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The Electro-Initiated Polymerization of Acrylamide in an Aqueous Solution of Trifluoroacetic Acid and Potassium Trifluoroacetate*

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The electro-initiated polymerization of acrylamide was investigated in an aqueous solution of trifluoroacetic acid and potassium trifluoroacetate. An oligomer with a molecular weight of 4000—6000 was thus obtained. The initiating ability of Kolbe's intermediate radicals was recognized by an analysis of the fluorine contained in the polymerized products as the end group. Kolbe's intermediate radicals, R·, react with monomers, M, to form RM·, which takes the paths of polymerization and other reactions. The rate of reaction to form RM· is so fast that no Kolbe's dimer, C_2F_6, is obtained. Gas analysis clarified the ratio of $CF_3COO\cdot$ to $CF_3\cdot$, which reacted with the monomer. The comparison of the molecular weights as measured by the two different methods suggests that the coupling reaction of radical ends terminates the propagation reaction. The rate of oligomer production was independent of the current density.

Over a period of years, much interest has been shown in electrolytic methods of initiating a polymerization, the so-called electro-initiated polymerization. A few papers have been reported concerning utilizing Kolbe's electrolysis as a source of free radicals for initiating polymerization. Yoshizawa *et al.*[1] obtained a polymerized acrylamide with a molecular weight of 700—1500 by the electro-initiated polymerization of acrylamide in an aqueous solution of acetic acid and potassium acetate. In this paper, the polymerization of acrylamide in an aqueous solution of trifluoroacetic acid and potassium trifluoroacetate was examined. The use of trifluoroacetate instead of acetate allows us to make sure whether Kolbe's radicals initiate the polymerization or produce the initiating species from an analysis of fluorine, which is considered to be present as the end group. From the results of the current efficiency of the production of oligomer and the relation between the rate of electrode reaction and that of polymerization, a path of the production of the oligomer may be suggested. Furthermore, information about Kolbe's intermediate radicals may be obtained.

Experimental

An H-shaped glass fitted with a fine fritted glass filter as a diaphragm was used as the electrolysis cell. Smooth platinum plates (3×3 cm^2) were used as electrodes. One of them was coated on one side with silicon resin for use as a working electrode, and this one was electrolyzed anodically and cathodically, alternately, and finally cathodically in 0.5 M H_2SO_4 at 20 mA/cm^2 as pretreatment. After that, it was washed with distilled water and electrolytes and then used immediately. Trifluoroacetic acid (commercial G.R. grade) was used.

The content of iron compound in it, which is known to affect the polymerization of acrylamide,[2] was less than 0.003 %, and this is low enough to have no effect on this experiment. Four mol of this reagent and 2 mol of potassium hydroxide (comercial G.R. grade) were dissolved in distilled water to 1 liter. This solution will be designated as TFA+TFK 4M from now on. The monomer of acrylamide was recrystallized from benzene and dried under air. The acrylamide thus refined, which will be designated as AAM, was stored in a dark and cold place and used within a week. The anolyte was prepared by dissolving a given amount of AAM in 100 ml of TFA+TFK 4M. TFA+TFK 4M was used as a catholyte without any addition of AAM. Electrolysis was carried out in an ice-water bath. Nitrogen was bubbled from 30 min before the beginning of the electrolysis to its end. The potential-current curve was potentiostatically obtained by the use of a rotating disk electrode (the surface area was 1 cm^2) in order to prevent the working electrode from being covered by the gas evolved. When the anolyte was poured into 1 liter of methanol after electrolysis, a white precipitate of an insoluble polymerized product came out. This was filtered through a ♯4 glass filter, dried at 60—80 °C under reduced pressure, and weighed. The viscosities were determined in an Ubellohde viscometer mounted in a thermostated bath held at 30.00±0.05 °C. The intrinsic viscosities were determined by means of the usual graphic plots. The weight-average molecular weight was calculated by means of the equation: $[\eta]=3.73\times10^{-4}\times M_w^{0.66}$.[3] To examine the possibility of the hydrolysis of the amide group to acid, the pH titration of the aqueous solution of the product was carried out. The results showed no hydrolysis occurring.

Results

Fluorine Content in Polymerized Products. The polymerized product obtained by the electrolysis of TFA+TFK 4M 100 ml+AAM 20 g at the anodic current of 400 mA/9 cm^2 was dissolved into the distilled water; this solution was poured into methanol in order to free the occluded fluorine from the product. The fluorine content in the product purified by repeating this process five times was examined by elemental analysis. Its content was between 2 and 3 percent. On the other hand, the polymerized product obtained by the electrolysis of a solution of acetic acid and its potassium salt was dissolved into TFA+TFK 4M, and then the fluorine content of this sample was examined. However, only a trace of fluorine was detected. These results clearly indicate that fluorine was included in the product *via* electrode processes.

Potential-current Relationship. The steady-state potential-current relationship was potentiostatically obtained. In this experiment, a rotating disk electrode

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* Studies of the Electro-initiated Polymerization. Part 3.

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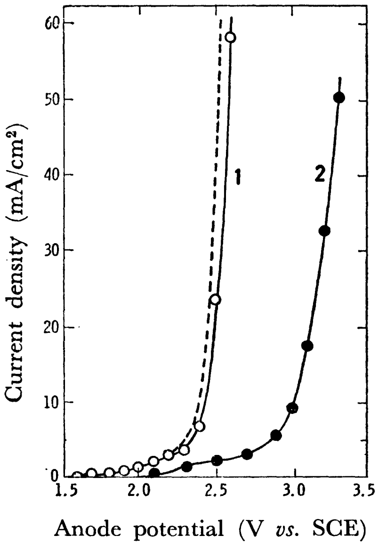

Fig. 1. Potentiostatic current-potential curves on the platinum rotating disk electrode in the solution of TFA+TFK 4M.
Rotating speed: 800 rpm.
-○-: without addition of AAM,
-●-: with addition of AAM 20 g
- - -: ohmic drop corrected

was used for the reason described above. The ohmic drop between the working and reference electrodes was not corrected in Fig. 1. This correction would cause Curve 2, measured in the solution containing AAM, to be almost the same as Curve 1, measured in the solution containing no AAM, as is shown by the dotted line. These curves show a current plateau which is characteristic of the Kolbe reaction.

Relationship between the Electrolysis Time and the Yield of an Oligomer. As is shown in Fig. 2, the yields of the oligomer increase linearly with the electrolysis time until four hours. This shows that the yield can be normalized independent of the electrolysis time, so that the induction period of oligomer production can be very short and the conditions can be kept constant during the electrolysis. Lying for eight hours under the same conditions except for a current passing through gave no polymerized product.

The Effect of the AAM Concentration on the Yields. The dependence of the yields on the concentration of AAM was examined at a current of 440 mA/9 cm^2.

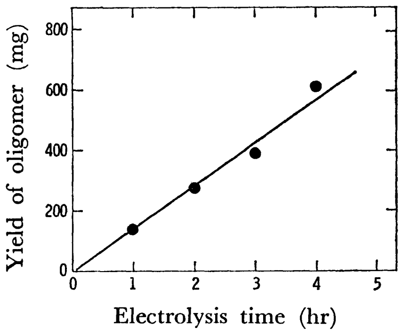

Fig. 2. Dependence of yields on electrolysis time in the solution of TFA+TFK 100 ml+AAM 20 g.
Current: 400 mA/9 cm^2

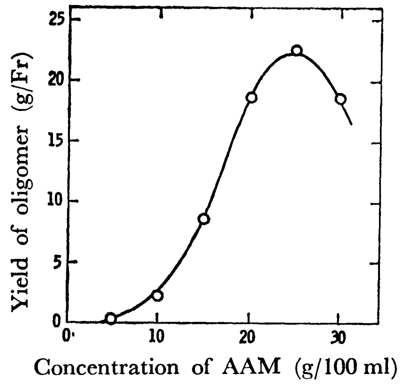

Fig. 3. Dependence of yields on the concentration of AAM in the solution of TFA+TFK 4M
Current: 400 mA/9 cm^2

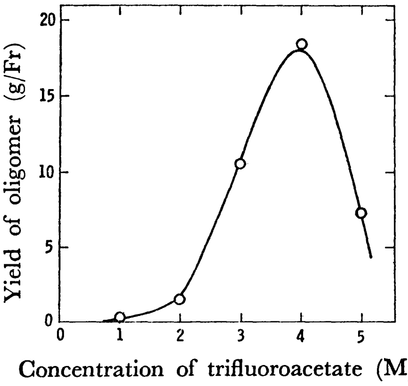

Fig. 4. Dependence of yields on the concentration of trifluoroacetate.
AAM 20 g per 100 ml of solution
Current: 400 mA/9 cm^2, $CF_3COOH:CF_3COOK=1:1$

The results are presented in Fig. 3.

The Effect of the Concentration of Trifluoroacetate on the Yields. The dependence of the yields on the concentration of trifluoroacetate was examined at the current of 400 mA/9 cm^2. In these experiments, the ratio of trifluoroacetic acid to potassium trifluoroacetate was kept constant at 1 : 1. The results shown in Fig. 4 show the maximum and the disagreement with the results obtained in the case of acetate, which shows a linear dependence.[1]

The Effect of the Current Density on the Yield. In order to investigate the effect of the current density on the yield, electrolysis was carried out at different current densities under the conditions of TFA+TFK 4M 100 ml+AAM 20 g. The results are shown in Fig. 5.

Analysis of Evolved Gases. A gas chromatographic technique was utilized to determine the gaseous products which were formed during electrolysis. The oxygen, tetrafluoromethane, hexafluoroethane, and carbon dioxide were analyzed by using the stationary phase of silica gel, Porapak K, and molecular-sieve 5A. The retention time was used for the qualitative analysis. The relative sensitivities, $N_2 : O_2 : CO_2 : CF_4 : C_2F_6 = 1.00 : 1.05 : 0.872 : 0.541 : 0.485$, were used for the quantitative analysis. Table 1 shows that both carbon dioxide and hexafluoroehane were evolved at high current efficiencies when no AAM was added, while,

Table 1. Current efficiency of gaseous products
Solution: TFA+TFK 4 M, Platinum electrode

AAM (g/100 ml)		0			20		
C. D. (mA/cm^2)		20	30	40	20	30	40
CE (%)	O_2	8.8	7.0	5.5	2.3	1.4	1.5
	CO_2	77.5	88.5	90.2	33.7	42.9	51.5
	C_2F_6	75.1	85.5	95.7	0	0	0

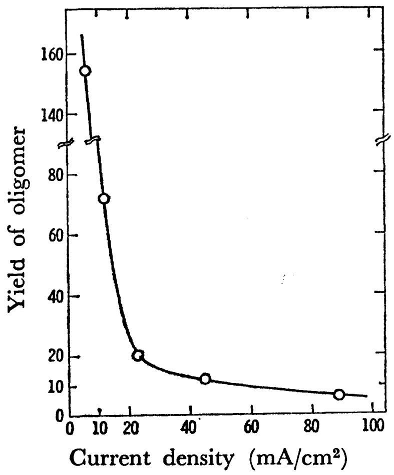

Fig. 5. Dependence of yields on current density in the solution TFA+TFK 4 M 100 ml+AAM 20 g.

on the other hand, the addition of AAM to anolyte caused a significant decrease in the current efficiency of the evolution of carbon dioxide and allowed the production of only a trace of hexafluoroethane. These results indicate that the intermediate radicals produced (R·) by electrolysis on the electrode do not further the normal coupling process of Kolbe's reaction, but react with the monomer (M) to form RM·. Whether CF_3-COO· or CF_3· of the intermediate radicals reacts with the monomer was determined by a comparison of the current efficiencies of the evolution of gases between the cases without and with the addition of AAM. The results are shown in Table 2.

Table 2. The ratio of radicals which react with monomer
TFA+TFK 4 mol/l, AAM 20 g/100 ml

C.D. (mA/cm^2)	Radical	
	CF_3COO%	CF_3%
20	44	33
30	45	43
40	37	52

Molecular Weight. The molecular weight was determined by means of two methods, one was based on viscosity measurements, and the other one, on a quantitative analysis of the end groups of the product by measuring the fluorine content. The results calculated by the two different measurements are listed in Table 3. The calculation in the latter method was carried out on the assumption that both ends of a product had a trifluoromethyl group. This table shows that the molecular weight does not depend on the current density.

Discussion

The facts that fluorine was detected in the polymerized products and that the molecular weights calculated from the fluorine contents were almost equal to those obtained by means of viscosity measurements indicate that Kolbe's electrochemical reaction produces the initiating species of polymerization and that termination is caused by a coupling reaction of radicals. It had previously been certified that the charge transfer of monomeric acrylamide on the anode does not take place under the experimental conditions adopted here. It has been reported that, in an experiment using acetic acid and potassium acetate, the oligomer with a molecular weight of about 1000 was produced.[1] On the other hand, in this experiment an oligomer with a molecular weight of 4000—6000 was obtained. This may be considered because of the difference in the possibilities of chain transfer to species in the electrolyte. The polymerized product was identified by means of IR spectroscopy as the oligomer of acrylamide. The electrochemical reaction of trifluoroacetate was extensively investigated in detail by Conway *et al.*[4] They proposed that trifluoroacetate furthers the process of Kolbe's reaction on the platiniumine electrode as follows, in the same way as in the case of acetate:

$$CF_3COO^- \longrightarrow CF_3COO\cdot + e \qquad (1)$$

Table 3. The effect of current density on the products
Solution: TFA+TFK 4 M, AAM: 20 g/100 ml

Current (mA/9 cm^2)	800	400	200	100	50	means
Yield (g/Fr)	5.70	12.06	20.44	72.38	154.2	—
Viscosity[η]	0.1125	0.1198	0.1165	0.115	0.1222	0.1172
M. wt.[a)]	5100	5700	5400	5300	5800	5460
F content	2.19	2.335	2.245	2.085	1.96	2.151
M. wt.[b)]	5210	4880	5080	5470	5820	5290

a) Calculated by using [η]. b) Calculated by using F content.

$$CF_3COO\cdot \longrightarrow CF_3\cdot + CO_2 \quad (2)$$

$$CF_3\cdot \longrightarrow 1/2C_2F_6 \quad (3)$$

or

$$CF_3COO\cdot \longrightarrow 1/2C_2F_6 + CO_2 \quad (4)$$

Many workers have proposed different mechanisms for Kolbe's reaction. We consider that the free radical mechanism is most reasonable. In this work, however, gas analysis has clearly shown that the addition of AAM to the anolyte resulted in preventing the evolution of Kolbe's coupling product, C_2F_6. This indicates that the intermediate species, $CF_3COO\cdot$ and/or $CF_3\cdot$, produced by the charge transfer of trifluoroacetate on the anode react with the monomeric acrylamide existing near the anode much faster than they react in the path of Kolbe's coupling process which produces C_2F_6 and forms RM·. The radicals, RM·, produces in this way react among themselves or with R· and monomers. The current efficiencies of the production of oligomers can be calculated from the yields and molecular weights of oligomers. As is shown in Fig. 6, a straight-line relation on logarithmic coordinates was obtained. This means that the rate of the production of the oligomer is independent of the rate of the electrode process and becomes a very slow and almost constant value compared with the latter. All this indicates that most of the RM· produced disappeared without furthering the polymerization. This result can be explained by considering in the same way as in the "cage effect theory," which is extensively used on the discussion of polymer chemistry. The RM· produced exists on the electrode surface or in the vicinity of the electrode, where the concentration of radicals is so high that the coupling reaction occurs easily. This is why the initiating efficiency of R· becomes very low. Thus, the polymerization may proceed as follows.

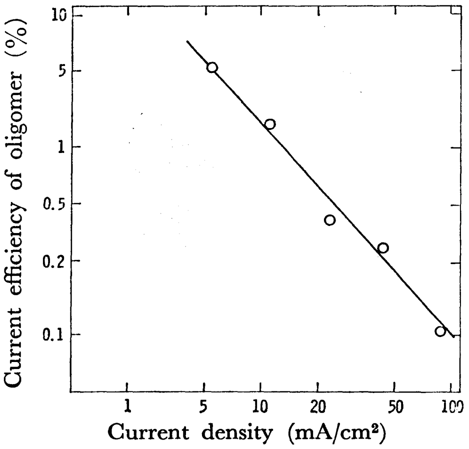

Fig. 6. Dependence of current efficiencies for polymerization on current density.

$$R\cdot + M \xrightarrow{\text{fast}} RM\cdot \quad (5)$$

$$2RM\cdot \longrightarrow RMMR \quad (6)$$

$$RM\cdot + R\cdot \longrightarrow RMR \quad (7)$$

$$RM\cdot + M \xrightarrow{\text{slow}} RMM\cdot \dashrightarrow \text{oligomer} \quad (8)$$

R· is $CF_3COO\cdot$ and/or $CF_3\cdot$, and the ratio of $CF_3COO\cdot$ to $CF_3\cdot$ can be calculated from the gas analysis as is shown in Table 2. The production of the high polymer of acrylamide caused by the addition of iron compounds to the solution adopted here has already been reported.[2] With reference to this evidence, intermediate radicals, RM·, and Kolbe's radicals can not exist as literally "free" radicals, because, if so, they would react to the high polymer, instead, they interact with the electrode. The region where polymerization takes place will be discussed in detail in following papers.

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