A TRACER STUDY OF THE KOLBE ELECTROLYSIS

Presented by

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ABSTRACT

The Kolbe electrolysis as a free radical source for the initiation of addition polymerizations of methyl methacrylate in dimethyl sulfoxide was investigated with zinc acetate labelled with C^{14} in the C_1 and C_2 positions. From the number average molecular weight and activity of the poly (methyl methacrylate) produced by zinc acetate-1-C^{14} as electrolyte, the average number of acetoxy initiator fragments per polymer molecule could be determined. Likewise, the number average molecular weight and activity of polymer produced with zinc acetate-2-C^{14} yielded the average number of methyl and acetoxy initiator fragments per polymer molecule.

The number of fragments per polymer molecule was determined for several polymerizations differing only in the initial monomer feed concentration. The fraction of acetoxy initiator fragments per polymer molecule to acetoxy and methyl initiator fragments per molecule was plotted as a function of monomer feed concentration. The graph was linear with a slope shown by simple kinetics to be given by the ratio of the rate constants for acetoxy free radical decomposition and monomer capture. The intercept at infinite monomer concentration did not have the value of unity predicted for the simple anode process postulated for the Kolbe electrolysis. A more complex anode process was proposed.

Acetic acid was used in place of zinc acetate to determine the effect of hydrogen atoms on the polymerizations. The same approach as in the zinc acetate case gave a linear graph with the same intercept but a different slope. This was attributed to transfer to initiator, hydrogen atom extraction from molecular acetic acid by polymer free radicals.

To determine the effects of solvent on the free radicals produced by the Kolbe electrolysis, dimethylformamide and dimethylacetamide were used instead of dimethyl sulfoxide. The efficiency of initiation by Kolbe electrolysis products was found to be considerably less in these solvents over that in dimethyl sulfoxide.

INTRODUCTION

The addition polymerization of unsaturated organic compounds is known to proceed via an ionic mechanism, free radical mechanism, or occasionally both, depending on whether the active centers capable of chain reactions are positively charged (carbonium ions), negatively charged (carbanions), or contain an unpaired electron (free radical). Since an ionic mechanism was not encountered in this study, the discussion will be restricted to free radical mechanisms.

The free radical mechanism of addition polymerization can be divided into three stages, initiation, propagation, and termination.

INITIATION

The initiation of free radical polymerization is intimately connected with the production of the free radical species. These free radicals provide the energy necessary to rupture the double bond of monomer molecules and thus initiate polymerization. Neglecting high energy radiation or mechanical methods, the radical production methods most often encountered are: (1) thermal, (2) oxidation and reduction, (3) photochemical and (4) electrolysis.

1. To produce free radicals at relatively low temperatures by thermal dissociation, the initiating species must contain a relatively weak bond such as the oxygen-oxygen single

bond in peroxides or the nitrogen-nitrogen single bond in azo compounds. Compounds such as the dialkyl peroxides, ROOR, or diacyl peroxides, $RC(=O)OOC(=O)R$, are the most commonly used peroxides. The dialkyl peroxides decompose thermally into alkoxy radicals which are then capable of initiating polymerization:

$$ROOR \longrightarrow 2RO\cdot$$

The diacyl peroxides decompose thermally to aroyloxy radicals which can themselves initiate polymerization or dissociate to alkyl radicals and carbon dioxide:

$$RC(=O)OOC(=O)R \longrightarrow 2RC(=O)O\cdot$$

$$RC(=O)O\cdot \longrightarrow 2R\cdot + 2CO_2$$

Azo compounds decompose thermally according to the reaction:

$$RNNR \longrightarrow 2R\cdot + N_2$$

Azoisobutyronitrile $(CH_3)_2C(CN)NNC(CH_3)_2CN$ is the best known of the azo initiators.

Other thermal initiators are the monosulfides and the disulfides RSR and RSSR.

2. Peroxides are often involved in oxidation-reduction free radical production. The free radicals are produced by a one electron transfer process:

$$H_2O_2 + Fe^{+2} \longrightarrow HO\cdot + HO^- + Fe^{+3}$$

The HO· radical is capable of initiating polymerization.

3. Photodissociation of stable molecules containing weak bonds by ultraviolet light is another important method of free radical production. Generally speaking, most substances that are suitable for thermally induced decomposition are also suitable for free radical production by photodissociation. However, the radicals produced by photodissociation may not be in their electronic ground states and as a consequence their reactivities may differ from those radicals generated thermally.

4. Free radical production by electrolysis has received little attention as a method of polymerization initiation. This method offers the advantages of molecular weight and yield programming.

The simplest free radical species produced electrolytically and capable of chain initiation is atomic hydrogen.

In 1949 Wilson et al [1] in attempting to reduce acrylic acid and methacrylic acid on a mercury cathode with sulfuric acid as electrolyte in an aqueous solution, found small amounts of the expected reduction product and fairly large yields of polymer. They presented evidence to show that this polymerization was a direct result of current passage and was a cathodic process uninfluenced by any anode process. The

authors suggested that the polymerization mechanism was free radical. Their investigation of polymerization initiation efficiency for various cathode materials suggested that the initiating species was atomic hydrogen. The efficiency increased with increasing hydrogen overvoltage due to the decreasing binding energy of atomic hydrogen with increasing overvoltage.

G. Parravano[2] in 1951 showed that hydrogen chemisorbed on metal surfaces or liberated during electrolysis can initiate the polymerization of methyl methacrylate when a 0.1 N sulfuric acid solution was used as electrolyte and metals such as platinum, palladium, lead, and mercury were used as cathodes. He concluded that the majority of hydrogen atoms released at the cathode escape as molecular hydrogen. Only a small fraction leave the electrode surface as atomic hydrogen and initiate polymerization in the body of the solution.

In 1953, Kern and Quast[3] were able to polymerize methyl methacrylate, acrylic acid, methyl acrylate and acrylonitrile in aqueous solutions by cathodic hydrogen. They also found the order of effectiveness of the cathode material to increase with increasing hydrogen overvoltage of the cathode material.

Fioshin and Tomilov[4] feel that Wilson and Kern and Quast are not justified in assuming the same mechanism for

cathodes with high hydrogen overvoltage and low hydrogen overvoltage. They agree that the Wilson mechanism probably proceeds at cathodes of low hydrogen overvoltage such as platinum, but for cathodes of high hydrogen overvoltage such as lead they propose a different mechanism:

$$CH_2 = CHCN + H^+ + e^- \longrightarrow \cdot CH_2CH_2CN$$

Recently Tsvetkov[5] studied the heterogeneous system methyl methacrylate, water, hydrochloric acid electrolyzed at lead electrodes. He found polymer product only at the cathode and an increasing polymer yield with increasing temperature. This he attributed to the fall in cathode hydrogen overvoltage with increasing temperature.

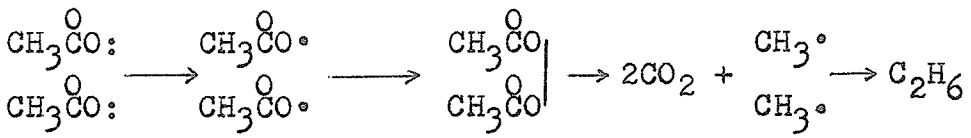
One interesting observation of Tsvetkov was that methyl methacrylate continued to polymerize for many hours after the current was shut off. This "after polymerization" was also noticed by Parravano and Kern and Quast. This is almost certainly not due to hydrogen atom initiation since this free radical species cannot be expected to exist in solution for several hours. A much more likely explanation is that initiation gives rise to radicals of long lives which are capable of adding monomer units over periods of hours.

The latest work on cathodic hydrogen initiation is that of Tsvetkov and Glotova[6]. They attempted to polymerize styrene by the electrolysis of a 0.4 M hydrochloric acid solu-

tion at lead electrodes. The results of their experiments showed that the polymerization of styrene does not occur under the influence of radicals formed at the electrodes. They attribute this to the low solubility of styrene in the aqueous solution, as a result of which there is not an efficient contact of monomer and free radicals. In order to test this conclusion, the authors made a number of experiments in which the monomer solubility was increased by using an alcohol, water mixture as solvent. Polymerization of styrene under the influence of cathodic hydrogen was observed when alcohol was introduced in the system.

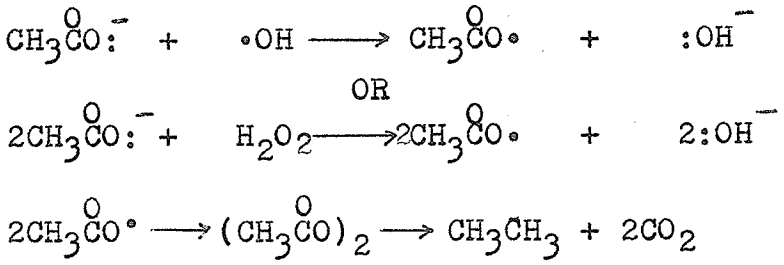
The last method to be discussed involves the production of free radicals by the Kolbe electrolysis.

In 1849, H. Kolbe [7] while atempting to isolate the methyl radical by the electrolysis of aqueous potassium acetate solution, discovered that ethane and small amounts of methyl acetate and carbon dioxide were released at the anode. Several theories have since been proposed to account for the products obtained. The first theory, the peroxide theory, was proposed by Schall and Fichter[8]. These investigators were of the opinion that the acetate ions were discharged at the anode, and the resulting free radicals reacted to form the diacetyl peroxide, which then decomposed to form the alkyl radicals and then the hydrocarbon:

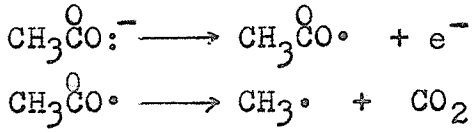


The peroxide theory is unable to explain the effects of anode material and added salts that are observed in the Kolbe electrolysis.

Another theory is the hydrogen peroxide theory, proposed by Glasstone and Hickling[9]. They suggest that hydrogen peroxide, which is first formed at the anode from hydroxyl radicals, or these hydroxyl radicals themselves prior to combination in pairs, react with the acetate ions to form acetate radicals. These then combine, possibly with the intermediate formation of diacetyl peroxide, to yield ethane and carbon dioxide:



The final theory is that of Brown and Walker[10], that the acetate ion is oxidized to the acetoxy free radical, which then decarboxylates to yield methyl free radicals and carbon dioxide:



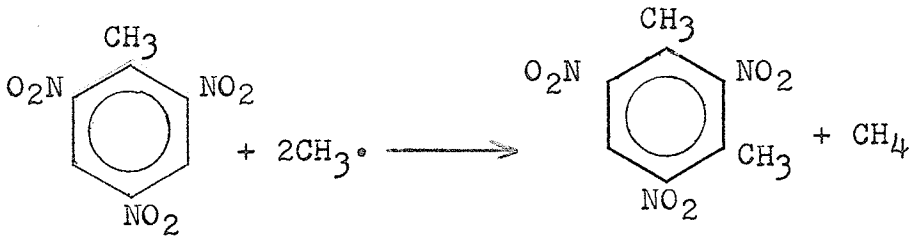
In nonaqueous medium, no hydroxyl ions are present and so neither hydroxyl radicals nor hydrogen peroxide can be formed. Therefore, the hydrogen peroxide theory is inapplicable. The remaining two theories differ only in the peroxide intermediate. There is no strong evidence to suggest such an intermediate exists[11] and most workers in the field[12,16,19] have accepted the free radical theory of Brown and Walker. The ethane and methyl acetate products of the Kolbe electrolysis can then be explained on the basis of primary radical termination:

$$CH_3\cdot + CH_3\cdot \longrightarrow C_2H_6$$

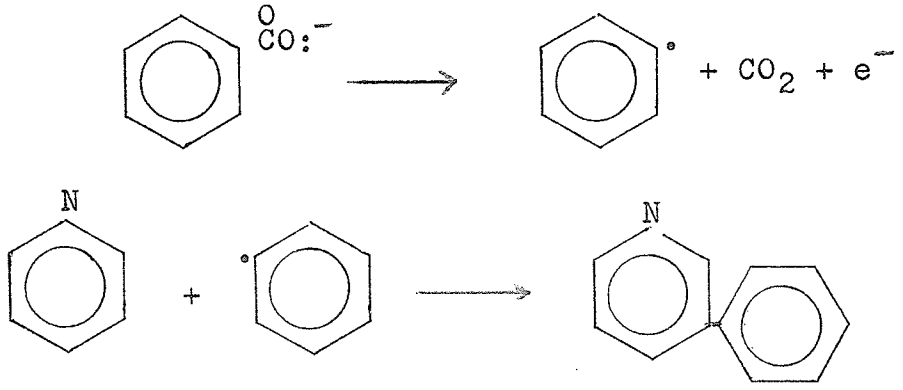
$$CH_3\cdot + CH_3\overset{O}{\overset{\|}{C}}O\cdot \rightarrow CH_3\overset{O}{\overset{\|}{C}}OCH_3$$

The Kolbe electrolysis was later found to be effective for other aliphatic carboxylic acids. It soon became a novel method of symmetrical alkane synthesis from carboxylic acids as well as for the production of olefins, dienes and esters from unsaturated dicarboxylic acids.

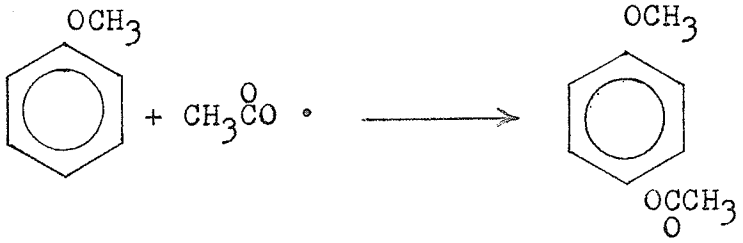
Many workers investigated the nature of the free radicals produced during the Kolbe electrolysis of acetates. Fieser and Clapp[13] reported that the electrolysis of sodium acetate in an acetic acid solution of trinitrotoluene leads to the formation of trinitro-m-xylene.



Fichter and Stenzel[14] found 4-phenylpyridine in the products of electrolysis of a benzoic acid, pyridine solution.

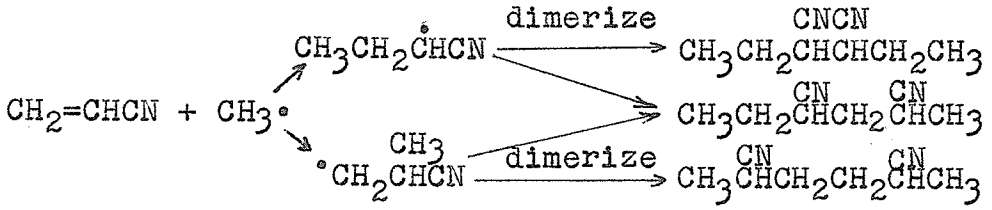


Wilson and Hayashi[15] reported a 30% yield of ortho and para acetoxyanisol formed by the electrolysis of potassium acetate in acetic acid and anisol. This is particularly interesting since it suggests a finite lifetime for the acetoxy free radical.

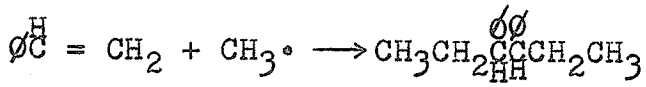


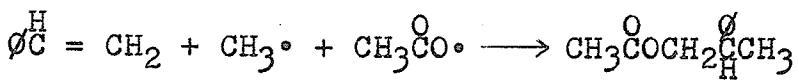
Goldschmidt and Stockl[16] also used product analysis to investigate the free radical species produced during the Kolbe electrolysis. They electrolyzed potassium acetate in

anhydrous acetic acid solution of acrylonitrile. They obtained products whose formation can only be described on the assumption that methyl free radicals are generated and then react with acrylonitrile.



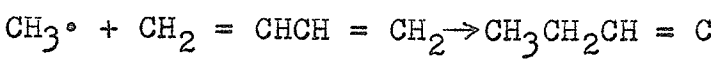
With styrene as monomer, they obtained products proving that both the methyl and acetoxy free radicals attacked styrene molecules then dimerized.

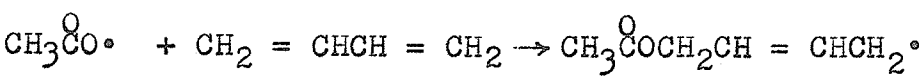




They also obtained similar products with propionic acid salts as electrolytes.

In 1959 Smith and Gilde[17] investigated the products obtained by the electrolysis of potassium acetate in methyl alcohol using butadiene as monomer. Two intermediate resonance stabilized radicals are possible:





By considering all possibilities for methyl and acetoxy free radical attack on these two intermediates, it was shown that only twenty-one products are possible (intermediate radical attack of butadiene was neglected). The authors were able to identify most of the twenty-one compounds in the electrolysis products by vapor phase chromatography.

Realizing that the Kolbe electrolysis was a useful source of free radicals in solution, Palit and Das[18] in 1950 attempted the polymerization of unsaturated monomer by free radicals generated by the Kolbe electrolysis.

They obtained poor yields of poly (methyl methacrylate) using a propylene glycol solution of sodium acetate. They found, however, that the polymer was produced at the cathode. They attributed the polymerization to hydrogen atom or sodium atom initiation.

Smith and Gilde [19] were successful in polymerizing vinyl acetate and methyl methacrylate by the electrolysis of aqueous and methanol solutions of potassium acetate. Smith and Manning[20] obtained good yields of poly (acrylic acid) by the electrolysis of aqueous solutions of acrylic acid and potassium acetate.

Smith and Gilde[21], as part of their study of the Kolbe electrolysis, examined the polymerization of vinyl acetate, methyl methacrylate, and vinyl chloride by the electrolysis

of their aqueous solutions using potassium acetate as an electrolyte. They found poly (vinyl acetate) formed only in the anode compartment and that the poly (vinyl acetate) and poly (methyl methacrylate) produced using potassium acetate-2-C^{14} as electrolyte were radioactive. Unfortunately some doubt exists as to the reliability of this tracer work since calculations on the values of polymer activity and molecular weight give over five hundred methyl and acetoxy end groups per polymer molecule. Since this value is unreasonable, the author suggests that the activity of the polymer was largely due to contamination.

Breitenbach and Srna[22] showed the free radical nature of methyl methacrylate polymerization by the electrolysis of an acetic acid solution of lithium acetate. This was accomplished by copolymerization studies with styrene and inhibition work with diphenylpicrylhydrazyl.

Funt and Williams[23] were able to polymerize vinyl pyrrolidone in a methanol solution of potassium acetate. They investigated initiation efficiency as a function of current density and found the efficiency to decrease as current density increased. This is consistent with the observation[24] that efficiency of methyl radical dimerization increases with current density.

Recently, Funt and Yu[25] investigated the Kolbe electrolysis in homogenous media in which both monomer and polymer

were soluble. This permitted a study of the electrolysis kinetics uncomplicated by polymer plating out on the electrodes. They used a dimethyl sulfoxide solution of zinc acetate and methyl methacrylate and obtained kinetics indicating a free radical mechanism.

One interesting property of the Kolbe electrolysis is the existence of a critical electrode current such that the reaction occurs significantly only above a certain limiting value of electrode current. This has been investigated by Conway and Dzieciuch[26] on the systems trifluoroacetic acid-potassium trifluoroacetate and formic acid-potassium formate using platinum electrodes. They found that a critical current was reached at 10^{-5} amps cm^{-2} and 10^{-4} amps cm^{-2} for the trifluoroacetic acid and formic acid systems respectively. The authors have attributed this critical current to the formation of passive films of metal "carboxylates" on the anode and the removal of this film is a prerequisite for subsequent steady-state occurance of the Kolbe decarboxylation.

TERMINATION

The propagation stage in radical addition polymerization merely consists of the polymer free radical attack upon a monomer molecule, forming a polymer free radical with an additional monomer unit:

$$Pn\cdot + M \longrightarrow Pn\dot{+}1$$

Where M is the monomer molecule and Pn· the polymer free radical. This process continues until the growing chain is terminated.

Except in a few cases, termination is by mutual deactivation of two free radicals. This deactivation can occur by combination or disproportionation.

If termination is by combination, the two polymer free radicals combine to give a single polymer molecule:

$$Pn\cdot + Pm\cdot \longrightarrow Pn+m$$

If initiation is entirely by initiator free radical attack, then each polymer free radical will contain one initiator fragment. If termination is now exclusively by combination, each resulting polymer molecule will contain two initiator fragments (end groups).

If termination is by disproportionation, a hydrogen atom is transferred between the polymer radicals to yield one saturated polymer molecule and one unsaturated.

$$Pn\cdot + PmCH_2CH_2\cdot \longrightarrow PnH + PmCH = CH_2$$

In this case, if initiation is entirely by initiator free radicals and termination entirely by disproportionation, the resulting polymer molecule will contain one initiator

fragment per molecule.

One further method of growing radical termination is chain transfer. A polymer free radical removes an atom, usually hydrogen, from a solvent molecule, monomer molecule, or dead polymer molecule.

$$Pn\cdot + SH \longrightarrow PnH + S\cdot$$

The growing polymer molecule has been terminated and in this case, a solvent free radical has been produced. This solvent free radical may or may not be reactive enough to add monomer units.

From this discussion it is obvious that the mode of termination can be determined by an analysis of the number of initiating groups per molecule of polymer. This, however, is based on the assumption that chain transfer does not occur to any appreciable extent.

NATURE OF THE RESEARCH

Recognizing that the great majority of free radicals generated by the Kolbe electrolysis either dimerize or transfer to the solvent, an attempt was made to determine the fate of the free radicals that escaped dimerization and transfer reactions. With the help of labelled acetate ions, the relative efficiencies of the methyl and acetoxy free radicals to initiation could be determined as well as the total number of each incorporated in the polymer molecules. It was decided to investigate this as a function of monomer feed concentration.

From the previous discussion, it was established that methyl and acetoxy free radicals are generated at the anode during the Kolbe electrolysis. These free radicals can react with monomer:

$$CH_3\overset{O}{C}O\cdot + M \longrightarrow CH_3\overset{O}{C}OM\cdot \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

$$CH_3\cdot + M \longrightarrow CH_3M\cdot \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

In addition, acetoxy radicals which escape reaction (1) are capable of dissociation:

$$CH_3\overset{O}{C}O\cdot \longrightarrow CH_3\cdot + CO_2 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3)$$

If x is the fraction of acetoxy radicals captured by monomer, then

$$x = \frac{\text{rate of reaction (1)}}{\text{rate of reaction (1)} + \text{rate of reaction (2)}}$$

Therefore

$$x = \frac{k_1(M)(CH_3\overset{O}{C}O\cdot)}{k_1(M)(CH_3\overset{O}{C}O\cdot) + k_3(CH_3\overset{O}{C}O\cdot)} \quad \ldots\ldots\ldots (4)$$

Where (M) is the concentration of monomer, $(CH_3\overset{O}{C}O\cdot)$ is the stationary concentration of acetoxy free radicals, k_1, k_2, and k_3, are the rate constants for reactions (1), (2), and (3) respectively.

Simplifying expression (4) and inverting, we find

$$\frac{1}{x} = 1 + \frac{k_3}{k_1(M)} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (5)$$

If we now consider all the methyl free radicals to be captured by monomer in the steady state, then the rates of reactions (2) and (3) are equal and

$$x = \frac{\text{rate of reaction (1)}}{\text{rate of reaction (1)} + \text{rate of reaction (2)}}$$

or

$$x = \frac{\text{Average number of acetoxy end groups per polymer molecule}}{\text{Average number of methyl and acetoxy end groups per polymer molecule}}$$

It is a simple matter to determine the factor x by the use of two labelled acetates. The activity of /the polymer produced from acetate-1-C^{14} as electrolyte is a measure of the number of acetoxy end groups per polymer molecule while the activity of /the polymer produced from acetate-2-C^{14} is a measure of the number of both methyl and acetoxy end groups per polymer molecule.

Inspection of expression (5) shows that a plot of 1/x vrs. 1/M should yield a straight line of intercept one and slope k_3/k_1.

An approach of this type for thermally initiated polymerization was used by Bevington[27] and Ayrey[28] with labelled peroxides.

inhibitors added by the manufacturer to prevent polymerization during storage and handling. The monomer was then distilled under reduced pressure. The middle portion was collected and stored at -25°C until used.

Methyl ethyl ketone used in viscometry and osmometry, was distilled at atmospheric pressure.

Sodium acetate-1-C^{14} and sodium acetate-2-C^{14} were obtained from New England Nuclear Corp., and converted to acetic acid by allowing acetate exchange between sodium acetate and anhydrous acetic acid then distilling off the acid. Zinc acetate-1-C^{14} and zinc acetate-2-C^{14} were prepared by the action of acetic acid-1-C^{14} and acetic acid-2-C^{14} on zinc carbonate. All salts were carefully dried before use.

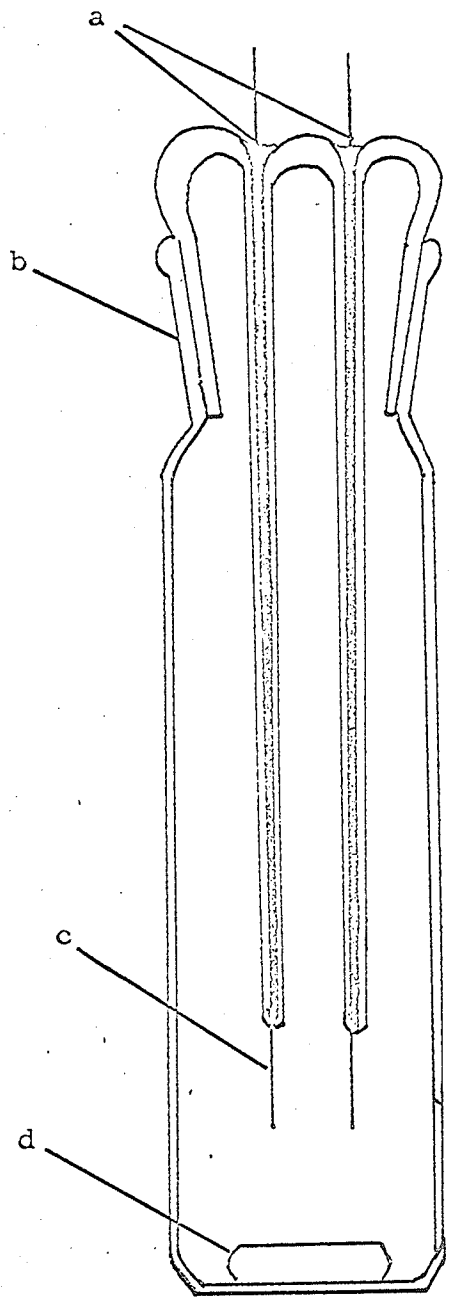
Diphenyl oxazole (PPO) and 1,4 di(2-(5-phenyloxazolyl)) benzene) (POPOP) scintillation grades were obtained from Nuclear Enterprises in 1962 and used in the liquid scintillators without further purification.

POLYMERIZATION

All polymerizations were carried out in a pair of polymerization cells (Figure 1). The platinum electrodes were 0.7 cms. apart, 2.5 cms square and sealed into glass capillary tubes. The electrode assembly was fitted with a ground glass stopper to form an air tight seal with the polymeriza-

FIGURE 1. Polymerization Cell.

(a) Mercury contacts.
(b) 35/45 ground glass joints.
(c) Platinum electrodes.
(d) Teflon stirring bar.


a
b
c
d

EXPERIMENTAL

MATERIALS

Dimethyl sulfoxide was dried over calcium hydride overnight, decanted, and distilled under vacuum. The middle portion was collected in a dry round bottom flask and stoppered in such a manner that volumes of dimethyl sulfoxide could be removed with a syringe. This prevented the hygroscopic solvent from absorbing moisture from the air.

Dimethylformamide[29] was mixed with 10% benzene which had previously been dried with calcium hydride. The mixture was allowed to stand twenty-four hours, then the benzene-water azeotrope was distilled off at a temperature of 80°C or less to prevent the decomposition of the dimethylformamide. The dimethylformamide was then distilled at atmospheric pressure and the middle portion boiling at 152°C collected. This was dried over barium oxide overnight, decanted, and distilled under vacuum. The middle portion was collected in a round bottom flask and stoppered in the same manner as dimethyl sulfoxide.

N,N-dimethylacetamide, rated at 0.006% water, was used without further purification but precautions were taken to prevent absorption of atmospheric moisture.

Methyl methacrylate was first passed through Fisher adsorption alumina in a chromatographic column to remove

tion vessel.

The cells were always used in pairs, both containing identical concentrations of monomer, solvent, and electrolyte. The only difference was in the labelled position of the acetate electrolyte. The cells were connected in series so the same current passed through both for the same length of time. Nitrogen was bubbled through each cell before electrolysis to remove atmospheric oxygen which would act as a retarder. Both cells were stirred vigorously and uniformly by means of teflon magnetic bars and thermostated at $30^{\circ} \pm 0.2^{\circ}C$. The same weight of electrolyte was used in all polymerizations.

The length of electrolysis was adjusted so that the percentage of monomer converted to polymer did not exceed 10% and the electrolyte concentration would not drop to zero. The power supply used in this research was a highly stable constant current supply specially designed by W.C. Hoyle of the National Research Council of Canada. It was capable of furnishing constant current of 15 ma. $\pm$ 0.04%. A constant current of 15 ma was used in all polymerizations.

The polymer solution after electrolysis was precipitated in methyl alcohol and filtered by suction onto Whatman #50 filter paper. The polymer was then dissolved in methyl ethyl ketone and reprecipitated in methyl alcohol. The procedure was repeated a third time to remove as much impurity as possible. The efficiency of the purification procedure

was checked for each system by mixing inactive polymer with active electrolyte for twenty hours and purifying. This polymer was then counted to ensure that all activity was removed. Polymer products, after purification, were dried overnight at 80°C in a vacuum desiccator. The activity of the purified polymer was determined by liquid scintillation counting and the molecular weight determined by viscometry and osmometry.

MOLECULAR WEIGHTS

In addition polymerization, the polymer chain length depends upon the number of monomer units a polymer radical can add before termination. Since termination is purely a random process, the polymer product will contain many molecules representing many different chain lengths. Any determination of molecular weight on such a polymer will give rise to an average molecular weight. Two such average molecular weights are of importance; the number average and the weight average molecular weight.

Any method of molecular weight determination that depends upon a colligative property (osmotic pressure, freezing point lowering) will count the number of molecules in a known mass of material. Through the use of Avagadro's Number, this information yields a number average molecular weight $\overline{M}n$.

On the other hand, many methods (ultra-centrifugation, sedimentation) depend upon properties in which the total effect of the molecule is a function of its weight. This will favor heavy molecules over light and yield a weight average molecular weight $\overline{M}w$.

From the nature of these molecular weights, $\overline{M}w$ must be equal to, or greater than, $\overline{M}n$. The ratio $\overline{M}w/\overline{M}n$ is a measure of the breadth of molecular weight distribution. Values of this ratio for typical polymers range between 1.5 to 2.0 and 20 to 50.

The molecular weight determination methods used in this research were viscometry and osmometry.

Viscometry

The viscosity of a solution is a measure of the size in space of the solute molecules. As such, any molecular weight determination based on solution viscosity will not yield $\overline{M}n$ or $\overline{M}w$. However, it is found experimentally that solution viscosity is related to $\overline{M}w$ by the Staudinger equation.

The apparatus used to obtain solution viscosity was the Ubbelohde viscometer (Figure 2). This viscometer has the advantages over other common viscometers in that measurements are independent of the volume of solution in the viscometer and that measurements at a series of concentrations can be made easily by successive dilutions in the viscometer. The viscometer was thermostated at $25 \pm 0.02^{\circ}C$.

The efflux time t, for the meniscus to pass between the two marks on the center tube was recorded for a series of solutions of different polymer concentration c, expressed in grams per 100 ml of solvent. The reduced viscosity Nr, was then calculated for each concentration by the expression

$$Nr = \frac{t/to - 1}{c}$$

Where to is the efflux time for pure solvent. Nr as a function of c was then plotted for each value of c and the linear graph extrapolated to zero polymer concentration. The intercept was taken as the intrinsic viscosity N. A typical viscosity curve is shown in Figure 3.

The intrinsic viscosity measures solution viscosity when polymer molecules behave independently of each other and effects of solvent-polymer interactions are minimized. As such, it is the quantity of interest and used in the Staudinger equation to determine weight average molecular weights $\overline{M}w$.

$$N = K\overline{M}w^{a}$$

Where K and a are empirical constants derived for every combination of temperature, solvent, and polymer type.

The values of K and a used in this research were

$$K = 6.8 \times 10^{-5} \qquad a = 0.72$$

FIGURE 2. Ubbelohde Viscometer.

(a) Reference marks.
(b) Capillary tube.
(c) Filling tube.

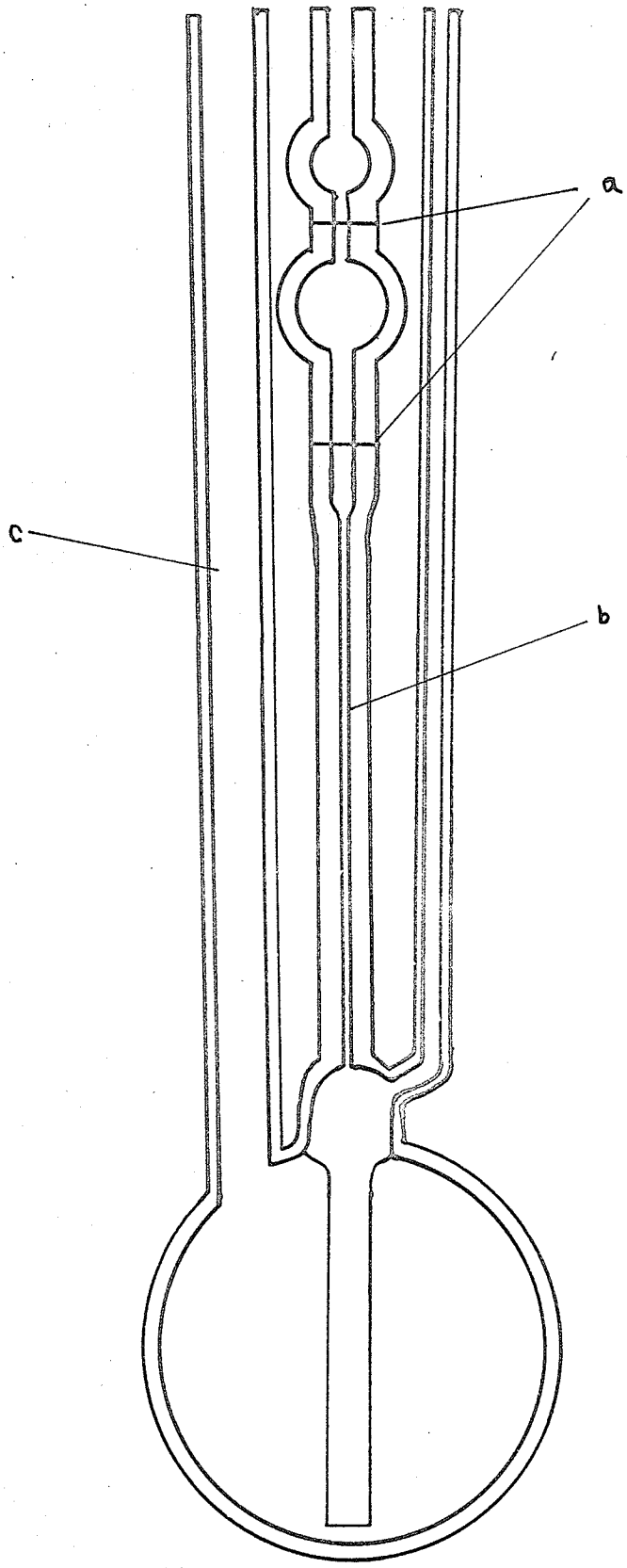
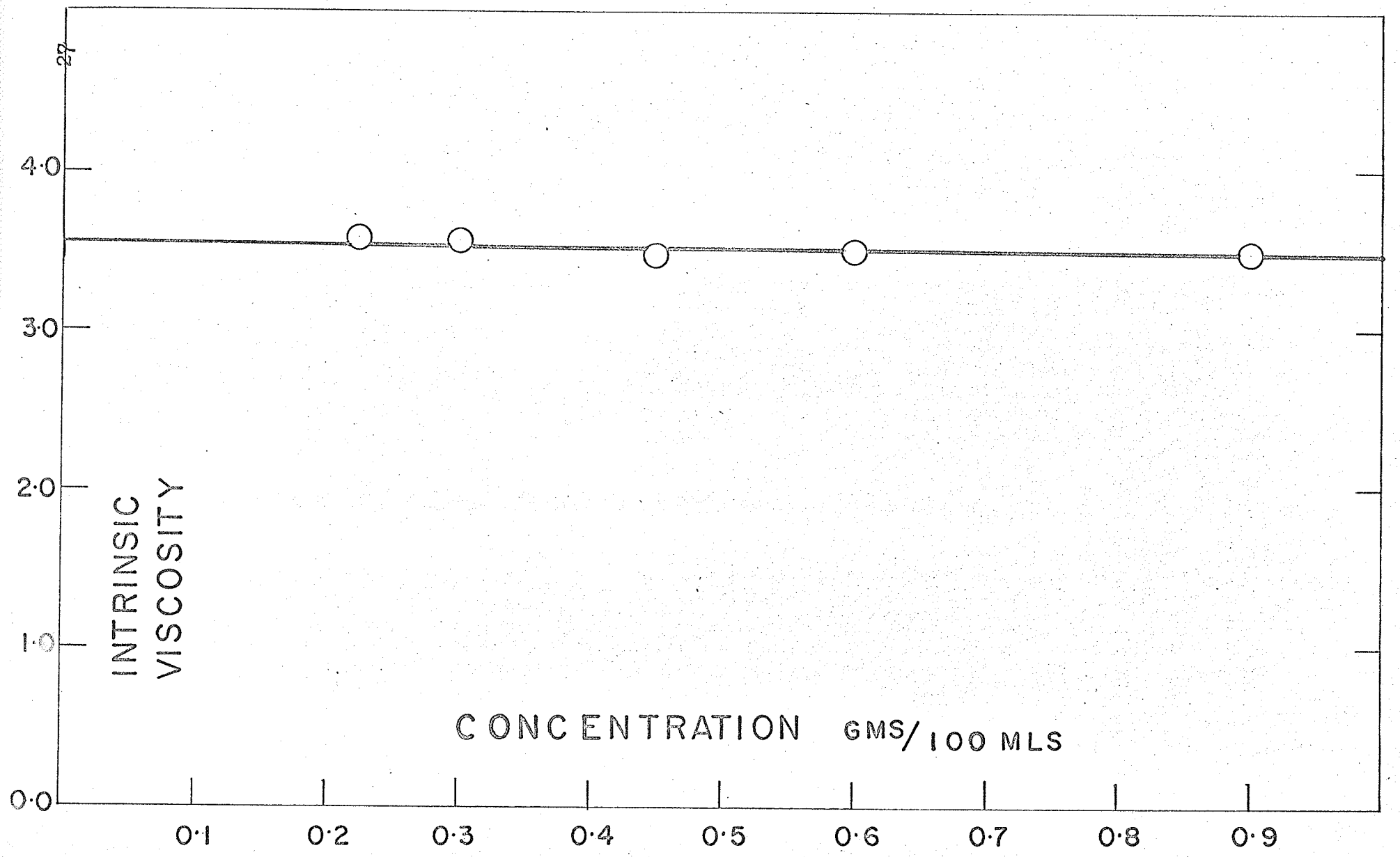

a
c
b

FIGURE 3. Viscosity Curves for Polymer Product "A" Produced in the Zinc Acetate System.


27
4·0
3·0
2·0
1·0
0·0
INTRINSIC VISCOSITY
CONCENTRATION GMS/100 MLS
0·1
0·2
0·3
0·4
0·5
0·6
0·7
0·8
0·9

These values apply at 25°C, methyl ethyl ketone as solvent, and poly (methyl methacrylate) with a weight average molecular weight in the range 3.5×10^4 to 10×10^6 [30, 31, 32].

Osmometry

The apparatus were modified Zimm Myerson osmometers (Figure 4). They consisted of a chamber containing the polymer solution and separated from pure solvent by a membrane permeable only to the solvent. The osmometers were operated by a static method whereby they were filled then allowed to come to their equilibrium osmotic height. The difference in height of the meniscus in the measuring and reference capillaries was taken as the osmotic height, and measured with a cathetometer to $\pm$ 0.01 cms.

A series of five osmometers, each containing a different concentration of polymer solution, were thermostated at 25 $\pm$ 0.02°C. The osmotic pressure π, in centimeters, divided by concentration c, in grams polymer per 100 ml. solvent, was plotted against c and the curve extrapolated to zero polymer concentration. The number average molecular weight $\overline{M}n$ was then determined from the value of the intercept $(\pi/c)_o$ by the use of Van't Hoff's equation for dilute solutions:

$$\overline{M}n = \frac{RT}{(\pi/c)_o}$$

A typical osmotic pressure curve is shown in Figure 5.

FIGURE 4. Modified Zimm Myerson Osmometer.

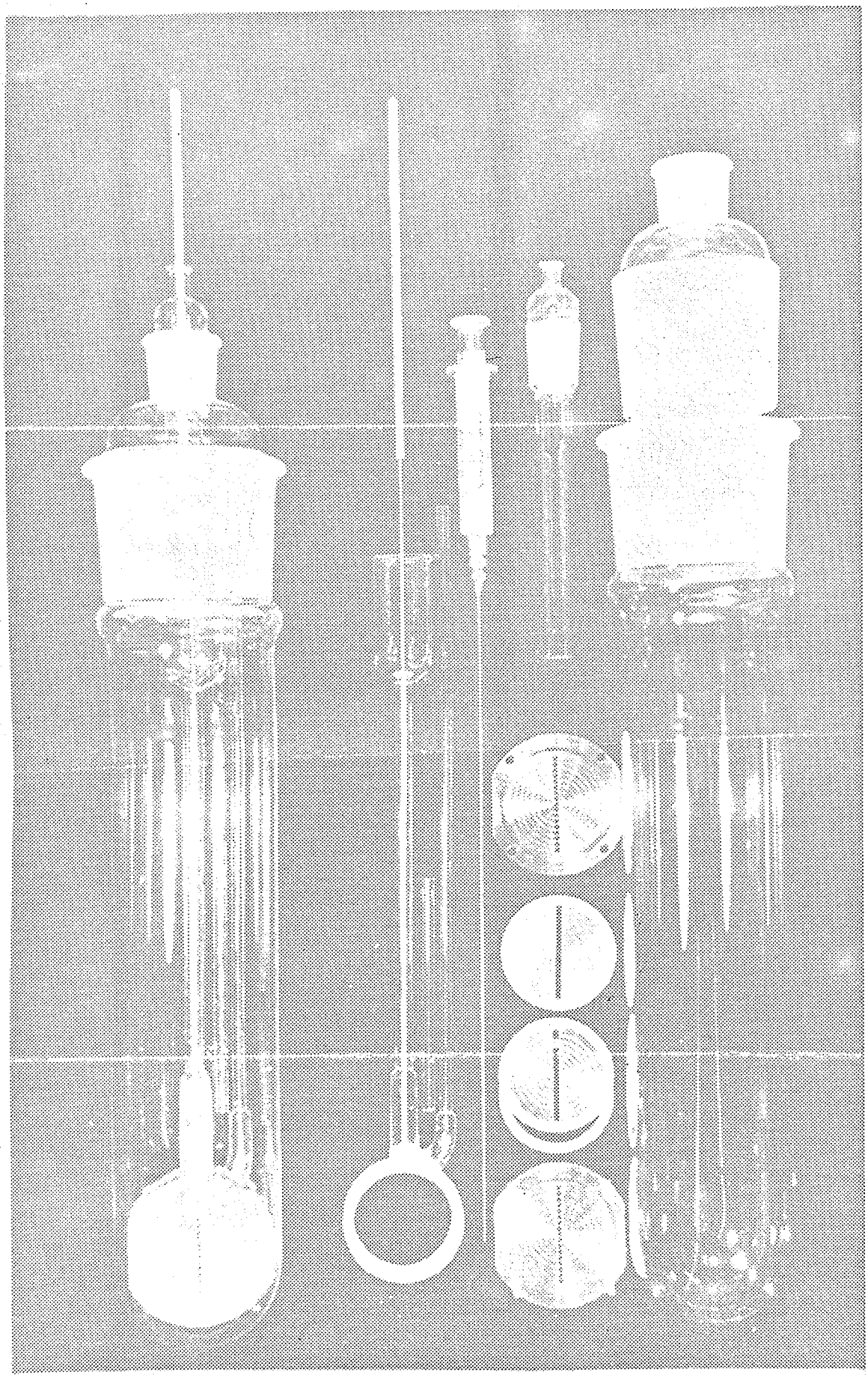
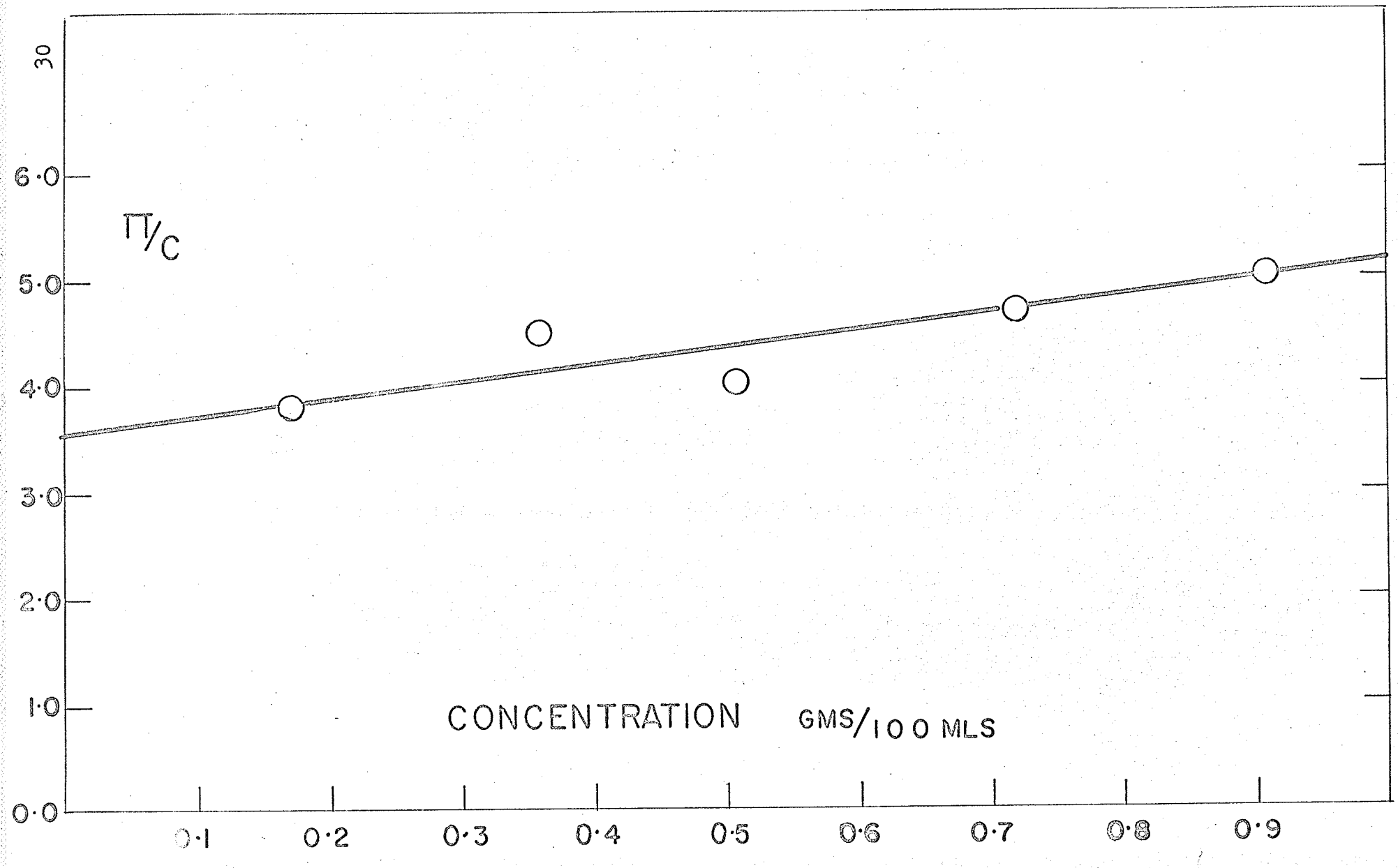


FIGURE 5. Osmotic Pressure Curve for Polymer Product "A" Produced in the Zinc Acetate System.


30
6·0
5·0
4·0
3·0
2·0
1·0
0·0
Π/C
CONCENTRATION GMS/100 MLS
0·1
0·2
0·3
0·4
0·5
0·6
0·7
0·8
0·9

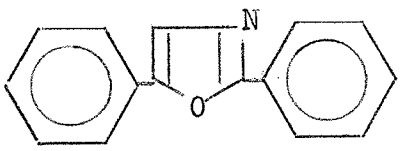
Counting

Of all the methods available for radioactive polymer assay, the most useful in this research at least is that of liquid scintillation counting. This technique offers the advantages of simplicity in sample preparation, negligible beta particle self absorption, and 4π geometry. Sample preparation consists simply of dissolving about 0.5 gms polymer in 20 ml of liquid scintillator contained in a special glass vial. Beta particles emitted by the sample will excite the liquid scintillator to fluorescence. It is the intensity of this fluoresence that is observed by the photomultiplier tubes and recorded as a measure of the beta particle activity of the sample.

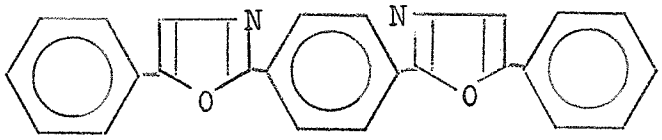
The liquid scintillator itself is always at least a two component system consisting of solvent and solute. The term "solvent" includes not only substances whose purpose is to solvate the sample and the solute but it also includes those substances that aid in the energy transfer process from solvent to the solute. The "solute" is the substance whose fluorescence emission is actually measured by the photo-multiplier tubes. Therefore, the emission spectrum of the solute must correspond to the sensitive region of the photomultiplier tube.

Normally, liquid scintillators are composed of two solvents and two solutes, called primary and secondary solvents or solutes depending on their relative concentrations. The

liquid scintillator found most useful for this study consisted of toluene and naphthalene as primary and secondary solvents respectively, and PPO (diphenyl oxazole) and POPOP (1,4 di (2-(5-phenyloxazolyl))benzene) as primary and secondary solute respectively.



PPO



POPOP

The naphthalene was added as a secondary solvent because of its excellent energy transfer characteristics and its low sensitivity to most external quenching agents such as water and oxygen. Even so naphthalene could not serve as a primary solvent since it is a solid at room temperature. POPOP was added as a secondary solute to shift the spectral band of fluorescence to longer wavelengths. This allowed a more efficient match of fluorescence spectra to the sensitive region of the photomultiplier.

The composition of the liquid scintillator found most suitable in this research was

100 gms naphthalene
9 gms PPO
0.15 gms POPOP
5000 ml toluene

Since the above scintillator was incapable of solvating the zinc acetate, it was necessary to develop another scintillator which would be able to solvate a small amount of water. The labelled zinc acetate could then be dissolved in water and a small amount of this added to the scintillator. The composition of the water solvating scintillator was

35 gms naphthalene
3 gms PPO
0.05 gms POPOP
300 ml ethyl alcohol 95%
500 ml para dioxane
1000 ml toluene

The ethyl alcohol was necessary to solvate the water but was responsible for the relatively low efficiency of 45-50% as against 60-70% for the former scintillator.

It was found that the water solvating scintillator was capable of dissolving up to 0.1 ml of water at the temperature of the Tri Carb sample changer.

The concentrations of PPO and POPOP are lower in these scintillators than that normally found in the literature. This resulted from our observation that, with normal solute concentrations, sample activity decreased rapidly for two or three hours and then continued a less rapid decrease for several days. It was found that decreasing the concentrations of the solutes and increasing the temperature of the Tri Carb sample changer from $-10^{\circ}C$ to $0^{\circ}C$ resulted in constant counting rates.

Since all samples were prepared at room temperature and counted at -10°C, the decrease in counting rate was attributed to the precipitation of one or both of the solutes at -10°C. All measurements in this research were made at 0°C.

A similar decrease was noted by Lohmann and Perkins[33] also using a Tri Carb and a scintillator with the normal concentrations of PPO and POPOP. They concluded that temperature effects and adsorption of radioactivity on the glass were responsible for the decline in counting rates.

Their explanation of these effects was not that of solute or sample solubility but rather that due to rupture of the weak interactions between the tritiated sample and the solvent. They confirm their theoretical interpretation by showing that counting rates no longer decline with time after the samples are irradiated with ultraviolet light before counting.

The counting system employed in this research was a Packard Series 314E Tri Carb Liquid Scintillation Spectrometer.

The Tri Carb has the advantages of two photomultipliers as well as two separate counting channels. The two photomultipliers and associated amplifiers allow coincidence counting whereby only light pulses received simultaneously by both photomultipliers will be counted. Since light pulses due to phosphorescence and cosmic rays will not be received in

coincidence except by accident, this results in a much lower background activity. The advantage of the two separate counting channels lies in the fact that the upper and lower energy discriminators are completely independent, permitting the counting rate of a sample to be determined for two different parts of the beta particle energy spectrum.

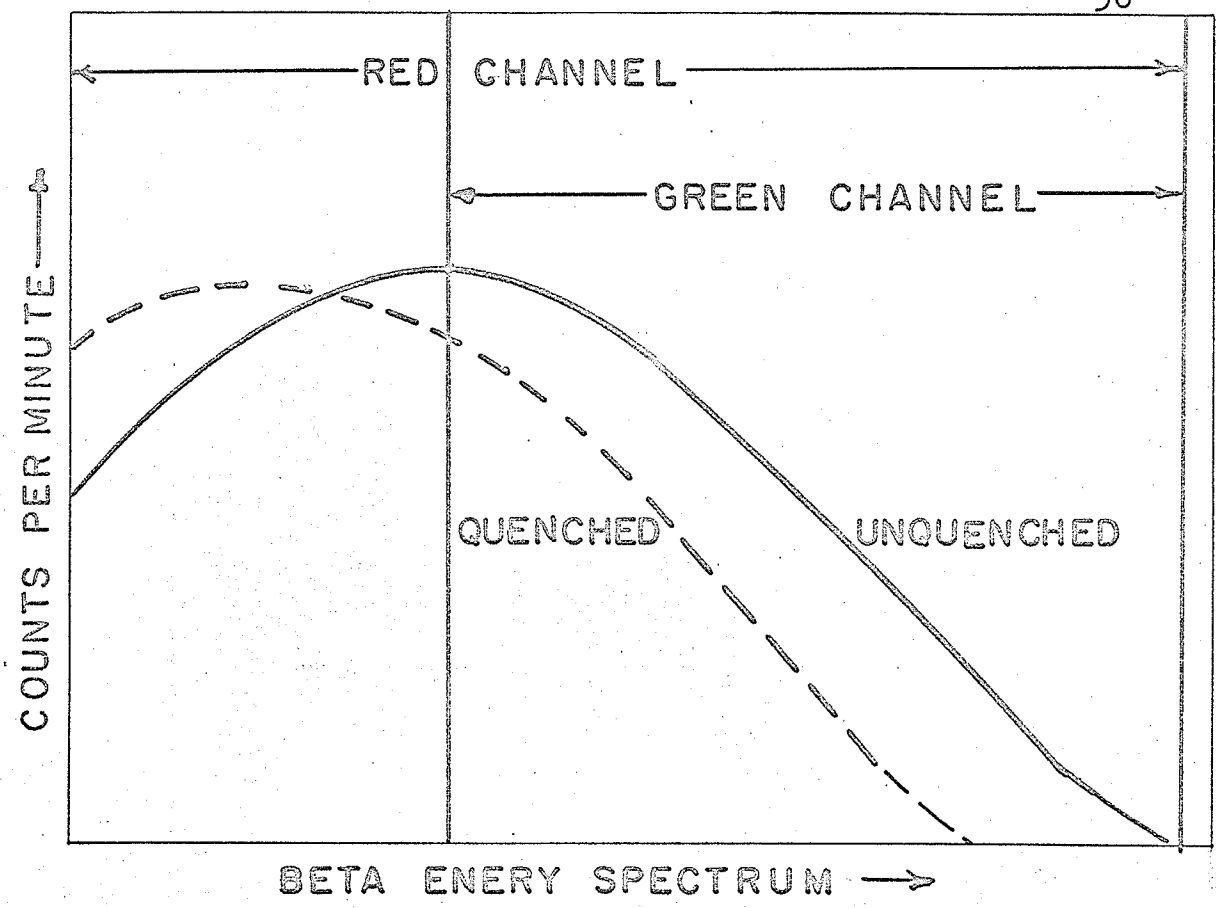
One disadvantage to liquid scintillation counting is that certain substances such as water and oxygen are capable of absorbing fluorescence radiation and degrading it to heat. In addition, coloured samples can increase the optical density of the liquid scintillator resulting in some absorption of the fluorescence. Whatever the cause such "quenching" results in a decrease of fluorescence emission and a corresponding decrease in counting efficiency.

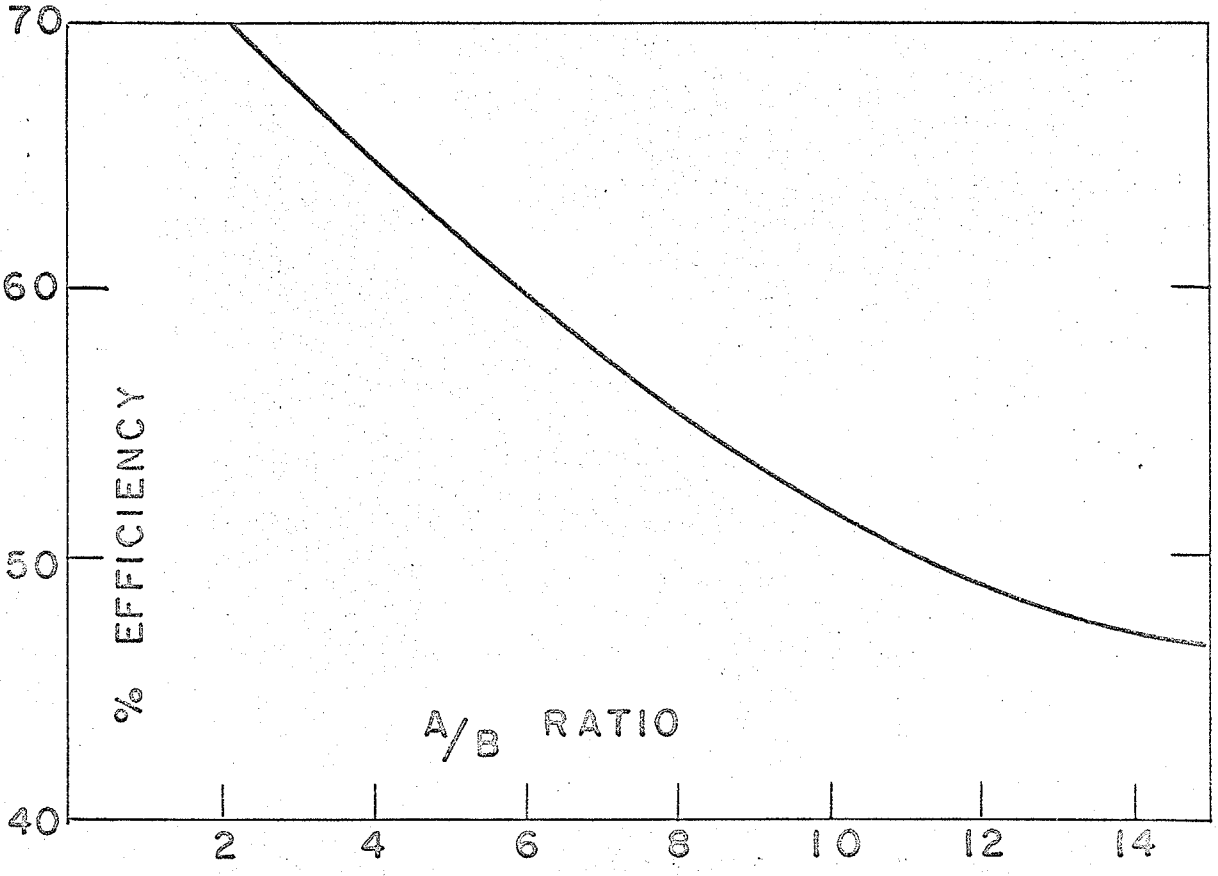
Since the liquid scintillation counter is a proportional counter, the output energy distribution from the amplifiers has a shape that is proportional to the input beta spectrum. When quenching occurs, the average energy of the light pulses is decreased and the output energy spectrum shifts to lower energy (Figure 6a).

If the discriminators are set so that one channel, the "red" channel on the Tri Carb, counts the total beta energy

FIGURE 6a. Effect of quenching on the output pulse-spectrum.

FIGURE 6b. A/B ratio vs. counting efficiency.


RED CHANNEL
GREEN CHANNEL
COUNTS PER MINUTE
QUENCHED
UNQUENCHED
BETA ENERY SPECTRUM


70
60
50
40
% EFFICIENCY
A/B RATIO
2
4
6
8
10
12
14

spectrum (after biasing out most of the electronic noise and high energy cosmic ray pulsss) and the remaining channel, the "green" channel on the Tri Carb, counts a fraction of the spectrum, then any shift in beta spectrum will change the count rate in each channel. The ratio of the two count rates, called the A/B Ratio, can then serve as a measure of counting efficiency.

In this laboratory, A/B ratios as a function of percent counting efficiency have been determined for the Tri Carb discriminator settings used in this research (Figure 6b). The efficiencies of all counts were determined by means of this correction curve.

Sample preparation involved weighing out 0.1 to 0.5 gms of polymer and adding this directly to 20 ml of liquid scintillator contained in a special, low K^{40}, glass sample bottle. After the polymer had dissolved, the samples were arranged in the Tri Carb sample changer so that the C^{14} sealed standard was always counted first. This was to leave a permenent record of the Tri Carb stability as well as to allow sufficient time for all light induced phosphorescence in the sample to decay. At least five ten-minute counts of each sample were taken, the counts per minute in each channel averaged for each sample, and the A/B ratio calculated. From the correction curve, the counting efficiency was found for each sample. The disintegration rate was then

calculated from the counting rate minus background on the red channel by multiplying the latter by the reciprocal efficiency.

$$DPM = CPM \times \frac{100}{\% \text{ EFF}}.$$

RESULTS AND DISCUSSION

ZINC ACETATE SYSTEM

The zinc acetate, dimethyl sulfoxide, methyl methacrylate system was previously studied by Funt and Yu[25]. On the basis of divided cell and inhibitor studies, they concluded the polymerization mechanism was predominately free radical.

Before beginning the tracer study, a blank was performed to check that the purification procedure was satisfactory on this system. Inactive poly (methyl methacrylate) was mixed with dimethyl sulfoxide, methyl methacrylate and active zinc acetate for twenty hours. The polymer activity after successive purifications is shown in Table I.

TABLE I. Results of successive precipitations on the polymer activity of the zinc acetate, dimethyl sulfoxide, methyl methacrylate system.

Number of Precipitations	Polymer Activity
One	1540 CPM/gm
Two	55
Three	60

Five polymerizations were attempted on this system each with different monomer concentration. For each polymer pro-

duct the weight average molecular weight was determined by viscometry following the procedure previously outlined. The results of the weight average molecular weight determination of polymerization "A" polymer are shown in Figure 3.

The number average molecular weight was attempted for each polymer product by osmometry. However, partial success was achieved only for polymerization "A" polymer since the other polymer products were of higher molecular weight and therefore gave a lower osmotic pressure. The results of the number average molecular weight determination of polymerization "A" polymer are shown in Figure 5.

From the results of these two molecular weights, the ratio $\overline{M}w/\overline{M}n$ was calculated for polymerization "A" polymer.

$$\frac{\overline{M}w}{\overline{M}n} = \frac{140,000}{89,000} = 1.6$$

On the assumption that the molecular weight distribution is essentially the same for each system and each polymerization, the factor 1/1.6 was applied to the weight average molecular weight of all polymer products to obtain a rough estimate of the number average molecular weight. These values were used in the calculation of the average number of initiator fragments per polymer molecule.

Sample calculations on polymerization "A" polymer

Activity of zinc acetate -2-C^{14}: 5.08×10^6 DPM

Weight of zinc acetate used: 1.51 gms.
Specific activity of polymer obtained: 11380 CPM/gm.
Sample counting efficiency: 69%.
Number average molecular weight: 89,000.

Disintegrations per minute per polymer molecule:

$$11380 \frac{\text{CPM}}{\text{gm}} \times \frac{100}{69} \frac{\text{DPM}}{\text{CPM}} \times 89{,}000 \frac{\text{gms}}{\text{mole polymer}}$$

$$= 1.47 \times 10^9 \frac{\text{DPM}}{\text{mole polymer}}$$

Disintegrations per minute per mole acetate ion:

$$5.08 \times 10^6 \frac{\text{DPM}}{1.51 \text{ gms}} \times \frac{183.5 \text{ gms}}{\text{mole zinc acetate}} \times \frac{1 \text{ mole zinc acetate}}{2 \text{ moles acetate ion}}$$

$$= 0.309 \times 10^9 \frac{\text{DPM}}{\text{mole acetate ion}}$$

Average number of methyl and acetoxy end groups per polymer molecule:

$$\frac{1.47 \times 10^9}{0.309 \times 10^9} = \frac{4.76 \text{ moles } CH_3\cdot \text{ and } CH_3\overset{O}{C}O\cdot}{\text{mole polymer}}$$

activity of zinc acetate-1-C^{14}:
1.40×10^7 DPM/
Weight of zinc acetate used: 1.51 gms.
Specific activity of polymer obtained: 4300 CPM/gm.
Sample counting efficiency: 69%.
Number average molecular weight: 89,000.

Disintegrations per minute per polymer molecule:

$$4300 \times \frac{100}{69} \times 89{,}000 = 5.55 \times 10^8 \frac{\text{DPM}}{\text{mole polymer}}$$

Disintegrations per minute per mole acetate ion:

$$\frac{1.40 \times 10^7}{1.51} \times 183.5 \times \frac{1}{2} = 8.51 \times 10^8 \quad \frac{\text{DPM}}{\text{mole acetate ion}}$$

Average number of acetoxy end groups per polymer molecule:

$$\frac{5.55 \times 10^8}{8.51 \times 10^8} = 0.652 \quad \frac{\text{moles } CH_3\overset{O}{C}O\cdot}{\text{mole polymer}}$$

$$x = \frac{\text{Average number of acetoxy end groups per polymer molecule.}}{\text{Average number of methyl and acetoxy end groups per polymer molecule.}}$$

$$x = \frac{0.652 \ \frac{\text{moles acetoxy}}{\text{moles polymer}}}{4.76 \ \frac{\text{moles methyl and acetoxy}}{\text{mole polymer}}} = 0.137$$

$$1/x = 7.30$$

The results for the zinc acetate system are shown in Table II.

The results show that the average number of methyl and acetoxy end groups per molecule vary from 2.4 to 4.8. This is higher than expected even if termination was exclusively by combination. However, values such as these can be explained in terms of hydrogen atom extraction from dead polymer. As polymerization proceeds and polymer accumulates in the system, there is an increased probability that transfer will take place between free radicals in solution and dead polymer. The resulting polymer radicals can then terminate

TABLE II. Molecular weights and activities of polymer produced in the system zinc acetate, dimethyl sulfoxide, methyl methacrylate.

Sample	Polymer Activity	$\overline{M}w$	$\overline{M}n$	Polymer Yield	Initiator Groups per Molecule	* M	1/M	x	1/x
	DPM/gm			gms		moles/liter			
AC_1	6,230	140,000	89,000	1.1	0.65	2.87	0.348	0.135	7.30
AC_2	16,490	140,000	89,000	1.0	4.8				
BC_1	3,830	126,000	80,100	1.3	0.43	3.33	0.300	0.153	6.53
BC_2	13,020	110,000	70,000	1.0	2.8				
CC_1	5,640	135,000	85,000	1.0	0.57	3.83	0.261	0.174	5.75
CC_2	9,910	164,000	104,000	1.2	3.3				
DC_1	4,470	200.000	127,000	1.7	0.59	4.78	0.209	0.202	4.94
DC_2	15,980	200,000	127,000	1.7	2.9				
EC_2	2,900	300,000	190,000	2.6	2.6	6.70	0.149	-	-
FC_1	2,440	350,000	222,000	1.3	0.63	7.69	0.130	0.260	3.84
FC_2	3,400	350,000	222,000	2.7	2.4				

*Monomer concentration. 1.5 grms of zinc acetate was used in each polymerization.

by combination or primary radical attack to increase the average number of initiator fragments per polymer molecule. The fact that a uniform trend exists between total groups per molecule and molecular weight substantiates this view since Schultz, Henrici, and Olive[34] have found that the reactivity of poly (methyl methacrylate) as a transfer agent can depend on molecular weight.

The polymer product labelled "E" in Table II was the result of one polymerization in which the rate of stirring was much slower than in the other polymerizations. The rate of stirring appears to have little if any effect on molecular weight or number of initiator groups per molecule.

Table II also shows that the molecular weights of the two polymer products BC_1 and BC_2 and also CC_1 and CC_2 are not identical although apparently the same conditions existed for each pair. An experiment was performed to see if this could be explained by a small amount of water in one cell and not the other.

A polymerization was repeated in which the same concentrations of zinc acetate-2-C^{14}, dimethyl sulfoxide, and methyl methacrylate were used in both cells, but 0.5 ml of water was introduced in one cell only. The results appear in Table III.

The presence of water, therefore, appears to explain the molecular weight differences in this system. The small

amounts of water necessary to decrease the molecular weight could have been present in an incompletely dry zinc acetate salt. It is interesting that the number of initiator end groups per polymer molecule did not change appreciably. This is an indication that hydrogen atoms are not discharged at the cathode due to the hydrogen overvoltage on platinium. Since the molecular weight decreased, it is probable that polymer radicals are able to extract hydrogen atoms from water and thus terminate the growing chains.

TABLE III. The effect of small amounts of water on molecular weight and end groups per molecule in the zinc acetate, dimethyl sulfoxide, methyl methacrylate system.

Cell	Polymer Yield	Mw	Initiator Groups per Molecule
Dry	2.0 gms	257,000	2.0
Wet	0.8	190,000	1.9

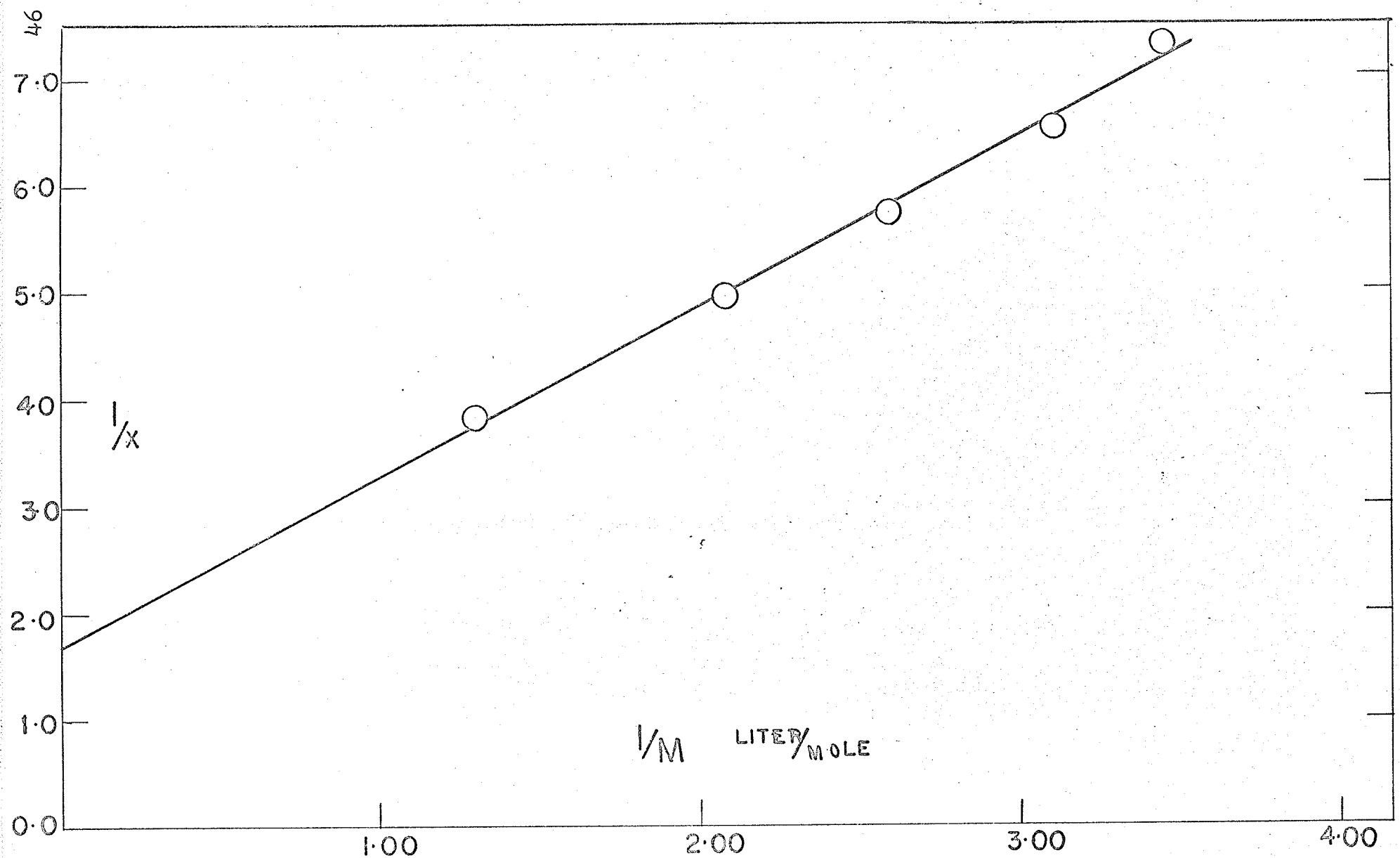
The values of 1/x and 1/M from Table II are plotted in Figure 7.

It is obvious from Figure 7 that the value of the intercept is not unity as expected from the expression:

$$\frac{1}{x} = 1 + \frac{k_3}{k_1(M)}$$

To explain this, it is proposed that the anode process does not proceed by simple oxidation of the acetate ions to

FIGURE 7. 1/x vs 1/M for the zinc acetate, dimethyl sulfoxide, methyl methacrylate system.


7·0
6·0
5·0
40
30
2·0
1·0
0·0
1/x
1·00
2·00
3·00
4·00
1/M LITER/MOLE

acetoxy radicals:

$$CH_3\overset{O}{C}O:^- \longrightarrow CH_3\overset{O}{C}O\cdot + e^-$$

Rather, than this, it is proposed that the acetate ions are oxidized to a mixture of acetoxy and methyl radicals:

$$CH_3\overset{O}{C}O:^- \quad (1-y)CH_3\overset{O}{C}O\cdot + yCH_3\cdot + yCO_2 + e^-$$

Then, the fraction of acetoxy radicals produced is (1-y) where y is the fraction of methyl radicals produced. In this case, x, the fraction of acetoxy radicals captured by monomer, will be (1-y) times the value of x if the acetate ions were simply oxidized to acetoxy radicals.

$$x = (1-y)\left(1 + \frac{k_1(M)}{k_3}\right)$$

inverting:

$$\frac{1}{x} = \frac{1}{1-y} + \frac{k_3}{k_1(1-y)(M)}$$

From Figure 7 the value of the intercept is 1.7.

Therefore $\frac{1}{1-y} = 1.7$ and $y = 0.41$

From the slope $\frac{k_3}{k_1} = 9.3 \ \frac{\text{moles}}{\text{liter}}$

It should be noted that these results are not inconsistent with the peroxide theory of the Kolbe electrolysis, for a peroxide could be formed at the electrode and decompose into a mixture of methyl and acetoxy free radicals:

$$CH_3\overset{O}{C}O\overset{O}{C}CH_3 \longrightarrow 2(1-y)CH_3\overset{O}{C}O\cdot + 2yCH_3\cdot + 2yCO_2$$

Again, however, there is no real justification for postulating the existence of such a peroxide.

Funt and Yu[25] found that dimethyl formamide appeared to be a suitable solvent for the polymerization of methyl methacrylate by the Kolbe electrolysis of zinc acetate. When dimethyl sulfoxide was replaced by dimethylformamide for the tracer study, it was found that the polymer product was virtually inactive (less than 150 CPM/gm). This was also noticed in the acetic acid system and will be discussed there.

ACETIC ACID SYSTEM

One further system studied was that of dimethyl sulfoxide, methyl methacrylate, and anhydrous acetic acid. Since this system had not been investigated previously, it was necessary to prove that the polymer produced by the electrolysis was not being polymerized thermally and that the polymerization mechanism was free radical.

Attempts were made to produce polymer by heating 50 volume percent of methyl methacrylate in dimethyl sulfoxide and acetic acid at 35°C for twenty-four hours and by electrolyzing such a mixture in the presence of 0.2 gms free radical retarder para benzoquinone. A polymer was not obtained in either case indicating that the polymer formation in this system occurred via a free radical mechanism initiated by electrolysis.

In keeping with the general procedure the purification technique was tested with inactive polymer and found to be satisfactory.

Table IV lists the results of three polymerizations on this system.

The acetic acid system shows the same trends of molecular weights and total groups per molecule with monomer concentration as did the zinc acetate system.

The values of 1/x and 1/M from Table IV are plotted in Figure 8.

The value of the intercept is again 1.7 as expected, however, the slope is definitely not the same as in Figure 7 and in fact is negative. This is surprising since the only apparent difference between the zinc acetate and acetic acid systems is in the source of acetate ions.

This observation can be explained on the basis of primary radical termination or transfer to initiator.

Consider the following reactions:

$$H\cdot + CH_3\cdot \longrightarrow CH_4$$

$$H\cdot + CH_3\overset{O}{C}O\cdot \longrightarrow CH_3\overset{O}{C}OH$$

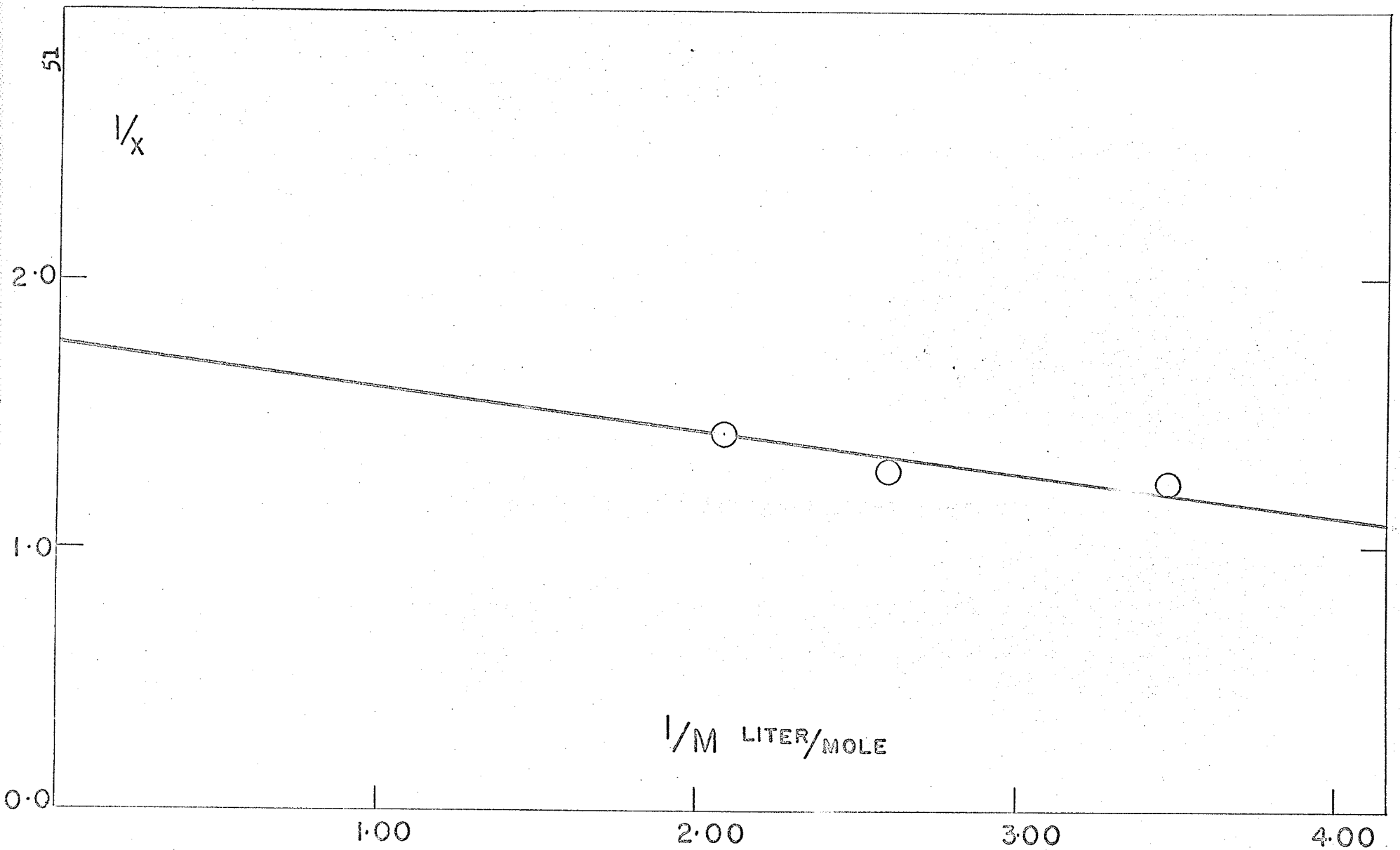
The hydrogen atoms are provided by the reduction of hydrogen ions furnished by acetic acid. Undoubtedly a high hydrogen atom concentration existed at the cathode and in a well stirred solution it is possible that such primary radical ter-

TABLE IV. Molecular weights and activities of polymer produced in the system acetic acid, dimethyl sulfoxide, methyl methacrylate.

Sample	Polymer Activity	$\overline{M}w$	$\overline{M}n$	Polymer Yield	Initiator Groups per Molecule	M	1/M	x	1/x
	DPM/gm			gms		Moles/Liter			
AC_1	22,240	170,000	108,100	0.9	3.51	2.87	0.348	0.806	1.24
AC_2	36,870	130,000	82,640	0.9	4.35				
BC_1	16,950	220,000	140,000	1.7	3.45	3.83	0.261	0.781	1.28
BC_2	21,900	220,000	140,000	1.4	4.41				
CC_1	4,240	300,000	190,700	0.9	1.78	4.78	0.209	0.699	1.43
CC_2	7,420	250,000	159,000	1.1	2.54				

2.1 gms of acetic acid was used in each polymerization.

FIGURE 8. 1/x vs 1/M for the acetic acid, dimethyl sulfoxide, methyl methacrylate system.


1/x
2·0
1·0
0·0
1/M LITER/MOLE
1·00
2·00
3·00
4·00

mination can occur. The effect of this termination is to lower the concentration of methyl radicals since the termination of methyl radicals yields methane which escapes from solution as a gas. The acetoxy radicals, however, yield molecular acetic acid on termination which can ionize to acetate ions and be oxidized at the anode to methyl and acetoxy radicals.

It is reasonable that as the monomer concentration increases, more methyl and acetoxy radicals will initiate polymerization rather than engage in primary radical termination. This would make the effect of primary radical termination less pronounced until at infinite monomer concentration it is negligible and the value of the intercept is the same for both systems. This would explain the negative slope.

Primary radical termination is not, however, a likely process. A better explanation for the different slope of the acetic acid system seems to be given by transfer to initiator whereby a polymer radical extracts a hydrogen atom from molecular acetic acid to form an acetoxy radical:

$$P\cdot + CH_3\overset{O}{C}OH \longrightarrow PH + CH_3\overset{O}{C}O\cdot$$

Many acetoxy radicals produced in this manner would become incorporated in polymer molecules either by initiation or recombination since the transfer occurs in the bulk of the

solution where the concentration of monomer and polymer is high and the probability of dimerization is small. This would decrease the factor 1/x. Again, the effect of transfer to initiator would become less pronounced as monomer concentration increases, for termination by combination or disproportionation is much more likely than transfer to initiator.

In an attempt to understand better why some solvents are effective in promoting polymer production by the Kolbe electrolysis and some not, the acetic acid system was investigated with dimethylformamide and dimethylacetamide as solvents. Both have essentially the same dielectric constant (36.7 and 37.8 respectively at 25°C), and appear to have the same solvating ability as dimethyl sulfoxide.

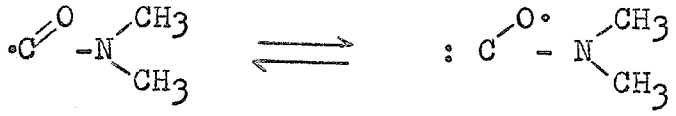
Table V lists the yields, molecular weights and groups per molecule for polymer produced with the three solvents in the acetic acid system.

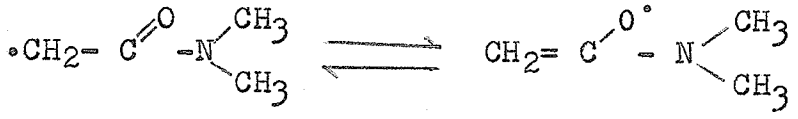
TABLE V. Molecular weights and activities of polymer produced in the acetic acid system using three different solvents.

Solvent	Polymer Activity	$\overline{M}n$	gms Yield	INITIATOR Groups per Molecule
Dimethylformamide	250 DPM/gm	860,000	0.4	0.31
Dimethylacetamide	52	3,800,000	2.0	0.28
Dimethyl sulfoxide	4900	150,000	1.1	2.4

The results shown in Table V suggest that initiation in the case of dimethylformamide and dimethylacetamide is by an indirect process in which the primary radicals produced by the Kolbe electrolysis extract hydrogen atoms from the solvent to give the initiating species. This would explain the higher molecular weights of the polymer produced with these two solvents, for the concentration of primary radicals in solution is lowered and chain termination by primary radical attack is less likely. Ayrey[35] found that much less radioactivity appeared in polymer produced by thermal dissociation of labelled peroxides when dimethylformamide was used as solvent. He concluded from this that initiation was by solvent free radicals.

It is reasonable that dimethylformamide and dimethylacetamide are relatively reactive towards loss of a hydrogen atom in view of the resonance stabilization available to the resulting radicals:





However, dimethyl sulfoxide would also be expected to be reactive towards loss of a hydrogen atom, for resonance

structures are possible:

It appears then that despite such resonance stabilization, dimethyl sulfoxide is less reactive towards loss of hydrogen atoms. This is probably associated with the increased difficulty of hydrogen atom removal from a primary carbon over that from either a secondary or tertiary carbon[37].

In addition to methyl methacrylate, styrene was used as a monomer in five polymerizations. The results were not encouraging as shown in Table VI.

Obviously, no uniform trend exists between 1/x and monomer concentration. This can be explained by polymer fractionation during purification since the molecular weights are low and difficulties were experienced in recovering the polymer product. It is interesting that the average number of end groups per poly styrene molecule are significantly less than that for poly (methyl methacrylate). This is reasonable since poly (methyl methacrylate) has more labile hydrogens available for extraction than has poly styrene.

Considerable time was devoted to an investigation of an interesting phenomenon observed in the dimethylformamide, acetic acid, methyl methacrylate system. It was originally decided to prepare the labelled acetic acid by mixing 2 ml inactive acetic acid and 0.1 ml aqueous active sodium acetate

TABLE VI. Molecular weights and activities of polymer produced in the system acetic acid, dimethyl sulfoxide, styrene.

Sample	Polymer Activity	$\overline{M}w$	$\overline{M}n$	Polymer Yield	Initiator Groups per Molecule	M	1/M	x	1/x
AC_1	3,120	32,000	20,300	0.45	0.19	5.00	0.200	0.11	9.2
AC_2	10,760	83,000	52,800	0.15	1.72				
BC_1	2,430	105,000	66,700	0.13	0.26	5.00	0.200	0.15	6.8
BC_2	19,800	89,000	56,600	0.13	1.78				
CC_1	5,390	40,400	25,700	0.4	0.19	5.95	0.162	0.15	6.8
CC_2	13,400	107,000	68,000	0.2	1.27				
DC_1	2,550	168,000	107,000	0.40	0.75	6.94	0.144	0.59	1.7
DC_2	4,720	152,000	97,000	0.55	1.27				
EC_1	4,140	200,000	127,000	0.47	0.78	8.00	0.125	0.37	2.7
EC_2	12,860	176,000	112,000	0.43	2.10				

2.1 gms of acetic acid was used in each polymerization

solution of high specific activity in dimethylformamide and allowing acetate exchange to take place between sodium acetate and acetic acid. When inactive poly (methyl methacrylate) was dissolved in this mixture and reprecipitated as with other blanks, the polymer was found to be very active even after a number of reprecipitations. The results of two such purification attempts are shown in Table VII.

TABLE VII. Results of successive precipitations on the activity of poly (methyl methacrylate).

Number of Precipitations	Trial I	Trial II
One	-	-
Two	4200 CPM/gm	2544 CPM/gm
Three	3800	1860
Four	3550	1120
Five	3600	930
Six	3550	970

The inactive polymer, the solvent, and acetic acid were checked for activity before mixing and were found to be inactive.

Various purification techniques were employed, all of which were unsuccessful in reducing the activity.

Four possibilities were considered in an attempt to explain these results:

1. Contamination by active polymer from some external source.
2. Radiolysis, the breaking of carbon-carbon bonds by beta particle bombardment and subsequent free radical combination resulting in active polymer.
3. Acetate exchange between acetic acid or sodium acetate and poly (methyl methacrylate).
4. Contamination of active acetic acid or sodium acetate in the purified polymer.

The first possibility was discounted by carrying out the purification in different laboratories using different equipment. The activity could not be removed in this manner.

Radiolysis was eliminated by proving that methyl methacrylate could not be polymerized by the amount of activity used in the blanks and that addition of para benzoquinone to the blanks did not improve the purification.

The third possibility was considered unlikely, in any event, active polymer from one blank was decomposed back to the monomer by heating the polymer in a vacuum system. The resulting methyl methacrylate was found to be inactive. This suggested that exchange was not taking place.

The last possibility was the most likely, however it was easily proven that the polymer was not contaminated with active acetic acid. This was done by mixing inactive acetic acid in the methyl ethyl ketone solution of polymer before

precipitation. This would allow acetic acid exchange between any contaminated active acetic acid in the polymer and inactive acetic acid and thus reduce the count. Furthermore, the purified polymer was dried overnight in a vacuum dessicator at 80°C to distill off any contaminated acetic acid. Neither procedure resulted in a significant decrease in polymer activity.

The conclusion then was that the polymer was contaminated with active sodium acetate. This is quite reasonable since the specific activity of the sodium acetate used was about 5×10^{10} DPM/gm then only 6×10^{-7} gms would be necessary to give the observed activity of 3000 DPM/gm polymer.

This requires that acetate exchange between sodium acetate and acetic acid not take place completely in dimethylformamide under the conditions used in this research. This was not investigated further since a contamination problem did not exist if active acetic acid was used instead of an inactive acetic acid-active sodium acetate mixture.

From the average number of methyl and acetoxy end groups per poly (methyl methacrylate) molecule, it is possible to calculate the fraction of these initiator fragments that find their way into the polymer. Using "A" polymer from the zinc acetate system as an example, from the polymer yield (1 gm.), current passed (15 ma. for 20 hours) and molecular weight of methyl methacrylate (100), it can be calculated

that 1.1 molecules of monomer are polymerized per acetate ion discharged. From the molecular weight of the polymer (89,000) and the average number of labelled end groups per polymer molecule (4.8) one finds that 180 monomer molecules are polymerized per initiator fragment incorporated. Thus only one initiator fragment in every two hundred becomes incorporated in the polymer.

ESTIMATION OF ERROR

The main sources of error in the determination of average number of initiator groups per molecule were polymer loses during purification and errors in the number average molecular weight determinations. Other sources of error such as isotope effects, counting errors, and measurements of volumes and weights are negligible compared to these. For example, the balance used in this research was capable of weighing to 0.0002 gms. Since most polymer samples weighed 0.5 gms, the error in weighing is about 0.04%. Likewise, the statistical error in counting is given by $n^{\frac{1}{2}}$ where n is the total number of counts. The polymer activity was never less than 1000 CPM representing a 1% error for a 10 minute count.

In tracer studies of this nature, it is essential that the low molecular weight polymer product makes its proper contributions and therefore it should not be lost during purification. Since low molecular weight product contains polymer chains that have terminated mostly by disproportionation or chain transfer, such losses would result in high values for the number of initiator fragments per polymer molecule. It has been estimated[28] that poly (methyl methacrylate) recovered by precipitation in methyl alcohol results in losses of up to 2% if the number average molecular weight is about 5×10^5. Losses are larger if the molecular weight is lower. In this research, the number average molecu-

lar weight was as low as 9×10^4. A rough estimate would place the error in the number of initiator groups per molecule due to fractionation at 10%.

Molecular weights have been measuring independently by osmometry at a number of laboratories and the deviations determined. It was thus established that the osmotic molecular weights could be determined with an error of 10% (36).

CONCLUSION

Zinc acetate and acetic acid were both used as electrolytes in the polymerization of methyl methacrylate by the Kolbe electrolysis. The results from the study indicate:

1. The average numbers of methyl and acetoxy end groups per poly (methyl methacrylate) molecule vary between 2 and 5 depending upon the initial monomer concentration. Calculations based on these values show that less than 0.5% of the initiator fragments discharged find their way into the polymer.

2. Appreciable hydrogen atom extraction from dead poly (methyl methacrylate) takes place as evidenced by the incorporation of 2 to 5 initiating groups per polymer molecule. In the case of poly styrene, the number of initiating groups per polymer molecule was between 1 and 2. This indicates that hydrogen atom extraction from dead poly styrene is less important.

3. The anode process of the Kolbe electrolysis is not the simple oxidation of the acetate ion to acetoxy free radicals but rather acetate ion oxidation to a mixture of acetoxy and methyl free radicals. Under the conditions employed in this research 41% of the acetate ions are oxidized directly to methyl free radicals and

carbon dioxide.

4. The ratio of rate constants for acetoxy radical decomposition to methyl radicals over that for acetoxy radical capture by monomer is about 9 under the conditions of this research.

5. Appreciable transfer to initiator is probably taking place in the acetic acid system resulting in a rate constant ratio differing widely from that of zinc acetate.

6. Dimethyl sulfoxide is a suitable solvent for the initiation of polymerization by primary radicals generated during the Kolbe electrolysis. Dimethylformamide and dimethylacetamide are not effective due to hydrogen atom extraction by primary radicals.

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