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Aqueous Polymerization of Acrylamide Initiated by Periodic Acid and Its Kinetics

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Abstract : The activity of periodic acid as an initiator for the polymerization of acrylamide in aqueous medium was investigated. The rate of polymerization was found to be proportional to the monomer concentration to the 1.5th power in the range of 1.41-5.64 mol/L. The reaction order to the periodic acid concentration was 0.49, which indicated a bimolecular mechanism for the termination reaction in the range of $0.5-4.0 \times 10^2$ mol/L. Propagation rate increased with raising the temperature according to an Arrhenius expression resulting in the exhibition of an apparent activation energy of 87.8 kJ/mol in the temperature range of 60-80°C. The addition of hydroquinone as a radical scavenger stopped the polymerization of acrylamide initiated by periodic acid. These results support that the polymerization proceeds via a radical chain mechanism.

Introduction

Polyacrylamides are a very important material in an industrial viewpoint: They have been widely applied as thickening agents of paper industry,¹ flocculants of aqueous suspensions,² soil stabilizers,³ and textile modifiers.⁴ They are also used in

emulsion or microemulsion form as cleaners and in enhanced oil recovery.⁵ It has been reported that hydrophilic modifications at the amide group in the side chain can convert the polymers into polyelectrolytes useful in the pharmaceutical, food and environmental industries.⁶⁻⁸

In the presence of free radical initiators, acrylamide is polymerized to high molecular weight polymers. Common initiators are water-soluble or

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organic-soluble initiators such as hydrogen peroxide, potassium persulfate, redox pairs, or azo compounds. Organic-soluble initiators such as azobisisobutyronitrile and benzoyl peroxide, however, produce a low molecular weight of polyacrylamide in organic solvent because of its low solubility.^{3,9} Therefore polymerization in aqueous solution is generally the preferred method. Redox catalysts are mainly used for aqueous polymerization of acrylamide. Common examples are persulfate/aliphatic diamine,¹⁰ ceric salt/aldehyde,¹¹ glycerol/Ce(IV),¹² cobaltous chloride/N,N-dimethylaniline,¹³ and so on.^{14,15} However, the transition metals in the redox catalytic systems affect the oxidative stability of the prepared polymers and lower their qualities.¹⁶ Furthermore, there are few studies on the initiator activity for polymerization of acrylamide in aqueous solution, except for potassium persulfate.^{17,18}

The present investigation deals with the polymerization of acrylamide with periodic acid initiator and its kinetics under various conditions. We will also discuss the effect of the initiator and monomer concentration on the molecular weight of the polymer formed.

Experimental

Materials. Acrylamide (97%) was recrystallized from acetone and then dried in vacuo (m.p. 84.5°C). Periodic acid (H₅IO₆, 99%; m.p. 121.5°C) was used as an initiator without further purification. Ferrous chloride tetrahydrate (99%) was deprived of crystal water by drying in vacuo at 40°C for 24 h. Cuprous chloride (99+%) and manganese chloride (99+%) were used as cocatalysts without

purification. All the chemicals were purchased from Aldrich Chemical Company. All solutions for polymerization were prepared by using double-distilled deionized water.

Polymerization. Acrylamide (1.0-4.0 g; 1.408-5.632 mole/L) and desired amounts of periodic acid (5.0×10^{-3} - 4.0×10^{-2} mole/L) as an initiator were charged into a 10 mL volumetric flask and then double-distilled deionized water was added to the flask to prepare a 10 mL solution. The solution was transferred into a 20 mL glass ampoule and embedded gas was removed by a vacuum-freeze-thawing technique. The ampoule was placed in a convection oven and the reaction proceeded at 60°C for a desired time. After the polymerization was completed, the viscous solution was precipitated into a large amount of methanol. The precipitated polymer was purified by a successive reprecipitation from water into methanol. The pure polyacrylamide was filtered and dried under reduced pressure at 50°C for 24 h.

Measurement of Viscosity. Intrinsic viscosity, $[\eta]$, of the polymers was measured in aqueous solution at 30°C by using a Ubbelohde viscometer. The number average molecular weights (M_n) of polyacrylamide samples were calculated from the following equation¹⁴:

$$[\eta] = 3.37 \times 10^{-4} M_n^{0.66}$$

Results and Discussion

Polymerization. To investigate the activity of the periodic acid as an initiator, we carried out the aqueous polymerization of acrylamide with changing the concentration of initiator and monomer,

Table I. Polymerization of Acrylamide with Periodic Acid Initiator^a

AA (mole/L)	H ₅ IO ₆ × 10 ² (mole/L)	Temp. (°C)	Conversion (%)	$[\eta]$ (dL/g)	Mol. Wt. ^b × 10 ⁴
1.408	2.0	60	57	0.41	4.76
2.816	2.0	60	73	0.67	9.95
4.224	2.0	60	79	0.82	13.55
1.408	2.0	70	79	0.36	3.88
1.408	2.0	80	87	0.24	2.05
1.408	0.5	60	22	0.59	8.03
1.408	4.0	60	81	0.26	2.27

^aPolymerization time, 8 h.

^bCalculated from $[\eta] = 3.37 \times 10^{-4} M_n^{0.66}$.

Table II. Effect of Hydroquinone on Polymerization^a

Hydroquinone $\times 10^2$ (mole/L)	0	0.4	0.8	2.0
Conversion (%)	79	6	2	nil

^a[AA] = 1.408 mole/L; [H₅IO₆] = 2.0×10^{-2} mole/L; polymerization time, 8 h; temperature, 70 °C.

Table III. Polymerization of Acrylamide with Periodic Acid/Transition Metal Halides^a

Transition Metal Halide	Conversion (%)	[η] (dL/g)	Mol. Wt. $\times 10^4$
MnCl ₂	91	1.11	21.37
FeCl ₂	86	0.95	16.88
CuCl	78	0.80	12.97

^aTemperature, 35 °C; polymerization time, 12 h; [AA]=1.408 mole/L; [H₅IO₆]= 2.0×10^{-2} mole/L; [transition metal halide]= 2.0×10^{-2} mole/L.

polymerization temperature, and additive concentration. Their results are listed in Tables I and II. The number average molecular weights of the prepared polymers were in the range of 20,000-140,000, when only the periodic acid was used as an initiator. When transition metal halides such as manganese chloride, ferrous chloride, and cuprous chloride were used together with the periodic acid, the high molecular weight polymers were obtained in the range of 120,000 to 220,000 (Table III).

Effect of Initiator Concentration on Polymerization Rate. Figure 1 shows the change of conversion against the reaction time with different concentrations of the periodic acid and the fixed concentration of monomer. Within 3 h after the polymerization, not only the initial rate of polymerization but also the maximum conversion increased linearly with increasing the concentration of periodic acid. The kinetic order of this reaction to the initiator concentration was determined by plotting the logarithm of the initial rate versus the logarithm of the periodic acid concentration, as shown in Figure 2. In the investigated concentration range ($0.5\text{-}4.0 \times 10^{-2}$ mol/L), the reaction order of periodic acid was 0.49, which indicated a half-order dependence of the polymerization rate on the periodic acid concentration. It is in fairly good agreement with the kinetic order of a typical radical chain polymerization illustrating the square-

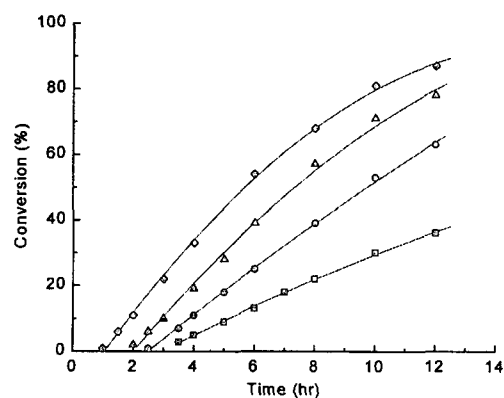


Figure 1. Time versus conversion curves for the aqueous polymerization of acrylamide with change of concentration of periodic acid (mol/L): [AA]=1.408 mol/L; temperature = 60 °C; (■) 5.0×10^{-3} ; (●) 1.0×10^{-2} ; (▲) 2.0×10^{-2} ; (◆) 4.0×10^{-2} .

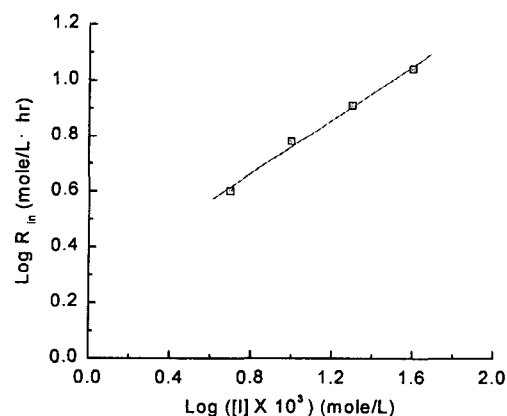


Figure 2. Double logarithmic plot of initial rates of polymerization versus periodic acid.

root dependence on initiator concentration.³

Effect of Monomer Concentration on Polymerization Rate. Figure 3 shows a typical plot of conversion against time with different monomer concentrations. The initial rate of polymerization within 3 h after the polymerization, as well as the maximum conversion, increased linearly with increasing the concentration of the monomer with the fixed concentration of the periodic acid. In all the cases, there are the induction periods for the polymerization. Figure 4 shows the effect of the monomer concentration on the polymerization rate. The rate of polymerization was found to be proportional to the monomer concentration to

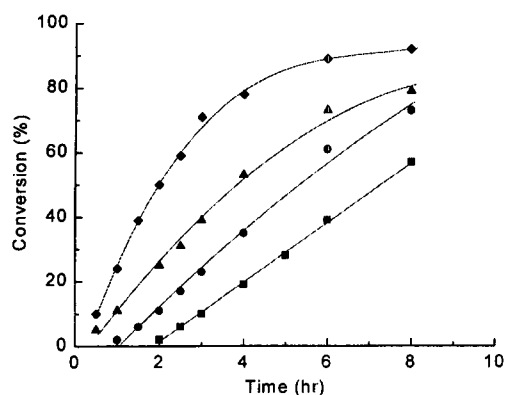


Figure 3. Time versus conversion curves for the aqueous polymerization of acrylamide with change of concentration of monomer (mol/L); $[H_5IO_6] = 2.0 \times 10^{-2}$ mol/L; temperature = 60°C ; (■) 1.408; (●) 2.816; (▲) 4.224; (◆) 5.632.

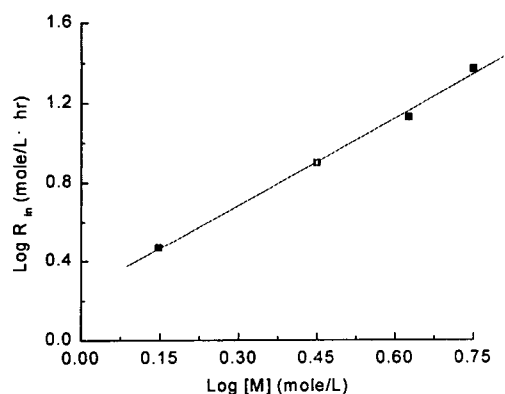
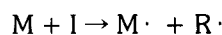


Figure 4. Dependence of polymerization rate on monomer concentration: $[H_5IO_6] = 2.0 \times 10^{-2}$ mol/L; temperature = 60°C .

the 1.5th power, in the range of 1.41–5.64 mol/L. These polymerizations exhibit a great deviation compared to the general behavior illustrating a first-order dependence of the polymerization rate on the monomer concentration. In general, the initiation of conventional radical initiators such as peroxide and azo compounds requires two step reactions; first, the homolytic dissociation of an initiator or catalyst species leads to the formation of a pair of radicals. The produced radicals initiate the first monomer molecule to yield the chain initiating species.

The $3/2$ -order dependence of the polymerization rate on the monomer concentration arises

from the monomer-enhanced decomposition which is first-order in both acrylamide and periodic acid initiator. The initiation reaction may be written as follows;



Based on the results shown in Figure 3, the induction period for the initiation of the aqueous polymerization can be quickly reduced by increasing the concentration of monomer in the range of 1.408 to 5.632 mol/L even with the fixed concentration of periodic acid. This indicates that the accelerated initiation arises from an intermolecular hydrogen bonding between the amide group in the monomer and the periodic acid. In other words, the increase of the monomer concentration leads to the enhancement of the interaction between the monomer and the initiator resulting in the exhibition of the high rate order dependence.¹⁸

On the other hand, the rate of polymerization on the monomer concentration was deviated from the linearity when the polymerization time was over 3 h in a high monomer concentration range (5.64 mol/L). It seemed to be due to the increased viscosity of the medium.

Effect of Polymerization Temperature. The conversion and the initial rate of polymerization increased with raising polymerization temperature from 60 to 80°C , as shown in Figure 5. However,

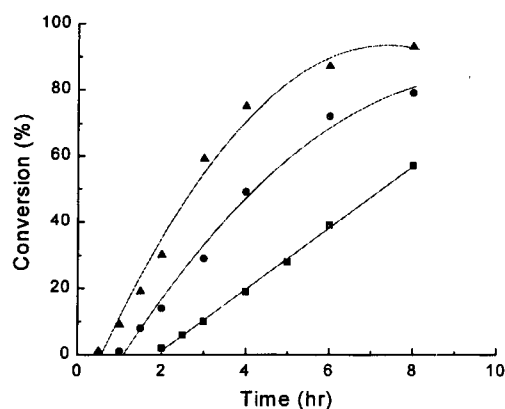


Figure 5. Time versus conversion curves for the aqueous polymerization of acrylamide with change of polymerization temperature ($^\circ\text{C}$): $[AA] = 1.408$ mole/L; $[H_5IO_6] = 2.0 \times 10^{-2}$ mole/L; (■) 60 ; (●) 70 ; (▲) 80 .

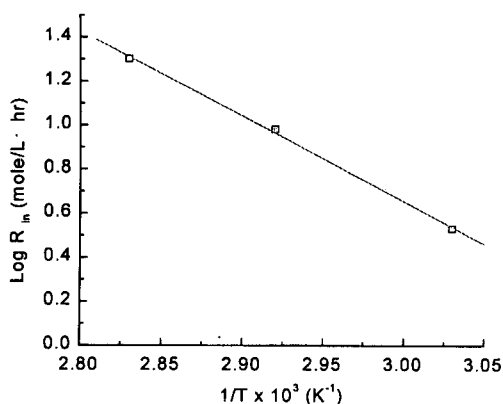


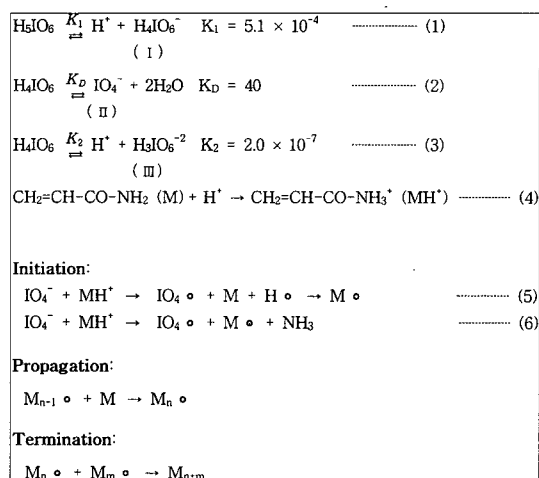
Figure 6. Logarithmic plot of rate of polymerization versus $1/T \times 10^3$ (in °K): [AA]=1.408 mole/L; $[H_5IO_6]=2.0 \times 10^{-2}$ mole/L.

the molecular weight (see Table I) and the induction period for the initiation of the aqueous polymerization decreased with raising the temperature. This is due to the increase of the number of radicals resulting from the monomer-enhanced decomposition during the initiation step.

To obtain a desirable molecular weight of the formed polymer, we carried out the polymerization at 60°C under various conditions. The activation energy (E_a) for the aqueous polymerization of acrylamide with the periodic acid was calculated from the Arrhenius expression using the least square method. The E_a from the slope shown in Figure 6 was 87.8 kJ/mol. The value was almost the same as the activation energy observed from general radical initiators.³ This informs us that the aqueous polymerization of acrylamide initiated by the periodic acid proceeds via a radical mechanism.

Effect of the Additive. Table II shows that the addition of hydroquinone as an inhibitor, to the system inhibits the polymerization by its complete consumption. For instance, the polymerization reaction completely stopped by the equimolar addition of hydroquinone to the concentration of the periodic acid used as an initiator. Consequently, it is concluded that the polymerization proceeds through a radical mechanism.

Polymerization Mechanism. Based on the results, a possible mechanism of the aqueous polymerization of acrylamide with periodic acid



Scheme 1. Polymerization mechanism.

may be proposed as shown in Scheme I.

Presumably, the periodic acid in aqueous solution exhibits the three equilibrium states as shown in the equations (1), (2), and (3).¹⁹ The constants for these ionization (K_1 , K_2) and hydration (K_D) equilibria have been evaluated at 25°C. The periodic acid is converted into the iodate ion (IO_4^-) as soon as the first ionization reaction occurred in the aqueous solution. The reaction may be accelerated in the presence of acrylamide monomer. For instance, the amide group of the monomer accepts the proton liberated from the first ionization leading to the formation of activated monomer (MH^+) shown in the equation (4). Thus, the activated monomer readily reacts with the iodate ion to produce free radicals through a equation (5) or (6). The radicals undergo the aqueous polymerization of acrylamide.

In addition, we also carried out the aqueous polymerization of acrylamide with the redox pairs from periodic acid and transition metal halides such as manganese chloride, ferrous chloride, or cuprous chloride. Figure 7 shows the results for polymer conversion as a function of time and various kind of transition metal halides with a fixed concentration of acrylamide and periodic acid. These cases exhibit an induction period to initiate the polymerization. The rate of polymerization with the redox systems at 35°C was much faster than that with the periodic acid only, and the prepared polymers had a very high molecular weight

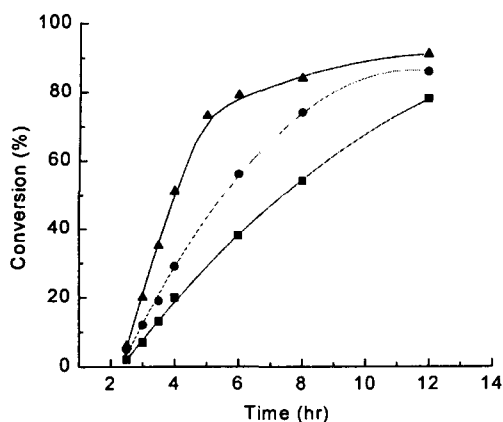


Figure 7. Effect of transition metal halides on rate of polymerization of acrylamide: temperature=35 °C; [AA]=1.408 mole/L; [H₂IO₆]=2.0 × 10⁻² mole/L; (▲), [MnCl₂]=2.0 × 10⁻²; (●), [FeCl₂]=2.0 × 10⁻²; (■), [CuCl]=2.0 × 10⁻² mole/L.

of 120,000-220,000 (Table III). The cocatalytic activity of transition metal halides for the polymerization was in the order of manganese chloride, ferrous chloride, and cuprous chloride. Detailed results including their kinetics and polymerization mechanism will be published elsewhere soon.

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