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Electrolytic Polymerization of Acrylonitrile. Kinetic Approach and Effect of Supporting Electrolytes

Teruzo ASAHARA, Manabu SENŌ and Mitsuru TSUCHIYA

The Institute of Industrial Science, The University of Tokyo, Roppongi, Minato-ku, Tokyo

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The electrolytic polymerization of acrylonitrile in constant current was examined by using several supporting electrolytes and the reaction mechanism was discussed. An explanation was given for the anomaly characteristic of the cathodic polymerization using sodium nitrate as a supporting electrolyte, which was reported by Funt. It was revealed that the polymerization is initiated by a radical mechanism at the anode and by an anionic mechanism at the cathode. The termination reaction of the anionic polymerization was analyzed by a kinetic approach and from the structural information of polymers obtained.

Recently, studies have been carried out on the electrode reaction and the following chemical reactions of acrylonitrile.[1] However, no definite conclusion has been obtained as to how many electrons are transferred in the electrolytic reduction, what chemical species are formed at the electrode, and what chemical reactions and termination follow.

In order to clarify these problems, the electrode reduction of acrylonitrile was studied by means of polarography, coulometry and electron spin resonance and the results were examined.

Experimental

Materials. Acrylonitrile was dried with barium oxide and calcium sulfate and distilled under reduced pressure. Sodium nitrate and sodium perchlorate of reagent grade were used without further purification. Tetrabutylammonium perchlorate was prepared from tetrabutylammonium hydroxide and perchloric acid and purified by recrystallization. Tetraethylammonium *p*-toluenesulfonate was synthesized by the reaction of ethyl *p*-toluenesulfonate and triethylamine and recrystallized.

Apparatus. The 500 m*l* cell used for electrolysis has no separatory membrane, because it has been confirmed that no polymer formation takes place in the anodic side. A source of direct current connected with a voltage stabilizer was used. The reaction temperature was maintained at 30°C and the solution was stirred with a magnetic stirrer. During electrolysis nitrogen gas was bubbled in. The electrolysis cell was equipped with a stirrer, a reflux condenser, an inlet tube of N_2 gas, a thermometer and a tube for sampling.

Reaction Kinetics. Every one hour, 10 m*l* of the reaction solution was taken out and poured into 100 m*l* of an aqueous sodium hydrosulfite solution. The resulting polymer precipitate was then separated and weighed after drying.

Measurement of ESR and Absorption Spectra. The ESR measurement was done on a Varian or a Japan Electron Optics Laboratory apparatus with an electrolysis cell. The anode was a platinum wire and the cathode a mercury pool. The measurement of absorption spectra was carried out with a Shimadzu Multipurpose Spectrophotometer using a 1 cm cell equipped with platinum electrodes. The viscosity of the

1) B. L. Funt and F. D. Williams, *J. Polymer Sci.*, **A2**, 865 (1964).

solution of resulting polymers in dimethylformamide was measured as usual at 30°C.

Results and Discussion

Electrode Reaction. Generally, an electrolytic reaction consists of two steps. One is the electrode reaction involving the electron-transfer reaction between ions or neutral molecules and the electrode. The other is the chemical reaction following or followed by the electrode reaction.

The reactivity on electrode changes with the electronic structure of reactants. It has been recognized in many cases that the electronic structures have certain relations to the half-wave potential.[2] The electronic energy state may be estimated by the molecular orbital theory.

The application of this procedure to vinyl compounds gives results as shown in Fig. 1. This shows a good correlation between the energy of the lowest unoccupied level and the half-wave potential of the polarographic reduction.

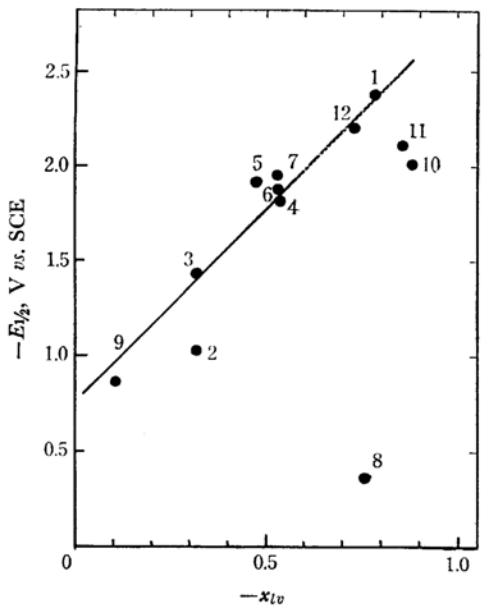


Fig. 1. The relation of coefficient of resonance integral in the lowest vacant orbital and the half-wave potential of various vinyl compounds.
1 styrene, 2 acrolein, 3 methyl vinyl ketone, 4 methyl acrylate, 5 acrylamide, 6 ethyl acrylate, 7 *n*-butyl acrylate, 8 vinyl acetate, 9 diethyl phthalate, 10 acrylonitrile, 11 methacrylonitrile, 12 1,2-dicyanoethylene

The ESR measurement during the electrolysis of acrylonitrile did not give any signal under the conditions shown in Table 1. The potentiostatic

Table 1. Conditions of ESR measurements

Acrylonitrile	Supporting elecrtolyte	Solvent	Cathode
10^{-3} mol/*l*	McKee's salt, 1(g/50 m*l*)	H_2O	Hg
10^{-3} mol/*l*	McKee's salt, 1(g/50 m*l*)	CH_3CN	Hg
10^{-3} mol/*l*	McKee's salt, 1(g/50 m*l*)	DMF	Hg
10^{-3} mol/*l*	$N(CH_3)_4I$ 1(g/50 m*l*)	$EtNH_2$	Hg
20 g	$NaNO_3$ 1 g	DMF 30 g	Hg
10 m*l*	$NaNO_3$ 1 g	DMF 40 ml	Pt

coulometry showed that two electrons were consumed for the reduction of one acrylonitrile molecule. The polarogram of acrylonitrile has a simple one-step reduction wave; the number of electrons for reduction was two from the limiting diffusion current density. On the other hand, the analysis of polarogram using the Nernst equation shows that the apparent number of electrons is 0.6. If the number of electrons is assumed to be 2, the transfer coefficient becomes 0.3, a reasonable value.[3] All these results lead to the conclusion that the two-electron reduction of acrylonitrile would be reasonable. Therefore, the following reaction mechanism could be proposed for the cathodic reduction:

$$CH_2=CHCN + 2e \rightarrow \overset{\ominus}{C}H_2-\overset{\ominus}{C}HCN$$

$$\overset{\ominus}{C}H_2-\overset{\ominus}{C}HCN + CH_2=CHCN \rightarrow$$

$$(2CH_2-\overset{\ominus}{C}HCN) \rightarrow NC\overset{\ominus}{C}H(CH_2)_2\overset{\ominus}{C}HCN$$

It is expected from the energy consideration that the reverse reaction, a disproportionation, hardly occurs. The formation of propionitrile and adiponitrile would take place according to the following reactions:

$$H_2O \rightleftarrows H^+ + OH^-$$

$$\overset{\ominus}{C}H_2-\overset{\ominus}{C}HCN + 2H^+ \rightarrow CH_3CH_2CN$$

$$NC\overset{\ominus}{C}H(CH_2)_2\overset{\ominus}{C}HCN + 2H^+ \rightarrow NC(CH_2)_4CN$$

It follows from this mechanism that the increase in water content gives rise to an increase in the yield of propionitrile. On the contrary, the decrease in water content gives an increase in the yield of adiponitrile and oligomers such as hydrotrimer. At a higher current density the formation rate of acrylonitrile dianion increases and the yield of propionitrile is depressed.

Beck[4] examined this reaction by the analysis of Tafel line in many systems containing acrylonitrile, and proposed the following reaction mechanism.

2) K. Higasi and H. Baba, "Quantum Organic Chemistry," Asakura Publishing Co., Tokyo (1965).

3) T. Asahara, M. Senō and H. Kaneko, *Denki Kagaku*, (*J. Electrochem. Soc. Japan*), **35**, 882 (1967).

4) F. Beck, *Chem. Ing. Tech.*, **37**, 607 (1967).

$$CH_2{=}CHCN + e + H_2O \xrightarrow{slow} \cdot CH_2CH_2CN + OH^-$$

$$\cdot CH_2CH_2CN + e \rightarrow :\overset{\ominus}{C}H_2CH_2CN$$

$$:\overset{\ominus}{C}H_2CH_2CN + CH_2{=}CHCN \rightarrow NCCH_2CH_2CH_2\overset{\ominus}{C}HCN$$

$$NCCH_2CH_2CH_2\overset{\ominus}{C}HCN + H_2O \rightarrow NC(CH_2)_4CN + OH^-$$

He considered that cyanoethyl iodide is reduced more easily than acrylonitrile, and that therefore cyanoethyl radical also would be reduced more easily than acrylonitrile, and reported that a weak signal was observed in the ESR measurement during electrolysis. However, there are ambiguities in his argument; for example, a cyanoethyl radical is an unstable primary radical and, if this was formed, it would enter into polymerization. Actually, polymer formation was scarcely observed. As to the ESR spectrum, the *g*-value and the hyperfine structure were not reported, and therefore the observed signal could not be assigned to a cyanoethyl radical. From these considerations, together with the polarographic result it could not be expected that the complex mechanism proposed by Beck is reasonable.

Electrolytic Polymerization of Acrylonitrile. Many researches have been carried out recently on the electrolytic polymerization of vinyl compounds. The principal feature of this method lies in the possibility of the control of the initiation reactions at electrodes by electrode potential and of the reaction rate by current density.

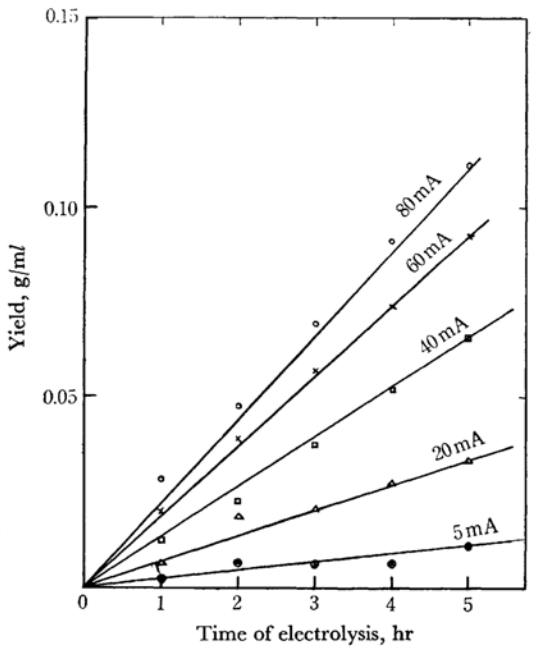


Fig. 2. The time dependence of the yield of polymers.

Funt and Williams[1] reported the anomaly in the electrolytic polymerization of acrylonitrile in dimethylformamide, using sodium nitrate as a supporting electrolyte. That is, there is a decrease in the rate of the formation of polymer with the increasing monomer concentration over a certain value. It should be noted that sodium nitrate is not soluble in acrylonitrile, but in dimethylform-

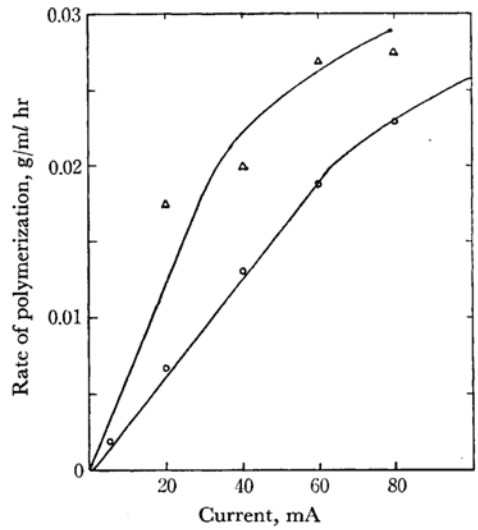


Fig. 3. The relation between the current and the rate of polymerization.

○ AN-$NaNO_3$, △ AN-McKee's salt

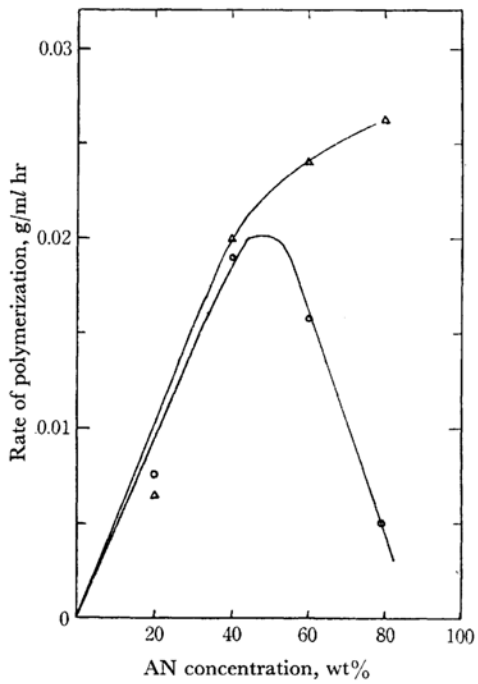


Fig. 4. The dependence of the rate of polymerization on AN concentrations.

○ AN-$NaNO_3$, △ AN-McKee's salt

amide, and sodium perchlorate is soluble both in acrylonitrile and dimethylformamide. It is of interest to use tetraethylammonium *p*-toluenesulfonate as a supporting electrolyte. However, Funt neither reported the structural analysis of the polymer obtained nor examined the reaction kinetics. As this reaction is interesting as a typical example of anionic addition reaction, the electrolytic polymerization of acrylonitrile was investigated.

AN-DMF-$NaNO_3$ System. A typical result in the system of acrylonitrile(AN)-dimethylformamide-(DMF)-$NaNO_3$ is shown in Fig. 2, where polymer yields are plotted against the reaction time corresponding to various current densities. When the molar ratio of AN to DMF is less than unity, the experimental results are expressed by the following equations (Figs. 3, 4, 5 and Table 2).

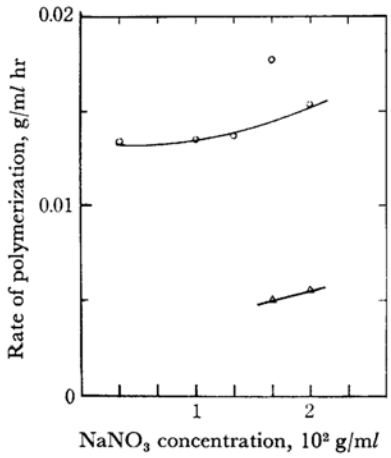


Fig. 5. The dependence of the rate of polymerization on $NaNO_3$ concentrations.
○ AN 60 wt%, △ AN 80 wt%

TABLE 2. INTRINSIC VISCOSITIES OF POLYMERS

AN-DMF-$NaNO_3$			AN-DMF-McKee's salt		
Current density mA/cm²	AN concn. wt%	$[\eta]$	Current density mA/cm²	AN concn. wt%	$[\eta]$
1.04*	40	1.2	4.16	40	0.18
2.08*	40	1.4	8.33	40	0.14
8.33	40	0.2	12.5	40	0.12
12.5	40	0.2	16.7	40	0.10
16.7	40	0.2			
8.33	20	0.2	8.33	20	0.11
8.33	60	0.2	8.33	60	0.24
8.33	80	0.3	8.33	80	
8.33	100	0.8	8.33	100	0.29

*In these cases, polymers are formed at anode and the analysis of IR spectrum of polymers suggests the following initiation mechanism:

$$NO_3^- \xrightarrow{-e} NO_3\cdot$$
$$NO_3\cdot + CH_2{=}CH{-}CN \rightarrow \text{polymers}$$

Rate of polymer formation: $\frac{d[P]}{dt} = k[M]\,[I]$

Degree of polymerization: DP = const.

The reaction might be assumed to consist of the following steps:

$$M + I \xrightarrow{k_i} C^* \quad (1)$$
$$C^* + M \xrightarrow{k_p} C^* \quad (2)$$
$$C^* + M \xrightarrow{k_{t1}} P \quad (3)$$
$$C^* \xrightarrow{k_{t2}} P \quad (4)$$

where M is monomer, C* active species with growing ends and P polymers. This reaction process was analyzed kinetically, using the stationary state method, and the following equations are obtained:

$$\frac{d[P]}{dt} = k_i\,[M][I]$$
$$DP = \frac{k_p\,[M]}{k_{t1}[M] + k_{t2}}$$

The experimental result requires that $k_{t1}[M]$ is much larger than k_{t2}. Therefore, the significance of the termination reaction (3) must be recognized. During electrolysis the bulk solution becomes yellow which remains after the electrolysis. This coloration would be caused not by reaction intermediates, but by resulting polymers, because polymers are yellow after purification. However, a question remains as to whether the color is due to the decomposition of supporting electrolytes. In order to confirm the possibility, the change in absorption

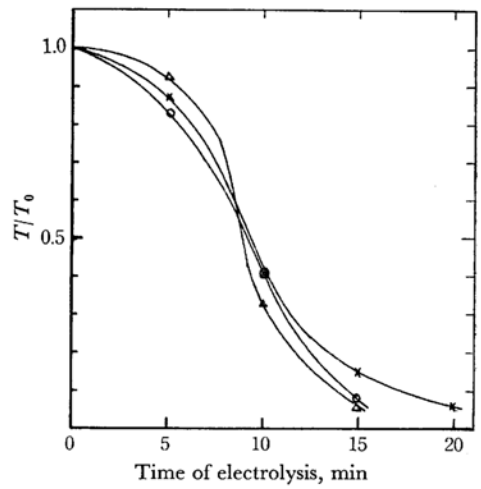


Fig. 6. Relation between the transmittance and the time of electrolysis.
○ 270 mμ, △ 310 mμ, ×340 mμ in DMF
T: Transmittance of sampe solution at given times
T_0: Transmittance of reference (t=0)

spectra of products was measured during electrolysis at various AN concentrations. The result is shown in terms of transmittance at the absorption peak (270 mμ) and other two wavelengths in Fig. 6. The change in transmittance T with time (t) obeys the exponential law $T=T_0e^{-\alpha/t}$, where T_0 is the transmittance at $t=0$. In Fig. 7, the values of α are plotted against the AN concentration. From this result it may be concluded that the decomposition of the supporting electrolyte has no correlation with the observed coloration.

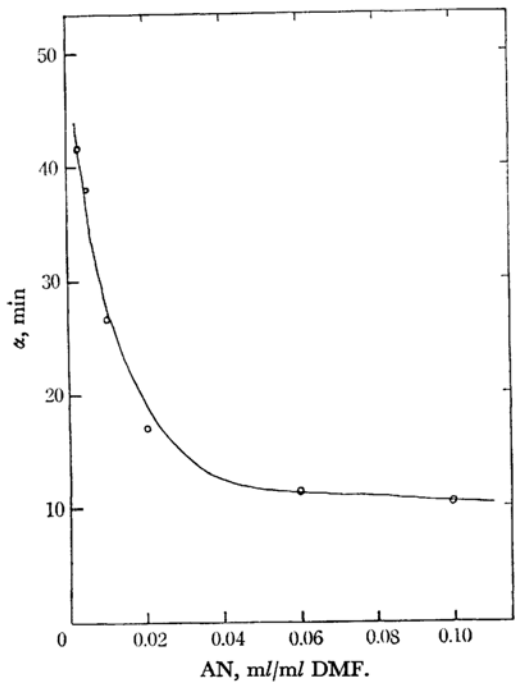
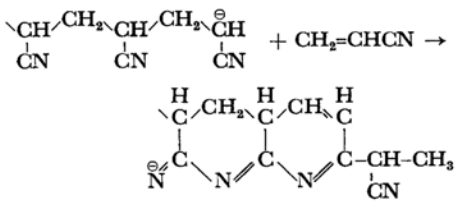


Fig. 7. The dependence of rate of coloration at 270 mμ on AN concentration in DMF.

Moreover, the identification of IR spectrum of polymers shows the existence of methyl and imino groups. Therefore, it seems that the coloration is due to the cyclization of nitrile groups. These observations suggest clearly the following termination reaction:



The anomaly in Fig. 4 might be attributed to the presence of the supporting electrolyte which is hardly soluble in acrylonitrile and causes an increase in the activation energy of the initiation step. This might be explained as follows. The dissociation of sodium nitrate is in equilibrium.

$$NaNO_3 \overset{K_1}{\rightleftarrows} Na^+ + NO_3^-$$

On the other hand, we have

$$[Na^+] = [NO_3^-] + [C^*]$$

An excess charge discharges at electrodes. If C* is small enough, we get

$$[Na^+] = \sqrt{K_1[NaNO_3]} \equiv K_1'$$

The following equilibrium would take place also for the active anions

$$C_f^* + Na^+ \overset{K_2}{\rightleftarrows} C_{nf}^*$$

where C^*_f and C^*_{nf} refer to the free active anions and the active ion-pairs respectively. C^*_f would be more active than C^*_{nf}.
Then

$$[C^*] = [C_f^*] + [C_{nf}^*]$$

$$= [C_f^*](1 + K_1'K_2)$$

Therefore

$$DP = \frac{k_p[C_f^*][M]}{k_{t1}[M][C^*] + k_{t2}[C^*]}$$

$$= \frac{k_p[M]}{(k_{t1}[M] + k_{t2})(1 + K_1'K_2)}$$

When the AN concentration increases, K_1' decreases and DP increases. In addition, it is suggested that the loss in the solvation energy of sodium cations results in the relative instability of the reactive point according to the linear free energy relationship, and the activation energy for the initiation reaction increases and the reaction rate decreases. This anomaly is not observed when McKee's salt is used as a supporting electrolyte.

AN-DMF-McKee's Salt System. In the system of AN, McKee's salt, and DMF, the polarogram of AN suggests the complex formation of AN with *p*-toluenesulfonate anion.[5] In this system, the current effect shows saturation for the rate of polymer formation at a certain current density as shown in Fig. 3. This would be interpreted on the assumption that the complex has a negative charge and the polymerization process in the neighborhood of the electrode is of the diffusion control even at a relatively low electrode potential. However, the decomposition of the supporting electrolyte would lead to the same result.

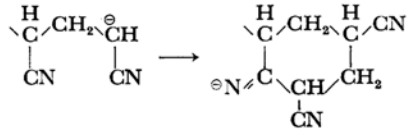
The increasing AN concentration causes an increase in the rate of polymer formation and the degree of polymerization as shown in Fig. 4 and

5) T. Arai, private communication.

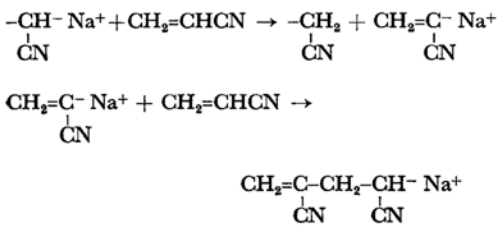
Table 2. This behavior may be described as follows:

$$\frac{d[P]}{dt} = k_i[M][I] \qquad DP = k[M]$$

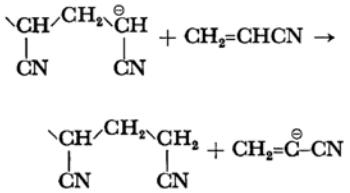
The kinetic analysis agrees with the result when $k_{t2} \gg k_{t1}[M]$, and suggests that the termination reaction (4), *i. e.*, the self-consumption of the reactive points, predominates. The IR spectrum of polymer obtained has no absorption assigned to methyl groups and the UV spectrum shows that the polymer has a cyclic unit. From these observations, the following termination seems reasonable.

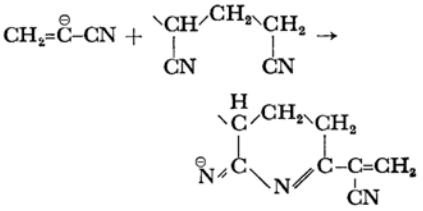


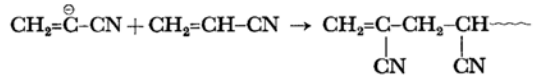
Electrolysis without Solvents. When sodium nitrate was used as a supporting electrolyte, the IR spectrum of the polymer obtained suggests the following reaction scheme:



The electrolysis of acrylonitrile at the cathode without solvent using sodium perchlorate as a supporting electrolyte would proceed according to the following scheme:







In this system, the polymerization proceeds at the anode through a radical mechanism, that is

$$ClO_4^- - e \rightarrow ClO_4\cdot$$

$$ClO_4\cdot + CH_2{=}CH{-}CN \rightarrow \text{polymers}$$

This is supported by the observation that the IR spectrum of the polymer formed at the anode has an absorption assigned to perchloro groups and the polymer has a very high molecular weight (the intrinsic viscosity in DMF is 4.0) and no coloration.

The information obtained in the present investigation is summarized as follows:

(1) The half-wave potentials and therefore the reactivity of vinyl compounds could be estimated from the molecular orbital calculation.

(2) Acrylonitrile undergoes a two-electron reduction in the cathode reaction.

(3) The lowering of the rate in the formation of polymer over a certain AN concentration in the system AN-DMF-$NaNO_3$ would be caused by the decrease in the rate constant of the initiation step.

(4) When the polymer is obtained at the cathode in the electrolysis of acrylonitrile, it is formed by the anionic polymerization mechanism. The termination reaction involves the cyclization of nitrile groups, and results in the formation of yellow-colored polymers.

(5) When the polymer is obtained at the anode it is initiated by the radical which is formed by the oxidation of supporting electrolytes. The degree of polymerization of polymers formed at the cathode is much lower than that of polymers formed at the anode.