

Electrochemical Polymerization of Acrylonitrile with Quaternary Salts

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SYNOPSIS

The electrochemical polymerization of acrylonitrile was carried out in the solutions of tetrabutylammonium bromide and tetrabutylphosphonium bromide in *N,N*-dimethylformamide in a divided electrolytic cell. The formation of polyacrylonitrile of high molecular weight (7.6×10^4) took place in the cathode compartment. The kinetics of the polymerization was investigated for different initial monomer concentrations, current levels, and electrode materials. The polymerization mechanism is anionic.

INTRODUCTION

The industrial application of electrolytic hydrodimerization of acrylonitrile (AN), developed by Baizer,¹ spurred considerable research on the electroinitiated polymerization of AN,²⁻⁹ as electrochemical process is found to be attractive to produce polymers. In this article we describe the cathodic polymerization of AN in *N,N*-dimethylformamide (DMF) containing tetrabutylammonium bromide (TBAB) and tetrabutylphosphonium bromide (TBPB) as supporting electrolytes. The aim of this work is to advance reaction mechanism and formulate kinetic expressions for the cathodic polymerization process of AN.

EXPERIMENTAL

Materials

DMF and AN were properly dried and then fractionally distilled. TBAB and TBPB were dried prior to use.

Polymerization Method

The polymerization was carried out in a simple H-shaped cell that could hold 25 mL of a solution and

accommodate two platinum electrodes of the area of $0.7 \times 2.5 \text{ cm}^2$. The cell was divided into two compartments by a fine fritted glass disk of 1 cm diameter. A known amount of supporting electrolyte was dissolved in a known volume of DMF. The solution was transferred to the electrolytic cell and a required amount of AN was added to the catholyte. The anolyte did not contain any monomer because AN did not polymerize in it. The volume of the catholyte was 12.5 mL at 35°C. The polymerization was carried out under the conditions of constant-current electrolysis using a stabilized dc power supply of 300 V, which gave current from 0 to 100 mA. The kinetics of the polymerization was followed gravimetrically at 35°C. In order to determine the amount of polymers for a desired time, the electrolysis was terminated at that time and the whole catholyte was poured into about 200 mL of distilled water. The polymer was recovered and properly washed with methanol. It was dried in air oven at 100°C. When 1 g of the polymer was dissolved in 10 mL of DMF, and the resulting solution was gradually poured into 200 mL of distilled water, the recovery of polymers was found to be satisfactory. Some loss of polymer during workup could not be avoided. The average molecular weights of the polymers were determined from the solution viscosity measurements in DMF at 30°C by Ubbelohde viscometer. The limiting viscosity numbers were converted into average molecular weights by the following correlation:¹⁰

$$[\eta] \text{ in dL g} = 2.303 \times 10^{-4} \times M^{0.75}$$

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RESULTS AND DISCUSSION

Blank Experiments

AN was added to the solution of TBAB or TBPB in DMF, and the solution was kept overnight at 35°C. When the resulting solution was heated at 80°C for 6 h, the polymerization did not occur, indicating that the salts did not initiate the polymerization. However, when the same solution was subjected to electrolysis, the polymerization took place.

Effect of Current Density

During electrolysis the catholyte turned from light yellow to deep orange with TBAB in DMF, and in case of TBPB the colorless catholyte became light orange. The cathode became heavily coated with yellow orange polymers. The polymer yield was not affected by the cathode coating if the current density remained constant. Tables I and II show that the yields and average molecular weights of polymers with different impressed currents and initial monomer concentrations are almost the same for both ammonium and phosphonium salts. An apparent decrease in molecular weight (Table I) at high current levels (20–25 mA) is assumed to be caused by the increase of concentration of initiator and depletion of the monomer in the catholyte.

Electrochemical Polymerization Kinetics

The polymerization was carried out at different constant currents with time in the solution of TBAB in DMF at 35°C, and the results are presented in

Table I Polymer Yields and Average Molecular Weights for the Cathodic Polymerization of Acrylonitrile (AN) (2.4 mol/liter)^a

Current (mA)	Polymer Yield (%)		Mol. Wt. ($\times 10^{-5}$)	
	I	II	I	II
5	24.5	19.8	0.73	0.73
10	37.4	34.6	0.73	0.73
15	49.5	44.5	0.73	0.68
20	55.7	48.3	0.68	0.66
25	59.5	52.3	0.66	0.56

^a In dimethylformamide (DMF) solutions of tetrabutylammonium bromide (TBAB)-I (3.72×10^{-2} mol/liter) and tetrabutylphosphonium bromide (TBPB)-II (3.54×10^{-2} mol/liter) at different impressed currents. Electrolysis time, 60 min; catholyte vol., 12.5 mL at 35°C.

Table II Polymer Yields and Average Molecular Weights for the Cathodic Polymerization of Acrylonitrile (AN)^a

AN Conc. (mol/liter)	Polymer Yield (%)		Mol. Wt. ($\times 10^{-5}$)	
	I	II	I	II
1.2	45.3	40.4	0.73	0.73
2.4	37.4	34.6	0.73	0.73
3.6	35.9	34.3	0.76	0.76
4.8	35.7	34.0	0.76	0.76

^a In dimethylformamide (DMF) solutions of tetrabutylammonium bromide (TBAB)-I (3.72×10^{-2} mol/liter) tetrabutylphosphonium bromide (TBPB)-II (3.54×10^{-2} mol/liter) at different acrylonitrile concentrations. Electrolysis time, 60 min; constant current, 10 mA; catholyte vol., 12.5 mL at 35°C.

Figure 1. The following assumptions are made to derive electrochemical polymerization kinetic expressions that fit the data in Figure 1.

1. Initiation is via direct electron transfer from cathode to the monomer, leading to the formation of radical anion.
2. Radical anion may not be capable of adding to monomer.

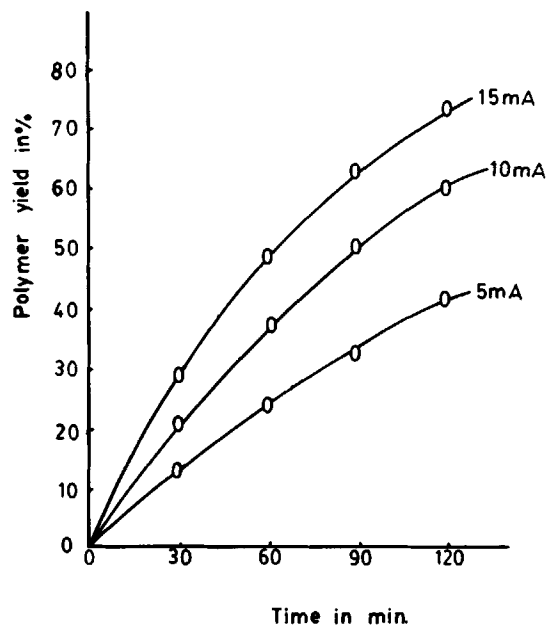
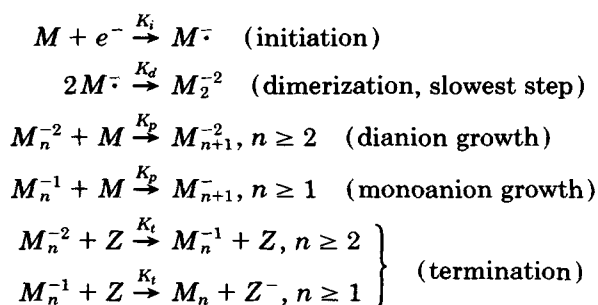


Figure 1 Time conversion curves for the cathodic polymerization of AN (2.4 mol/liter) at different current levels in DMF containing TBAB (3.72×10^{-2} mol/liter) at 35°C.

3. Monomeric radical anion dimerizes and the dimerization is the slowest step.
4. Termination is only by reaction with solvent or other agent (Z), and their reaction products are not capable of initiating polymerization.
5. Consumption of monomer is primarily by polymer growth, i.e., high molecular weight polymers are produced.
6. Concentration of solvent or chain terminating agent (Z) is essentially constant.
7. Steady concentration of polymeric anion is achieved.

The reaction steps may then be written as:¹¹



where K_p 's are equal and K_t 's are also equal. The rates of initiation, growth, and termination at steady state are, respectively,

$$\begin{aligned}
 R_i &= K_d[M^{\cdot-}]^2 \\
 R_p &= K_p[M] \sum_{n=1}^{\infty} 2[M_n^{\cdot-2}] \\
 &\quad + K_p[M] \sum_{n=1}^{\infty} [M_n^{\cdot-1}] - [M^{\cdot-}] \\
 &= K_p[M] \sum_{n=1}^{\infty} [2[M_n^{\cdot-2}] + [M_n^{\cdot-1}]] - [M^{\cdot-}]
 \end{aligned}$$

Thus

$$R_p = K_p[M][P^-]$$

where

$$[P^-] = \sum_{n=1}^{\infty} [2[M_n^{\cdot-2}] + [M_n^{\cdot-1}]] - [M^{\cdot-}]$$

Similarly,

$$R_t = K_t[Z][P^-]$$

Since the initiation takes place by the direct cathodic reduction of the monomer, the initiation rate is proportional to the quantity of the current in faraday per unit volume available in the electrode process, i.e., I/FV where I = constant current in amperes, V = volume of catholyte, and F = faraday.

Therefore, under steady-state condition,

$$\frac{I}{FV} - 2K_d[M^{\cdot-}]^2 = 0$$

$$\frac{I}{FV} = 2K_d[M^{\cdot-}]^2$$

$$[M^{\cdot-}] = \left(\frac{I}{2K_d FV} \right)^{1/2}$$

When the number of chain growth initiated equals the number of chain growth arrested, the rate of initiation is equal to the rate of termination, i.e.,

$$R_i = R_t$$

Thus

$$K_d[M^{\cdot-}]^2 = K_t[Z][P^-]$$

or

$$[P^-] = \frac{K_d[M^{\cdot-}]^2}{K_t[Z]}$$

Substituting the value of $[M^{\cdot-}]$,

$$[P^-] = \frac{K_d}{K_t[Z]} \times \frac{I}{2K_d FV}$$

or

$$[P^-] = \frac{I}{2K_t FV [Z]}$$

Rate of consumption of monomer, i.e.,

$$-\frac{d[M]}{dt} = \frac{I}{FV} + K_p[M][P^-]$$

Since the consumption of monomer in the initiation process is negligible compared to the growth process leading to formation of high molecular weight polymer, then

$$-\frac{d[M]}{dt} = K_p[M][P^-] = \frac{K_p[M]}{K_t[Z]} \left(\frac{I}{2FV} \right)$$

Therefore the rate of polymerization, R_p , is directly proportional to the electrolysis current, I , when M and Z are constant. Now on integration of the preceding equation, when I and Z are constant, $M_t = M_0$ when $t = 0$, we get

$$\ln[M_0]/[M_t] = Kt$$

where

$$K = \frac{K_p}{2K_t} \frac{I}{FV} \frac{1}{[Z]}$$

or

$$\frac{K}{I} = \frac{K_p}{2K_t} \frac{1}{FV[Z]}$$

and K/I is constant when $[Z]$ is constant.

Indeed, the least-square analysis plot of $\log_{10}[M_0]/[M_t]$ versus t for the data, presented in the conversion curves of Figure 1, gives a straight line passing through the origin, as shown in Figure 2. The overall rate constant, K , obtained from the

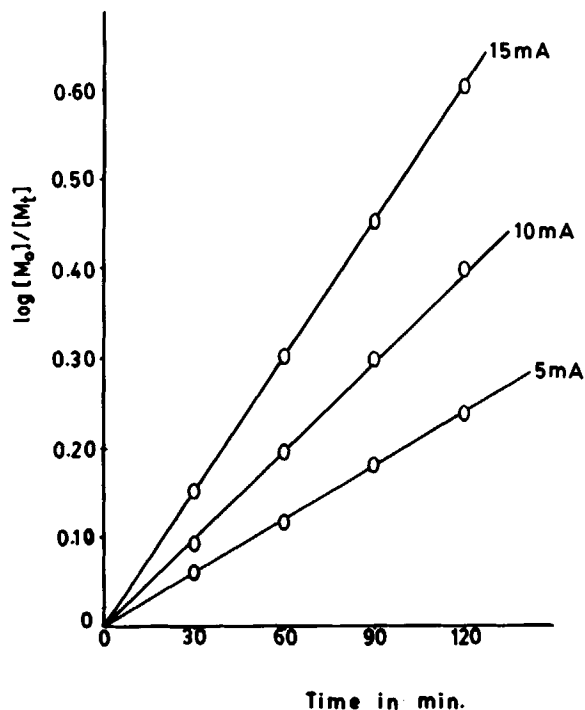


Figure 2 Plot of $\log_{10}[M_0]/[M_t]$ vs. t for the conversion curves of Figure 1.

Table III Rate Constant, K , of the Cathodic Polymerization of Acrylonitrile (AN) (2.4 mol/liter)^a

Current (mA)	Slope 10^3 (min^{-1})	K 10^3 (min^{-1})	K/I (10^{-3})
5	2.00	4.60	0.92
10	3.25	7.48	0.74
15	5.06	11.57	0.77

^a In dimethylformamide (DMF) solution of tetrabutylammonium bromide (TBAB) (3.72×10^{-2} mol/liter) at different currents at 35°C. Electrolysis time, 60 min; catholyte vol., 12.5 mL at 35°C.

slopes of the lines of Figure 2, increases with the impressed currents, and values of K/I are roughly constant, as is evident from Table III. This is expected from the rate expression. The polymerization was also carried out at different initial monomer concentrations with time at a fixed current of 15 mA at 35°C and data are shown in Figure 3. Then least-square analysis plot of $\log_{10}[M_t]$ versus t (data being obtained from Fig. 3) gives a set of approximately parallel lines as shown in Figure 4, suggesting that the rate constant does not vary with the monomer concentration at a constant-current density. There-

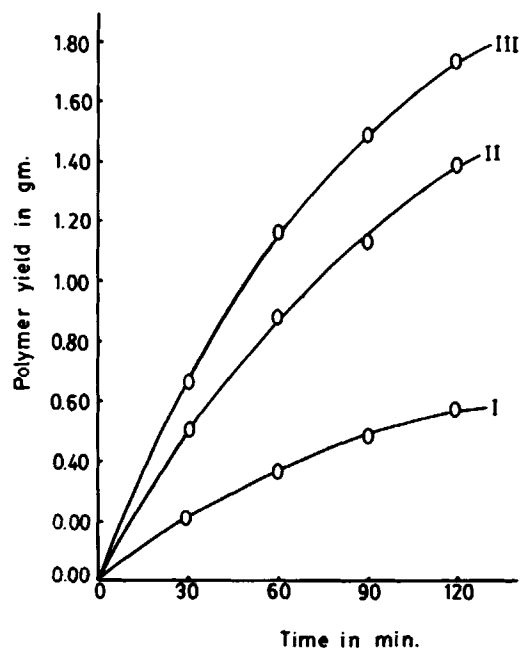


Figure 3 Polyacrylonitrile formation at fixed current of 10 mA in DMF containing TBAB (3.72×10^{-2} mol/liter) at 35°C. The concentration of AN being (I) 1.2 mol/liter, (II) 3.6 mol/liter, and (III) 4.8 mol/liter.

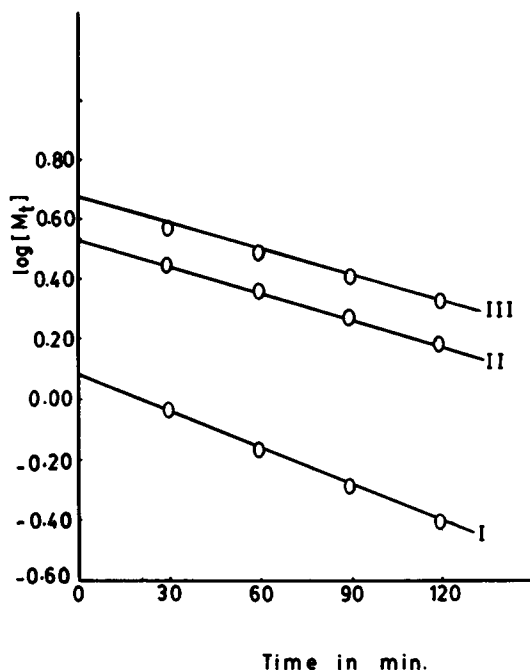


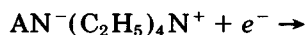
Figure 4 Plot of $\log_{10}[M_t]$ vs. t for the conversion curves of Figure 4.

fore, the kinetics studies substantiate that the proposed reaction mechanism is plausible.

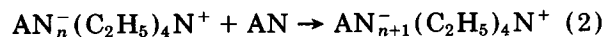
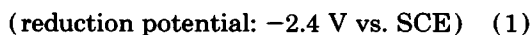
Polymerization with TBPB

The kinetic study of electrochemical polymerization of AN with TBPB in DMF at different current levels and several initial monomer concentrations were also studied and almost the same results were obtained as with TBAB. Collins et al.⁹ examined the influence of tetraalkylammonium and tetraarylphosphonium cations on the rate of acrylonitrile (AN) polymerization in the catholyte. A higher yield of polyacrylonitrile with phosphonium salt was obtained in the same electrolysis time even though there was only one-tenth as much phosphonium salt as the ammonium salts. Contrary to this, in the present work slightly higher polymer yield was obtained with TBAB (Table II). On the basis of an intimate ion pair model, and the difference in cathodic potentials of the salts, the following propagation mechanism has been advanced.⁹

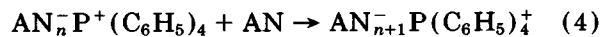
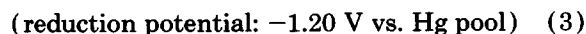
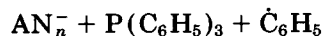
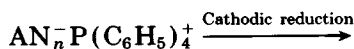
Propagation with alkylammonium salt:



no cathodic reduction of cation



Propagation with phosphonium salts:



The reduction of the cation in reaction (3) results in the formation of a polymeric free ion (5), which might have been responsible for the observed large increase in the overall rate of the electrochemical polymerization with the aromatic phosphonium salt. No such free ion appears to be generated electrically in the case of alkylquaternary ammonium or alkylquaternary phosphonium cations.

Inhibition of Polymer Formation

A free radical inhibitor, 2,2-diphenyl picryl hydrazyl did not inhibit the polymerization of AN in the solution of ammonium and phosphonium quaternary salts in DMF, but the proton donating substances such as water, methanol, and acid completely inhibit the polymerization suggesting an anodic polymerization.

Polymerization at Electrodes of Different Metals

The polymerization of AN in the solution of ammonium and phosphonium quaternary salts in DMF

Table IV Polymer Yields and Average Molecular Weights for the Cathodic Polymerization of Acrylonitrile (AN) (2.4 mol/liter)^a

Electrode	Polymer Yields (%)		Mol. Wt. ($\times 10^{-5}$)	
	I	II	I	II
Ni	36.8	34.3	0.81	0.78
Fe	34.0	31.0	0.82	0.78
Cu	32.0	30.0	0.82	0.79
Pb	29.3	9.0	0.76	0.76

^a In dimethylformamide (DMF) solutions of tetrabutylammonium bromide (TBAB)-I and tetrabutylphosphonium bromide (TBPB)-II at electrodes of different materials. Electrolysis time, 60 min, constant current, 10 mA; cathodic vol., 12.5 mL at 35°C.

were carried out at Ni, Fe, Cu, and Pb electrodes at 10 mA for 1 h. The results are given in Table IV, which shows that the yields and average molecular weights are nearly the same at each electrode for both electrolytes except for Pb electrodes with TBPB where the yield was only 9%. The repeated experiments gave almost the same results. The reason for the low yield is not immediately known.

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