INHIBITION AND RETARDATION OF

ETHYL METHACRYLATE POLYMERIZATION

AND

ELECTROLYTICALLY INITIATED POLYMERIZATIONS

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To my Grandparents

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ABSTRACT

INHIBITION

Combination of C¹⁴-tagged or inactive benzoquinone with tagged or inactive azobisisobutyronitrile was used to study the kinetics of polymerization of ethyl methacrylate. The course of the reaction was followed by dilatometry, and the resultant polymers were assayed for C¹⁴ content by liquid scintillation techniques. Molecular weights were obtained by osmometry in order to determine the number of tagged fragments per polymer molecule. A transition from a retarded polymerization to one showing an inhibition period was found at a critical concentration of p-benzoquinone. This transition was accompanied by a marked change in the C¹⁴ content of the polymers. The magnitude of chain transfer or copolymerization was directly estimated from the number of tagged fragments incorporated per polymer molecule. These indicated that no more than two molecules of p-benzoquinone could copolymerize or that a limit could be set of one chain transfer step per kinetic chain. Hence, neither, of these processes can be considered as highly significant in the mechanism. The formation of a transient adduct between primary radicals of initiation and benzoquinone is postulated, and the transition from retarded to inhibited polymerization in this system is discussed on this basis. These ideas were extended to a consideration of the role of primary radical capture and

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radical reactivity for other monomers, such as styrene and vinyl acetate.

ELECTROLYTIC

Electrolytically produced CH₃ radicals have been used to initiate vinyl pyrrolidone polymerization. Because polymer formed insolubly, efficiencies in the form of yield per faraday were determined. The efficiency was found to decrease with increasing current density and to increase to a limit with increasing monomer concentration.

Polymerization of acrylonitrile, methyl methacrylate, and styrene has been electrolytically activated in dimethyl formamide solution saturated with various inorganic salts. A detailed study of acrylonitrile polymerization indicated a direct electron transfer as the initiation mechanism followed by an anionic propagation mechanism. The molecular weight of the polymer was independent of temperature, monomer concentration, and current and was explained on the basis of chain transfer to monomer. Evidence has been found that the simultaneous occurrence of free radical and anionic polymerization is dependent upon the accompanying cation. The effect of the gegen ion on anionic polymerization has been discussed.

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CHAPTER I

GENERAL INTRODUCTION

Polymerizations, like all chain reactions, involve three basic steps: initiation, propagation and termination. The initiator, whether it induces free radical, cationic, or anionic polymerization, must form active centres on the monomer which are capable of propagating further by addition with other monomer molecules. Control of the initiation step by affecting its rate of active site production or the type of site formed, will result in virtual control of the polymerization.

FREE RADICAL

Free radicals may be formed by the thermal or photolytic decomposition of labile compounds, oxidation and reductions by inorganic ions, thermal activation of a monomer, or electrolysis.

thermal decomposition (1)

 $CH_3 - C^{\neq 0} - 0 - 0 - C^{\neq 0} - CH_3 \longrightarrow 2CH_3 - C^{\neq 0} - 0$ (1) photolytic decomposition (2)

oxidation and reduction(3)
HOOH + Fe⁺⁺ _____ FeOH⁺⁺ + OH•.....(3)
thermal monomer activation (4)

electrolysis (Kolbe synthesis) (5)

 $CH_3 - C^{=0} - 0^- \longrightarrow CH_3 - C^{=0} - 0^{\circ} + e^{\circ} (5)$

In addition to the normal rate dependence on temperature and concentration, the reactions of equations two and five are also functions of light intensity and current, respectively. In this respect the production of radicals by these reactions are subject to an additional degree of control. The photolytic production of free radicals has been extensively investigated (6) whereas electrolysis has been, by comparison, almost entirely neglected (7).

The initiation step may be substantially affected by the introduction to the polymerizing solution of foreign molecules, which are capable of competing with monomer for the initiator radicals. However, a great many complications including an increased rate of termination are involved, and a discussion of this extremely complex question will be reserved for another section.

A radical formed by any of the above mechanisms may add to the double bond of a monomer molecule, which in turn adds to other monomer and so propagates the chain. If the initiator radical is represented by I., the propagation steps may be written as follows:

Propagation

 $I \cdot + CH_2 = CHR \longrightarrow I - CH_2 - CHR \cdot \dots (6)$ $I - CH_2 - CHR \cdot + NCH_2 = CH_2R \rightarrow I(CH_2CHR)_N CH_2 - CHR \cdot \dots (7)$

The growth of the molecule continues until interaction with another radical terminates the chain by either a combination or disproportionation of the radicals involved.

Termination

Combination

 $I \xrightarrow{\text{CH}_2 - \text{CHR}} + \cdot \text{CHR} - \text{CH}_2 \xrightarrow{\text{CHR}} I \xrightarrow{\text{CHR}} \text{CH}_2 \xrightarrow{\text{CHR}} \text{CHR} \xrightarrow{\text{CHR}} \xrightarrow{\text{CHR}} \text{CHR} \xrightarrow{\text{CHR}} \text{CHR} \xrightarrow{\text{CHR}} \text{CHR} \xrightarrow{\text{CHR}} \text{CHR} \xrightarrow{\text{CHR}} \xrightarrow{\text{CHR}} \text{CHR} \xrightarrow{\text{CHR}} \xrightarrow{$

Disproportionation

A polymer molecule may be formed without the destruction of the chain carrying radical by the process of chain transfer.

<u>Chain Transfer</u> $I \sim CH_2 - CHR_{\bullet} + SH \longrightarrow I \sim CH_2 - CH_2R + S_{\bullet} \dots (10)$

where SH may be a monomer, solvent or a dead polymer molecule

The initiation, propagation, and termination steps are succinctly written below (8)(9):

In -	>	2R•	k _d		(11)
R• + M	>	RM•	ki		(12)
R-M• +	M →	ŔМ-М•	^k p	- 100 ya ga	(13)
R-Mn•+	M>	RMn+1°	kp	an es as as	(14)
2RMn•	>	combinati produc	lon or disproporti	.onati	on (15)

In represents an initiator molecule which decomposes to form two free radicals, R., M represents monomer molecules, and M. the monomer radical.

The rate of formation of polymer is equal to the rate of loss of monomer.

That is: $dP/dt = -dM/dt = k_i(R^{\bullet})(M) + k_p(RM_n^{\bullet})(M) ---(16)$ Assuming steady state condition,

 $dM^{\bullet}/dt = k_{i}(R^{\bullet})(M) - 2 k_{t} (RM_{n^{\bullet}})^{2} = 0$ ----(17) and

$$dR'/dt = 2f k_d In) - k_i (R \cdot)(M) = 0$$
 ----(18)

The term ''f'' is an efficiency factor which represents the fraction of initiator radicals that initiate polymer chains. Adding equations seventeen and eighteen, one obtains 2 f $k_d(In) = 2 k_t (RM_n \cdot)^2$

$$(RM_n \cdot) = (k_d/k_t)^{1/2} (In)^{1/2} f^{1/2}$$
 ---- (19)

Assuming that the kinetic chains are long, the term $k_i(R \cdot)(M)$ in equation sixteen represents an insignificant monomer destroying reaction.

Therefore:

$$\frac{dP}{dt} = -\frac{dM}{dt} = k_{p} \left(\frac{k_{H}f}{k_{t}}\right)^{1/2} (In)^{1/2} (M) \qquad ---- (20)$$

Inherent in the derivation of the above rate expression is the assumption that k_p for RM_n is exactly the same as that for RM_{n+1} - that is, the radical reactivity is independent of the length of the chain. This assumption has been demonstrated as unequivocally correct (10).

Two terms in addition to $\frac{dP}{dt}$ used in the elucidation of reaction mechanism are kinetic chain length and degree of polymerization. The kinetic chain length, v, represents the average number of monomer units consumed for each chain started.

v = -dM/dt/ Rate of initiation ---- (21) At the steady state, the rate of initiation is equal to the rate of termination.

v = -dM/dt/ Rate of termination ---- (22)

 $v = k_{p}(RM_{n} \cdot)(M) / 2 k_{t}(RM_{n} \cdot)^{2}$ = $k_{p}(M) / 2 k_{t}(RM_{n} \cdot)$ = $k_{p}(M) / 2(k_{t} k_{d} f)^{\frac{1}{2}}(In)^{\frac{1}{2}}....(23)$

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The degree of polymerization, \overline{DP} , is the average number of monomer units consumed per polymer molecule formed. For simple reactions, \overline{DP} is equal to 2v if two kinetic chains terminate by combining, and it is equal to v if the chain radicals terminate by disproportionation. When chain transfer occurs, a dead polymer molecule is formed without termination of the chain propagating radical, making a simple relationship between v and \overline{DP} impossible.

IONIC POLYMERIZATION

In comparison to free radical polymerizations, cationic and anionic mechanisms are not as thoroughly understood.

Although cationic initiation of polymerization has been known for many years (11), its exact nature has been confused by the complex phenomenon of co-catalysis. Strongly electrophilic substances such as $AlCl_3$, BF_3 , SnCl₄, and TiCl₄ are used as initiators, but the presence of trace amounts of co-catalysts such as water, alcohols, or acids, may or may not be required (12)(13). Because no carbonium ion mechanism was encountered in this research no further discussion will be made.

The polymerization of olefins by anionic mechanisms has only recently received much attention. The polymerization of methacrylonitrile through carbanionic intermediates was obtained in 1948 by the action of Grignard reagents, triphenylmethyl sodium and sodium in liquid ammonia (14), although earlier anionic polymerizations had been successful(15)(16)(17)(18).

The first quantitative study of anionic polymerizations was performed on the NH_2^- initiation of styrene (19), methylmethacrylate, and acryonitrile in liquid ammonia (20). The following mechanism was proposed (21) and found satisfactory for styrene concentrations up to 0.03 M (19).

Initiation: $NH_2^- + CH_2 = CHR \longrightarrow NH_2 - CH_2 - CHR^-$(24) Propagation: $NH_2 - CH_2R^- + nCH_2 = CHR \longrightarrow$ $NH_2^- (CH_2 - CHR)_n - CH_2 - CHR^-$(25)

Chain transfer: $NH_2 - (CH_2 - CHR)_n - CH_2 - CHR^- + NH_3 \longrightarrow$ $NH_2^- + NH_2 - (CH_2 - CHR)_n - CH_2 - CH_2R.....(26)$

In this reaction scheme, the initiation step is a direct addition of NH_2^- to the double bond of the monomer in a manner similar to free radically induced polymerizations (see equations six and twelve).

In contrast to the above addition mechanism, Szwarc has proposed an initiation step which involves an electron transfer to the monomer molecule (22)(23). This initiation mechanism has been confirmed in subsequent publications (24)(25)(26). Substances which act as good electron donors are alkali metals and alkali metal-aromatic hydrocarbon adducts, such as sodium naphthalide (27) and triphenylmethyl sodium (14). The initiation mechanism may be written as follows:



The electron occupies the lowest unfilled \mathcal{T} orbital of the monomer, forming an ion radical which, in general, dimerizes to a dianion.

- RCH - CH2-CH2-RCH-

The resultant dianion grows in both directions until all the monomer is exhausted. If stringently purified materials are employed, termination of the dianion in inert solvents will occur to negligible extent. When this condition of no termination exists, "living polymers" are formed (22)(23)-that is, polymers whose reactive growing ends are not destroyed. In such situations, if monomer is added to a reaction which has polymerized to completion, further reaction will occur until all the unreacted monomer is exhausted. The reactive or "living" end of the polymer persists until destroyed by the addition of a proton donating substance.

 $CH_2-CHR^- + SH \longrightarrow CH_2-CH_2R + S^-....(28)$ The polymer formed from "living" systems has been found to have a very narrow molecular weight distribution.

MOLECULAR WEIGHT DETERMINATION

The determination of molecular weights and molecular weight distributions provides valuable evidence for the elucidation of polymerization reaction mechanisms.

The molecular size of polymeric materials and the evaluation of their molecular weights, however, presents problems peculiar to macromolecular substances. Because of the random nature of propagation and termination reactions, polymer molecules have a molecular weight distribution.

The actual value of an average molecular weight for a particular sample depends upon the property used for the measurement (28). For example, an investigator who knows the amount of material present and the value of some colligative property, knows in effect the number of particles associated with this material. A molecular weight determined by a measurement of any colligative property is called a number average molecular weight and is defined by the expression

 $\mathbb{M}_{n} = \left\langle n, \mathbb{M} \right\rangle / \left\langle n, \dots \right\rangle$ (29)

Similarly, if a molecular weight is determined by measuring a property which is proportional to the mass of the particles as well as the concentration, a value called the weight average molecular weight defined by

 $\overline{M}_{w} = \sum n i M i^2 / \sum n i M i \dots (30)$ is obtained.

The determination of number average molecular weights by cryoscopic and ebullioscopic measurements is practicable only when the molecular weight is less than 2000. Larger number average molecular weights are estimated by osmotic pressure measurements of dilute polymer solutions using the van't Hoff equation for dilute solutions: $M = RT/(\pi/c)_0$ (29).

Osmosis is described by Glasstone as "the spontaneous flow of solvent into a solution, or from a more dilute to a more concentrated solution, when the two liquids are separated from each other by a suitable membrane", whereas osmotic pressure is defined as "the excess pressure which must be applied to a solution to prevent the passage into it of solvent when separated from the latter by a perfectly semi-permeable membrane". (30).

When pure solvent is placed on both sides of a membrane, an "asymmetry" pressure often is developed. The only explanation of this pressure known to the author assumes that the osmotic pressures are generated by forces within a few molecular diameters of the membrane and that the polymer chains of the membrane material become detached at one end. The asymmetry pressure then, is a measure of disengaged polymer chains on the two sides of the membrane (31).

When a series of molecular weights for a particular polymer has been determined absolutely by some method such as osmometry or cryoscopy, a relationship to the intrinsic viscosities of the polymers is readily attainable through the semi-empirical expression $m = KM^{\prec}$. In this modified form of Staudinger's equation, m is the intrinsic or ideal specific viscosity, M is the molecular weight of the polymer and K and \ll are experimentally determined constants. Because of the comparitive ease with which intrinsic viscosities can be determined, this method of establishing molecular weights is extensively used when the constants K and \ll are available.

CHAPTER II

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CHAPTER II

INHIBITION AND RETARDATION

The rate of a vinyl polymerization can be substantially affected by certain materials called either inhibitors or retardants. If a compound completely suppresses any polymerization, it is called an inhibitor. If, on the other hand, the compound merely reduces the rate, it is a retarder. Whether a given compound behaves as a retarder or inhibitor depends wholly upon the reactants and reaction conditions; thus p-benzoquinone is a retarder for the thermal polymerization of styrene (32), but is an inhibitor for peroxide initiated styrene polymerizations (33).

In general, the inhibitor or retarder molecule interacts with the radical intermediates of a normal polymerization. The newly formed radical, because of its increased stability, will reduce the rate of reaction by decreasing the rate of initiation or propagation or by increasing the rate of termination. The phenomenon of inhibition is considered to be due to a greatly reduced rate of initiation, whereas retardation may be the result of either a decreased rate of propagation or an increased rate of termination (34)(35).

The previous kinetic expression (equation twenty) is vastly complicated by terms arising from the addition of retarder or inhibitor to the monomer. Some of all of the following reactions may be of importance.

$\mathbb{R} \bullet + \mathbb{Q} \longrightarrow$	RQ•	
$\mathbb{M}^{\bullet} + \mathbb{Q} \longrightarrow$	MQ•	
$RQ \bullet + M \longrightarrow$	M•	
$MQ \bullet + M \longrightarrow$	M•	
$M\bullet + MQ\bullet \longrightarrow$	Ρ	••••••(35)
$MQ \bullet + MQ \bullet \longrightarrow$	P	
M• + RQ• →	P	
MQ• + RQ•>	P	

Q represents the inhibitor or retarder molecule and Q. its radical. Kice has proposed a mechanism which is adaquate for slightly retarded polymerizations but which is unsatisfactory when the rates are greatly reduced (36)(37). No complete quantitative scheme has yet been established for retarded polymerizations (38).

The influence of different retarder molecules has received a great deal of attention. One type of inhibitant is free radicals, which are so remarkably stable that they may be isolated in a pure form. An example of such a compound is 2,2-diphenyl-l-picrylhydrazyl (DPPH)(39).



This radical does not initiate polymerization but has been

shown to completely inhibit both polyvinyl acetate (40) and polystyrene formation (41).

Generally, materials which cause retardation and inhibition are those which form a stable unreactive species through reaction with free radicals. Halogenated compounds (42), phenols (43)(44)(45)(46), aromatic nitro compounds (43)(47), amines (43), polyaromatics (48)(49) and quinones (40)(50)(51) are some of the most common inhibitants or retardants.

Although benzoquinone has been one of the most extensively studied inhibitants (41)(43)(50)(52)(53)(54) (55), a thorough understanding of the reasons for its relative effectiveness on various monomers has remained unclear. Cohen has claimed that quinone inhibits styrene polymerization by chain radical capture (33), whereas other monomers could conceivably be inhibited by consumption of initiator radicals (56). Further, Mayo and Gregg's results indicate copolymerization of benzoquinone (59), whereas a chain transfer mechanism is advocated by Schulz and Kammerer (58).

Much of the kinetic confusion arising from the complexities of polymer radical-benzoquinone interactions may be avoided by the utilization of auxilliary measurements. A case in point is the study of c^{14} tagged initiator and retarder molecules during the polymerization of methyl methacrylate (59) and styrene (60). By compar-

ing experiments employing radioactive 2,2'-azobisisobutyronitrile and inactive benzoquinone with its duplicate using inactive initiator and active retarder, Bevington, Ghanem, and Melville obtained results which determined the fate of both the initiator and retarder molecules. Their results indicated that the retarded polymerization of methyl methaat crylate termined by polymer radical-quinone radical combinations.

 $I \xrightarrow{q} Q \cdot + M \cdot \xrightarrow{} P$ (cf equation thirty-five)

Their results with styrene inhibition indicated a slight copolymerization of benzoquinone.

 $I \sim Q \circ + M \longrightarrow I \sim QM \circ (cf equation thirty-four)$

With the above results in mind, the role of benzoquinone under conditions of extremely heavy retardation has been investigated in this laboratory (61)(62). Because a unique transition from retardation to inhibition was obtained with methyl methacrylate, it was thought necessary to confirm this work using ethyl methacrylate as an alternate monomer.

EXPERIMENTAL

The experimental methods were almost identical to those used in the previous investigation (61)(62). Reaction rates were determined dilatometrically by utilizing the fact that ethyl methacrylate contracts 26.6% of its total volume when it polymerizes 100% (63). Number average molecular weights were estimated osmotically with a bank of five modified Zimm-Myerson osmometers (64). Radioactive assays were performed by liquid scintillation techniques (66)(65).

MATERIALS

Scintillation chemicals, p-terphenyl and 1,4 di (2-(5 phenyloxazoly!)) benzene (POPOP), were obtained from Nuclear Enterprises Ltd., Winnipeg, and were used without further purification.

Monomeric ethyl methacrylate (EMA) was obtained from Matheson, Coleman and Bell, and 250 ml portions were treated with 5% NaOH solution containing NaCl in five successive washes to remove inhibitor. After repeated shakings with distilled water, the monomer was dried over CaSO₄ and then distilled at 43-44°C at 37-38 mm Hg, and the middle fraction collected ($n^{20} = 1.4143$).

The radioactive initiator, 2,2'-azobisisobutyronitrile (dicyano C¹⁴) (100µc) (AIBN) was purchased from the

Commissariat a l'Energie Atomique, France. Inactive AIBN (Eastman Organic Chemicals) was used to dilute the radioactive material to 1.30μ c/mmole prior to purification by three precipitations from toluene. Inactive AIBN was similarly purified.

c¹⁴ tagged benzoquinone (100µc) (BQ) (Commissariat a l' Energie Atomique, France) was diluted with inactive BQ (Matheson, Coleman and Bell) to form a stock activity of 4.12µc/mmole. BQ was purified by recrystallizations from ether followed by a sublimation.

POLYMERIZATIONS.

Initiator and retarder were admitted to the polymerization tubes in chloroform solution and the chloroform was evaporated off at low temperatures. EMA was added to the tubes and degassed by repeated freezing and thawing cycles. The monomer was transferred to the dilatometer under vacuum (Figure One) in order to avoid contact with oxygen (67)(68).

Duplicate tagging experiments were used to determine the fate of both the initiator and retarder molecules. One set of experiments using C^{14} tagged AIBN and inactive BQ was used to discover the termination mechanism. If termination is by <u>combination</u>, there will be two initiator fragments per polymer molecule (equation eight); however, if termination is by disproportionation, there

will be one initiator fragment per polymer molecule (equation nine). A second set of identical experiments employed inactive AIBN and active BQ. These experiments served to determine the fate of the BQ molecules.

Polymerizations were conducted in bulk with 20 ml portions of monomer at $60 \pm .05^{\circ}$ C and were carried to less than 10% conversion. Blank runs, identical to the above but containing no initiator, were simultaneously performed, and they indicated a negligible amount of thermal polymerization.

Polyethyl methacrylate was precipitated in cold *ethyl* methanol. Precipitation from methyl ketone (MEK) was repeated three times in order to remove any traces of unreacted C¹⁴ tagged material (59)(61).

RADIOACTIVE ASSAYS.

The sample of polymer, which had been precipitated, purified, and dried, was dissolved in liquid scintillator consisting of 0.40 g. p-terphenyl and 0.01 g. POPOP in 100 ml toluene. Oxygen was removed by bubbling argon through the solution for fifteen minutes before the counts were determined (69). The counting cell was shielded by two inches of lead.

An integral counting method was employed so that all disintegrations of energy in excess of approximately 10 kev were counted. Possible variations in light quenching

FIGURE 1. Dilatometer and Filling Device.

The monomer solution was degassed in e. The mercury in the dilatometer was sucked into the capillary to stopcock a which was then closed. The dilatometer and degassing cell were connected and the system was evacuated through d while the monomer remained frozen. After melting, the monomer was poured into the dilatometer under vacuum. When thermal equilibrium had been attained, stopcock b was closed and a opened and the drop of the mercury column was measured.



as well as electronic drift were eliminated by counting an internal standard (70)(71) of AIBN or BQ immediately after the determination of the sample counting rate.

An EMI type 9536S phototube, factory selected for low noise characteristics, was employed, and absolute counting efficiencies of 90% for C^{14} could be obtained with this apparatus (Figure two).

MOLECULAR WEIGHT DETERMINATIONS.

Two modified Zimm-Myerson osmometers (64) were purchased from the J. V. Stabin Co., Brooklyn, New York, and three were constructed locally.

Grade 300 (0.002 inches thick), undried gel-cellophane was obtained from American Viscose Co., cut to the proper diameter, and washed for several days in cold running water. The membranes were conditioned by successive 15 minute immersions in 25, 50, 75 and 100% ethanol; the ethanol was replaced by similar 15 minute washings in 25, 50, 75 and 100% ethanol - MEK solutions. The membranes were left for several days in 1-2% solutions of polyethyl methacrylate in MEK before being sealed into the osmometers.

The five osmometers were placed into a thermostat regulated at 25 \pm .02°C and filled with 0.02, 0.04, 0.06, 0.08 and 1.00% polymer solutions respectively. The pressures which developed were read to 0.001 cm. by a Griffin and
FIGURE 2.

Block Diagram of Counting Apparatus.

- (a) Potentiometer Unit.
 (b) Linear Amplifier with Discriminator.
 (c) Model 105 Scaler.
 (d) Power Unit.
 (e) Lead Shield.
 (f) Photomultiplier tube.
 (g) Cathode Follower.



George Ltd., cathetometer.

Intrinsic viscosities were determined at $25 \pm .05^{\circ}C$ with an Ubbelohde viscometer.

RATE DATA.

The rates of polymerization as determined by dilatometry at 60° C are presented in Figure three.

Each polymerization was initiated by 1.62×10^{-4} moles AIBN/mole EMA and had incremented quinone concentrations from 0 to 89.76 x 10^{-5} moles/mole EMA. The rates, as evaluated from the graph, are listed in Table one.

TABLE I

BQ Concentration moles/mole monomer x 10+5 Rate %/min. x 10+3 No. 1 0 68.7 2 11.22 13.8 3 22.44 33.66 4 6.12 5 2.82* 56.10 6 67.32 2.81* 7 78.54 2.80 8 89.76

Rates of Polymerization at 60° C at Various BQ Concentrations and Constant AIBN Concentration (1.62 x 10^{-4} moles/mole EMA)

* Rates obtained after inhibition period.

MOLECULAR WEIGHTS.

Number average molecular weights were determined osmotically at 25 \pm .02°C by using the van't Hoff limiting law: M = RT/ (π/c)₀ . If π is expressed in centimeters of solvent and c in grams of polymer per 100 millilitres of solvent, then R becomes equal to 848/d, where d is the solvent density at temperature T. For MEK at 25°C, M = 316.45 x 10³/(π/c)₀. (π/c)₀ is determined by extrapolation of π/c values to infinite dilution. The osmotic pressure data are shown in Figure four.

Because osmotic molecular weight determinations are both difficult and time consuming, an intrinsic viscosity relationship was determined for the molecular weight range encountered in this research. If the intrinsic viscosities are known for a series of molecular weights, the constants K and \ll may be graphically determined.

> $\mathfrak{A} = KM^{\checkmark}$ $\log \mathfrak{A} = \log K + \ll \log M$

A plot of $\log \eta$ vs log M will yield a straight line whose slope is \propto and whose intercept is log K. The results are presented graphically in Figure five.

The line in Figure five is defined by the equation $n=1.44 \times 10^{-5} \text{ M} \cdot 88$ as determined by a least squares calculation.

The molecular weights are given in Table two and Table three.

FIGURE 3.

Retarded and inhibited rates of polymerization of EMA at AIBN concentration of 1.62 x 10-4 moles/mole monomer and various BQ concentrations as described in Table one.



FIGURE 4.

Osmotic Pressure Data for Samples Described in Tables two and three.



FIGURE 5. Plot of Log η vs Log M for EMA.



TABLE II

Polymers Prepared with Labeled AIBN and Inactive BQ (Concentrations as in Table one)				
Sample Number	Weight Counted gm	Molecular Weight	Activity Counts/ Min.	AIBN Fragments/ Polymer*
1A 2A 3A 4A 6A 7A	0.1656 0.1644 0.1571 0.1468 0.1596 0.1301	369,700 170,800 91,800 90,300 75,000	226 431 931 1450 1701 1856	1.28 1.35 1.22 1.34 1.43

* Calculated on the basis of 6.09 x 10-6 moles AIBN producing 9059 counts/min.

TABLE III

Polymers Prepared with Labeled BQ and Inactive AIBN (Concentrations as in Table one)

Sample Number	Weight Counted gm	Molecular Weight	Activity Counts/ Min.	BQ/ Polymer*
2Q	0.1461	286,000	507	0.74
3Q	0.1542	146,200	1939	1.36
4Q	0.1474	91,100	4210	1.86
5Q	0.1611	101,400	4360	2.04
7Q	0.1795	52,500	72,802	2.08
8Q	0.0540	54,700	2,814	2.06

* Calculated on the basis of 9.24 x 10-6 moles BQ producing 12,476 counts/min., except for sample 7Q with 102,379 counts/min.

TABLE IV

Sample Number	Reaction Time, hr.	Molecular Weight	Weight Counted gm	Activity Counts/ Min.	BQ Polymer ⁺
4Q	24	96,200	0.1918	39 , 25 <u>5</u>	1.91
	30	95,800	0.1493	30,457	1.90
	55	96,200	0.2188	45,364	1.94
	74	95,800	0.1550	30,881	1.85
7Q	24	50,900	0.1313	105,331	3.83
	30	51,700	0.1641	93,096	2.86
	55	52 , 500	0.1516	72,292	2.42
	75	52 , 500	0.1795	72,802	2.08

Variation with Time of BQ in Polymer

+ Calculated on the basis of 9.24×10^{-6} moles BQ producing 12,476 counts/min., except for sample 7Q with 102,379 counts/min.

RADIOACTIVE DATA.

The results of the tagged AIBN experiments are assembled in Table II.

Although neither the combination nor the disproportionation of radicals occurs to the complete exclusion of the other, the results are essentially constant at 1.32 AIBN fragments per polymer molecule. This was interpreted as meaning that 49% of the chains terminate by combination whereas 51% terminate by disproportionation.

The above percentages were calculated on the basis of the following derivation (72).

Let x be the fraction of molecules with two labelled end groups. Let y be the fraction of molecules with one labelled end group. Let n be the average number of end groups/molecule.

x + y = 1 and 2x + y = nTherefore,

x = n - 1 and y = 2 - nThe fraction of polymer molecules formed by disproportionation and combination is 2-n/n and 2(n-1)/n, respectively.

The results of tagged BQ experiments are presented in Tables three and four.

RATE OF INITIATION.

The rate of initiation may be calculated from rate and kinetic chain length data. Since v = Rp/Ri, then Ri = Rp/v. The kinetic chain length, v, was calculated by the expression

(molecular weight of polymer)

(molecular weight of monomer)(number AIBN fragments/ polymer)

v may also be calculated exclusively from the radioactive data by the expression (75)

(weight counted)

(molecular weight of monomer)(total number of AIBN fragments)

Sufficient data for calculation of Ri were available for 1A, 2A and 4A (Table five).

TABLE V

Num- ber	BQ Concen- tration moles/mole monomer x 10 ⁵	v Count- ing Data	Ri % initia- ted/min x 10 ³	▼ M.W. Data	Ri % initia- ted/min.x 10 ³
1	0	4780	14.40	-	_
2	11.22	2490	5.54	2532	5.45
4	33.66	660	9.28	1279	4.80

Variation of Ri with Initial BQ Concentration

ERROR

The maximum error in calculating the number of initiator fragments and benzoquinone molecules per polymer was assessed at 13%. This rather high value is a result of a generally accepted 10% uncertainty in osmotic molecular weight determinations (73)(74). All other errors arising from counting data, weighings, impurities, et cetera, were estimated at 3%.

SUMMARY

The results of this research are in complete agreement with those previously obtained with methyl methacrylate (61)(62). These observations immediately reveal that neither copolymerization (equation thirty-four) nor chain transfer reactions (equation ten) are highly significant in BQ retarded polymerizations of EMA.

Again it was noted that BQ did not affect the ter-

mination mechanisms - the ratio of combination to termination - although the amount of BQ in the polymer, to a limited extent, was proportional to its initial concentration. At BQ concentrations which caused inhibition, a constant value of about 2.06 BQ molecules per chain was present in the polymer formed after the inhibition period.

The results of Table four indicate that the rate of BQ incorporation into the polymer is constant for retarded reactions. For inhibited reactions, the amount of BQ in the polymer is greatest immediately after the inhibition period.

Although the molecular weight decreases with increasing BQ concentrations (Tables two and three), it is sensibly constant during either an inhibited or retarded run (Table four).

DISCUSSION

It is necessary to simultaneously explain the effect of retarder on the rate, termination mechanism, and BQ content of the polymer. As a first approximation, one normally conceives of an initiated polymer radical rapidly propagating until interaction with a BQ molecule. The stabilized adduct will remain in solution until termination occurs.

 $I \cdots M \bullet + Q \longrightarrow I \cdots MQ \bullet$

 $I \cdots MQ \bullet + radical \longrightarrow polymer$

Increasing the BQ concentration increases the probability of BQ interaction occurring at an earlier stage of the propagation. This mechanism accounts for the reduction of both the rate and molecular weight with increasing BQ concentrations, and with elaborations, it may be able to partially explain the inhibition period. Unfortunately, however, incorporation of BQ at terminal positions of growing radical chains will cause a variation of the ratio of combination to disproportionation (59). Because no variation was found in this or the previous research (61)(62), it is necessary to postulate that the increased amounts of BQ in the polymer were incorporated at positions other than chain ends.

An examination of rates of initiation might be propitious at this time. Although the results of Table five are insufficient, they do reveal that BQ decreases the uninhibited rate of initiation. Values determined previously for MMA indicate diminished rates of initiation that extrapolate to zero at the BQ concentration at which inhibition was first encountered. Because of the great similarity of the present results with those previously obtained, it is highly probable that the initiation step is partially reduced by low BQ concentrations and becomes totally inhibited at higher concentrations.

The inhibition product formed by the interaction of AIBN radicals and BQ has the structure

$$R - 0 - - - 0 \cdot ,$$

where R is the 2-cyanopropyl group. The high stability of this radical precludes permanent formation of a peroxide by combination with a similar radical. The adduct exists in solution and will be destroyed by termination with growing polymer radicals.

 $I \cdots M \cdot + IQ \cdot \longrightarrow I \cdots QI$

 $I \cdots M \cdot + IQ \cdot \longrightarrow I \cdots M + IQ (non-polymeric)$

This, however, accounts for only one BQ per polymer if termination is by combination, or none if termination is by disproportionation.

To logically explain a constant termination mechanism of 49% combination and 51% disproportionation and a

maximum of two BQs per polymer, it is necessary to postulate that the initiator - quinone adduct, $R-0-\oint-0$, is capable of initiating polymerization. Accordingly, to reactions described in the previous paragraphs, must be added the reaction

$$R - 0 - \not 0 - 0 + \begin{matrix} H \\ C \\ H \end{matrix} = \begin{matrix} H \\ R^* \end{matrix} \longrightarrow R - 0 - \not 0 - 0 - \begin{matrix} H \\ -C \\ H \end{matrix} \qquad (39)$$
(see equation thirty-three).

During retardation, BQ simultaneously interrupts the growth of active polymer chains and intercepts initiator fragments. The initiator radical-BQ adduct acts both as a terminator and a weak initiator.

During inhibition, BQ reacts with all the AIBN fragments formed preventing any normal initiation. The only radicals present are the BQ adducts which, because of their high stability, have a low initiation efficiency. When a monomer is initiated, however, the resulting radical rapidly propagates to a reasonably high degree of polymerization before either termination with another radical or interaction with free BQ occurs. Thus BQ becomes incorporated into the polymer during the initiation as well as the termination of the radicals.

The constant ratio of combination to disproportionation is a result of a termination mechanism which always involves unlike radicals.

 $0-\phi-0$ + $\overset{H}{\overset{C}{\overset{}}_{H}}$ $\overset{Combination and disproportionation}{\overset{}}_{---}$ (40)

It is normally assumed that inhibition is a limiting case of retadation (76). This cannot be true for EMA inhibitions since the length of the inhibition period would be comparable to the length of the retardations. The brevity and sharp definition of the inhibition period must be due to a phenomenon which does not occur during retardations. Although reduction of the BQ concentration in the solution by copolymerization is suggested by Table V, more work is definitely required.

A kinetic scheme representing some possible steps in the retardation mechanism is given in equations forty-one to fifty.

In>	2I º	k	(41)
I• + M →>	M∙	ki	(42)
I• + X>	ୢୄୄୄୄ	k _x	(43)
Q• + M>	M•	kq	(44)
$M_n \cdot + M \longrightarrow$	^M n+1°	^k p	(45)
$M_n \cdot + X \rightarrow$	X•+Pn	^k tr	(46)
$M_{n} \cdot + X \longrightarrow$	M _n X•	^k c	(47)
X• + M• →>	P	^k tx	(48)
Q• + M•>	Р	^k tq	(49)
2X• →	X ₂	K _x	(50)
2Q•>	Q ₂	Kq	(50a)

Here I represents initiator, M monomer, X benzoquinone,

P Polymer; and I., M., X. are the respective radicals. The postulated adduct between initiator and BQ is denoted by Q. and in its molecular form as Q_{2} .

The degree of polymerization is given by

DP = - dM/dt/dP/dt

 $DP = \frac{k_{p} (M \cdot)(M)}{k_{tr}(M \cdot)(X) + k_{tx} (X \cdot)(M \cdot) + k_{tq} (Q \cdot)(M \cdot)} ---(51)$

The kinetic chain length, v, is the ratio of the rate of monomer loss to rate of initiation

v = dM/dt/Rate of initiation

At the steady state, the rate of initiation equals the rate of termination.

Therefore v = dM/dt/Rate of termination

$$\frac{k_{p} (M \cdot)(M)}{k_{tx} (X \cdot)(M \cdot) + k_{tq} (Q \cdot)(M \cdot)} ---(52)$$

Hence

$$1/DP - 1/v = \frac{k_{tr}(X)}{k_{p}(M)}$$
 ---(53)

This relationship is plotted in Figure six and is found to be linear for the present data and for the previous measurements of methyl methacrylate under similar conditions.

The novel feature of this scheme is the distinction drawn between initiator-BQ (equation forty-three) and polymer radical - BQ interactions (equations forty-six and forty-seven). The relative importance of each of these reactions is dependent upon the reactivities of the various

species involved. A discussion of this point with respect to the three common monomers, styrene, vinyl acetate, and methyl methacrylate follows immediately.

Styrene is a relatively unstable monomer which, when initiated, forms a highly resonance stabilized radical.

 $\operatorname{R-CH}_2 - \overset{\circ}{\operatorname{H}} - \overset{\circ}{\underset{\operatorname{H}}{\bigcirc}} \longleftrightarrow \operatorname{R-CH}_2 - \overset{\circ}{\underset{\operatorname{H}}{\bigcirc}} \cdot \overset{\circ}{\underset{\operatorname{H}}{\bigcirc}} \cdot \longleftrightarrow \operatorname{etc.}$

In contrast, vinyl acetate is a very stable monomer which forms a highly reactive radical. Methyl methacrylate is less stable than vinyl acetate but more than styrene. The radical produced has a reactivity intermediate to that of vinyl acetate and styrene, due possibly to the single resonance structure written below.



If these views, originally conceived from copolymerization studies regarding both monomer and radical reactivity are extended, (77) it is possible to qualitatively explain inhibition and retardation of free radical vinyl polymerizations by BQ. Vinyl acetate has been shown to be a very stable monomer which, when activated, becomes an extremely reactive radical. When p-benzoquinone is added to an initiated polymerization, the initiator frag-

ments will react with the quinone in preference to the stable vinyl acetate monomer. The reaction will be inhibited until the benzoquinone is exhausted. The mechanism of inhibition for initiated styrene polymerizations is basically different. The initiator radicals will attack the easily activated styrene monomers forming the stable styryl radical, which adds monomer relatively slowly. Benzoquinone adds to the short chain styrene radical and forms an extremely stable intermediate that rapidly terminates. Inhibition in the former case is the result of an unreactive monomer, and in the latter, of a stable monomer radical.

Retardation will occur if the monomer is sufficiently active to add initiator in competition with benzoquinone. The radical thus formed must be reactive enough to grow to a reasonable extent before interference by p-benzoquinone takes place. This appears to be the case with methacrylates.

In summary:

- (a) a very stable monomer will be inhibited,
- (b) an unstable monomer which forms a stable radical will also be inhibited.
- (c) a substance which has intermediate monomer stability and radical reactivity will retarded.In the above discussion it has been assumed that the

initiator radicals are those formed from the decomposition of azo nitriles. Such radicals have a rather high stability and are, therefore, relatively unreactive (78). If a highly reactive radical could be generated in benzoquinone solutions of each of the above three monomers, a different relative behaviour may be obtained. Styrene and methyl methacrylate polymerizations will exhibit a kinetic behaviour similar to that previously described. Vinyl acetate polymerization, however, will probably show retardation instead of inhibition. This prediction is based upon the assumption that the reactive initiator radicals will attack vinyl acetate monomers, which then grow significantly before interaction with benzoquinone and the ensuing termination can take place.

FIGURE 6.
$$\frac{1}{DP} - \frac{1}{v}$$

•

Concentration.

vs

Χ

at Constant Monomer



CHAPTER THREE

CHAPTER III

ELECTROLYTIC INITIATION OF POLYMERIZATION

INTRODUCTION

Although it had an early beginning (79) one of the least studied means of activating polymerization is by the formation of reactive intermediates from the electrolytic discharge of certain substances in the presence of monomer. In general, the electrolysis of complex materials produces radicals, which, because of their high concentration at the electrode surface, have a strong tendency to dimerize (80). If radicals can be produced with a sufficiently long lifetime, they will be capable of diffusing from the electrode into the bulk of a monomer containing solution where initiation of polymerization can take place.

The electrolytic initiation of polymerization can be divided into several classes.

1) Kolbe Reaction.

Free radicals are produced at the anode during an electrolytic oxidation of carboxylic acids. This reaction, commonly known as the Kolbe synthesis, is used to produce dimerized hydrocarbons by the following sequence:

$$R - C^{\neq 0} - 0^{-} \longrightarrow R - C^{\neq 0} - 0^{\circ} + e$$

$$R - C^{\neq 0} - 0^{\circ} \longrightarrow R^{\circ} + C0_{2}$$

$$2R^{\circ} \longrightarrow R - R$$

where R must be aliphatic for dimerization (5). When a vinyl compound is present, either the $R-C^{\neq 0}$ 0 or R radical can initiate a polymerization. Styrene (81), vinyl acetate (82) methyl methacrylate (82)(83), vinyl chloride (82), and acrylonitrile (83) have been polymerized by electrolysis of potassium acetate in acidic of methanolic solutions. The polymer in these cases formed insolubly on the anode, insulating it from any further flow of current, and thus arresting the initiation of polymerization.

Recently a similar type of initiation was reported using zinc acetate as the conducting salt in dimethyl sulphoxide and other non-aqueous solvents of high dielectric constant (84). Polymer of high molecular weight formed homogeneously in the solution with no interference of the electrode process. The results using methyl methacrylate monomer indicated a linear dependence of the rate and the inverse relationship of molecular weight with the current density. This was kinetically interpreted by a reaction scheme involving formation of radical at the anode which initiates polymerization. The growing radical rapidly

propagates, but termination occurs with primary radicals formed in high concentrations at the electrode.

In a related study, it was found by C^{14} tagging of the acetate ion on both the one and two positions that the methyl radical caused 99% of the initiation whereas the acetoxy radical was responsible for about 1% (85).

One of the most useful applications of Kolbe electro-initiation is the activation of polymerization of halogen containing olefins (86). Under normal conditions, olefins such as trifluorochloroethylene and tetrafluoroethylene require high temperatures and pressures in order to yield high molecular weight products. When these halo-olefins are initiated by electrolysing trifluoracetic acid solutions containing its potassium salt, low pressures and temperatures may be employed. It was found that the yield of polymer decreased at high current densities due to the formation of low molecular weight products, but increased with increasing monomer concentra-The efficiency of the initiating species, CF_3 , tion. increased at low temperatures.

Although not a Kolbe reaction, results strikingly similar to those described above were obtained when solutions of potassium fluoride in hydrofluoric acid were electrolysed in the presence of halo-olefins (87). In this case, the initiating species is apparently the F. radical.

2) Electrolytic Reduction.

Electrolytic initiation of polymerization may be attained by the partial hydrogenation of vinyl compounds such as methyl methacrylate (88)(89)(90)(91), methyl acrylate (88)(90), methacrylic and acrylic acids (88)(90), and acrylonitrile (90). A reaction of this type requires the cathodic production of hydrogen atoms, usually from acidic solutions, followed by a transfer to monomer adsorbed on the metal surface. In general, this type of initiation is inefficient with respect to the total number of hydrogen atoms produced.

 $H^{+} + e \longrightarrow H^{\bullet}$ $2H^{\bullet} \longrightarrow H_{2}$ $H^{\bullet} + CH_{2} = CH_{2} \longrightarrow CH_{3} - CHR^{\bullet}$

Dineen, Schwann and Wilson, (88), Kern and Quast (90) and Parravano (89) have reported a dependence of the efficiency of initiation on the overvoltage of the cathode material. It was noted that Pb, Sn, Hg, Pt, Bi, Fe, and Al caused initiation in order of effectiveness, whereas no polymerization resulted when the cathode material was Cu, Cd, Ni, W, Ta, Mo, Cr, Ag, or Zn. These results are in complete agreement with the general idea that hydrogen atoms formed from a high overvoltage metal have a greater reactivity and hence a greater probability of efficiently adding to a double bond.

Parravano (89) and more recently Tsvetkov (91) have noted that the polymerization of acidic solutions of methyl methacrylate continued after the electrolysing current had been disrupted. This was apparently due to migration of monomer into emulsified polymer radical particles under conditions of negligible termination - a situation quite analogous to the preparation of monodisperse polystyrene (92).

Tsvetkov further has reported that the amount of polymethyl methacrylate formed by cathodic hydrogen varies directly with the size of lead electrode, current density and temperature, and that the induction period which preceded each polymerization could be shortened by increasing the current density.

The electrolytic reduction of certain organic compounds produce free radicals (93) which, under judiciously chosen conditions, have been used to initiate the polymerization of olefin's (94). Ketones, quinones, and nitro compounds were successfully employed as reducible organic materials in solvents capable of simultaneously dissolving the olefin and conducting current. Electrolytes such as lithium chloride, sodium chloride, acids, tertiary ammonium halides, and tertiary alkyl halides were used to carry the electric current between electrodes

of platinum, mercury, stainless steel, nickel, lead, copper, carbon, or graphite.

Results were dependent to a degree on the cathode material. Polymers were formed with molecular weights from 7,000 to 100,000, depending upon the olefine concentration, the electrolyte, the nature of the solvent, and particularly upon the current density. At low current densities, high molecular weight product formed, whereas lower molecular weights were obtained at high current density.

OXIDATION AND REDUCTION REQUIRING A TWO ELECTRON CHANGE.

The oxidation or reduction of substances which require a change of at least two electrons for a transition from an initial to a final stable state, undoubtedly proceeds through free radical intermediates. The attempted utilization of such intermediates as initiators of polymerization by electrolytically reducing persulphates and peroxides has proved unsuccessful (95).

$$S_{2}O_{8}^{\bullet} + e \longrightarrow SO_{4}^{\bullet} + SO_{4}^{\bullet}$$

$$SO_{4}^{\bullet} + e \longrightarrow SO_{4}^{\bullet}$$

$$ROOR + e \longrightarrow RO:^{\bullet} + RO^{\bullet}$$

$$RO^{\bullet} + e \longrightarrow RO:^{\bullet}$$

Negligible amounts of polymer formed, indicating an insufficient lifetime for the transitory RO• and SO_4^{-} radicals under the experimental conditions.

SECONDARY ACTIVATION.

This method employs oxidation-reduction couples typified by the reaction of Fenton's reagent (3):

 Fe^{++} + HOOH \longrightarrow Fe^{+++} + OH - + HO•

In the electrochemical modification, ferric ion is reduced to ferrous at the cathode, and the ferrous ion so formed undergoes the above reaction in peroxide solutions, producing the initiating HO• radicals (95). Thus the initiating species, HO•, is the result of secondary activation which is dependent upon the initial electrode reaction.

Reasonable rates of acrylonitrile polymerization were obtained with the ferric ion - hydrogen peroxide system, but considerably higher yields were obtained at higher currents using potassium persulphate and cumene hydroperoxide-ferric ion couples. A sample calculation indicated that 1.3×10^3 moles of acrylonitrile were polymerized for each mole of ferrous ion produced. The attempted polymerization of styrene and isoprene was unsuccessful.

IONIC POLYMERIZATION.

Although free radical mechanisms are more common, electrolysis may be employed to induce ionic polymerizations in solution. The cationic polymerization of styrene, vinylbutyl ether, and N-vinyl carbazole by the anodic discharge of BF_4^- and ClO_4^- in nitrobenzene solution has been reported (83)(96). BF_4^- is oxidized to BF_3 which undoubtedly forms a catalyst-cocatalyst complex with trace amounts of water present in solution (97). The BF_3OH_2 dissociates to form a complex anion and a proton which is capable of cationic initiation.

 $2BF_4 \rightarrow 2BF_3 + F_2 + 2e^-$

 $BF_3 + H_2^0 \rightleftharpoons BF_3^{0H_2} \rightleftharpoons BF_3^{0H_2} + H^+$

The initiating effectiveness of the oxidation product of ClO_4^- has been questioned (98) since ClO_4^- is a powerful cationic initiator in the absence of electrolysis (99)(100).

In 1959, Breitenbach reported the initiation of acrylonitrile polymerization by the cathodic discharge of tetraethyl-ammonium perchlorate (101). At that time the reaction mechanism was believed to be free radical as a following result of the reaction, but later it was proved to be anionic (83)(96).

 $(C_2H_5)_4N^+ + e^- \longrightarrow (C_2H_5)_4N^ (C_2H_5)_4N \longrightarrow (C_2H_5)_3N + C_2H_5^{\bullet}$

The polymerization of styrene initiated by electrons supplied directly from the cathode had been reported earlier (102). Although in this latter case no mechanism was presented, it is reasonable to assume that both reactions were the result of a direct electron addition followed by an anionic polymerization.

Detailed studies of electrolytic initiation were carried out in very few of the above examples. It was, therefore, the purpose of this research to explore more fully both Kolbe and anionic initiation mechanisms.

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EXPERIMENTAL

MATERIALS.

1-Vinyl-2-pyrrolidone (VP), stabilized with NaOH, from Matheson, Coleman and Bell, was twice distilled at 87-88°C and 3.5 mm Hg and middle fraction collected. The purified monomer was frozen solid and stored at -25°C for no more than one week before it was used.

Monomeric acrylonitrile (AcN) (Eastman Organic Chemicals) was fractionally distilled at reduced pressure the and middle portion stored over CaSO₄ and BaO for several days before redistillation.

Methyl methacrylate (MMA) was freed of phenolic inhibitors by repeated washings with 5% NaOH solutions containing NaCl. After mixing with distilled water, the monomer was dried over CaSO₄ for twenty-four hours and then fractionally distilled at reduced pressures.

Dimethyl formamide (DMF)(Matheson, Coleman and Bell) was purified by fractional distillation, stored over CaSO₄ and BaO for several days, and redistilled before use.

Absolute methanol (99.8%) and potassium acetate (Baker Analysed Reagent) was used without further purification.

Polarographic grade tetramethyl ammonium iodide (TMAI)

(Southwestern Analytical Chemicals) was used without further purification.

Unless otherwise indicated, inorganic salts of the highest available purity were dried for a minimum of twenty hours at 180°C under vacuum.

POLYMERIZATIONS.

Polymerizations were initiated electrochemically in cells which had two basic designs. For reactions which require the anode and cathode polymer to be analysed individually, a cell separated by a sintered glass disk of medium porosity was employed (Figure seven). Circular platinum electrodes of diameter 2.5 cm were sealed into the glass as close as possible to the glass disk in order that the IR drop be a minimum. The total volume of the cell was approximately 80 ml.

Reaction cells used in all kinetic runs had a total volume of approximately 150 ml and were cylindrical in shape with side arms for the admission of nitrogen and the withdrawal of samples (Figure eight). The platinum electrodes had a surface area of one square inch and were sealed into a removable top of the cell.

The cell and electrodes were dried and flamed before each polymerization.

Two distinctly separate electrochemical initiations

FIGURE 7. Divided Polymerization Cell.

- (a) mercury contacts
- (b) medium porosity sintered glass disk
- (c) platinum electrode



FIGURE 8. Polymerization Cell Used for Rate Determination.

(a) platinum electrodes

(b) self-sealing gasket



were investigated. Reactions studying Kolbe initiations were conducted at room temperature. Vinyl pyrrolidone solutions of varying concentrations were prepared in methanol containing 1.33 moles of potassium acetate per litre. Oxygen and other dissolved gases were removed by bubbling with predried nitrogen prior to the start of the electrolysis. Agitation was accomplished by magnetically stirring the solution.

The anionic series was conducted at $30 \pm .05^{\circ}$ C in dimethyl formamide containing monomer and saturated with the inorganic salt under consideration. Dissolved gases were again removed by vigorously bubbling the solution with predried nitrogen. In order to maintain the exclusion of oxygen and carbon dioxide, bubbling with nitrogen at a reduced rate was continued throughout the reaction.

A constant rate of initiation was achieved by the use of highly stabilized currents. A constant current supply designed by W. G. Hoyle of the National Research Council of Canada was used for the range between 1.5 and 15 milliamperes (Figure nine). Stable currents up to 500 milliamperes could be attained by an Ambitrol 4005 when the total resistance of the solution was less than eight ohms.

In the "Kolbe" series, polyvinyl pyrrolidone formed

insolubly on the anode, negating any possibility of determining rates of reaction. In this case the polymer was removed from the electrode, dried and weighed. Because of its complete insolubility in all the solvents tested, no further characterization of the polymer was attempted.

Kinetic curves were determined gravimetrically. Samples were removed by a special hypodermic syringe with a 38 cm needle through a self-sealing gasket and precipitated in 50% methanol. Dimethyl formamide was removed by slurrying the polymer several times in methanol and drying in a strong current of air.

COPOLYMER ANALYSIS.

The acrylonitrile-methyl methacrylate copolymer compositions were determined by Kjeldahl analyses as described by Cole and Parks (103).

INFRA-RED SPECTRA.

Nujol mulls of polymer samples were prepared and distributed between two flat NaCl disks. Infra-red spectra were determined with a Perkin-Elmer infra-red spectrometer, model twenty-one.

POLAROGRAPHY.

Polarographic analyses were accomplished in cylin-

drical cells using a mercury pool as the anode. Nitrogen was admitted at the top of the cell through a tube which permitted either bubbling the solution or blanKeting it during an experiment. The polarographic curves were obtained with a Radiometer, Copenhagen instrument which had a current scale calibration of $0.00035 \,\mu$ A/mm at maximum sensitivity.

The dropping mercury electrode was operated from a height of 42.2 cm and had a droptime of 2.58 seconds in dimethyl formamide at zero potential. The m 2/3 t 1/6value was 2.30 mg 2/3 sec -1/2.

Well defined waves were obtained without the necessity of adding small percentages of water.

INTRINSIC VISCOSITY.

Intrinsic viscosities were determined at $25 \pm .05^{\circ}$ and $30 \pm .05^{\circ}$ C with an Ubbelohde viscometer.

X-RAY.

X-ray powder photographs were obtained. They revealed the characteristically hazy pattern of amorphous polymers.

FIGURE 9. Constant Current Supply.



RESULTS AND CALCULATIONS

KOLBE

Polymer (polyvinyl pyrrolidone) was produced at the anode by the oxidation of carboxylic anions in methanolic solution. Although the polymer formed in insoluble sheets on the electrode making a true kinetic study impossible, it neither increased the resistance of the solution nor hindered electrolysis. The reactions, therefore, were stopped when polymerization reached approximately 1% and the yield of polymer was determined as a function of both current density and monomer concentration. The relative efficiencies of the reactions were determined by calculation of the yield per faraday and plotting them against the current density (Figure ten) and weight percent monomer concentration (Figure eleven).

ANIONIC.

Polymer was produced by electrolysis of dimethyl formamide (DMF) solutions containing monomer. Salts were added to reduce the resistance of the solution.

In order to initially determine which electrode was producing polymer, the homo-polymerization of styrene, MMA, and AcN was effected in divided cells. The results are presented in Table six.

FIGURE 10.

Efficiency (Yield per Faraday) vs Current Density.

At a constant vinyl pyrrolidone concentration of 23.4 weight percent in methanol-potassium acetate.



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FIGURE 11. Efficiency (Yield per Faraday) vs Monomer Concentration.

At a constant current density of 31.1 mA/cm².



TABLE VI

· · · · · ·			· · · · · · · · · · · · · · · · · · ·
Monomer	Mole % in DMF	Weight Cath- ode Polymer (gm)	Weight Anode Polymer (gm)
Styrene	25.2	2,583	1.067
Methyl Methacryl ate	- 26.8	9.509	1.765
Acrylonitrile	37.0	12.102	less than 0.200
Vinyl Acetate	29.4	no polymer	ization

Amounts of Anode and Cathode Polymer Formed by Electrolysis in Divided Cells of Styrene, MMA, AcN, and Vinyl Acetate in DMF Saturated with NaNO₃

The determination of the mechanism of propagation was accomplished by copolymerizations in DMF solutions saturated with the salt under investigation. These reactions were carried out in a cell with divided anode and cathode compartments. For each copolymerization there were 38.6 mole % MMA to 61.4% AcN.

When an equimolar mixture of AcN and MMA is free radically initiated, the resulting polymer will contain approximately equal proportions of both monomers (77). Anionically polymerized AcN-MMA mixtures will contain predominantly AcN (104)(105), whereas cationically initiated AcN and MMA does not yield polymer readily (106). to percentage AcN by the factor:

% AcN = (% N in polymer)(100/26.4)
The copolymerization analyses on the cathode polymer are
represented by Figure twelve. The high AcN concentrations indicates an anionic mechanism.

Anodic copolymers, in general, had AcN compositions slightly in excess of that theoretically expected for free radical copolymerizations. Since the cathode compartment contained at least ten times as much polymer as the anode, it is believed that these deviations were due to diffusion of cathodic polymer into the anode compartment.

Not all salts were equally efficient as "initiators" of polymerization. The results of reactions at the cathode of divided cells are presented in Table seven. The salts are listed in the relative order in which their cations appear in the electromotive force series. Although there is no justification for this order in DMF, it probably does represent a first approximation (107).

The polyacrylonitrile which formed at the anode and cathode compartments appeared physically different. Anodic polymer was colorless in the reaction solution and precipitated white. The cathodic polymer, however, colored the reaction solution a dark orange and precipitated in various shades of yellow. In addition, small amounts of insoluble polyacrylonitrile which formed on the cathode had darker shades of yellow than the soluble polymer. To

investigate the insolubility and coloration, homopolymers of acrylonitrile were cathodically produced and their infra-red spectra were compared to anodic polyacrylonitrile (Figure thirteen).

TABLE VII

Effectiveness of Salts as "Initiators" of Polymerization in Divided Cells (67.8 mole % DMF, 19.8 mole % AcN, and 12.4 mole % MMA).

Salt	Result	Initial Potential (volts)	Current
LiN03	polymer	••• ·	15
KClO4	polymer	10	15
KAc	polymer	33	4
srcl ₂	polymer	23	15
NaNO3	polymer	11	10
NaCl	polymer	-	-
MgCl ₂	polymer	-	-
$Zn(NO_3)_2$	polymer	36	6
ZnCl ₂	polymer	10	6
FeCl ₂	no polymer	18	25
TlNO3	polymer	200	15
CoCl ₂	sludge	15	5
NiCl ₂	sludge	9.5	15
SnCl ₂	no polymer	50	15
PbN03	no polymer	-	-
FeCl ₃	no polymer	18	12

cont'd

Salt	Result	Initial Potential (volts)	Current (mA)
HAC	no polymer	64	15
CaCl ₂	no polymer	8.6	25
cus0 ₄	polymer	400	15
AgN03	no polymer	13	25

TABLE VII CONT'D

The kinetics of cathodic (anionic) acrylonitrile polymerization were studied as a function of concentration, current and, to a limited extent, temperature. Reactions, unless otherwise stated, were conducted at $30 \pm .05^{\circ}$ C in DMF solution saturated with NaNO₃. The effect on AcN concentration on the rate at 15 milliamperes is shown in Figures fourteen and fifteen. The rates as a function of current at a constant AcN concentration of 37.0 mole % are presented in Figures six-The variation of intrinteen, seventeen and eighteen. sic viscosity with AcN concentration at 15 milliamperes is given in Table eight. The intrinsic viscosities at constant AcN concentration and variable current are presented in Table nine.

The influence of three temperatures on the rate of polymerization of 37.0 mole % AcN in DMF saturated with NaNO₃ at 15 milliamperes is given in Table ten.

FIGURE 12. Copolymerization Analyses of Cathodically Formed Polymers (Table VII).



FIGURE 13. Infra-red Spectra of Polyqcrylonitrile.

(1) colorless polyacrylonitrile

(2) soluble cathodic polymer

(3) insoluble cathodic polymer



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FIGURE 14. Rate (gm/l/min) vs Monomer Concentration for AcN at 15 mA.



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FIGURE 15. Rate (% Polymerization) vs Monomer Concentration for AcN at 15 mA.



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FIGURE 16. Rates (gm/l/min) for Various Currents (Current written above each line) for 37.0 mole % AcN in DMF.



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FIGURE 17. Rate of Polymerization as a Function of Current for 37.0 mole % AcN in DMF.



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FIGURE 18. Rate of Polymerization as a Function of the Square Root of Current for 37.0 mole % AcN in DMF.



TABLE VIII

AcN Concentra- tion (mole % AcN)	Rate (gm/l/min) x 10	Intrinsic Viscosity (dl/gm)
12.4 20.8 32.0 37.0 54.0 62.3 70.0 75.1 79.5 100	1.01 1.94 3.17 3.43 6.06 7.04 7.29 1.57 0.65 0.00	• 054 • 051 • 050 • 052 • 053 • 051 • 053 • 055 • 155

Effect of AcN Concentration on the Intrinsic Viscosity at 15 Milliamperes and 30°C.

TABLE IX

Effect of Current on the Intrinsic Viscosity at 37.0 Mole % AcN and 30°C.

والمراجع والمستحد والمراجع والمستكف المستكرة والمتراجع المحافل ومحتها والمتراجع والمراجع والمتكر المتكر المتعا		
Current (mA)	Rate (gm/l/min) x10	Intrinsic Viscosity (dl/gm)
0.90 4.4 9.1 15 40 75 125	0.76 1.74 3.03 3.43 6.18 9.54 16.20	• 059 • 053 • 054 • 052 • 055 • 054 • 050

TABLE X

Temperature	Rate	Intrinsic
(00)	(gm/l/gm) x 10	(dl/gm)
0	2.92	.060
30	3.43	•052
60	2.62	•052

The Influence of Temperature on the Rate of 37.0 Mole % AcN in DMF at 15 Milliamperes Saturated with NaNO3

Absolute efficiencies of anionic initiation may be calculated from a knowledge of the number of moles of polymer produced and the number of faradays required for their production. In the present research, rates were obtained as a function of monomer concentration and current. The molecular weights have been found constant (Tables eight and nine) and for the purposes of the present calculations have been assumed to be 4000. As a sample calculation at a current of 0.9 milliamperes, a rate of 0.076 gms/1/min That is, in one minute $0.9 \ge 60 \ge 10^{-3}/$ was obtained. $96,494 = 5.57 \times 10^{-7}$ faradays produce 0.076/4000 =1.90 x 10⁻⁵ moles of polymer. The efficiency, therefore, is $(1.90 \times 10^{-5})/(5.57 \times 10^{-7})$ or 3410%.

The results of efficiency calculations as a function of monomer concentration and current are shown in Figures nineteen and twenty respectively.
FIGURE 19. Efficiency of Initiation Vs Monomer Concentration.



FIGURE 20. Efficiency of initiation Vs Current.



The effect of eight salts on the intrinsic viscosity and rate of polymerization at constant AcN concentration (37.0 mole %) and constant current (15 milliamperes) is listed in Table eleven.

TABLE XI

The Effect of Eight Salts as Efficient "Initiating" Electrolytes at 37.0 mole % AcN, 15 milliamperes and 30°C.

عيها مناصل ببيناه البيدية				
_Salt	Initial Potential (volts)	Current (ma)	Rate (gm/l/min x 10)	Intrinsic Viscosity (dl/gm)
LiNO3	4.8	15	0.76	0.310
KClO4	4•2	15	4.16	.115
SrCl ₂	4•5	15	3.00	.132
NaNO3	4.0	15	3•43	•052
NaCl	10	15	3.57	.114
MgCl ₂	3.7	15	2.92	.057
ZnCl ₂	2.9	15	-	_
TINO3	3.2	15		- ,

Polarographic curves for the monomers in DMF are reproduced in Figure twenty-one. These data, as well as that obtained for a number of salts in DMF, are presented in Table XII. The results obtained for polarography in dimethyl sulphoxide are given in Table thirteen.

FIGURE 21. Polarographic Curves.

Diffusion current (300 x height in centi-meters x .0035) μ A vs applied potential using a mercury anode.

Vinyl Acetate
Acrylonitrile
Methyl Methacrylate
Styrene
NaNO₃



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TABLE XII

Polarographic Data in DMF saturated with TMAI

Compound	Concentra- tion (mmoles/l)	E% vs Hg pool (volts)	id (nA)
Acrylonitrile	1.51	- 1.69	5.46
Styrene	0.90	- 1.99	2.15
Methyl Methacrylate	0•94	- 1.79	5.04
Vinyl Acetate	1.10	no wave	
LiN03	-	- 1.95	7.88
KClO4	1.37	- 1.58	4.20
NaNO3	3.20	- 1.55	10.17
NaCl	2.27	- 1.57	4.31
MgCl ₂	2.12	- 1.90	5.25
$z_n(NO_3)_2$	0.66	- 0.55	6.62
CoCl ₂	1.05	- 0.64	2.21
sncl ₂	1.96	+ 0.21	67.20
CuCl ₂	1.19	+ 0.20	75.60
CuSO ₄	1.05	+ 0.23	73.50

The equation of the polarographic waves can be shown to be $E = E_{2}^{\prime} - (.0591/n) \log (id-i/i) + K'$ at $25^{\circ}C$ (108). E represents the potential on the electrode and E_{2}^{\prime} the value at the midpoint of the polarographic wave; id is the diffusion current and i is the current at any point on the wave. The number of electrons taking part in the reaction is n. The value of K', a ratio of diffusion coefficients, is so small that it usually can be neglected. Therefore a plot of log (id-i/i) vs E should yield a straight line whose slope is -0.0591/n. For reversible reactions n will be a whole number. Values of n below approximately 0.7 indicate that the reaction is taking place irreversibly.

A plot of log (id - i/i) vs E for styrene, MMA, and NaNO₃ is given in Figure twenty-three and for AcN in Figure twenty-four.

TABLE XIII

			1
Compound	Concentra- tion (mmoles/l)	E½ vs Hg pool (volts)	id (mA)
Acrylonitrile	1.51	- 1.58	1.35
Styrene	0.90	- 1.99	3.58
Methyl Methacrylate	0.94	- 1.69	l.40
NaNO ₃	2.18	- 1.57	4.57

Polarographic Data in Dimethyl Sulphoxide Saturated with TMAI

FIGURE 22. Log <u>id-i</u> vs E for Styrene, Methyl Methacrylate, and NaNO₃.



FIGURE 23. Log $\frac{id-i}{i}$ vs E for Acrylonitrile.



DISCUSSION

KOLBE.

Although there has been confusion as to its exact nature (109), the mechanism of the Kolbe reaction at present is believed to obey the following equations:

R -	c ^{≠0} —	0>	R -	c≠ ⁰ - 0•	+ (9
R -	c≠ ⁰ —	0•>	R∙	+ CO ₂		
2R•	. <u></u>	>	R -	R		(5)(110).

Utilization of the radical intermediates as initiators of polymerization has received limited attention (81)(82)(83). For the most part, investigators were content to demonstrate that the radicals could activate the double bond, and as a result, did not quantitatively study the factors influencing the reaction. A recent study from this laboratory will soon be published on the production of polymer homogeneously in solution (84). The present work has investigated the influence of current density and monomer concentration on the production of insoluble polymer.

Vinyl pyrrolidone monomer was initially chosen because of the high solubility of its polymer in most solvents including water and methanol. Therefore, the

nature of the insoluble polymer which formed must, in some way, be dependent upon the conditions of electrolysis. Since electrolytically generated radicals have been shown to initiate polymerization (81)(82) (83)(84), linear chains of polyvinyl pyrrelidone undoubtedly were formed. Cross linking to the extent of a few percent is responsible for the formation of insoluble polymer (111). It is reasonable to believe, therefore, that cross linking of polymer chains has caused insolubilization of polyvinyl pyrrelidone - particularly in view of the following arguments.

For the case of acetate anions, at a current of 0.1 amps, there are approximately 6 x 10^{17} CH₃. radicals produced per second. The majority of these radicals dimerize to form ethane. Some add to the double bond initiating polymerization (equation six), whereas still others abstract labile hydrogens from neighbouring molecules. When hydrogen abstraction occurs, a cross link may be formed.

The molecular structure of polyvinyl pyrrölidone is shown below:



There are three positions, marked by an asterisk, from which a hydrogen may be readily removed. The resulting radical in each case will have some resonance stabilization.







Because of the high methyl radical concentration at the anode and because of the stability of the various pyrrolidone radicals formed, the abstraction of hydrogen atom will take place often and with relative ease, yielding completely insoluble polymer.

It was stated previously that the majority of all methyl radicals produced dimerize to form ethane. Indeed studies on the Kolbe reaction have revealed that at high

current density approximately 90% of all the radicals dimerize (112) but that the percentage yield of dimer decreases at lower values (113)(114). Presumably the fewer radicals generated at low current densities interact with solvent before dimerization can occur. It can be predicted, therefore, that the efficiency of radicals as initiators of polymerization will be completely opposite to that of dimerization. That is, there will be a high efficiency of initiation at low current densities.

Figure eleven indicates the variation of initiation efficiency with monomer concentration. As one would expect, increasing the concentration of monomer initially increases the efficiency of electrolysis. There is, however, little effect on the ratio of yield/faraday at monomer concentrations in excess of 20 weight per cent. Presumably this limit is governed by the rate of diffusion of monomer to the electrode surface as well as an increased rate of termination.

The maximum attainable efficiency of initiation can be shown to be exceedingly low. If, for example, one assumes that at an efficiency of four grams per faraday the molecular weight of polymer is 4000, the number of moles produced is 0.001. This is equivalent to an efficiency of 0.1%. Unless current densities less than 1 mA/cm² are used, efficiencies less than this value will be obtained (Figure ten).

ANIONIC.

Polymerization, activated by a cathodic discharge, has been the subject of a number of investigations (83)(88)(90)(91)(94)(95)(96)(101). In several cases polymerization was initiated by hydrogen atoms formed from the reduction of hydrogen ions in acidic solution (88)(89)(90)(91). In another, initiating HO• radicals were produced by generating Fe^{++} which induced the decomposition of HOOH (95). Free radicals. produced by the electrolytic reduction of certain organic substances, also have been used to cause polymerization There are, however, only four publications which (94). bear directly on the present research: Breitenbach has reported anionic polymerization initiated by the cathodic discharge of tetra alkyl ammonium ions (83)(96): Yang, McEwen, and Kleinberg have indicated in a letter that styrene can be initiated by electrons supplied from a magnesium electrode (102): Polyacrylonitrile formed on a dropping mercury cathode in dimethyl formamide solution (115).

In the present research, we have demonstrated that styrene, methyl methacrylate, and acrylonitrile will polymerize at a cathode during electrolysis whereas vinyl acetate remains unaffected (Table six). We have further shown by copolymerization studies that the reaction takes

place anionically (Figure twelve) forming polymer of relatively low molecular weight.

A polarographic study to determine the initiation mechanism was performed. The distinct waves which were obtained (Figure twenty-one) are entirely analogous to those of other unsaturated hydrocarbon reductions (116) (119)(118) and as such are interpreted as due to a direct electron addition to the double bond. Values of n for the three monomers indicate that the reaction is reversible for styrene and methyl methacrylate but irreversible for acrylonitrile.



The n for acrylonitrile (0.32) is in reasonable agreement with the value previously reported (115).

No wave was obtained with vinyl acetate monomer.

This may be interpreted as indicating a lack of an initiation step which, of course, would explain the absense of any polyvinyl acetate formation.

Direct electron addition to monomer is the initiation mechanism postulated by Szwarc for anionic polymerizations activated by sodium-aromatic hydrocarbon adducts (equation twenty-seven)(22)(23). Although this mechanism is generally accepted, the present work offers direct evidence as to its validity. It also has been found that anionic initiation will take place in the relative order acrylonitrile) methyl methacrylate) styrene (104). An inspection of the halfwave potentials of these monomers (Tables twelve and thirteen) shows a lower potential for acrylonitrile, followed by methyl methacrylate and sty-This clearly indicates that the rene, respectively. ease of electron transfer to these monomers is greatest for acrylonitrile and least for styrene, and offers direct proof for the previously obtained order.

Comparison of half wave potentials of a number of inorganic salts with those of the three polymerizable monomers (Table twelve) might give a clue as to their initiating effectiveness. Table eleven indicates that, of the salts used as electrolytes, ZnCl₂ and TlNO₃ did not yield polymer whereas the salts of Mg⁺⁺, Na⁺, Sr⁺⁺, K⁺, and Li⁺ did. The half wave potentials of these salts in dimethyl formamide (Table thirteen) reveal a

distinctly higher potential for Zn⁺⁺, Co⁺⁺, Sn⁺⁺, and Cu⁺⁺ than the other salts studied. It appears, therefore, that when the reduction potential is sufficiently low, the inorganic cations will be discharged to the complete exclusion of electron addition to the double bond. At higher negative potentials there will be competition for electrons from the vinyl groups resulting in the activation and subsequent polymerization of the monomer.

Qualitative confirmation of the view that initiation is due to a direct electron transfer independent of cations present in solution has been obtained. Electrolysis of acrylonitrile solutions in dimethyl formamide and dimethyl sulphoxide in the complete absence of salts produced polymer at the cathode. Extremely high voltages and low unstable currents as well as the insolubility of the polymer made a quantitative investigation impractical.

The results for LiNO₃ appear anomalous in that the rate of polymerization is slowest and yet its reduction potential is highest. One would justifiably expect that, because of the high negative potential, the initiation efficiency with this salt would be greatest. Although this is true, the rate is dependent not only upon the initiation but also upon the propagation and

termination of polymerization. Both the slow rate and copolymerization data indicate a high percentage of free radical polymerization when lithium salts are used as electrolytes. In fact, it has been reported that metallic lithium induces significant free radical copolymerization (119)(120), whereas other group one metals promote purely anionic reactions (see for example (121)(122)). This automatically disallows any comparison with other reactions whose mechanisms are predominantly anionic.

The half wave potentials obtained in dimethyl sulphoxide indicate that the reduction potential of acrylonitrile and methyl methacrylate is lower by 0.1 volts compared to dimethyl formomide. Styrene and NaNO₃ remained unchanged.

Table VII indicates the effectiveness of salts on the initiation of copolymerization of acrylonitrile and methyl methacrylate. The salts, listed in the order in which the cations appear in the electromotive force series, show a transition from effective to non-effective initiating electrolytes between Zn⁺⁺ and Sn⁺⁺. These results, however, cannot be directly compared to those of Table XI. The presence of a sintered glass disc separating the anode and cathode compartments increased the resistance of the solution and thereby

the potential (at a constant current) at least $2\frac{1}{2}$ times more than when no separation was employed. It is believed that electron transfer to the monomer will occur at this increased potential in the presence of $2n^{++}$ but will not take place when the potential is lower.

The intrinsic viscosities of polyacrylonitrile formed in dimethyl formamide in the presence of NaNO₃ are shown to be independent of temperature (Table ten), monomer concentration (Table eight), and current (Table nine). Values of about 0.053 for the intrinsic viscosities are identical with those previously reported for anionic acrylonitrile polymerizations in dimethyl formamide (123).

A closer examination of the copolymerization data (Figure twelve) might be propitious at this stage of the discussion. Firstly, the four independent determinations of acrylonitrile concentration in NaNO₃ "initiated" polymers indicate a purely anionic propagation mechanism. The deviations from ideal anionic copolymer structure of the polymers formed in the presence of other salts cannot be attributed to the experimental error of the analysis. Some free radical polymerization must be occurring.

The initiation step, as indicated by the equations

on page 89, produce species which are simultaneously radical and an ion (124).

$$\begin{array}{cccc} H & H & H & H \\ \hline & & & & \\ \hline \vdots C & - & C \cdot & \longleftarrow & \cdot C & - & C \vdots \\ \hline & & & & & \\ H & R & & H & R \end{array}$$

Pure anionic polymerization results when dimerization,

is followed by propagation at both ends. This is the normal situation for anionic polymerizations, initiated by an electron. However, it is possible that under conditions in which dimerization does not occur, anionic polymerization will take place from one end and free radical from the other. Indications of thisphenomenon have been reported (119)(120), and it is conceivably the explanation for deviations from ideal anionic copolymer structure in Figure twelve.

Since the initiation mechanism is in every case a direct electron addition to the double bond, the varying extent of free radical and anionic reactions must depend upon the nature of the gegen ion in solution. The difficulty in knowing the effect of the gegen ion has been discussed by Szware (124). One may argue that the electrostatic field of the growing ion polarizes the approaching monomeric molecule, and this process is responsible for the addition. According to this point of view the presence of gegen ions would inhibit the reaction since they weaken the strength of the polarizing field. On the other hand, the polarization of the monomeric molecule might result from a concerted action of negative and positive ions interacting with its opposite ends. In this case the presence of a gegen ion should enhance the propagation, since the ions reinforce each other's action.

It is tempting to utilize the present results to resolve this problem. For instance, one may argue that anionic polymerization in the presence of a divalent cation such as Mg⁺⁺ will be significantly different from that for the corresponding sodium salt. A comparison of the copolymerization (Figure twelve) and rate data (Table eleven) of MgCl, and NaCl polymerizations reveal a slightly lower per centage of anionic reaction for the divalent cation. More significantly, however, is the slower rate for the magnesium ion. (Ionic reactions are much more rapid than free radical). These results may be explained by assuming that the larger cation hinders the anionic reaction thereby slowing the overall rate and increasing the relative proportion of free radical Further, a similar comparison of LiNOz and polymer. NaNO3 polymerizations indicates definite free radical characteristics for the lithium salt. In this example, LiNOz is less ionic than NaNOz in dimethyl formamide, and

therefore the lithium ions would be expected to associate more strongly with the propagating anion. Both examples seem to indicate that the gegen ion hinders propagation.

An electropositive gegen ion may also stabilize the radical ion by complexing with the three electron bond, in much the same way as some metal salts form complexes with olefings or aromatic hydrocarbons (125).

$$\mathbb{M}^{n+} + \frac{H}{\mathbf{C}} - \frac{H}{\mathbf{C}} + \frac{H}$$

When the first addition takes place, there will be a definite separation of the radical and anion.

$$\overset{\mathrm{H}}{\overset{\mathrm{I}}{_{\mathrm{C}}}} - \mathrm{CH}_{2} - \mathrm{CH}_{2} - \overset{\mathrm{H}}{\overset{\mathrm{C}}{_{\mathrm{C}}}} \overset{\mathrm{H}}{_{\mathrm{C}}} \overset{\mathrm{H}}{\overset{\mathrm{I}}{_{\mathrm{C}}}}$$

The cation and anionic end of the polymer will form an ion pair. Definite conclusions concerning these effects, however, cannot be made until auxiliary data regarding the nature of the cations in solution are obtained.

Figures fourteen and fifteen indicate that the rate is dependent upon the first power of the monomer concentration. Since the molecular weight is constant, more molecules are necessarily being formed at the faster

rates. A calculation, assuming a molecular weight of 4000, reveals that approximately twenty polymer molecultes are produced per electron at seventy mole per cent acrylonitrile, whereas about four are formed at twenty mole per cent at a constant current of fifteen milliamperes (Figure nineteen). A kinetic scheme utilizing the initiation and propagation steps previously discussed and a chain transfer mechanism to explain the above facts is presented.

Initiation

 $M + I \longrightarrow M^{\bullet}$ kl

where I is the current and M. is an ion radical.

Dimerization

2M• - _ M - M k2

Propagation of dianion

 $M - M_{n-1} - M + M \longrightarrow M - M_n - M$ k3

Chain transfer of dianion

 $M - M_m - M + M \longrightarrow M_{m+1} - M + M$ k4

Propagation of anion

$$M_{n-1} + M \longrightarrow M_n \quad k5$$

Transfer of anion

 $M_m + M \longrightarrow Pm + M - k6$

The rate of propagation is $Rp = k3 (-M-M_{n-1}-M)$ $(M) + k5 (M_{n-1})(M)$. If anionic polymerization reactions of dianions occur at each active site independent of the other, the rate constants for the individual steps will be equal to those for the mono-anions (that is k3 = k5and k4 = k6) although the rate of dianionic reactions will be twice as great. Therefore we may write

$$Rp = 2k3 (M_{n-1})(M) + k3 (M_{n-1})(M)$$

= 3k3 (M_{n-1})(M)

The rate of termination or chain transfer is given by Rt = k6 (M_m^-)(M)

The degree of polymerization, DP= Rp/Ri

$$\overline{\text{DP}} = \frac{3k3 \ (\text{M}_{n-1}^{-})(\text{M})}{k6(\text{M}_{m}^{-})(\text{M})}$$

If the assumption that the reactivity of the anion is independent of the length of the chain is made, then for kinetic purposes $M_{n-1}^- = M_m^-$ and $\overline{DP} = 3k3/k6$, a constant.

Chain transfer to monomer is the critical reaction. At a constant rate of initiation, the rate of propagation $\omega:th [m]$ increases but the ratio of Rp/Rt remains constant - a fact in complete accord with the experimental results.

If transfer with solvent took place,

 $\mathbb{M}_{n}^{-} + \mathrm{SH} \longrightarrow \mathrm{Pn} + \mathrm{S}^{-} \qquad \mathrm{k7}$

the expression $\overline{DP} = 3k3(M)/k7(SH)$ may be derived. The molecular weight in this case would be a function of the ratio of monomer to solvent concentration.

The independence of molecular weight on initiator and monomer concentration for acrylonitrile has been reported due to chain transfer to monomer in a previous publication (123). The authors were able to demonstrate that the tertiary hydrogen was responsible for the transfer by repeating experiments with methacrylonitrile. In this case no tertiary hydrogen is available and a direct dependence of molecular weight on monomer concentration was obtained.

The derivation of a rate scheme which would be half order with respect to current at low amperages, but first order at higher values (Figures seventeen and eighteen) has proved extremely difficult. In the author's opinion, the most acceptable mechanism assumes that the rate determining step of the polymerization is the dimerization of radical ions to form dianions. The stabilization of the radical ions by resonance forms (page 94) corroborates this assumption although unequivocal justification is not available.

Rate = $k2(M \cdot)^2$

Applying the steady state condition

 $dM \cdot /dt = kl(M/t) - k2 (M \cdot)^2 = 0$

Therefore the rate = kl(M)(I).

Because strict adherence to first order kinetics with respect to current was not found at low amperages, efficiencies of initiation have been calculated by comparing the total number of moles of polymer formed with the number of faradays passed through the solution. An efficiency of 3400%, therefore, indicates that one faraday has produced thirty-four moles of polymer. In these examples then, efficiencies may be considered as alternate indices of chain transfer.

An inspection of the efficiency of reaction as a function of current (Figure twenty) indicates extremely high efficiencies of chain transfer at low currents. At higher currents it rapidly decreases and becomes sensibly constant at about 510%. These large variations of efficiency are believed responsible for the deviation from first order kinetics at low currents.

The polymers of methyl methacrylate and styrene were white and in every respect (except possibly intrinsic viscosity) indentical to their respective polymers formed by other means. Electrolytically produced polyacrylonitrile, however, was yellow in contrast to the normally white polymer which is produced by free radical initiation. Furthermore, insoluble polyacrylonitrile which formed had deeper shades of yellow than the soluble polymer. A comparison of the infra-red spectra of the colored and colorless polyacrylonitrile indicated little difference (Figure thirteen). The insoluble polymer, however, has a very sharp absorption at 1670 cm^{-1} corresponding to -C = N - absorption (126). A broad absorption at 1570 cm^{-1} could possibly be due to the existence of $-(C = N)_n^-$ chains (126)(127).

These results are good general agreement with a recent paper on thermal coloration and insolubilization of polyacrylonitrile by Grassie and Hay (126). The amount of color formation was found to parallel the degree of -C = N- and conjugated -C=N- absorption. Although an inter- or intramolecular process could not be distingui-shed, the authors argued that intramolecular rearrangements are more favourable. In the present case, removal of the tertiary hydrogen may be catalysed by an electron.



As confirmation, white soluble polymer formed by a free radical polymerization was dissolved in dimethyl formamide containing NaNO₃ and electrolysed. The solution, in accordance with the above views, turned red and insoluble polymer formed at the cathode. They(126) further propose that insolubilization is a result of "propagation crosslinks" due to the successive combination of nitrile groups to form the following type of network:



This suggestion appears quite reasonable . Coloration and the accompanying insolubilization can be initiated by the removal of a tertiary hydrogen as in the previously discussed chain transfer reaction.





The crosslinking is due to an intermolecular reaction

CLAIMS TO ORIGINAL WORK AND CONTRIBUTIONS TO KNOWLEDGE

INHIBITION.

- The details of a transition from a retarded to an inhibited polymerization of ethyl methacrylate were studied.
- 2. Retardation was found to be due to the simultaneous occurrence of primary initiator radical capture and growing polymer chain interaction.
- 3. Inhibition was found to be due exclusively to primary radical capture.

ELECTROLYTIC.

- Polymerizations of acrylonitrile, styrene, and methyl methacrylate were initiated electrolytically in dimethyl formamide solutions saturated with inorganic salts.
- 2. The initiation was found to be a direct electron addition from the cathode to the double bond.
- 3. Propagation was essentially anionic although some free radical character was found in the presence of certain salts.

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