An Application of Current-pulse Electrolysis to an Electro-initiated Polymerization of Acrylamide*

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(Received August 13, 1975)

A unidirectional current pulse was applied to the electro-initiated polymerization of acrylamide in a Kolbe system, and the behavior of intermediate was investigated. The formation rate of the oligomer during the current-on pulse was not affected by the pulse length, and it was almost the same as that under steady conditions. An oligomer was also formed during current-off pulse. The formation rate of the oligomer during the current-off pulse was calculated on the base of the mechanism presented in previous papers; the calculated results agreed well with the experimental results. The half-life time of intermediate radical, [RM·], was about 10 ms.

In previous papers[1,2] it was clarified that the concentration of an intermediate at an electrode interface had an important influence on the current efficiency of the oligomer formation and that the current density was more important than the electrode potential. Current-pulse electrolysis was applied to an electro-initiated polymerization of acrylamide in the system of Kolbe electrolysis based on the prediction that the intermediates had a finite lifetime.

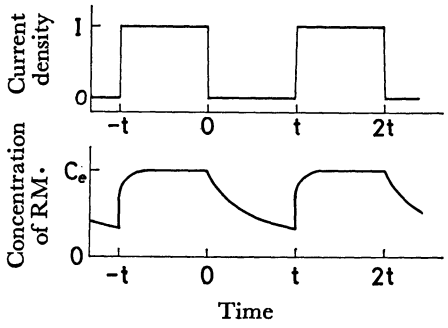

Fig. 1. The concentration change under unidirectional pulse conditions.

The concentration of an intermediate will be changed by electrolysis under unidirectional pulse conditions (Fig. 1). The concentration of the intermediate increases rapidly at the current-on pulse up to a steady value, C_e, depending on the current density and decreases at the current-off pulse depending on the rate of the following chemical reaction. If the pulse electrolysis is applied to the system in which a rise-up time is negligibly short compared with the length of the current-on pulse, the electrode reaction during the current-on pulse may be considered to be the same as that under steady conditions. In this case the formation rate of a product during the current-off pulse can be calculated. If the reaction mechanism is known, the concentration change of intermediate may be calculated using the formation rate obtained above. In the present paper, a unidirectional current pulse was applied to an electro-initiated polymerization of acrylamide in the Kolbe system.

* Studies of Electro-Initiated Polymerization. Part V.

Experimental

An H-shaped glass cell fitted with an anion-exchange membrane as a diaphragm was used as the electrolysis cell. A smooth platinum plate (3×1.5 cm^2) and a smooth platinum cylinder electrode (1.3 cm diameter, 3 cm height, 10 cm^2 area) were used as working electrodes. As a cathode, a smooth platinum electrode (3×3 cm^2) was used. The working electrodes were pretreated prior to use, as has been described before.[1] A solution prepared by dissolving 1 mol of acetic acid and 1 mol of potassium acetate in distilled water to 1 liter was used and will be designated as the 2 M acetate solution from now on. The electrolyte was prepared by dissolving a given amount of acrylamide in this solution. The acrylamide was refined by recrystallization. A current interrupter (Hokuto Denko CI253) was used as the current source. The details of the experimental procedure were described in a previous paper.[1]

The amount of the polymerized product, an oligomer, was measured as follows. 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 yield of the oligomer thus produced was also calculated as follows. The yield during electrolysis time, T_t, is Y_t. The real time of current flowing, T_{on}, is the sum of the current-on time. The yield per unit of time by electrolysis under steady conditions at the current density equal to it in the current-pulse electrolysis is Y_s. It is assumed that the rate of oligomer formation during the current-on pulse under pulse conditions is the same as under steady conditions. The yield for the total current in time Y_{on} is calculated from Y_s and T_{on}. The yield, Y_{off}, for the total current-off time, T_{off}, can also be calculated by means of Y_{on} and Y_t:

$$Y_{off} = Y_t - Y_{on} \quad (1)$$

$$Y_{on} = Y_s \times T_{on} \quad (2)$$

The yield per current-off pulse, y, is calculated as follows:

$$y = Y_{off}/(T_t/t_t) \quad (3)$$

t_t is the pulse length (on time+off time). The quantity of electricity passed through was measured by means of a hydrogen/oxygen coulometer and a transistorized coulometer manufactured by Hokuto Denko Co., Ltd.

Results and Discussion

Kolbe Reaction under Galvanostatic Pulse Conditions. Constant current pulse electrolysis was first of all applied

Table 1. The current efficiency of carbon dioxide in the case of current-pulse electrolysis at 200 mA/9 cm^2 in a 2 M acetate solution on a smooth platimum plate electrode
Current-on time/current-off time=1/1.

Pulse length (ms)		2	10	20	40
Current efficiency of CO_2 (%)	91.2[a]	89.7	90.8	91.0	91.2

a) Steady-current electrolysis.

to the Kolbe electrochemical reaction, and the effect of current pulse on the charge-transfer reaction in the system of the electro-initiated polymerization of acrylamide was investigated. The current efficiency of carbon dioxide was examined on a smooth platinum plate electrode in a 2 M acetate solution. The carbon dioxide was measured by using 0.1 M $Ba(OH)_2$. The current efficiency does not depend on the pulse length and is almost the same as that in steady-current electrolysis (Table 1). Wood[3] has reported that acetate is completely oxidized to carbon dioxide and water in an acidic aqueous solution on a platinum electrode at a potential less positive than that where the electrode surface is completely covered with oxide. Fleischmann *et al.*[4] have investigated the Kolbe electrolysis under pulse conditions where they have used the potential pulse between E_h (2.2 V *vs.* NHE) and E_l (−0.15 V *vs.* NHE). Under these conditions, the surface oxide formed on the electrode at E_h is reduced at E_l. The state of the electrode surface just after setting the potential at E_h is considered to be different from the state which is normally attained as the Kolbe reaction proceeds. Accordingly, the Kolbe reaction does not proceed at the beginning of the setting at E_h. Complete oxidation, as in Eq. 4, and surface-oxide formation proceed simultaneously until the surface state necessary for the Kolbe reaction is attained:

$$CH_3COO^- + 2H_2O \longrightarrow 2CO_2 + 7H^+ + 8e \quad (4)$$

Moreover, these reactions result in lowering the current efficiency of the Kolbe reaction and in decreasing the formation of carbon dioxide.** Hickling and Wilkins[5] and Wilson and Lippincott[6] have investigated the application of the alternating current pulse to the Brown-Walker and Kolbe reactions. They examined the effect of the pulse length on the current efficiency of the dimerized product and ascertained that the current efficiency was independent of the pulse length and was equal to that obtained by steady-state electrolysis when the reverse (cathodic) current was zero, that is, when the pulse current was applied instead of the alternating current. On the other hand, when the alternating pulse current with a small reverse current was applied, the current efficiency decreased and depended on the coulombic amount of reverse electricity. When the reverse electricity exceeded a critical value, the current efficiency again became high. However, in the present system, the current efficiency of carbon dioxide did not depend on the pulse length and almost coincided with the value obtained by steady-current electrolysis (Table 1). This fact indicates that the formation of surface oxide and the complete oxidation described by Eq. 4 do not occur, differing from the result of the potential pulse electrolysis of Fleischmann *et al.*[4] and also from results reported by Hickling and Wilkins,[5] and Wilson and Lippincott.[6] It is a possible to conclude that, under the present pulse conditions, a usual Kolbe reaction proceeds during the current-on pulse.

An Oligomer Production and the Effects of Some Electrolysis Conditions. The above investigation made it clear that, by electrolysis using a unidirectional pulse current, carbon dioxide was produced at the same current efficiency as with steady-current electrolysis. The change in the surface state under the pulse conditions was examined by measuring the electrode potential. The electrode potential is considered to change with the change in the electrode surface state and not to attain the steady-state value until the electrode surface reaches the steady state. The measurement was carried out by using a cathode-ray oscilloscope. The measuring circuit is shown diagramatically in Fig. 2. The potential was referred to SCE. The potential change is shown representatively in Fig. 3. The time, τ, which was required for attaining the steady potential and the potential difference, ΔE, were measured and tabulated in Table 2 in the system with and without the addition of acrylamide. The potential change, ΔE, increased with the pulse length; the time, τ, also increased in the

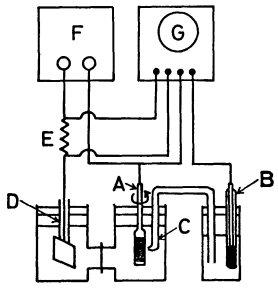

Fig. 2. Experimental equipment.
A: Working electrode. B: Reference electrode (SCE).
C: Luggin capillary. D: Counter electrode.
E: Standard resistor. F: Current pulse generator.
G: Cathode ray oscilloscope.

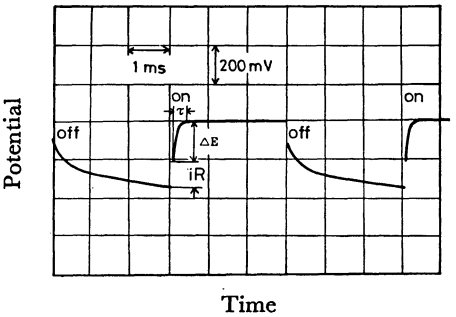

Fig. 3. Typical potential change in current pulse electrolysis at 200 mA/10 cm^2 on a rotating cylinder electrode (2000 rpm). *iR* means an ohmic drop.

** In Reaction 4, only 1 mol of CO_2 is produced by the electrolysis of 4 Faraday, but in the Kolbe reaction ($2CH_3COO^- \rightarrow CH_3{-}CH_3 + 2CO_2 + 2e$), 4 mol of CO_2 are produced by this electrolysis.

Table 2. Dependence of the rise-up time, τ, on the pulse length on a rotating cylinder electrode (2000 rpm) at 250 mA/10 cm² 2 M acetate solution, 100 ml.

Pulse length (ms)	Without acrylamide		With acrylamide (20 g)	
	ΔE (mV)	τ (ms)	ΔE (mV)	τ (ms)
0.4	160	0.08		
1	200	0.10	280	0.08
2	250	0.12	340	0.09
6	320	0.14	400	0.10
10	355	0.16	410	0.11
14	400	0.18	420	0.12
20	440	0.20	480	0.14
30	480	0.23	510	0.15
40	530	0.25	580	0.15
60	580	0.25	590	0.16
100	610	0.26		
	760	0.24		

same manner. The ratio of τ to the pulse length is easily calculated; its value is small and decreases as the pulse length becomes longer. The ratio is especially very small in the system with acrylamide added. Furthermore, the steady potential after the rise-up was independent of the pulse length and was 2.4 and 3.2 V in the systems with and without acrylamide respectively. As has been described above, the surface state required for the occurrence of the Kolbe reaction might be destroyed during the current-off pulse. This would lower the current efficiency of the Kolbe reaction. However, the potential drop during the current-off time, which is equal to ΔE, is so small, and the steady potential attained during the current-on time is so high (2.4 or 3.2 V), that the destruction of the surface state does not occur (Table 2). This consideration might allow us to conclude that the Kolbe reaction proceeds during the rise-up time, τ, except for a small current for the charging of the double layer. In addition to this, it has already been established that, in the electro-initiated polymerization of acrylamide in the Kolbe system, the formation rate of the polymerized product hardly depended on the current density at the potentials large enough for the Kolbe reaction.[1,2] Accordingly, it can reasonably be presumed that the formation rate of the oligomer during the rise-up time is almost the same as in the steady state. In order to confirm this assumption, the dependence of the oligomer-formation rate on the current-on pulse length was examined at a constant current-off pulse length. The measurement was carried out in a 2 M acetate solution containing 20 g of acrylamide by utilizing a rotating cylinder electrode (1450 rpm) at 200 mA/cm². The length of the current-on pulse had little effect on the yield (Fig. 4). This fact shows that the oligomer production during the rise-up time proceeds almost at the same rate as the steady state. From now on the ratio of the current-on time to the current-off time will be set at 1 unless specifically stated.

An effect of the rotation rate was next examined on a cylinder electrode and compared with the results

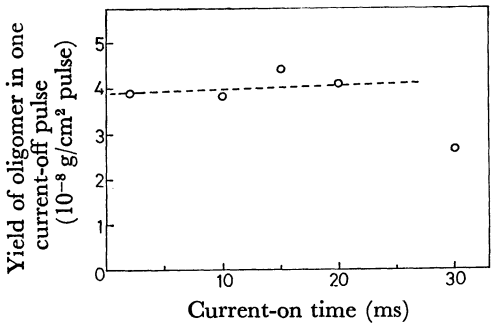

Fig. 4. The effect of current-on pulse length on the oligomer yield at 200 mA/10 cm² on a rotating cylinder electrode (1450 rpm) in the solution 2 M acetate solution 100 ml+acrylamide 20 g. Current-off pulse= 10 ms.

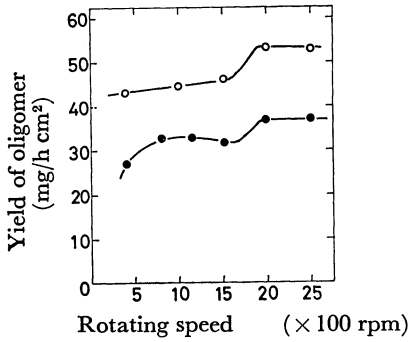

Fig. 5. Dependence of the yield on rotation rate on a rotating cylinder electrode at 200 mA/10 cm² in the solution 2 M acetate solution 100 ml+acrylamide 20 g. a —●—: With pulse current of 20 ms, b —○—: with steady current.

obtained by steady-current electrolysis (Fig. 5). Curve a in this figure represents the yield per hour, including the current-off time under pulse conditions of a 20 ms pulse length at 200 mA/10 cm². Curve b represents the yield under steady conditions at the same current density. On both curves an abrupt change is observed between 1500 and 2000 rpm; above and below this range, the change is not remarkable. The yield during the current-off pulse can be calculated from Fig. 5 (Fig. 6). The rotation rate has no effect on the yield except for a point at 400 rpm, and no abrupt change is observed in

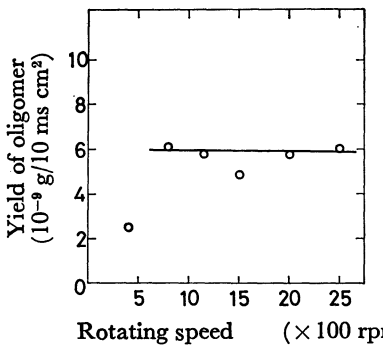

Fig. 6. The effect of rotation rate on the yield during current-off pulse in the solution 2 M acetate solution 100 ml+acrylamide 20 g on a rotating cylinder electrode at 200 mA/10 cm².

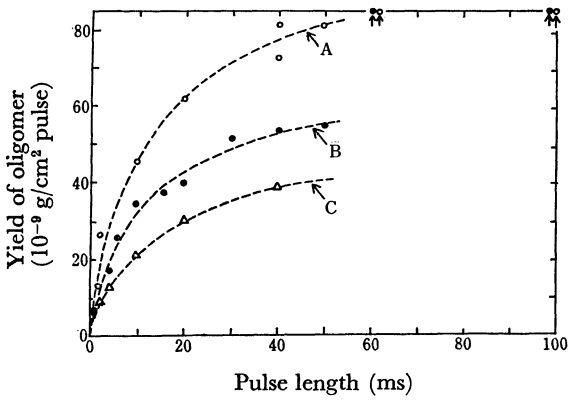

Fig. 7. Relationship between pulse length and the oligomer yield during one current-off pulse on a rotating cylinder electrode in the solution 2 M acetate solution 100 ml+acrylamide 20 g.
A: 250 mA/10 cm², 2000 rpm.
B: 200 mA/10 cm², 2000 rpm.
C: 200 mA/10 cm², 400 rpm.

Fig. 6. Thus, the formation of the oligomer during the current-off pulse is not remarkably affected by the mass-transfer rate to the electrode.

The relationship between the current-pulse length and the yield of the oligomer during the current-off pulse was also examined (Fig. 7). The yield increased with the pulse length in the region of short pulse lengths. However, the yield suddenly reached a high value at pulse lengths longer than 60 ms. In this case, a high polymer was observed besides an oligomer. The high polymer is considered to be formed through a different process, which is still ambiguous, from that of oligomer formation.

Behavior of Intermediate Radicals and a Theoretical Treatment of It. In the Kolbe system two intermediate radicals, $CH_3\cdot$ and $CH_3COO\cdot$, are considered to exist on or near an electrode surface. In spite of vigorous investigations by many workers, however these intermediates have never been directly detected. The electrode surface is covered with oxide and intermediates. Bruno and Dobois[7] reported that a hydrophobic polymer film like polyethylene covered the surface, and authors also found that, in an electro-initiated polymerization of acrylamide in an aqueous solution of trifluoroacetate, an electrode surface was covered with a hydrophobic film which was not easily removed.[9] Kolbe intermediates are considered to exist at the interface under interaction with the above species adsorbed on the surface. As has been reported in the previous papers,[1,2] the polymerized product in the Kolbe system is formed by the reactions of intermediates. A low current efficiency of polymerization was ascribed to that polymerization was initiated on or just near the electrode surface, where the radical concentration was high. The fact that an oligomer was formed during current-off pulse explicitly shows that some intermediate species which have the ability to initiate the polymerization have a finite lifetime. Taking this into consideration the mechanism of oligomer formation under pulse conditions was examined. The reaction proceeds as follows:[1]

$$CH_3COO^- \longrightarrow R\cdot + e \quad (5)$$

R· represents two Kolbe intermediate radicals, $CH_3\cdot$ and $CH_3COO\cdot$.

$$R\cdot + R\cdot \xrightarrow{k_1} R\text{–}R \quad (6)$$

$$R\cdot + M \xrightarrow{k_2} RM\cdot \quad (7)$$

$$R\cdot + RM\cdot \xrightarrow{k_3} RMR \quad (8)$$

M represents an acrylamide monomer. The RM· thus formed reacts further into polymerized products as follows:***

$$RM\cdot + M \xrightarrow{k_4} RMM\cdot \quad (9)$$

$$RMM\cdot + nM \xrightarrow{k_p} RM_{n+2}\cdot \dashrightarrow \text{Oligomer} \quad (10)$$

$$RM\cdot + RM\cdot \xrightarrow{k_5} RMMR \quad (11)$$

$$RM\cdot + B \xrightarrow{k_6} RMX + B' \quad (12)$$

B represents some impurity *etc.*, RMX includes a stable radical which can not initiate polymerization. B′ can not initiate polymerization, either. The formation rate of R·, v, is expressed as follows:

$$v = g\cdot I/F \quad (13)$$

I and g represent the current density and the current efficiency respectively. F is the Faraday constant. The change in the R· concentration is:

$$d[R\cdot]/dt = v - 2k_1[R\cdot]^2 - k_2[R\cdot][M] - k_3[RM\cdot][R\cdot] \quad (14)$$

The change in the RM· concentration is:

$$d[RM\cdot]/dt = k_2[R\cdot][M] - k_3[RM\cdot][R\cdot] - k_4[RM\cdot][M] - 2k_5[RM\cdot]^2 - k_6[RM\cdot][B] \quad (15)$$

In the above expressions, it was assumed that mass-transfer did not cause any probelms in any reaction. The rate of oligomer formation is:

$$v_p = k_4[RM\cdot][M] \quad (16)$$

It is considered for the sake of simplification, that all the R· formed in Eq. 5 proceeds Reaction 7 into RM·, because it was clarified in a previous paper[2] that no dimerized Kolbe product, R–R, was produced in this system, and the contributions of Reactions 8 and 12 are considered to be small when acrylamide is used at concentrations higher than 2.5 mol/l (see another previous paper).[2] In this experiment, the concentration of acrylamide was about 2.8 mol/l. Therefore, $k_3[RM\cdot]\times[R\cdot]$ and $k_6[RM\cdot][B]$ in Eqs. 14 and 15 can be neglected.

Then,

$$k_2[R\cdot][M] = v \quad (17)$$

By replacing [RM·] and [M] with C and m respectively, Eq. 15 is written as follows:

*** As lower-molecular-weight products are formed in our system, RMR, RMMR, and RMX were mainly detected.[2] The other reactions besides Eqs. 8, 11, and 12 (*e.g.*, $RM\cdot + RM_2\cdot \rightarrow RM_3R$) were thus not considered as terminating reactions.

$$dC/dt = v - (k_4'C + 2K_5C^2) \quad (18)$$

Here, $k'_4 = k_4 m$. The concentration at the interface should be taken as m. Under steady conditions at constant-current electrolysis,

$$dC/dt = 0. \quad (19)$$

Then C_e, the steady value of C, is

$$C_e = (-k_4' + \sqrt{k_4'^2 + 8k_5 v})/(4k_5). \quad (20)$$

At the current-off time under pulse conditions, $v=0$. Then, from Eq. 18 under the condition that $C=C_e$ at $t=0$,

$$C = k_4'/(2k_5 \times [\exp\{k_4'(K+t)\} - 1]). \quad (21)$$

$$K = \ln\{k_4'/(2k_5C_e) + 1\}/k_4' \quad (22)$$

Using the average molecular weight, M_0, the yield of the oligomer is:

$$y = M_0 \int_0^t v_p dt. \quad (23)$$

The yield at the current-off time is calculated from Eq. 23 using Eqs. 16 and 21 as follows:

$$y = M_0 \frac{k_4'}{2k_5} \ln \frac{1 - \exp\{-k_4'(K+t)\}}{1 - \exp(-k_4'K)} \quad (24)$$

When the pulse is very long,

$$y|_{t\to\infty} = M_0 \frac{k_4'}{2k_5} \ln\left(1 + \frac{2k_5C_e}{k_4'}\right). \quad (25)$$

On the other hand,

$$\left.\frac{dy}{dt}\right|_{t=0} = M_0 k_4' C_e = v_{p0} M_0. \quad (26)$$

Here v_{p0} represents the rate of oligomer formation at a steady current which is equal to the value at the current-on pulse. If the values of M_0, v_{p0}, v, $y|_{t\to\infty}$ are experimentally known, k'_4, k_5, and C_e can be calculated from Eqs. 20, 25, and 26. This calculation was carried out for Curve B (Fig. 7) as one example. Also, the relationship between the pulse length and the yield during the current-off pulse was obtained.

The molecular weight of the oligomer obtained under pulse conditions was almost the same as that obtained under steady conditions. Hence, M_0 was assumed to be 1000 based on the result by Yoshizawa *et al.*[8] v_{p0} was obtained from $dy/dt|_{t=0}$ or the observed rate of oligomer formation under steady conditions. v was calculated form the current density, assuming a 100% current efficiency. $dy/dt|_{t=0}$, can be obtained from Fig. 7. On the other hand, the yield suddenly became a high value beyond a pulse length at 60 ms (Fig. 7). It is impossible to obtain $y|_{t\to\infty}$ from the experimental results. Therefore, it is necessary to calculate the values of k'_4, k_5, and C_e based on the supposed $y|_{t\to\infty}$ (Table 3). In this calculation v_{p0} was obtained from Fig. 7 as 1.3×10^{-8} mol

Table 3. C_e, k_5, and k'_4 parameters at different $Y|_{t\to\infty}$ values

$Y\|_{t\to\infty}$ (10^{-8} g/cm^2)	C_e (10^{-10} mol/cm^2)	k_5 (10^{12} cm^2/mol/s)	k'_4 (10 s^{-4})	Fig. 8
3.4	1.6	0.35	12.5	a
5.4	2.9	1.2	4.5	b
9.5	5.4	3.3	2.4	c

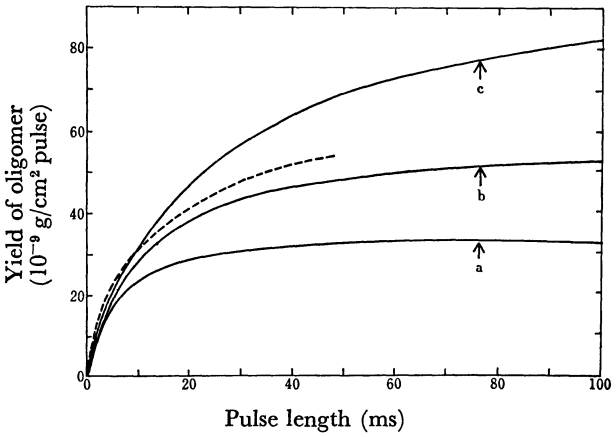

Fig. 8. Relationship between pulse length and the oligomer yield during one current-off pulse calculated by using Eq. 24. a, b, and c represent those in Table 3 respectively. A dotted line represents curve B in Fig. 7.

cm^{-2} s^{-1}, which agreed well with the value, 1.5×10^{-8} mol cm^{-2} s^{-1}, obtained from a steady-state electrolysis at 200 mA/10 cm^2. Using these values, the relationship between the yield, y, and the pulse length, t, was calculated (Fig. 8). The dotted line in this figure shows the experimental result. The calculated curves does not agree perfectly with the experimental results, but the agreement is fairly good. From these calculated results, the half-lifetime of the intermediate, RM·, can be calculated; it becomes about 10 ms. This value is much larger than the half-lifetime of $CH_3\cdot$ (10^{-10} s). An experiment to detect this intermediate was attempted by utilizing the cyclic voltammetry technique at a high scanning rate. However, the reduction current due to intermediates was never observed. Accordingly, the intermediates are considered to be electrochemically inactive.

Conclusion

The following results were obtained from an application of current-pulse electrolysis to an electro-initated polymerization of acrylamide by the Kolbe electrochemical reaction in an aqueous acetate solution.

(1) Under unidirectional current-pulse conditions, the current efficiency of the Kolbe reaction is independent of the pulse length and equal to that under steady conditions.

(2) In the electro-initiated polymerization under pulse conditions, polymerized products are formed not only during the current-on pulse, but also the current-off pulse.

(3) The behavior of intermediates, namely, the production path of polymerized products during the current-off pulse, can be explained well by assuming the rate-determining step to be a simple chemical reaction on or near an electrode.

(4) Intermediate species are electrochemically inactive and have a half-life of about 10 ms.

(5) The application of pulse electrolysis to electrode reactions, in which successive chemical reactions have a decisive influence on the current efficiency of the

intended reaction, allows us to improve the reaction selectivity and the current efficiency and, moreover, to analyze the following chemical reactions in more detail.

(6) In a current-pulse electrolysis the current loss for nonfaradaic processes, such as double-layer charging, *etc.*, has only an insignificant effect.

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