

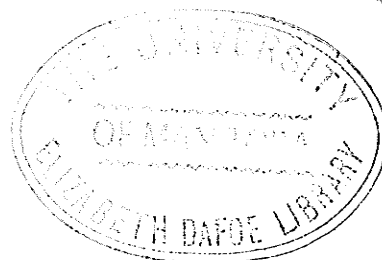
ELECTRODEGRADATION AND ELECTROPOLYMERIZATION
OF METHACRYLIC ACID
AND DERIVATIVES

Presented by
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Faculty of Graduate Studies and Research
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To my Parents

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LIST OF ABBREVIATIONS

MONOMERS:

AAm	acrylamide
AA	acrylic acid
AcN	acrylonitrile
BU	buta - 1,3 - diene
ET	ethylene
FCET	fluorochloroethylenes
IS	isoprene
MAA	methacrylic acid
MA	methyl acrylate
MMA	methyl methacrylate
ST	styrene
VAC	vinyl acetate
VC	vinyl chloride
VP	vinyl pyrrolidone

POLYMERS:

PAAm	polyacrylamide
PMA	poly(methacrylic acid)

INITIATORS:

AIBN	α, α' - azobisisobutyronitrile
Bz ₂ O ₂	benzoylperoxide

SOLVENTS:

Ac ₂ O	acetic anhydride
DMF	N,N- dimethylformamide
DMSO	dimethyl sulfoxide
H Ac	acetic acid
Pr Gl	propylene glycol

ELECTRODES:

+	anode
-	cathode

OTHER SYMBOLS:

A ⁻	anion
AC	alternating current
B	undesignated molecule
C ⁺	cation
DC	direct current
e	electron
M	monomer molecule
M•	monomer radical
Me	metal
η_{sp}	specific viscosity
η_{sp}/C	reduced specific viscosity (viscosity number)
$[\eta]$	intrinsic viscosity
N	neutral molecule
P _s , P _t	dead polymer molecules where s and t are the number of repeating units in the molecule

$R_s \cdot, R_t \cdot$	living polymer radicals where s and t are the number of repeating units
$R \cdot$	primary radical (generated in a primary electrode process)
S	solvent
$\sim C$	extended polymer chain

ABSTRACT

ELECTRODEGRADATION

A study of the electrolytically induced degradation of aqueous solutions of poly(methacrylic acid) and of polyacrylamide was made.

Three samples of poly(methacrylic acid) were prepared - two by thermal methods and one in an electroinitiated polymerization - and subjected to electrolysis at various constant currents. The viscometric behavior of the polyacid solutions as a function of electrolysis time was found to be dependent on the preparative history of the polymer. A sample of completely neutralized peroxide-initiated polymer, made thermally, underwent a dramatic reduction in viscosity during electrolysis. A sample of electroinitiated poly(methacrylic acid) underwent a comparatively little change in viscosity. For a sample of the polyacid, prepared thermally using α, α' -azobisisobutyronitrile, measurements of carbon dioxide evolution, unsaturation, viscosity, molecular weight, pH and total acidity were made as a function of duration of electrolysis and current density. The unneutralized polymer solution, initially containing an apparently large number of unsaturated links, evolved carbon dioxide at the anode, while the viscosity, molecular weight, and degree of unsaturation decreased. The total acid content of the solution increased whereas the pH remained essentially constant throughout the electrolysis. A degradative mechanism involving the generation of macroradicals by a Kolbe electro-synthesis was postulated. Anodically generated oxygen which pro-

bably led to hydroperoxide intermediates was believed to be important in the degradation.

The viscosity of aqueous solutions of polyacrylamide was measured as a function of electrolysis time, current density and initial polymer concentration. Potassium acetate was added to the solution in most of the electrolysis experiments. In such cases, a Kolbe oxidation of the low molecular weight carboxylate anion produced free radicals which were believed to initiate a degradative process.

ELECTROPOLYMERIZATION

A study of the electroinitiated polymerization of methacrylic acid in a homogeneous aqueous solution was also undertaken. A series of preliminary experiments explored the reaction conditions suitable for the polymerization process. A kinetic study of the variation of monomer concentration, determined in a bromometric titration, with the duration of electrolysis was made at a given current density in buffered solutions. An irreproducible and highly inefficient linear decrease of monomer concentration with time was observed.

CHAPTER I

INTRODUCTION

PURPOSE OF THE RESEARCH

It is well established that free radicals generated electrolytically are able to induce the polymerization of vinyl monomers. It is not so thoroughly established, however, that free radicals similarly produced, may interact with dead polymer molecules and consequently modify their chain structure. The purpose of this research was to study both of these free radical processes in a homogeneous aqueous medium.

Several reactions are conceivable when dead polymer solutions are subjected to high radical concentrations generated at the electrodes. On the one hand, aggregative processes such as chain transfer, chain branching and cross-linking could be promoted. Epstein and Bar-Nun¹, for example, succeeded in electrografting methyl methacrylate on to cellulose and F. D. Williams² reported an increase in the solution viscosity of poly (methacrylic acid) upon electrolysis. On the other hand, disaggregative processes such as chain scission and depolymerization are possible. Smets^{3,4}, for example, degraded poly(methacrylic acid) solutions by electrolytic means. A compromise situation of a simultaneous occurrence of both aggregative and disaggregative processes, perhaps with a predominance of one over the other, cannot be overlooked. The first

and main objective of this research was to study the behavior of polymer solutions subjected to electrolysis.

The second aim of this research was to study electroinitiated free radical polymerization processes in homogeneous aqueous media, exploiting, if feasible, the advantages of not only aqueous systems to physiochemical measurements, but also of homogeneous systems to kinetic studies. All reported radical polymerizations in aqueous media were heterogeneous in character until Smith and Manning⁵ apparently obtained a good yield of poly(methacrylic acid) by a homogeneous reaction. Soviet workers show continued interest in free radical processes as evidenced by their numerous publications in recent literature.

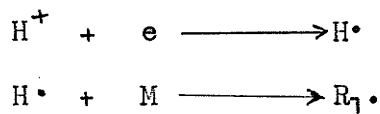
The Kolbe electrosynthesis provides a convenient source of radical species to study these processes. Low molecular weight monocarboxylic acids undergo anodic oxidation to produce intermediate free radicals which may attack vulnerable links of a dead polymer chain or, conversely, may initiate the polymerization of monomeric species. Furthermore, the Kolbe electrolysis of poly(carboxylic acids) provides a unique source of macroradicals which may initiate either degradative or aggregative reactions of the polyacid solutions.

REVIEW OF ELECTROINITIATED FREE RADICAL POLYMERIZATION PROCESSES

Historically, the first successful electroinitiated polymerization by a free radical mechanism was reported in 1949 whereas ionic polymerizations induced by electric currents remained unknown until 1957. Thus the early literature was devoted entirely to radical pro-

cesses. German and American researchers published most of the early reports while the more recent Russian publications indicate continued interest in this field. Table 1.1 reviews historical developments in a chronological manner.

In 1949, using H_2SO_4 in aqueous methanol as an electrolyte, Wilson⁶ successfully polymerized acrylic acid, methylacrylate, and methyl methacrylate at a Hg cathode. It was deduced that polymerization was initiated by a primary electron transfer at the cathode or some closely related process. The mechanism of polymerization initiation was believed to involve hydrogen radicals generated at the cathode:

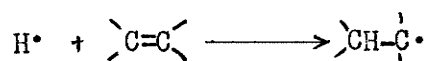


The effectiveness of the electrode metal for inducing polymerization was, with few exceptions, compatible with the overvoltage sequence.

One year later, Palit and Das⁷ produced highly crosslinked poly(methyl methacrylate) using propylene glycol as solvent. Sodium acetate was used as electrolyte and it was believed that polymerization at the cathode may have been due to initiation by sodium or hydrogen atoms.

In 1951, Parravano⁸ reported that metals loaded with hydrogen, either electrolytically or by processes of chemisorption, initiate the polymerization of aqueous solutions of methyl methacrylate. Sulfuric acid

was used as electrolyte. The efficiency of the initiation process was extremely small in terms of total hydrogen produced or present, being of the order of 10^{-8} . In agreement with Wilson's results, the effectiveness of the cathode material paralleled hydrogen overvoltage of the metal. The mechanism either involves an escape of hydrogen atoms from the cathode to the methyl methacrylate solution,

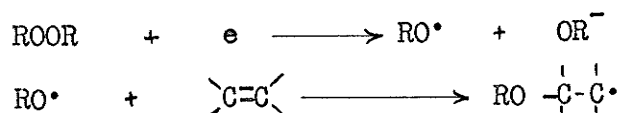


or a reaction of monomer molecules with hydrogen atoms adsorbed on the electrode surface and liberation of monomer radicals to the solution,



Parravano makes the surprising postulate that polymer radicals stay alive over a period of hours. He observed polymerization in monomer solutions inoculated with the cathode liquor for several hours after the current was stopped.

In the same year, Kolthoff and Ferstandig⁹ polymerized acrylonitrile by passing an electric current through solutions of perdioxy compounds. Very small yields were obtained in the electroreduction of H_2O_2 , $\text{K}_2\text{S}_2\text{O}_8$ and cumene hydroperoxide according to the scheme:



However, extremely large yields (1.3×10^3 moles AcN polymerized per mole of Fe^{++} ion produced) were obtained using free radicals formed in a secondary reaction which is dependent on a primary reaction at the

HEMICAL FREE RADICAL POLYMERIZATION PROCESSES

<u>E</u>	<u>ELECTRODE MATERIAL</u>	<u>LOCUS*</u>	<u>MECHANISM</u>	<u>REF</u>
	Hg	-	H•	(6)
	Pt	-	H• or Na	(7)
	Pt	-	H•	(8)
+	Pt	-	perdioxy	(9)
	Pt	+	Kolbe	(10)
		-	H•	(11)
lts		+ & -	no polymer	(12)
	Ni-Al		radical	(13)
	Pt ⁺ /Ag ⁻	+	Kolbe	(14)
	C		radical	(15)
l	Pt	-	radical	(16)
	Pt	+	dimers	(17)
	Pt	+	dimers	(18)

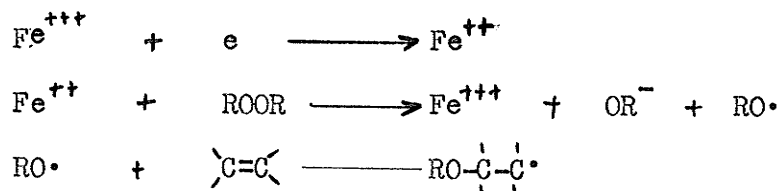
(continued)

Table 1.1: Electrochemical Free Radical Polymerization Processes (continued)

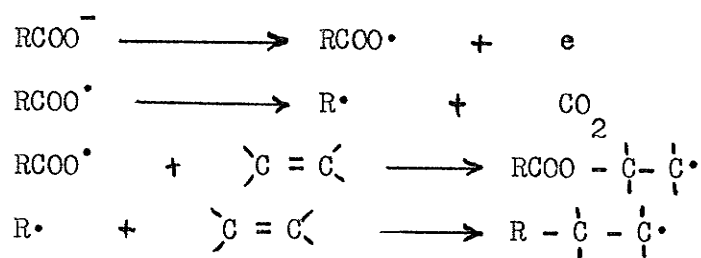
<u>YEAR</u>	<u>MONOMER</u>	<u>MEDIUM</u>	<u>ELECTROLYTE</u>	<u>ELECTRODE MATERIAL</u>	<u>LOCUS*</u>	<u>MECHANISM</u>	<u>REF</u>
1960	MMA, VAc, VC	water	CH_3COO^-	Pt	+	Kolbe	(19)
1961	MA	water	H_2SO_4	Pt^+/Hg^-	-	HO_2^\bullet	(20)
1961	MA	water	HCl	Pt^+/Pb^-	-	H^\bullet	(21)
1962	AcN, MA, ST	HAc, Ac_2O	CH_3COO^-	Pt	+	Kolbe	(22)
1962	MMA	DMSO	CH_3COO^-	C	+	Kolbe	(23)
1962	AA	water	CH_3COO^- , CdCl_2	Pt	+	Kolbe	(5)
1963	VP	CH_3OH	CH_3COO^-	Pt	+	Kolbe	(24)
1963	MMA, ST	water	HCl, NaCl	Pt^+/Pb^-	-	H^\bullet	(25)
1964	MMA	DMSO, DMF	tagged NaAc	Pt	+	Kolbe	(26)
1964	MMA	water	H_2SO_4	Pd^+/Hg^-	-	peroxide	(27,28)
1964	BU	water	NaAc	Pt	+	BU adsorbed no polymer	(29)
1964	AAm	water	$\text{K}_2\text{S}_2\text{O}_8$	Pt	-	$\text{SO}_4^{\bullet -}$	(30)

* Locus of Polymerization

electrode:



One year later, Goldschmidt and Stockel¹⁰ obtained semi-colloidal polystyrene of molecular weight 3200 by a Kolbe electrolysis in a sodium acetate-acetic acid system. Yields at the anode were poor with the main products being dimers and trimers. The initiation mechanism follows the scheme:



In 1953, the German chemists, Kern and Quast¹¹, were able to polymerize methyl methacrylate, acrylonitrile, acrylic acid and methyl acrylate by the cathodic generation of hydrogen atoms using 1/10 N HCl as solvent. The reaction was inhibited by oxygen and hydroquinone indicating a free radical mechanism. These workers agree with Parravano that the reaction occurs between species adsorbed on the metal surface.

In the same year, Marvel and coworkers¹² investigated several reactions, cathodic and anodic, which should produce free radicals. The intermediates formed at the electrodes were too transient to react with styrene in aqueous solutions.

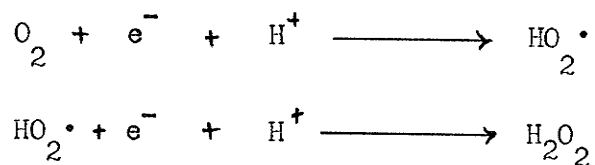
Patent literature in the period 1955-58 contains examples of highly efficient electroinitiated polymerizations. Goerrig, Jonas and

Moschel^{13,14} reported the polymerization of fluorochloroethylene monomers and Gehrke and Feckenheim¹⁵ polymerized ethylene at carbon electrodes under high pressure. Loveland¹⁶ polymerized ethylene at platinum electrodes at atmospheric pressure.

In 1958, Lindsey and Peterson¹⁷ generated radicals in a Kolbe electrolysis which attacked 1,3-dienes to give butenyl radicals which dimerize or react with other radical species at the anode. These free radical synthesis reactions were termed electrochemical additive dimerizations. No high polymers were formed.

Smith and Gilde¹⁸, in 1959, electrolyzed methanolic solutions of potassium acetate in the presence of butadiene and isoprene. Both methyl and acetoxy radicals added to the acceptor monomer molecules and dimers resulted. The following year, these authors¹⁹ reported the polymerization of vinyl acetate, methyl methacrylate and vinyl chloride in aqueous solutions of potassium acetate. Divided cell experiments showed the anode to be the locus of polymerization. Electrolysis of potassium acetate -2-C¹⁴ produced radioactive polymer indicating initiation by both acetoxy and methyl radicals. Coating of the polymer on the electrode stopped the reaction, illustrating the disadvantages of heterogeneous effects. In some cases, ethyl alcohol was added to increase the solubility of the monomer and polymer.

In a paper published in 1961²⁰, Federova and coworkers dramatically demonstrated the importance of electrode potential and the role of oxygen in electrochemical initiation. Methyl methacrylate was polymerized in acid solutions at a mercury cathode by electrolytic reduction of oxygen, which in acid environment takes place as follows:



Oxygen is claimed to have a dual role:

1) initiation of polymerization by intermediate

$\text{HO}_2 \cdot$ radicals.

2) inhibition of propagation.

In the same year, Tsvetkov²¹ studied the polymerization of methyl methacrylate by cathodic hydrogen in a heterogeneous system. The polymerization was accelerated by an increase in size of the cathode, in current density and in reaction temperature. Furthermore, they showed that stirring the reaction mixture retards the rate and degree of polymerization considerably. This effect is presumably due to an increased rate of coalescence of polymer particles containing active chains. These workers also reported a very peculiar and remarkable after-effect. Polymerization occurred up to six hours after the current was switched off, after which time no radicals could be formed electrochemically. An after-effect is described as that non-stationary state involving the decay of radical concentration as soon as the initiating reaction is stopped. Clearly, Tsvetkov's observation is out of harmony with our conventional ideas of average lifetimes of free radicals, ordinarily being in the neighbourhood of a few seconds or less. This phenomenon was also reported by other workers. Parravano⁸ produced polymer radicals which continued to add monomer units over a period of hours away from the initiation center. Kern and Quast¹¹ reported a post-polymerization which could be arrested

by molecular oxygen, hydroquinone and picric acid. A similar effect was reported by Brietenbach²² in an anodic cationic polymerization of styrene in nitrobenzene. None of these workers attempted to offer an explanation for this phenomenon. Perhaps the large living polymer radicals become stabilized, by a decreased mobility relative to monomer and other low molecular weight species, in the viscous matrix, bimolecular chain termination being retarded. A more likely explanation in the case of the radical processes is a subsequent thermal decomposition of peroxidic materials. In the cationic case, perchloric acid may be initiating the after-polymerization.

Several significant publications appeared in 1962. Breitenbach²² produced high molecular weight polymers at the anode by electrolysis of acetate solutions of acrylonitrile, methylmethacrylate, and styrene. Current efficiencies were of the order of 10^{-2} and the radical nature of the polymerization was demonstrated by inhibition with diphenylpicrylhydrazyl.

Funt and Yu²³ studied the rate of polymerization of methyl methacrylate in a homogeneous organic medium of high dielectric constant. The yield of polymer was proportional to the electrolysis time and current density. The influence of the nature of the salt and electrode material was conveyed and the molecular weight varied inversely as the current density. The fact that radical inhibitors retard rather than stop the reaction suggests an ion-radical mechanism.

Smith and Manning⁵ reported that acrylic acid could be polymerized in good yield by a Kolbe mechanism. They used potassium acetate and cadmium chloride as their electrolytes. This is probably the first and only report of a completely homogeneous polymerization in aqueous medium.