THE ELECTROLYTICALLY INITIATED POLYMERIZATION

OF STYRENE

presented by

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A Thesis Submitted to the

Faculty of Graduate Studies and Research

in Partial Fulfillment of the

Requirement for the Degree of

Master of Science

University of Manitoba

April 1964

To Mr. Eugene C. Laurent

ACKNOWLEDGMENTS

ABSTRACT

Styrene was polymerized by electrolysis of solutions containing monomer and alkali metal nitrates in dimethylformamide. Potassium nitrate was found to give the highest yields of polymer. The polymerization reaction was studied with this salt as a function of current, monomer concentration, and time. The anionic nature of the polymerization mechanism was established by a polymerization and inhibitor studies. The molecular weights were obtained and found to have number average values in the range from 2000 to 5000.

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INTRODUCTION

The electrolytic initiation of polymerization did not attract much interest until the last decade, although the production of free radicals by the electrolysis of carboxylic acid salts was known as early as the mid 19th century (1). The Kolbe reaction was not used as a method of polymer initiation until 1949 (2). The initiating species in the first studies (2) (3) (4) were found to be hydrogen ions. The effectiveness of the alkyl free radicals as initiators was not demonstrated till 1952 (5). Free radical, anionic, and radical anion processes have since been identified as polymerization electrode reactions (6) (7).

The attractive feature of this mode of initiation is the control which it offers. The ability of electrical processes to be programmed, varied and measured and the inherent simplicity of the electrode processes contribute to the interest of electrolytic initiation.

The most successful application of the electro-initiation process has been the polymerization of halo-olefins (8). Previous methods of polymerization required that olefins such as tetrafluoro ethylene and trifluorochloroethylene be subjected to high temperatures and pressures for initiation of high molecular weight polymers.

The electro-initiation may be carried out under normal

conditions by the electrolysis of trifluoroacetic acid in the presence of its potassium salt and the halo-olefin monomer. The initiating species is CF_3.

Similar results have been obtained by electrolysis of potassium fluoride and hydrofluoric acid in the presence of halo-olefins (9). In this reaction F· is the initiating species.

The object of this project was to study the system styrene monomer and KNO_3 in dimethylformamide. The reports of previous investigations of styrene systems are few and their authors' interests were mainly the formation of polymer as a proof of an initiation mechanism.

A brief review of the papers published in the electro-lytic field and a description of the anionic initiation mech-anisms follow.

A REVIEW OF THE ELECTROLYTIC INITIATION OF POLYMERIZATION

Free radical initiation is due to a number of varied initiators. Polymerization due to the discharge of H· atoms at the cathode has been reported by several authors. The electrolytic reduction of acidic solutions usually produces H· atoms which react with the monomer to initiate polymerization. There are reports of the polymerization of methyl methacrylate (2) (3) (4) (10), methyl acrylate (2) (4), methacrylic and acrylic acids (2) (4), as well as acrylonitrile (4), by this method.

Some authors report an aftereffect of continued polymerization after the current has been stopped. Tsvetkov (10) reports an after-polymerization which he claims is due to cathodic hydrogen. His results show a reduction of yield on stirring and a decrease in aftereffect on lengthening electrolysis time due to agitation by gases released at the cathode. In many cases a dependence of the efficiency of the H· initiation has been found to vary with the over-voltage of the cathode metal (1) (3) (4). The metals of the series Pb, Sn, Hg, Pt, Bi, Fe and Al are increasingly effective as cathode material in the order given. Other metals with which polymerization does not occur are Cu, Cd, Ni, W, Ta, Mo, Cr, Ag and Zn. The reason for the varied activity of the H· atoms is probably the varying over-voltages of the metals. The H·

released from the cathode of the highest over-voltage is the
most reactive.

A second type of radical polymerization is due to the
production of radicals at the anode by a Kolbe electrolysis
of acetates in acidic or methanolic solutions. Alkyl R$\cdot$ or
alkoxide $R - C \overset{\displaystyle O}{\diagup} - O\cdot$ free radicals are produced at the anode
and diffuse into the solution to initiate polymerization.
The polymerization of styrene (5), acrylonitrile (6), methyl
methacrylate (6) (11), vinyl acetate (11), vinyl chloride (11),
and vinyl pyrrolidone (12), have been reported. These systems
are complicated by the coating of the anode with polymer caus-
ing the flow of current to cease. In the case of vinyl pyr-
rolidone current flow did not cease but the polymer coating
trapped the radicals and polymerization ceased.

Similar free radical initiation in homogeneous solu-
tions has produced high molecular weight polymer without
cessation of current. The salt used was Zn acetate in non-
aqueous media such as dimethyl sulphoxide and dimethylformamide,
which have high dielectric constants. The rate of polymer-
ization of methyl methacrylate varied directly with current
density while the molecular weight of the polymer varied in-
versely with the current density (13). The kinetics indicate
the formation of radicals at the electrode which diffuse into
solution initiating polymerization. An increase in current
density results in a corresponding increase in the number of

radicals formed. Thus the molecular weight of the polymer decreases as the number of growing chains increases and monomer concentration remains constant.

There are fewer examples of polymerization by an anionic mechanism. Breitenbach (14) first reported the polymerization of acrylonitrile by electrolysis of tetraethyl-ammonium perchlorate as a free radical polymerization. Later studies (6) using copolymerization analysis showed the mechanism to be anionic.

A more detailed study of the anionic polymerization of acrylonitrile in the presence of $NaNO_3$ in dimethylformamide was reported (15). The polymerization of methyl methacrylate and styrene in dimethylformamide in the presence of inorganic salts was also reported (15). The acrylonitrile system was studied intensively and the initiation mechanism was proposed to be direct electron addition to monomer. The author suggests that initiation of the monomers methyl methacrylate and styrene follows the same mechanism and also is independent of the salt present. The difficulty in carrying out polymerization of styrene and methyl methacrylate is attributed to the reversibility of the initiation step.

$$\text{CH}_2\!=\!\underset{\underset{\text{OCH}_3}{|}}{\overset{\overset{\text{CH}_3}{|}}{\text{C}}}\!\!\overset{\nearrow^O}{\text{C}} \quad +e^- \;\rightleftarrows\; \cdot\text{CH}_2\!-\!\underset{\underset{\text{OCH}_3}{|}}{\overset{\overset{\text{CH}_3}{|}}{\text{C}}\!:}^-\overset{\nearrow^O}{\text{C}} \quad \rightleftarrows\; {}^-\!\!:\!\text{CH}_2\!-\!\underset{\underset{\text{OCH}_3}{|}}{\overset{\overset{\text{CH}_3}{|}}{\text{C}}\cdot}\overset{\nearrow^O}{\text{C}}$$

$$\text{CH}_2\!=\!\underset{\underset{\text{H}}{|}\,(\text{C}_6\text{H}_4)\,\overset{\text{H}}{|}}{\overset{\overset{\text{H}}{|}}{\text{C}}} \quad +e^- \;\rightleftarrows\; {}^\circ\text{CH}_2\!-\!\text{C}\!:^- \quad \rightleftarrows\; {}^-\!\!:\!\text{CH}_2\!-\!\text{C}\cdot$$

$$\text{CH}_2\!=\!\underset{\underset{\text{CN}}{|}}{\overset{\overset{\text{H}}{|}}{\text{C}}} \quad +e^- \;\longrightarrow\; \cdot\text{CH}_2\!-\!\text{C}\!:^- \quad \rightleftarrows\; {}^-\!\!:\!\text{CH}_2\!-\!\text{C}\cdot$$
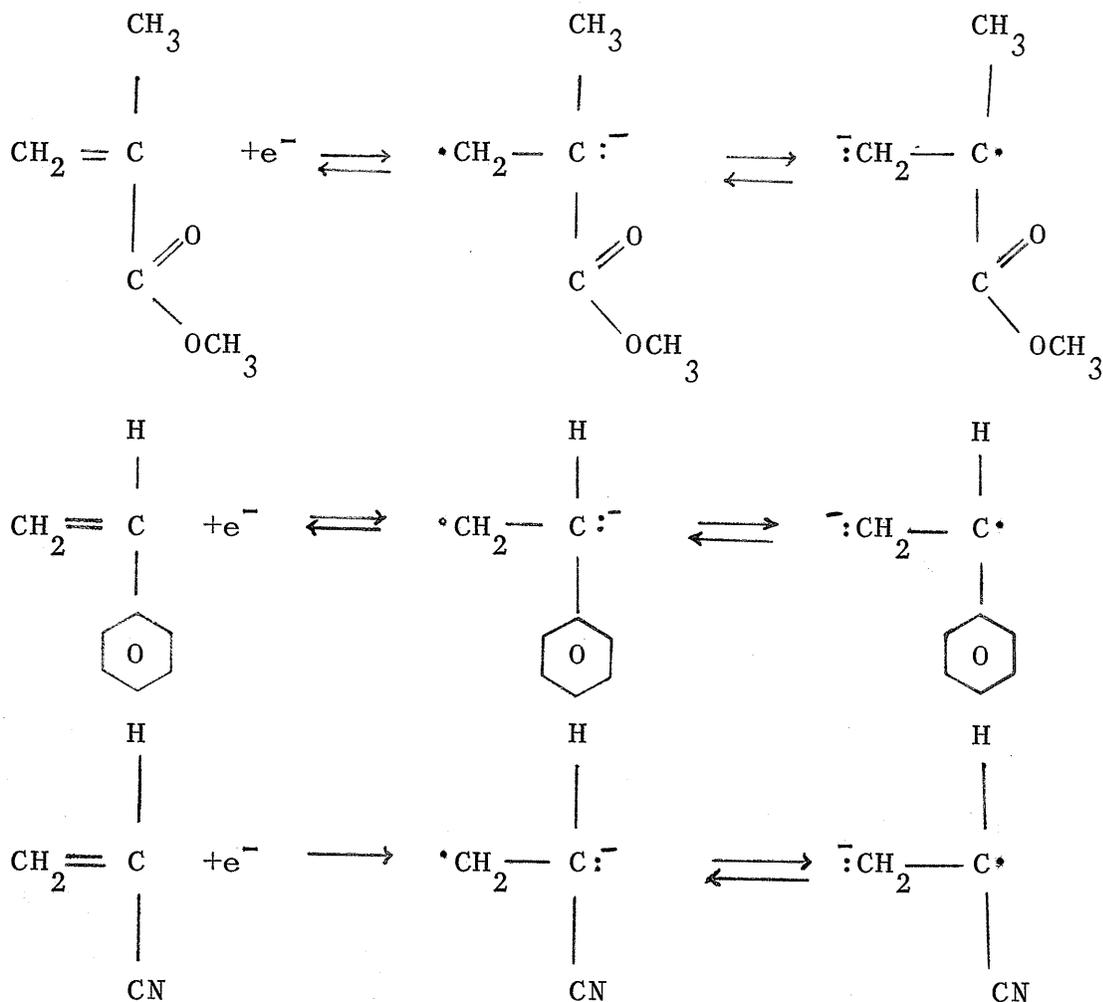
The reversibility is assumed from values of n--the number of electrons taking part in the reaction from the Ilkovic equation $E = E\,1/2 - (0.0591/n)\log(i_d - i/i) + K'$ (34). The order of their polarographic halfwave potentials is interpreted as the order of the ease of electron transfer to monomer, hence the ability to be polymerized. Polymers were obtained with acrylonitrile and dimethylformamide in the presence of the following salts: LiNO_3, KClO_4, SnCl_2, NaNO_3, NaCl and MgCl_2. The

polarographic data obtained with dimethylsulphoxide as
solvent indicate that styrene should polymerize if the initi-
ation mechanism is correct.

The polyacrylonitrile was reported to have a molecular
weight of approximately 4000. The low molecular weight was
thought to be due to chain transfer.

A Review of the Electrolytic Polymerizations of Styrene

The polymerization of styrene by the electrolytic
method has been mentioned briefly in the literature. In
1952 Goldschmidt and Stockel (5) reported the polymerization
of styrene during the electrolysis of fatty acid salts in
anhydrous fatty acids. The polystyrene was produced at the
anode. Analysis of low molecular weight products showed that
initiation was due to $CH_3 \cdot$ radicals. They reported a high
molecular weight of thirty-two hundred, yet termed the pro-
ducts semi-colloidal.

Styrene polymerization at the cathode was reported
in 1957 by Yang, McEwen and Kleinberg (16). The polymer was
formed in pyridine solution with NaI as electrolyte using
magnesium electrodes. The authors concluded that the styrene
was polymerized by direct electron addition because the poly-
mer was free of nitrogen. The polymers formed from addition
of styrene to pre-electrolyzed solutions of NaI in pyridine,
and from solutions of monomer in pyridine to which metallic

sodium was added, contained nitrogen. From these results
the authors concluded that in the latter cases the sodium
metal combines with pyridine to produce an organo-metallic
initiator. The molecular weights of the products were found
to vary from eighteen hundred at a current density of 0.004
amp. per sq. cm. to twenty-eight hundred at a current den-
sity of 0.007 amp. per sq. cm.

ANIONIC POLYMERIZATION

The anionic mechanism of polymerization is characterized by a number of properties:

1) the basicity of the catalyst.

2) the varied hues of the reaction mixture.

3) the termination of the reaction on the introduction of proton donating substances, e.g. water or methanol.

4) the inability of radical traps such as benzoquinone to affect the reaction.

5) the individual copolymer ratios which vary from those of the free radical and cationic mechanisms for the same monomer.

Anionic polymerizations may be divided into three categories which are dependent on the type of catalyst used as initiator. The catalyst in all cases is a negative fragment which may be either an ion or an electron. These categories are
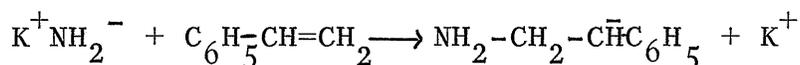
1) the conventional anionic system.

2) the metal-alkyl initiator systems.

3) the ion-radical systems.

1) The conventional anionic system

The conventional system is that of Higginson and Wooding (17) in which styrene is polymerized by KNH_2 in liquid ammonia. The mechanism postulated is consistent with
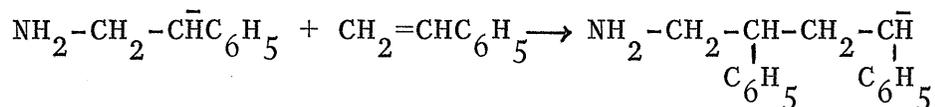
experimental data. The initiation is due to NH_2^- ion and K^+ ion exists in solution as a gegen ion, the role of which is not clearly defined.

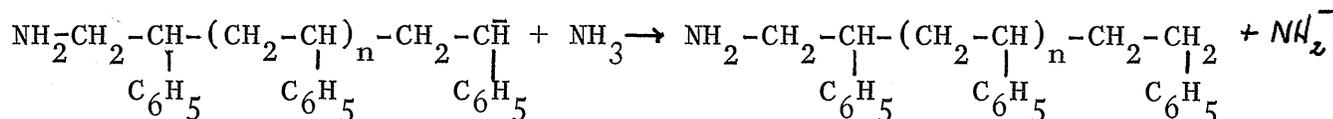The mechanism which seems best suited is the following (18):

Initiation

$$K^+NH_2^- + C_6H_5CH{=}CH_2 \longrightarrow NH_2{-}CH_2{-}\bar{CH}C_6H_5 + K^+$$

Propagation

$$NH_2{-}CH_2{-}\bar{CH}C_6H_5 + CH_2{=}CHC_6H_5 \longrightarrow NH_2{-}CH_2{-}\underset{C_6H_5}{CH}{-}CH_2{-}\underset{C_6H_5}{\bar{CH}}$$

Termination

$$NH_2^-CH_2{-}\underset{C_6H_5}{CH}{-}(CH_2{-}\underset{C_6H_5}{CH})_n{-}CH_2{-}\underset{C_6H_5}{\bar{CH}} + NH_3 \longrightarrow NH_2{-}CH_2{-}\underset{C_6H_5}{CH}{-}(CH_2{-}\underset{C_6H_5}{CH})_n{-}CH_2{-}\underset{C_6H_5}{CH_2} + NH_2^-$$

The rate of polymerization and the molecular weight of polymer increase with decreasing temperature. The role of the catalyst is such that the molecular weight is independent of catalyst concentration. The catalyst concentration is constant because each polymer chain regenerates one molecule of NH_2^- on termination. The rate equation of the reaction is

$$-d(\text{styrene})/dt = k(\text{styrene}) (KNH_2)^{1/2}$$

2) The metal-alkyl initiator systems

There are a number of metal-alkyls which will initiate polymerization. The mechanisms of initiation by butyl lithium, phenyl lithium, phenyl sodium and benzyl sodium (19)

depend on the nature of the solvent used. Stereoregular

polymers may result from these polymerizations.

Lithium metal is particularly effective in causing

stereoregularity. The effectiveness of lithium compounds

is attributed by Tobolsky (20) to the varying polarity of

the M-R bond where M is the metal and R the organic portion

of the initiator molecule. The view of Mark (21) is that

an ionic quadrupole, which orientates the addition of monomer,

is formed, i.e. $R_1-CH_2-\underset{\underset{R_2}{|}}{CH} \wedge\wedge CH_2-\underset{\underset{R_2}{|}}{\overset{-}{C}H} \ Li^+$

$$Li^+R_1^-$$
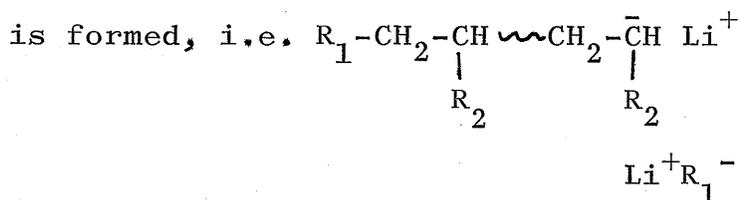
The solvent dependence of the type of polymer formed

suggests the ionic nature of these catalysts. The polymer-

ization of isoprene with n-butyl lithium gives the following

results (19).

Catalyst	Solvent	Configuration of Polymer			
		%1,2	%3,4	%cis 14	%trans 14
N-Butyl Li	n-heptane	0	7	93	0
N-Butyl Li	tetra-hydro-furan	16	54	0	30

There is also the possibility of association of the

initiator in some solvents. Butyl lithium in benzene may

associate with initiated growing polystyrene and result in

dormant chains (22).

The rate of polymerization in these systems may also