The Initiation Reaction of Electro-initiated Polymerization of Acrylamide in the Kolbe Electrolysis System*

Zempachi Ogumi, Isao Tari**, Zenichiro Takehara, and Shiro Yoshizawa
Department of Industrial Chemistry, Faculty of Engineering, Kyoto University, Yoshida, Sakyo-ku, Kyoto 606

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The mechanism of electro-initiated polymerization of acrylamide in the Kolbe electrolysis system was investigated in detail and the reaction path of the intermediate radicals was clarified by product analysis and a measurement of the consumption rate of the monomer. The Kolbe intermediate radical, $CF_3\cdot$, reacts first preferentially with the monomer. Next, the radical thus formed reacts with other species to produce $CF_3CH_2CH_2CONH_2$, $CF_3CH_2CH(CF_3COO)CONH_2$ and $CF_3CH_2CH(CONH_2)CH(CF_3CH_2)CONH_2$. The first reaction is fast, but the reaction of $CF_3COO\cdot$ with the monomer appears to be unreasonable. These reactions proceed on the electrode surface and in the layers below the diffusion layer, *i.e.*, in layers of the same order as the depth of unevenness on the platinized platinum electrode.

A few papers have been published concerning the utilization of Kolbe electrolysis as a source of free radicals for initiating polymerization and papers explaining the process of initiating polymerization are very few. The authors have also investigated the production of an oligomer[1,2] and a high polymer[3,4] of acrylamide utilizing the Kolbe reaction in a system of acetate and trifluoroacetate solutions. In a preceding paper[2], they have proposed the following reaction path as the most probable process of initiating polymerization of acrylamide in an aqueous solution of trifluoroacetic acid and potassium trifluoroacetate.

$$R\cdot + M \longrightarrow RM\cdot \tag{1}$$

$$RM\cdot + X \longrightarrow RMX \tag{2}$$

$$2RM\cdot \longrightarrow RMMR \tag{3}$$

$$RM\cdot + R\cdot \longrightarrow RMR \tag{4}$$

$$RM\cdot + M \longrightarrow RMM\cdot \overset{M}{\dashrightarrow} \text{oligomer} \tag{5}$$

where $R\cdot$ represents Kolbe intermediate radical, $CF_3COO\cdot$ and/or $CF_3\cdot$. Reaction (1) was assumed to be very fast. If this assumption is correct, one mol of the monomer will be consumed for every Farady of electricity in addition to that required for oligomer formation. The low current efficiency of oligomer production was ascribed to the fact that reaction (5), which leads to the formation of the oligomer, competes with reactions (2)—(4) which are considered to be fast. Therefore, it is expected that the products with low molecular weight represented by RMX, RMR and RMMR are formed during the oligomer formation. These compounds are examined in this paper in order to verify the above reaction path which was proposed by the authors. Also the kind of radicals taking part in initiating reactions and the manner by which the reactions of the intermediate radicals proceeds are discussed. Furthermore, the site of the polymerization reaction is examined. This is very important from the standpoint of improving of the current efficiency of the oligomer formation and of reaction system for the production of high polymers. This problem may concern the state of the Kolbe intermediate radicals.[5] The experiments were conducted using a rotating cylindrical electrode and platinized platinum electrodes.

Experimental

The same equipment as that used in previous work was used for the electrolysis[2]. A cylindrical platinum electrode (1.3 cm in diameter, 10 cm^2 in area) was used in the rotating electrode experiment. Platinized platinum electrodes having various degrees of roughness were used. Besides a TFA and TFK 4M solution***, a 2M acetate solution was used, which includes 1 mol acetic acid and 1 mol potassium acetate in 1 liter. The measurement of the acrylamide content in the solution was carried out following the bromate-bromide method, which was modified so that the addition of bromide was performed in a nitrogen atmosphere and in the dark to eliminate the effect of oxygen.

Results

Low Molecular Weight Products. As shown in a preceding paper[2], neither normal Kolbe coupling products nor other gaseous products are formed in a system of electro-initiated polymerization in spite of the low current efficiency of oligomer formation. This fact and the above reaction path imply the existence of products such as RMX, RMR and RMMR in the electrolyte. On the basis of this prediction, the electrolyte was analysed after electrolysis. After electrolysis of a TFA and TFK 4 M solution containing 20 g/100 ml of acrylamide at 400 mA on a platinum electrode (3×3 cm^2), the electrolyte was analyzed using the gel filtration chromatographic technique. Peak b of curve A in Fig. 1 indicates the existence of products with low molecular weight. Peaks a, c and d correspond to products with high molecular weight, monomeric acrylamide and trifluoroacetate, respectively. Curve B corresponds to an aqueous solution of the acrylamide monomer. The following low molecular weight products were detected. $CF_3CH_2CH(CF_3COO)CONH_2$, $CF_3CH_2CH_2CONH_2$ and $CF_3CH_2CH(CONH_2)CH(CF_3CH_2)CONH_2$. These were isolated using the gas-chromatographic technique and identified using mass and infrared spectrophotometric techniques. The gas chromatogram also exhibited traces of products with

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** Present address: Department of Synthetic Chemistry, Faculty of Engineering, Okayama University, Tsushima, Okayama 700.

*** This is an aqueous solution of 2 mol trifluoroacetic acid and 2 mol potassium trifluoroacetate in 1 liter.

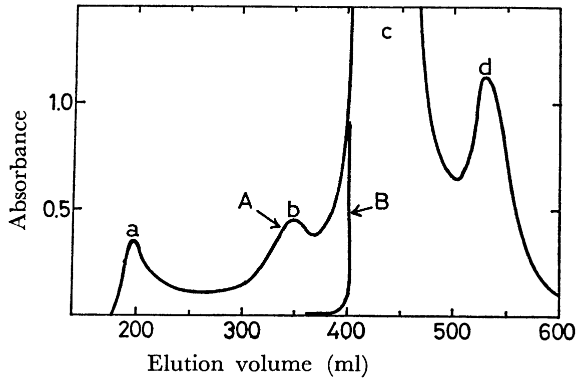

Fig. 1. Gel filtration chromatograms.
Column: Sephadex G-10, 4 cmϕ, 40 cm hight, V_r = 195 ml
A: Electrolyte after electrolysis, B: an aqueous solution of monomeric acrylamide.

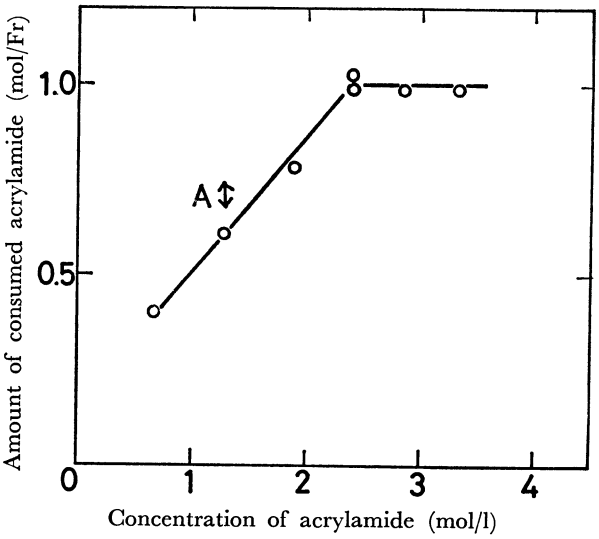

Fig. 2. Relationship between the amount of consumed monomer and monomer concentration.
Electrolyte: TFA+TFK 4 M, Electrode: Smooth platinum (3×3 cm^2), Current: 400 mA.

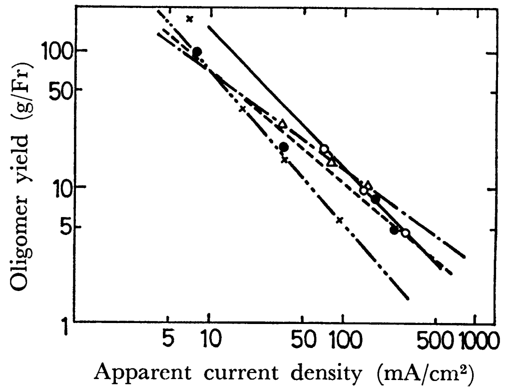

Fig. 3. The effect of surface roughness on the oligomer yield.
Electrolyte: 2 M acetate solution 100 ml+acrylamide 20 g, Electrode: Platinized platinum (1.5×3×2 cm^2)
r; ○: 1300, △: 175, ●: 60, ×: 45.

molecular weights higher than the above three compounds.

The Amount of Consumed Acrylamide. In order to confirm the participation of the intermediate radical R· in the Kolbe reaction with the monomer forming RM·, the amount of consumed monomeric acrylamide was measured based on the modified bromate-bromide method. The amount of the monomer consumed and of the polymer produced were measured. From these measurements, the amount of monomer consumed for reactions other than oligomer formation was calculated. This value per Faraday is illustrated in Fig. 2. The higher the concentration of acrylamide up to 2.4 M, the more acrylamide is consumed. At concentrations above 2.4 M, about one mol of monomer is consumed per Faraday. At concentrations lower than 2.4 M, the Kolbe dimer, ethane, is formed. In this case, R· produced by charge transfer on the electrode reacts to form the oligomer, ethane and other products. The amount of R· consumed other than that for oligomer and ethane formation were calculated in order to obtain the amount of consumed acrylamide per mol of R· which resulted in products in the electrolyte with lower molecular weight. This amount is illustrated by A in Fig. 2.

The Effect of Electrode Surface Unevenness. The effect of electrode surface roughness was examined in order to obtain information about the area where the oligomer formation occurred. Platinum electrodes (1×2 cm^2), coated on one side with silicon resin, were plated with platinum black in a solution of chloroplatinic acid so as to produce a surface of different roughness. The real surface area (A_1) was calculated from the amount of adsorbed hydrogen measured based on the charging curve method in 0.5 M H_2SO_4. The ratio of A_1 to the apparent surface area is designated the roughness factor (r). The relationship between the oligomer yield and the apparent current density on electrodes with different roughness factors was examined. As shown in Fig. 3, the yield increases with roughness factor in the region of relatively high current densities. The effect of roughness, however, is not great. The apparent current density at a given potential increases with r in a 2 M acetate solution without acrylamide but this increase is not great in comparison with the increase of r, and is less than in a solution containing acrylamide. This fact implies that only a part of the surface measured by the hydrogen adsorption method is effective for charge transfer on the electrode.

The Effect of Electrode Rotation. The relation between the area where the polymerization occurs and the thickness of the diffusion layer and the effect of the mass transfer rate to the electrode on oligomer formation were examined using the rotating cylindrical electrode in a 2 M acetate solution. As shown in Fig. 4, below 1500 rpm and above 2000 rpm only a small effect is observed, but there exists a marked increase between 1500 and 2000 rpm. This jump may be ascribed to a change from laminar to turbulent flow.

The Effects of Monomer Concentration and Current Density. The effect of current density was examined at different monomer concentrations in a 2 M acetate solution

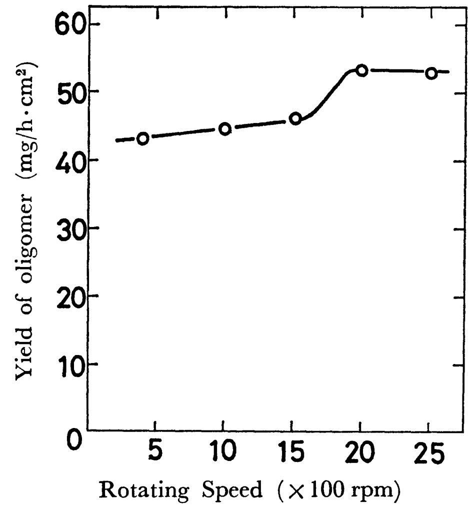

Fig. 4. Dependence of oligomer yield on rotating speed. Electrolyte: 2 M acetate solution 100 ml+acrylamide 20 g, Electrode: Cylinder electrode (10 cm²), Current: 200 mA.

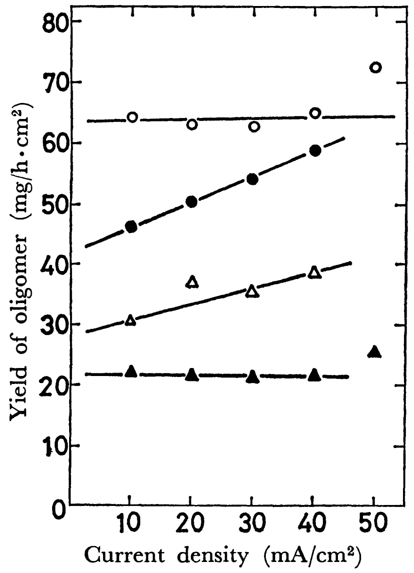

Fig. 5. Dependence of oligomer yield on current density and monomer concentration. Electrode: Cylinder electrode (10 cm²), Rotating speed: 1450 rpm, Electrolyte: 2 M acetate solution 100 ml+acrylamide, Acrylamide; ▲: 10 g, △: 15 g, ●: 20 g, ○: 25 g.

using a cylindrical electrode. Figure 5 shows that at the acrylamide concentrations of 25 g/100 ml and 10 g/100 ml, the yield does not depend on the current density, in agreement with the case of the TFA and TFK 4 M solution[2]. As concentrations of 15 g/100 ml and 20 g/100 ml, however, the yield increases linearly with current density but does not exceed the value at 25 g/100 ml.

Discussion

Three compounds, $CF_3CH_2CH_2CONH_2$, $CF_3CH_2CH(CF_3COO)CONH_2$ and $CF_3CH_2CH(CONH_2)CH(CF_3CH_2)CONH_2$ were detected as products with low molecular weight, RMX, RMR and RMMR. These products indicate the occurrence of reactions (1)—(4). It was observed that 1 mol of the monomer was consumed per Faraday in addition to the consumption required for oligomer formation at high monomer concentrations. This fact supports the assumption that reaction (1) is so fast that almost all of the Kolbe intermediate radicals react with the monomer. In this consideration the current efficiency of the acetate discharge can be considered to be 100%. There exist two kinds of radical species, $CF_3\cdot$ and $CF_3COO\cdot$, as Kolbe intermediates. The fact that $CF_3COOCH_2CH_2CONH_2$ and $CF_3COOCH_2CH(CONH_2)CH(CF_3COOCH_2)CONH_2$ were not detected, but that $CF_3CH_2CH_2CONH_2$ and $CF_3CH_2CH(CONH_2)CH(CF_3CH_2)CONH_2$ were produced clearly shows that $CH_3\cdot$ reacts first with the monomer and the RM· thus formed produces farther reactions. This indicates that the reaction of the radical with the monomer is not as fast as the decarboxylation reaction of $CF_3COO\cdot$. Radical RM· is more active than the monomer and it can react fast with $CF_3COO\cdot$ or RM·, or it can extract hydrogen from other species. From these results we can deduce the reaction path of intermediate radicals as shown in Fig. 6. We have considered that the region where polymerization occurs is just in the vicinity of electrode, but it is still a question as to how far from the electrode this region extends. Some investigators have considered that it occurs on the electrode surface.[6]

The correlation between the height of the rough surface and the thickness of the reaction region in the experiment with the platinized platinum electrode is schematically shown in Fig. 7. In case A, where the thickness is small and the reaction layer is parallel to

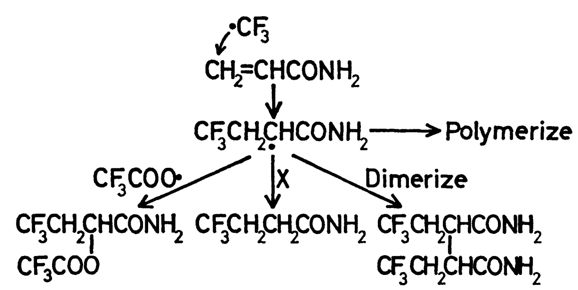

Fig. 6. Reaction path of intermediates.

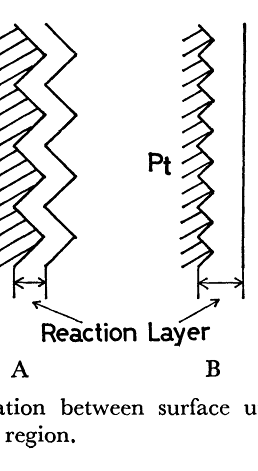

Fig. 7. The relation between surface unevenness and polymerization region.

the uneven surface of the electrode, the volume of the reaction region increases proportionally with an increase of the electrode surface on which the electrode reactions proceed. Thus the radical concentration is this region changes with the surface roughness at the same apparent current density. This causes an increase in the current efficiency of oligomer formation with an increase in surface roughness, because the current efficient of oligomer formation decreases with an increase in current density. In case B, where the reaction layer is thick enough so that the unevenness of the surface does not affect the deepest surface of the layer, the volume of the reaction layer does not increase even if the surface roughness increases. Accordingly, no change in oligomer yield will be caused by a change in the surface roughness. As is shown in Fig. 3, only a slight effect of surface roughness was observed at high current densities, while none was observed at low current densities. This indicates a state between A and B in Fig. 7, *i.e.*, the reaction layer is very thin and that of the same order of thickness as the unevenness of the platinized platinum electrode. Furthermore, this consideration is supported by the results using the rotating cylindrical electrode in which only a slight effect of the rotational speed was observed above 2000 rpm and below 1500 rpm. Namely, the reaction layer is very thin and does not extend into the diffusion layer which is influenced by the electrode rotational speed.

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