a wide range of 4 to 23 dl/g. A similar linear relation has been reported⁵ in the intrinsic viscosity range lower than 5 dl/g, and an intrinsic viscosity dependence higher than first order was reported⁶ in the range of 1 to 8 dl/g. It should be noted that some polyacrylamides prepared by radiation polymerization in this study show sedimentation speeds much higher than commercial nonionic flocculants.

The relation between sedimentation speed and amount of flocculant added is shown in Figure 3 for polyacrylamides of various molecular weights. The sedimentation speed increases with concentration of flocculant, but levels off in the range larger than 10 ppm for samples with intrinsic viscosity less than 10 dl/g. The required amount of polyacrylamide is decreased by using the increased molecular weight polymer. Figure 3 also shows the excellent flocculation effect of the radiation-polymerized polyacrylamide with large molecular weight.

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