JOURNAL OF APPLIED ELECTROCHEMISTRY 6 (1976) 147–153

Formation of a high polymer of acrylamide by utilizing Kolbe's electrolysis

S. YOSHIZAWA, Z. TAKEHARA, Z. OGUMI, C. NAGAI

Department of Industrial Chemistry, Faculty of Engineering, Kyoto University, Yoshida, Sakyo-ku, Kyoto, Japan.

Received 3 March 1975

During the electro-initiated polymerization of acrylamide by utilizing Kolbe's electrolysis as a source of free radicals in an aqueous solution of acetic acid and potassium acetate, only an oligomer with a molecular weight of 4000–6000 was obtained. However, by the addition of ferric ion, a high-polymer with a molecular weight of a few millions was obtained. The effective action of ferric ions was retarded by the presence of ferrous ion and a large amount of chloride ion. The optimum amount of ferric ion for the formation of high-polymer and the effects and roles of various ions on the process of polymerization are discussed.

1. Introduction

Over a period of years, much interest has been shown in the field of electro-initiated polymerization by utilizing the free radicals formed anodically or cathodically in electrolytic cells. Yoshizawa *et al.* [1] examined the polymerization of acrylamide, where the monomer as well as the polymer is soluble in aqueous solution, by utilizing Kolbe's electrolysis as a source of free radicals for initiating polymerization, and found that only an oligomer with a molecular weight of a few thousands was formed by the anodic reaction in aqueous solutions of CH_3COOH–CH_3COOK [1] or CF_3COOH–CF_3COOK [2]. Also, it was confirmed that polymerization proceeds via the Kolbe reaction from the fact that an oligomer with $-CF_3$ as the end group was produced by the electrolysis in aqueous solution of CF_3COOH–CF_3COOK [2]. Also, it was found that a polymer with a high molecular weight of a few millions was formed by adding a certain amount of ferric sulfate to the CH_3COOH–CH_3COOK anolyte [3]. In this paper, the effects of the amounts of added ferric ions and the addition of various cations and anions will be reported, and the roles of various ions dissolved in the anolyte on the electro-initiated polymerization process of acrylamide will be discussed.

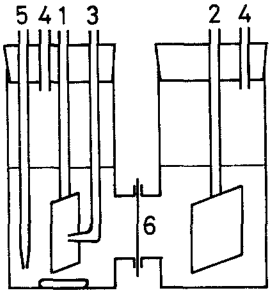


Fig. 1. Experimental cell. 1–Anode; 2–cathode; 3–Luggin capillary; 4–gas outlet; 5–gas inlet; 6–ion exchange diaphragm.

2. Experimental

An H-shaped glass cell with an anion exchange membrane was used (Fig. 1). The volumes of the anode and the cathode compartment were about 200 ml respectively. Smooth platinum plates were used as anodes and cathodes; a platinum disc (1·3 cm diameter) was used as a rotating anode. As a pretreatment, the platinum anode was polarized anodically and cathodically, alternately, in 1 N H_2SO_4 for about 30 min (plate) and for more than 90 min (disc) at 30 mA cm^{-2}. After that, it was washed with distilled water and electrolytes and then used immediately.

The monomer of acrylamide was recrystallized from benzene and dried under air, stored in a dark and cold place and used within a week. 1 litre of electrolyte solution was prepared by dissolving 1 mol of potassium acetate and 1 mol of acetic acid (commercial G.R. grade) in distilled water. This solution will be designated as 2 M acetate solution from now on. The anolyte was prepared by dissolving a given amount of ferric or ferrous salt and 15 g of acrylamide in 150 ml of 2 M acetate solution. 2 M acetate solution was used as a catholyte without any addition. Electrolysis was carried out in an ice bath, under bubbling nitrogen from 30 min before the beginning of the electrolysis to its end. Galvanostatic electrolysis at a current density of 30 mA cm^{-2} was employed in most work reported here. During electrolysis, the anode potential was about 2·3 V (versus SCE).

After electrolysis, the anolyte was poured with stirring into 2 l of methanol containing 2 g of hydroquinone as a polymerization inhibitor. An insoluble polymerized product precipitated; it was filtered through a No. 2 grade glass filter, dried at 60–80° C under reduced pressure, and weighed. The viscosities of the products were determined in an Ostwald viscometer mounted in a thermostated bath held at 30·00 ± 0·05° C. The weight-average molecular weight (M_w) was calculated from the intrinsic viscosities ($[\eta]$), according to the following equation [4]:

$$[\eta] = 3{\cdot}73 \times 10^{-4} \times M_w^{0{\cdot}66}. \qquad (1)$$

3. Results

When electrolysis was carried out without adding any ferric salt to the anolyte, an oligomer whose intrinsic viscosity was about 0·1 was obtained. Its molecular weight was calculated to be a few thousands. On the other hand, a polymer of high molecular weight (a few millions) was obtained by the electrolysis of the anolyte containing a few milligrams of ferric sulphate.

In order to investigate the effects of various iron compounds on the polymerization process, cyclic voltammetry was employed, and the result is shown in Fig. 2. It is clear that ferric ion has no effect on the current-potential curves, and that the addition of acrylamide to the Kolbe's system caused the suppression of the current density. The addition of ferrous sulphate to the Kolbe's system led to the oxidation of the ferrous ion to the ferric ion at about 1·6–1·7 V. The polymer of a high molecular weight was produced at an electrode potential beyond 2·1 V, where the Kolbe's reaction was occurring.

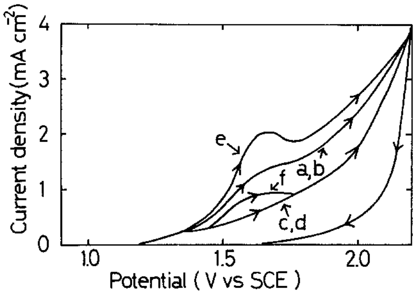


Fig. 2. Current-potential curves for different iron compounds. a–0·5 M acetate solution (100 ml); b–a + $Fe_2(SO_4)_3 \cdot 7H_2O$ (100 mg); c–a + acrylamide (5 g); d–b + acrylamide (5 g); e–b + $FeSO_4 \cdot 5H_2O$ (100 mg); f–d + $FeSO_4 \cdot 5H_2O$ (100 mg).

The mechanism of the Kolbe's reaction is explained either by

$$RCOO^- \longrightarrow RCOO\cdot + e^- \qquad (2)$$

$$RCOO\cdot \longrightarrow R\cdot + CO_2 \qquad (3)$$

$$R\cdot \longrightarrow 1/2\ R\text{–}R \qquad (4)$$

or

$$RCOO\cdot \longrightarrow 1/2\ R\text{–}R + CO_2. \qquad (5)$$

Acetate ion discharges and gives the dimeric product, ethane, and carbon dioxide. In our aqueous solution, the possibility of ionic polymerization is neglected. Polymerization in our system proceeds via a radical polymerization process in which the Kolbe's intermediate radical is utilized as a radical source.

For the case where both ferrous and ferric ions are present, the relationship between the induction period of the polymerization and the amounts of the added iron compounds is shown in Fig. 3, [the total amount of dissolved ferrous and ferric ion was maintained constant (100 mg)]. When only the ferrous ion was present, a high polymer was obtained about 110 min after electrolysis started. The induction period of polymerization was decreased by increasing the amount of dissolved ferric sulphate. Finally, a high polymer was formed in 5 min when only the ferric ion was present. The polymerization was retarded in the presence of ferrous ion and a high polymer could only be obtained after ferrous ion was completely oxidized to ferric ion. The induction period of polymerization may be explained in terms of the

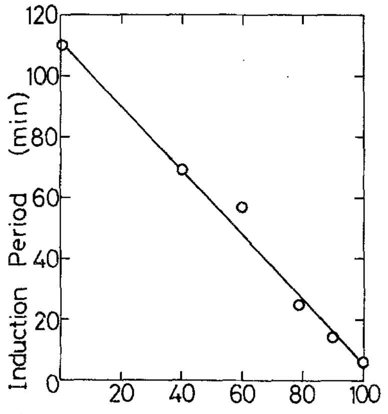


Fig. 3. Relationship between the induction period of polymerization and the ratio of Fe^{2+} ion and Fe^{3+} ion. Anolyte: 2 M acetate solution (100 ml) + acrylamide (10 g) + iron compounds (total 100 mg).

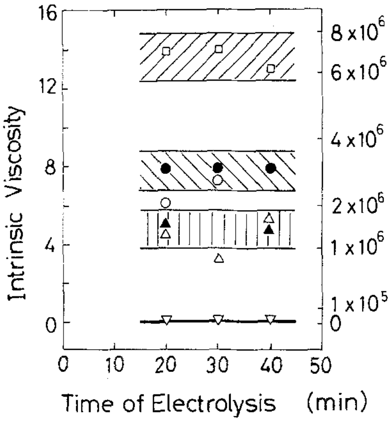


Fig. 5. Relationship between the intrinsic viscosity and the time of electrolysis for various amounts of dissolved $Fe_2(SO_4)_3 \cdot 7H_2O$. Anolyte: 2 M acetate solution (100 ml) + acrylamide (10 g) $Fe_2(SO_4)_3 \cdot 7H_2O$; ▽–0 mg; △–10 mg; ▲–15 mg; □–25 mg; ○–50 mg; ●–75 mg.

time needed for the ferrous ion to be completely oxidized to ferric ion at the platinum anode.

When only ferric sulphate was added to the electrolyte, a high polymer was formed. The longer the time of electrolysis, the more copious was the polymer that was produced. In Fig. 4, the polymer yield is plotted against the amount of added ferric sulphate, with the time of electrolysis maintained constant. As shown in Fig. 4, the optimum amount of added ferric sulphate that gave the maximum polymer yield irrespective of time of electrolysis was 25 mg 100 ml^{-1}. This interesting phenomena will be discussed in detail in Section 4.

The relationship between the intrinsic viscosities and the times of electrolysis with various amounts of dissolved ferric sulphate was also examined (Fig. 5). The average molecular weight is also shown on the ordinate. Without the addition of ferric sulphate, the intrinsic viscosity was about 0·1. When 25 mg 100 ml^{-1} of ferric sulphate was added, the viscosity was between 12–14, when less

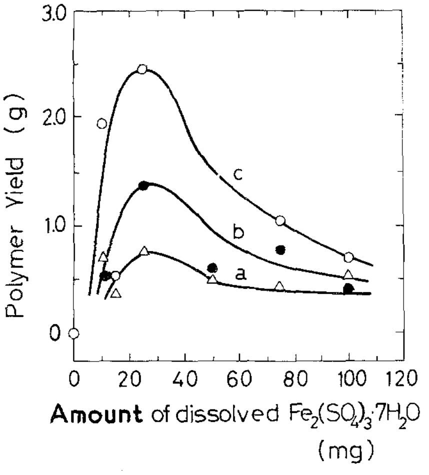


Fig. 4. Relationship between the polymer yield and the amount of dissolved $Fe_2(SO_4)_3 \cdot 7H_2O$ at different electrolysis times. Anolyte: 2 M acetate solution (100 ml) + acrylamide (10 g) a–20 min; b–30 min; c–40 min.

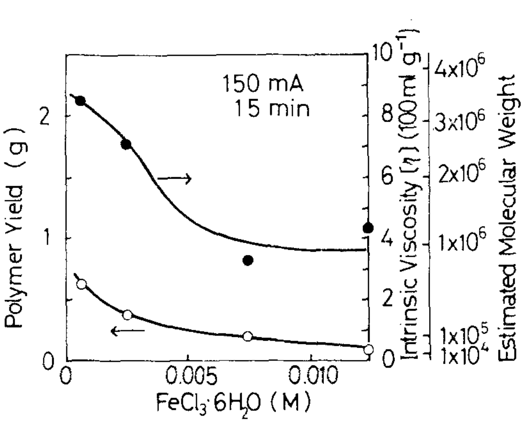


Fig. 6. Relationships between the polymer yield, and corresponding intrinsic viscosity and the added amount of ferric chloride. Electrolysis: 150 mA, 15 min.

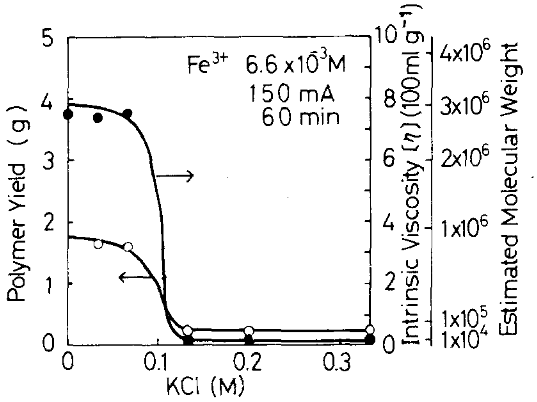


Fig. 7. Relationships between the polymer yield, the corresponding intrinsic viscosity and the added amount of potassium chloride. Electrolysis: 150 mA, 60 min; Fe^{3+}: 6·6 × 10^{-3} M.

than 25 mg, about 4–6, and when more than 25 mg, 7–9. The polymer of the highest molecular weight was obtained when 25 mg of ferric sulphate was added. It can be seen in Fig. 5 that the intrinsic viscosity and the corresponding estimated molecular weight were approximately constant regardless of the electrolysis time. Thus the number of polymer molecules increases with the time of electrolysis as long as the concentration of ferric sulphate is maintained constant. If ferric chloride is added instead of ferric sulphate, a polymer of high molecular weight is produced. However, increasing quantities of added ferric chloride retard the production of polymer (Fig. 6). This shows that ferric chloride has a retarding effect as well as an initiating effect on the polymerization. In order to confirm this result, potassium chloride was added to 2 M acetate solution containing ferric ion from the anodic dissolution of iron. A polymer of high molecular weight was obtained when the concentration of chloride ion was more than three times that of the ferric ion concentration, as shown in Fig. 7. When the chloride ion concentration became more than about 0·1 M, a polymer was not obtained. This may be due to the discharge of chloride ion in place of acetate ion. This phenomenon was also observed by adding perchlorate ion.

Experiments were also conducted to see whether or not ferric ion influenced the initiation reaction (the electrode reaction), or the propagation reaction (the chemical reaction in the bulk of solution). An adsorbed acetate radical on the oxide film on the platinum electrode might be desorbed by ferric ion. Thus, electrolysis was carried out in the non-aqueous CH_3COOH CH_3COOK solution, where oxide films would only be sparingly formed on the platinum anode. By increasing the water content in the electrolyte, it was found that there exists a critical value for polymer formation between the ratio $H_2O/CH_3COOH = 3/7$ and the ratio $H_2O/CH_3COOH = 2/8$. The former solution produced a high polymer, whereas the latter produced only an oligomer. Cyclic voltammetry was carried out as shown in Fig. 8. It will be seen that voltammograms in the

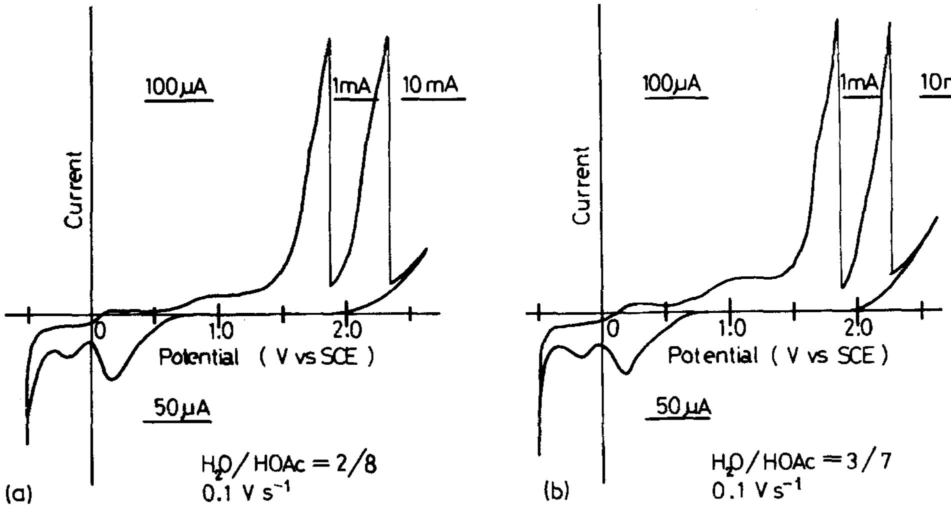


Fig. 8. Cyclic voltammograms. Sweep rate: 0·7 V s^{-1}. (a) $H_2O/HOAc = 2/8$; (b) $H_2O/HOAc = 3/7$.

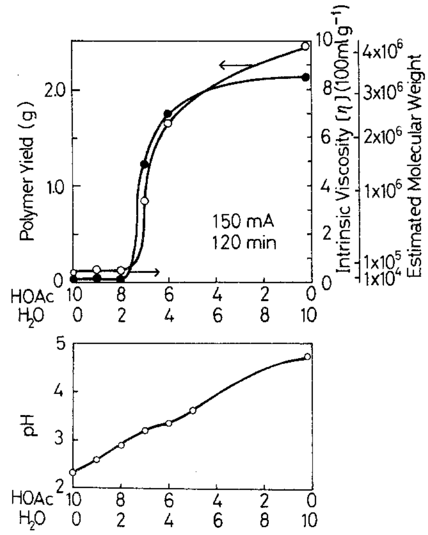


Fig. 9, Relationships between the polymer yield, the corresponding intrinsic viscosity and the $H_2O/HOAc$ ratio, and the relationship between the pH value and the $H_2O/HOAc$ ratio. Electrolysis: 150 mA, 120 min.

two cases were the same. The surface oxide film does not appear to play an important role in the high polymer formation process. The electrolysis was also performed by increasing the amount of H_2O in the non-aqueous acetate solution in the presence of ferric ion. The result is shown in Fig. 9; the corresponding pH value of the solution is also shown in Fig. 9. Polymers of high molecular weight are not obtained until the H_2O content in the anolyte exceeds 30%. The polymer yield increases as the H_2O content is increased, and the intrinsic viscosity also increases for H_2O contents in excess of 30%. The pH effect on the high polymer formation was uncertain, though at pH 3·2 high polymer was obtained which could not be formed at pH 2·9. A pH effect might be responsible for the fact that the polymer of high molecular weight could not be formed in 2 M CF_3COOH–CF_3COOK solution even if ferric sulphate was added. The variation of an u.v. absorption peak of ferric ion in 2 M acetate solution at various pH values was also investigated after adding sulphuric acid to the anolyte. The result is shown in Fig. 10. Due to the strong absorbance of acrylamide, it is not possible to say if the ferric ion absorption peak shifts or not. However, there might be some difference in the position of the absorption peak of ferric ion that seemed to have a tendency to shift toward the

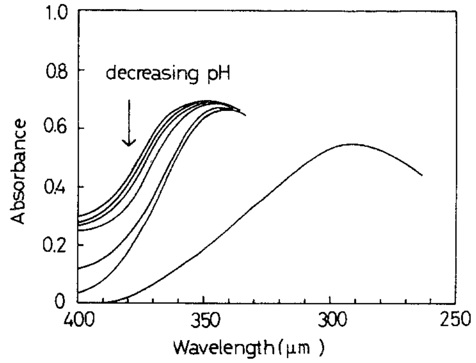


Fig. 10. Ultra-violet spectra of Fe^{3+} with various pH values.

shorter wave length. The brown-coloured 2 M acetate solution was decoloured at pH 2·7 where polymer could not be obtained. The position of the absorption peak of ferric ion in water is also shown in Fig. 10 for comparison. From the above experiments it is clear that ferric ion has an effect on the propagation reaction. In order to see if the electrode reaction is affected by ferric ion, the following electrolysis was performed using a rotating disc electrode, and a current density of 30 mA cm^{-2}. The polymer of high molecular weight was obtained at any rotation speed and its yield remained at a constant value, irrespective of rotation speed. The relationship between the intrinsic viscosity and the rotation speed is shown in Fig. 11. Open circles, dots, and triangles in Fig. 11 represent different batches of acrylamide monomer. The intrinsic viscosity number was inclined to decrease as the rotating speed increased

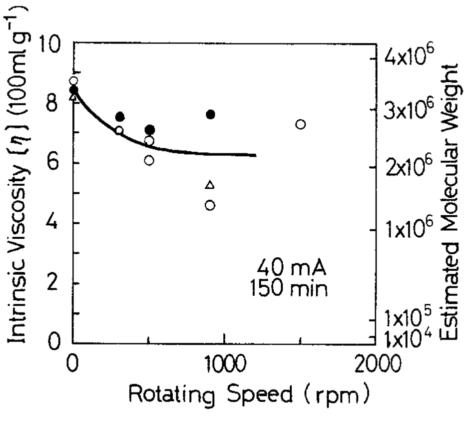


Fig. 11. Relationship between the intrinsic viscosity and the rotating speed. $Fe_2(SO_4)_3 \cdot 7H_2O$: 75 mg 150 ml^{-1}; electrolysis: 40 mA, 150 min.

at first, but then reached a constant value. It can be said that the number of polymer molecules formed increases as the rotating speed increases during the first stage. Which has the greater effect on the polymerization process, the diffusion of ferric ion toward the electrode surface, or the diffusion of a growing polymer radical into the bulk of the solution is not clear yet. It seems to be possible to neglect the coupling reaction between two growing polymer radicals but some ambiguity remains. It might be concluded that the effect of diffusion is the result of a competitive reaction between the oligomer forming reaction and the forming reaction of ferric complex ions.

4. Discussion

Redox reactions are often utilized for initiating polymerization. For instance, the following reaction

$$H_2O_2 + Fe^{2+} \longrightarrow HO\cdot + HO^- + Fe^{3+} \qquad (6)$$

which is called Fenton's reaction, can initiate polymerization. Besides iron compounds, copper and cerium compounds etc. are used for this purpose. The ion which is effective is the lower valence one (c.f. ferrous ion in the above example). But as shown in this paper, ferric ion can also initiate polymerization. Therefore, polymerization by ferric ion is clearly different from redox polymerization, and in addition the inhibiting action of ferrous ion can also not be explained from the standpoint of redox polymerization.

The ferric ion seems to affect the reaction in two steps:

(1) in the process of the formation of initiator, namely, electrode reaction;

(2) in the process of propagation.

In case 1, a different kind of initiator is produced, which migrates from the electrode surface into the solution bulk and initiates the polymerization. In case 2, ferric ion stabilizes the radical end of the propagating oligomer or retards the coupling reaction of radicals formed at the electrode and helps it to migrate from the reaction area just next to the electrode surface to the bulk, where the propagation reaction continues.

As shown in Fig. 9 there exists a limiting value in the water content for the high polymer formation. Beyond $H_2O/CH_3COOH = 2/8$, ferric ion does not cause the formation of a high polymer. The presence of ferrous ion, furthermore, causes a strong inhibition of the effect of the ferric ion. Considered along with the fact, however, that the electrode potential where the electro-initiated polymerization proceeds is positive enough for the ferrous ion present near the electrode to be oxidized to ferric ion, the difference between ferric ion and ferrous ion would never play a part in case 1, which can thus be eliminated.

Cavell *et al.* showed that ferric chloride could initiate the polymerization of acrylamide by itself but that ferric sulphate could not [5]. On the other hand, the effect of ferric ion described in this paper was shown by ferric sulphate and no polymer was formed without electrolysis. So this effect is quite different from that of Cavell *et al.*

As previously described, the polymerization proceeds in the acetate solution only when the water content is beyond the limiting value and not in the trifluoroacetate solution [2]. Also, ferrous ion causes inhibition. These facts suggest that the ferric ion is concerned in the propagation process by preventing the propagating radical end from reacting with other radicals and helping it to migrate from the area of high radical concentration near the electrode to the bulk. The interaction between ferric ion and the propagating radical end had been investigated as follows. Collinson *et al.* investigated the polymerization of acrylamide induced by X-rays or γ-ray in aqueous solutions [6]. They found that ions such as Fe^{3+}_{aq} and $FeOH^{2+}$ terminated the polymerization. They determined the value of the termination rate constant, k_t. This value is different from ion to ion as shown in Table 1.

Table 1. The terminating rate, the frequency factor, and the activation energy of various Fe^{3+} complexes in the polymerization of acrylamide [6]

Ion	*k* ($mol^{-1}\ s^{-1}$)	*A* ($mol^{-1}\ s^{-1}$)	E_a (kcal)
$Fe(H_2O)_6^{3+}$	$2{\cdot}8 \times 10^{3}$	$1{\cdot}5 \times 10^{5}$	2·3
$FeOH^{2+}$	$2{\cdot}1 \times 10^{4}$	$4{\cdot}0 \times 10^{4}$	0·3
$FeCl^{2+}$	$8{\cdot}1 \times 10^{4}$	$2{\cdot}7 \times 10^{5}$	0·7
$FeCl_2^{+}$	$1{\cdot}7 \times 10^{4}$		
$FeCl_3$	$1{\cdot}0 \times 10^{6}$		

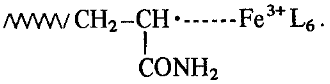
Narita *et al.* reported that the iron compound was involved in the polymer formed in the presence of ferric ion [7]. In our investigation, acetate solutions were used, and acetate ion can also act as a ligand. Thus, iron compounds formed complexes such as

$$[Fe(H_2O)_l \cdot (CH_3COO^-)_m \cdot X_n]^{(3-m-n)^+}$$

or

$$[Fe(H_2O)_l \cdot (CH_3COO^-)_m \cdot X_n]^{(2-m-n)^+}.$$

In the case of chloride, X might be Cl^-. The acetate solution is buffered at about pH 4·7. These complex ions could interact with the radical ends of propagating polymer. The strength of this interaction is different from ion to ion as we can guess from the different rates of termination shown in Table 1. When it is not so strong, the termination reaction will dominate the propagation and these ions will stabilize the radical end and prevent it from coupling with other radicals, as follows:



$$\sim\!\sim\!\sim CH_2-\underset{\displaystyle CONH_2}{\underset{|}{CH}}\cdot\cdots\cdots Fe^{3+}L_6.$$

This effect assists the radical end to migrate into the bulk of electrolyte, where the high polymer formation proceeds. When the concentration of ferric ion is low, the stabilizing effect is marked; when it is high, the terminating action is prominent. This is the reason why there exists an optimum value of added ion concentration for the high polymer formation. The optimum value might be different, we guess, depending on the species of iron compound. The ferrous ion inhibits the effect of ferric ion. The reason for this inhibition effect is considered below.

(1) It forms a redox couple as

$$Fe^{3+} + e \rightleftharpoons Fe^{2+} \qquad (7)$$

This buffers the Fe^{3+} concentration and prevents it from interacting with the radical ends.

(2) It interacts with radical ends more effectively than ferric ion.

The fact that only a small amount of ferrous ion can inhibit the high polymer formation suggests that the latter explanation is the correct one.

References

[1] S. Yoshizawa, I. Tari and M. Suhara, *J. Electrochem. Soc., Japan.* **40** (1972) 650.

[2] Z. Ogumi, I. Tari, Z. Takehara and S. Yoshizawa, *Bull. Chem. Soc., Japan.* **47** (1974) 1843.

[3] S. Yozhizawa, Z. Takehara, Z. Ogumi and C. Nagai, *J. Electrochem. Soc., Japan.* **40** (1972) 724.

[4] 'Polyacrylamide', American Cyanamid Co., New Products Bull No. 34, (1955) p. 2.

[5] E. A. S. Cavell and I. T. Gilson, *J. Polymer Sci. A1* 4 (1968) 14.

[6] E. Collinson, F. S. Dainton, B. Mile, T. Tazuke and D. R. Smith, *Nature* **198** (1963) 26.

[7] H. Narita, S. Okamoto and S. Machida, *J. Polymer Sci. A1* 8 (1970) 2725.