

ELECTROCHEMICAL INITIATION OF POLYMERIZATION

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INTRODUCTION

The possibility of initiating the polymerization of vinyl compounds by means of electrolytic processes has not received very much attention. A survey on the existing work is given in *Table 1*. The first report on this

Table 1. Electrochemical initiation of polymerization

<i>Electrode</i>	<i>Ion</i>	<i>Monomer*</i>	<i>Medium</i>	<i>Mechanism</i>	<i>Ref.</i>
Cathode	H ⁺	MMA	Aqueous methanol	Radical	1
Cathode	?	MMA	Propane-1,2-diol	Radical	2
Cathode	H ⁺	MMA	Aqueous	Radical	3
Cathode	Fe ³⁺ +K ₂ S ₂ O ₈	AN	Aqueous	Radical	4
Anode	CH ₃ COO ⁻	ST	Acetic acid	Radical	5
Cathode	H ⁺	MMA	Aqueous	Radical	6
Cathode	Na ⁺	ST	Anhydrous pyridine	Anionic	7
Anode	CH ₃ COO ⁻	BU, IS	Methanol	Dimerizat'n	8
Anode	CH ₃ COO ⁻	BU, IS	Methanol	Dimerizat'n	9
Anode	CH ₃ COO ⁻	MMA, VAC, VC	Water (heterogeneous)	Radical	10

* MMA = methyl methacrylate; AN = acrylonitrile; ST = styrene; BU = butadiene; IS = isoprene; VAC = vinyl acetate; VC = vinyl chloride.

kind of initiation was from Wilson *et al.*¹ in 1949. As electrolyte they used sulphuric acid in aqueous methanol, and, by cathodic discharge of the hydrogen ion, they were able to initiate the polymerization of acrylic acid, methyl acrylate and methyl methacrylate. The cathode was mercury, and, with a current density of 30 mA/cm², five moles of monomer were polymerized per mole of hydrogen ion discharged. The proposed mechanism was that a hydrogen atom, formed at the electrode, was added onto the monomer, followed by the growth of the resulting free radical by further addition of monomer. Little, if any, reduction of the monomer was observed.

Cathodic polymerization was also observed by Palit² in 1950. He tried to polymerize methyl methacrylate in propane-1,2-diol solution with acetate free radicals generated anodically in the Kolbe electrolysis of alkali metal acetates. In this he did not succeed, but he obtained at the smooth platinum cathode poly(methyl methacrylate), apparently in a crosslinked state, which he attributed to an initiation by hydrogen or sodium atoms. On similar lines to Wilson's work are some experiments by Parravano.³ Here, an aqueous solution which was 0.1 N in sulphuric acid and 0.1 M in methyl methacrylate was used. At a current density of 2.57 mA/cm² polymer was formed at a mercury cathode after 1.5 h, and at a lead cathode after 2 h; at a platinum cathode more than 24 h were needed.

An indirect electrolytic method was used by Kolthoff⁴. He reduced cathodically ferric ions to ferrous, which reacted with persulphate present in the solution to initiate the polymerization of acrylonitrile.

The first successful anodic polymerization was reported by Goldschmidt and Stöckel⁵ in 1952. By the electrolysis of sodium acetate in acetic acid solution at a current density of 1–4 mA/cm², styrene was converted mainly into dimer and trimer at the anode, but some low molecular weight polymer was also formed. The dimerization of acrylonitrile was similarly achieved.

Cathodic polymerization of methyl methacrylate was also carried out in aqueous hydrogen chloride by Kern⁶. He reported the polymerization of 270 moles of monomer per mole of hydrogen ion discharged.

Another type of cathodic polymerization was observed by Yang, McEwen and Kleinberg⁷, who polymerized styrene to low molecular weight polymers (DP = 20–30) by electrolysis of sodium iodide in anhydrous pyridine at magnesium electrodes. These authors assumed a direct initiation by electrons supplied by the cathode; this would, of course, be an anionic process.

The anodic dimerization of butadiene and isoprene initiated by acetate radicals has been reported by Lindsey and Peterson⁸, and also by Smith and Gilde⁹. The last-named authors were also able to get high molecular weight polymers in a heterogeneous aqueous system from methyl methacrylate, vinyl acetate and vinyl chloride by anodically generated acetate radicals¹⁰.

CATHODIC POLYMERIZATION OF ACRYLONITRILE WITH TETRA-ALKYLAMMONIUM SALTS

Our first experiments in this field were started as early as 1950 with the electrolysis of alkali metal acetates in acetic acid in the presence of different monomers. Some water was always added to improve the solubility of the salt. The polymerization was very poor and not reproducible. As this might possibly have been due to the presence of anodically-generated oxygen, we continued our experiments (after an interval of several years) in anhydrous systems. To make our system as simple as possible, we used a pure monomer as solvent. Acrylonitrile was found to be suitable because tetra-alkylammonium salts are partly soluble in it^{11, 12}. For the initial

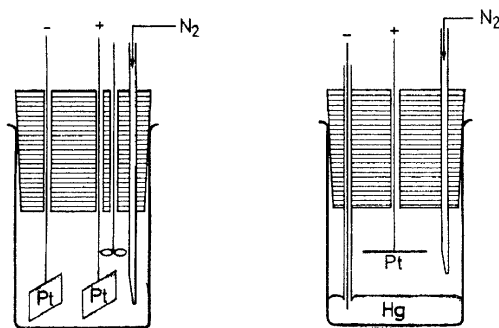


Figure 1. Simple set-up for the electrochemical polymerization of acrylonitrile

ELECTROCHEMICAL INITIATION OF POLYMERIZATION

experiments, a very simple set-up was used (*Figure 1*). The electrical resistance for the solutions of tetra-alkylammonium salts in acrylonitrile was of the order of 10,000 Ω . During the electrolysis, the solutions became yellow, and solid polyacrylonitrile was formed at the cathode. The results of some experiments are summarized in *Table 2*. The polymerization was

Table 2. Polymerization of acrylonitrile (20 ml) initiated by cathodic discharge of tetra-alkylammonium ions

<i>Salt</i>	<i>Initial moles</i> $\times 10^{-5}$	<i>Average current</i> ($A \times 10^{-3}$)	<i>Time</i> (min)	<i>Electro-chemical equi-valents</i> $\times 10^{-5}$	<i>Moles monomer polymerized</i> $\times 10^{-5}$	$[\eta]$ (ml/g)	<i>Reference</i>
$(Me_4N)^+(ClO_4)^-$	4.3	0.3	142	2.7	210	6.8	1
$(Et_4N)^+(ClO_4)^-$	2.5	1.2	60	4.5	70	7.8	2
	9.0	0.82	1,620	83	860	4.4	3
	4.4	6	90	34	1,500	5.4	4
$(Et_4N)^+(BF_4)^-$	4.2	7	100	44	410	7.4	5
	3.8	7	280	120	1,200	4.9	6
$1/2(Et_4N)_2^+C_2O_4^{2-}$	9.4	0.2	1,045	13	160	12	7
$(Et_4N)^+I^-$	3.7	1	240	15	60	8.0	8
$(Me_4N)^+Br^-$	(Satd.soln.)	3.5	305	66	2,000	4.7	9

always at the cathode. The cation was tetramethyl- or tetraethylammonium ion. The anions were perchlorate, borotetrafluoride, oxalate, iodide, and bromide. The concentrations of the salts were 1–5 mmol/l. The cathode surface area was 1 cm², and, therefore, the current (A) and the current density (A/cm²) used were numerically identical. The first experiment shows that about 80 moles of monomer were polymerized per electrochemical equivalent passed through the solution. The viscosity number of the polymer, 6.8, corresponds to a D.P. of about 20. Therefore, if every ion discharged at the cathode had initiated a polymer chain, four polymer molecules would have been formed per primary act. This might be due to an effective chain-transfer reaction, which might also be responsible for the short chain-length of the polyacrylonitriles formed. Another remarkable feature of these experiments is that the number of electrochemical equivalents converted may be several orders of magnitude greater than the initial amount of salt; there must be a very effective regeneration of ions, and a very small amount of salt may initiate the polymerization of a practically unlimited amount of monomer.

In one experiment at 60°, a still higher current efficiency was found: about 400 moles of acrylonitrile were polymerized per electrochemical equivalent; $[\eta] = 5.5$ ml/g; polymerization also occurred at –70° with the same current (5 mA). In a mixture of equal volumes of acrylonitrile and methanol (or ethanol), polymerization was completely inhibited. The presence of small amounts of water causes induction periods and reduces the current efficiency, especially at low current densities.

With platinum, copper, mercury, aluminium, silver, and lead, no noticeable influence of the electrode material on the polymerization could be observed.

With methyl methacrylate, the solubility of the tetra-alkylammonium salts was too low, but the addition of 15 to 20 per cent of *N*-dimethylformamide was sufficient to allow a current of 5 mA to be obtained with tetraethylammonium borotetrafluoride. In this case, after 40 h, about 1 g of polymer had been formed with a viscosity number $[\eta] = 8.4$. Here also a higher molecular weight portion with $[\eta] = 48.5$ was isolated.

Similar polymerizations were effected by the cathodic discharge of tetrapropylammonium, tetrabutylammonium, trimethylanilinium and cetylpyridinium ions.

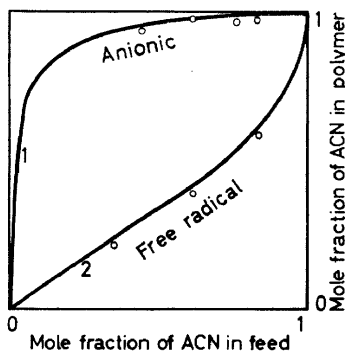
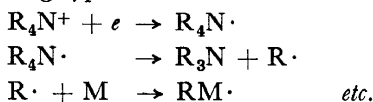


Figure 2. Copolymerization of acrylonitrile (ACN) and methyl methacrylate

At first, the mechanism of polymerization was thought to be a free radical mechanism of the following type:



However, since the addition of diphenylpicrylhydrazyl did not suppress polymerization, an ionic mechanism seems more probable. Some copolymerization experiments were carried out, therefore, to decide this point (see Table 3). The system acrylonitrile–methyl methacrylate was

Table 3. Copolymerization of acrylonitrile and methyl methacrylate, initiated by electrolysis of $(Et_4N)^+(BF_4)^-$ (initial current 10 mA)

Time of electrolysis (min)	Conversion of feed (%)	Molar fraction of acrylonitrile	
		In the feed	In the copolymer
150	0.40	0.45	0.95
75	0.19	0.62	0.98
65	0.15	0.76	0.98
120	0.30	0.83	0.98

investigated and the compositions of the copolymers obtained from different feeds were determined. These correspond clearly to an anionic mechanism, as can be seen by inspection of Figure 2. Curve 1 is calculated for an

ELECTROCHEMICAL INITIATION OF POLYMERIZATION

anionic mechanism according to Foster¹³. All four points fall very close to this curve. Curve 2 is calculated according to Lewis, Mayo and Hulse¹⁴ for a free radical mechanism. The points on this curve come from polymers obtained by electrolysis of lithium acetate at the anode.

An anionic mechanism can also explain the low molecular weights obtained. It has been shown¹⁵ that, in the anionic polymerization of acrylonitrile initiated by tetra-alkylammonium hydroxides, polymers with $[\eta] = 5$ are formed, and that this is due to an effective chain-transfer by the monomer.

DEPENDENCE OF POLYMERIZATION ON CURRENT DENSITY

During an electrolysis there was often a change in current due to changes in the electrolyte content and viscosity of the solutions, and to coating of the electrode by the polymer.

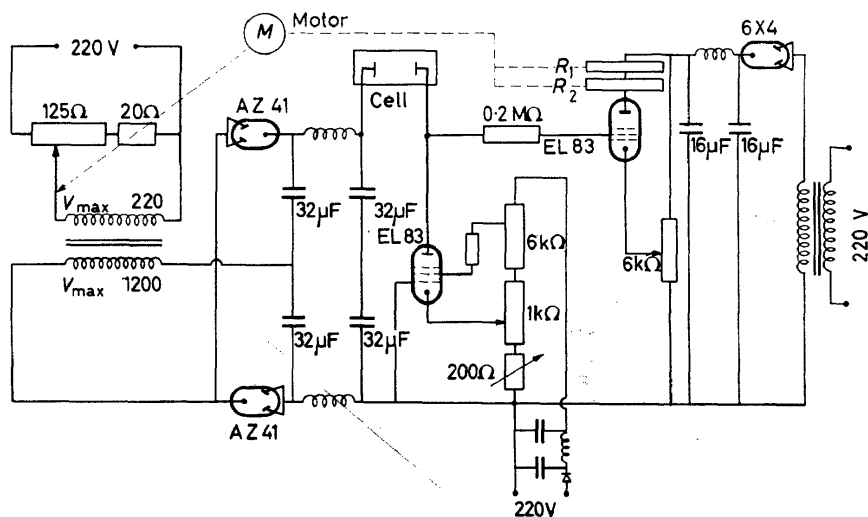


Figure 3. Current stabilization main circuit diagram

For quantitative kinetic measurements, an apparatus was constructed to keep the current automatically at a certain value. Figure 3 gives the wiring diagram for this apparatus. It consists principally of a motor-driven potentiometer which gives a variable voltage up to 220 V. This voltage is transformed (up to 1,200 V) and rectified. Direct currents up to 50 mA can be used. A valve and two relays are used to keep the motor driving the potentiometer at a standstill for a chosen current value, and to let it turn in two opposite directions at lower and higher currents respectively.

In Figure 4, some conversion curves are given for different currents in homogeneous systems (5 ml acrylonitrile + 20 ml *N*-dimethylformamide). The yields of polymer go up to 42 per cent. This means that up to 330 moles of monomer have been polymerized per initial mole of salt. The plot of initial rate against current is linear (see Figure 5), but does not go through the

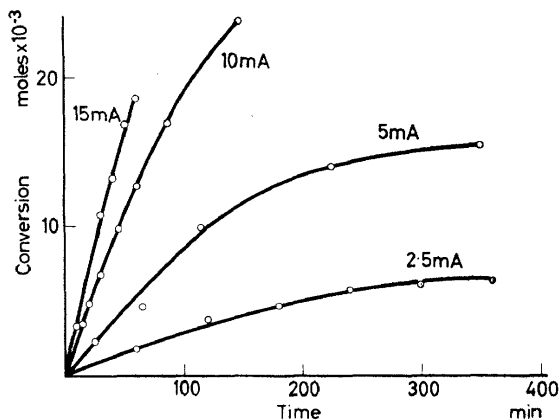


Figure 4. Cathodic polymerization of acrylonitrile

origin. The intercept is nearly 1 mA, and it was confirmed experimentally that, with currents below 1 mA, no polymerization occurred under these conditions. It is assumed that, in our systems, 1 mA is used up by non-initiating electrode processes, *e.g.* the electrolysis of water. It must be stressed that the rate of polymerization shows a pronounced dependence on the presence of very small amounts of water in the medium. Therefore, the data in *Figure 4* have only a poor reproducibility.

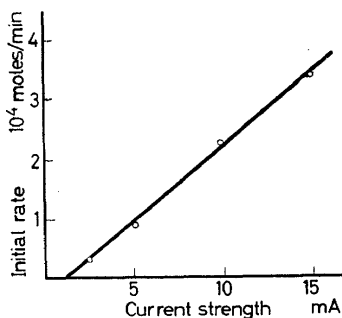


Figure 5. Variation of initial rate with current

POLYMERIZATION BY FREE RADICALS GENERATED AT THE ANODE

The initiation of a free radical polymerization at the anode by electrolyzing an acetate solution has already been illustrated in *Figure 2*. Similar results were obtained in the system styrene–methyl methacrylate: the curve in *Figure 6* is plotted according to Lewis, Mayo and Hulse¹⁴ for a free radical mechanism.

Polymerization was also carried out with single monomers. *Table 4* gives some results with acrylonitrile, methyl methacrylate and styrene.

ELECTROCHEMICAL INITIATION OF POLYMERIZATION

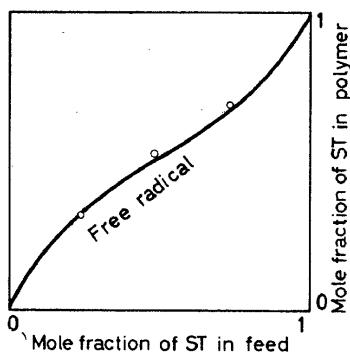


Figure 6. Copolymerization of styrene (ST) and methyl methacrylate

Table 4. Anodic polymerization by electrolysis of acetate solutions (free radical mechanism)

Monomer	Time of electrolysis (h)	Current (mA)	Moles monomer polymerized per electrochemical equivalent	$[\eta]$ (ml/g)
Acrylonitrile*	23	0.07	1	100
Methyl methacrylate*	4	7	10	104
Styrene†	15	3	0.8	27

* Composition of initial solution: monomer, 25 ml; acetic acid, 5 ml; acetic anhydride, 5 ml; saturated with lithium acetate.

† Composition of initial solution: monomer, 18 ml; acetic acid, 5 ml; acetic anhydride, 13 ml; saturated with lithium acetate.

In the case of methyl methacrylate, the free radical nature of the polymerization was also demonstrated by the inhibiting action of diphenylpicrylhydrazyl. In the experiments shown in Table 4, very high molecular polymers were formed. The current efficiencies (moles of polymer per faraday) are, therefore, very low, being of the order of 10^{-2} , in contrast to those found in cathodic anionic polymerization. This indicates that polymerization initiation is only a minor reaction of the primary radicals formed at the anode.

CATIONIC MECHANISM

Surprising results were obtained in the copolymerization of acrylonitrile and styrene initiated by electrolysis of tetraethylammonium borotetrafluoride (see Figure 7). The free radical and the anionic curves were plotted according to Lewis, Mayo and Hulse¹⁴ and Zutty and Welch¹⁶ respectively. Whereas the polymers of compositions 2 and 3 could possibly be the result of superposition of an anionic and a free radical mechanism, this seemed impossible for point 1. Experiments with a three-compartment vessel showed the simultaneous occurrence of polymerization in the cathode and anode compartment. The polymers of a feed corresponding to 2 were isolated separately and their composition is given by 2a and 2c. Thus the superposition of an anionic and a free radical mechanism is confirmed.

In a run on a feed corresponding to 1, there was practically no polymerization at the cathode, and the only possible explanation is the occurrence of a cationic polymerization (according to Walling, Mayo *et al.*¹⁷) in addition to the free radical process.

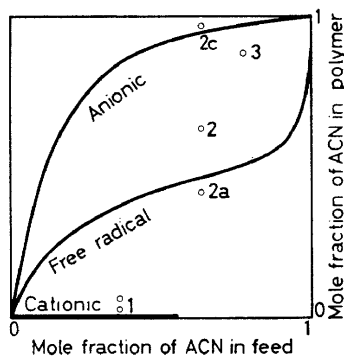


Figure 7. Copolymerization of acrylonitrile (ACN) and styrene

For the cationic polymerization of styrene, acrylonitrile is a bad solvent owing to its electron-donating character; so it was thought that better polymerization yields might be obtained in more suitable solvents. Nitrobenzene proved to be very useful both for styrene and for other monomers (Table 5). isoButyl vinyl ether and *N*-vinylcarbazole gave a good yield of

Table 5. Anodic (cationic) polymerization in nitrobenzene solution

Monomer	Monomer (vol %)	Electrolyte	Current (mA)	Time (min)	Yield of polymer (g)	$[\eta]$ (ml/g)
Styrene	64	$(Et_4N)^+(BF_4)^-$	0.35	60	0.86	9
isoButyl vinyl ether	67	$(Et_4N)^+(ClO_4)^-$	10	3	4.93	7.5
<i>N</i> -Vinylcarbazole	14	$(Et_4N)^+(ClO_4)^-$	2	5	1.20	9.1

low molecular weight polymers. In similar experiments, an oily polymer was obtained from α -methylstyrene only after much longer electrolysis and with a very low current efficiency, but no polymerization took place with vinyl acetate. Tetraethylammonium perchlorate was sufficiently soluble in *N*-vinylpyrrolidone without the addition of nitrobenzene, and, on electrolysis of the solution, an oily (probably dimeric) product was formed at the anode.

Some electrolysis experiments in styrene and isobutyl vinyl ether were carried out with silver perchlorate. Silver perchlorate has two advantages: it is soluble in the pure monomer without addition of any solvent; and it leads to the deposition of metallic silver (which does not interfere with the growing chains in the solution) at the cathode.

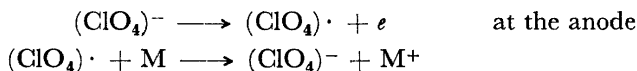
Electrolyses carried out with silver perchlorate in the pure monomer, or in the presence of nitrobenzene, showed remarkable current efficiencies.

ELECTROCHEMICAL INITIATION OF POLYMERIZATION

It was possible to polymerize 3.7×10^{-8} moles of styrene by the passage of 3×10^{-6} faradays. In the case of isobutyl vinyl ether, even 2×10^{-7} faradays effected violent polymerization of 10^{-1} moles of monomer during electrolysis with the strong evolution of heat. Without cooling the electrolyte, a dark-green semi-solid rubber-like material was obtained. *N*-Vinylcarbazole is solid at room temperature and can only be polymerized in a solvent. Its reactivity in nitrobenzene solution lies between that of styrene and that of isobutyl vinyl ether.

The viscosity numbers of the polymers are in the order of 5–10 ml/g, irrespective of whether nitrobenzene is present or not. In the case of styrene about 20 polymer chains are generated per discharge. *N*-Vinylcarbazole and isobutyl vinyl ether show a similar behaviour. These facts strongly support an effective chain-transfer with the monomer. A similarly high chain-transfer in the polymerization of isobutyl vinyl ether with Friedel-Craft catalysts (99 per cent of the polymer terminated by chain-transfer) was found by the use of labelled diethyl ether as a co-catalyst¹⁸.

All these experiments prove a cationic mechanism for the polymerization quite conclusively. The mechanism of initiation might be of the following type:



with a cationic growing chain.

The presence of a very active species in the electrolyzed solution was proved by a remarkable after-effect. A mixture of 1 ml styrene and 10 ml nitrobenzene containing silver perchlorate was electrolyzed with 15 mA for 1 min at the melting temperature of nitrobenzene. Then the current was interrupted, and, after 3 min a solution of 3 g *N*-vinylcarbazole in 5 ml nitrobenzene was added. A strong evolution of heat was observed, and, by precipitation with methanol, 3.3 g of polymer was isolated. Thus it seems possible that something like "living" polymers are produced in a cationic system. This, of course, has to be proved by further experiments. Not only in this, but also in most other respects, we are at the very beginning of our studies in this field, but I hope to have shown here that a broad field has been opened up.

Summary

A short review is given of the existing work on the initiation of polymerization by electrolysis. The possibility of initiating polymerization of unsaturated compounds by discharging suitable ions at an inert electrode is well established. Free radical mechanisms have been generally proposed for this polymerization. In the present work, a study of the polymerization mechanism has been carried out by the copolymerization method, and it has been shown that the reaction mechanism depends on the ions used in the electrolytic discharge, and on the monomer present in the system.

The discharge of tetra-alkylammonium ions at the cathode in the presence of acrylonitrile gives an anionic polymerization of acrylonitrile. Some conversion curves for this type of reaction are reported. High current efficiencies are observed, and the number of polymer molecules formed is several orders of magnitude greater than the initial amount of salt.

Cationic processes are initiated in a solution of styrene in nitrobenzene by the anodic discharge of perchlorate and borotetrafluoride ions. Free radical copolymerization of acrylonitrile and methyl methacrylate is initiated by discharge of acetate ions in acetic anhydride

solution, but polymerization initiation seems to be only a minor reaction of the primary radicals formed at the electrode.

Under suitable conditions the three different mechanisms occur simultaneously in the same system. This is demonstrated in the system acrylonitrile-styrene by using a diaphragm to divide the electrolytic cell into separate compartments. With anodic cationic polymerization, there is a remarkable after-effect.

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