INHIBITION AND RETARDATION OF METHYL METHACRYLATE POLYMERIZATION

presented by

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To my Parents

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ABSTRACT

The influence of p-benzoquinone on the polymerization of methyl methacrylate has been investigated.

The rates of reaction were determined on $\alpha\alpha'$azobis-iso-butyronitrile initiated polymerizations which had incremented concentrations of quinone.

A tracer study was effected by employing C^{14} tagged initiator and inactive retarder in one series of experiments and C^{14} tagged retarder and inactive initiator in an identical series of experiments. Radioactive assays were accomplished by means of liquid scintillation counting techniques.

Number average molecular weights were determined by osmotic pressure measurements.

It was found that the reaction was retarded at low concentrations of p-benzoquinone but showed a definite transition to inhibition at higher concentrations. Analysis of the data showed that the number of initiator fragments incorporated per polymer molecule was independent of retarder concentration, but that the number of retarder molecules per polymer molecule increased.

The results indicate that p-benzoquinone has a dual function in the inhibition of methyl methacrylate. It combines with the end of growing polymer chains as well as intercepts primary initiating radicals.

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INTRODUCTION

INTRODUCTION

a) Polymerization i) Historical

The first recorded polymerization of a vinyl compound dates back to E. Simon who reported in 1839 that styrene could be converted into a gelatinous mass. Polymers were thought to consist of aggregations of smaller units held together by mysterious intermolecular forces and somewhat later the structure of certain polymeric substances was believed to be cyclic.

In 1920 Staudinger postulated that vinyl polymers were linear chains consisting of smaller units held together by ordinary covalent bonds (1). He stated that they were formed by means of a chain reaction involving intermediates with free valences at each end of the molecule. It was not necessary at that time to propose any termination mechanism for the free ends since it was thought that the large size of the molecule would "absorb" the radical electrons.

As the theory of free radical chain mechanisms evolved, it became apparent that the reactivity of the radical end of the growing polymer chain was largely independent of the size of the chain. It was for this reason that a definite termination mechanism had to be established. P. J. Flory, recognizing that free radicals can be created or destroyed in pairs only, suggested the bimolecular combination or disproportionation of polymer radicals (2).

The first clear example of the free radical mechanism was given by Taylor and Jones (3) on the gaseous polymerization of ethylene. Free radical reactions in solution have since been

established by the following facts:

a) vinyl polymerizations are catalysed by substances which give off free radicals on decomposition.

b) stable free radicals and known free radical intercepters decrease the rate of polymerization.

c) theoretical analysis on the basic kinetics of polymerizations agree in all respects with that predicted by a free radical mechanism.

According to the theory established by Staudinger and slightly modified by Flory, a polymer molecule would consist of a linear arrangement of monomer units held together by covalent forces with end groups of normal valence structure.

ii) Theoretical

An all inclusive treatment of polymerization must include those polymers formed by addition and condensation processes as well as those formed by the more specific ionic mechanisms. Although condensation and ionic polymers are certainly important, they have no direct bearing on the addition mechanism of a free radical vinyl polymerization. For this reason they will be omitted from any further discussion.

The following pages will treat the known effects which could reflect on the analysis of the results obtained in this research.

Free radical vinyl polymerization

The formation of a polymer molecule involves three quite distinct steps: initiation, propagation and termination. Initiation of a chain may be accomplished by adding certain compounds which decompose to free radicals or it may be caused by a contribution of photochemical or thermal energy to the vinyl monomer thereby causing the formation of a free radical. The free radical now adds to monomer molecules and so propagates a growing polymer.

$$\left.\begin{array}{lll} \text{Initiator} \longrightarrow & 2R\cdot & \\ R\cdot + M \longrightarrow & RM\cdot & \end{array}\right\} \text{Initiation}$$

$$RM\cdot_{n-1} + M \longrightarrow RM\cdot_{n} \quad \text{Propagation}$$

The cessation of growth of the polymer chains may take place by several possible mechanisms. The complete destruction of a free radical must, however, involve a mutual

interaction with another radical by either combination or disproportionation.

Combination

$$\sim\sim CH_2\text{-}CHX\cdot + \cdot XC\text{-}CH_2\sim\sim \longrightarrow \sim\sim CH_2\text{-}CHX\text{-}CHX\text{-}CH_2\sim\sim$$

Disproportionation

$$\sim\sim CH_2\text{-}CHX\cdot + \cdot XHC\text{-}CH_2\sim\sim \longrightarrow \sim\sim CH{=}CHX + XH_2C\text{-}CH_2\sim\sim$$

$$RM_n\cdot + RM_{n'}\cdot \longrightarrow RM_nM_{n'}R$$
$$RM_n\cdot + RM_{n'}\cdot \longrightarrow RM_n + RM_{n'} \qquad \text{Termination}$$

Whether a specific monomer will terminate its polymerization by combination or disproportionation is, at the present, subject to speculation.

A method by which a polymer molecule may be formed without destruction of a radical is by the process of chain transfer.

Chain Transfer

$$\sim\sim CH_2\text{-}CHX\cdot + CH_2{=}CHX \longrightarrow \sim\sim CH_2\text{-}CH_2X + CH_2{=}CX\cdot$$

or

$$\sim\sim CH_2\text{-}CHX\cdot + CH_2{=}CHX \longrightarrow \sim\sim CH{=}CHX + CH_3\text{-}CHX\cdot$$

$$RM_n\cdot + M \longrightarrow RM_n + M\cdot$$

The monomer radical M· is now capable of further polymerization.

In applying the steps given for initiation, propagation and termination to a kinetic scheme, the assumption was made that the reactivity of the end radical is independent of the

length of the polymer. Although this initially received some criticism its validity has been justified by the good agreement found with the results of critically chosen experiments. The steady state assumption is also made; that is, the rate of appearance and disappearance of radicals is equal.

A third and obvious assumption for molecules having large kinetic chain lengths is that the rate of propagation is equivalent to the rate of loss of monomer. The validity of this assumption is substantiated by its general applicability and by the obvious triviality of the chain initiation step to the propagation steps, for long chain molecules.

The termination mechanism of three compounds, vinyl acetate, sytrene and methyl methacrylate, have been studied under conditions of negligible chain transfer by analysing the number of end groups in the polymer. By tagging the initiator with C^{14} it is possible to ascertain whether one or two initiator fragments are present in each polymer molecule proving either disproportionation in the first case or combination in the latter.

TABLE I Termination Data

Polymer	Temp.°C	Average Number of End Groups	Reference
Poly Methyl Methacrylate	60	1.08	(4)
"	60	1.27	(5)
"	25	1.18	(6)
"	0	1.25	(4)
Poly Vinyl Acetate	60	1.06	(7)
Polystyrene	60	2.00	(4)(7)
"	25	2.05	(6)

The results of these experiments indicate that the termination mechanism for polystyrene and polyvinyl acetate is combination and disproportionation respectively, whereas polymethyl methacrylate terminates by various proportions of each depending upon the temperature of polymerization. A more significant observation is, however, that either combination or disproportionation will occur depending upon the radical involved.

Effect of a Foreign Compound.

Radical propagated chain reactions are greatly affected by low concentrations of foreign compounds. It has been found that halogenated compounds (8), phenols (9), aromatic nitro compounds (9)(10), and amines (9) either diminish the rate, molecular weight or both or completely inhibit the reaction.

A compound which lowers the rate of polymerization

is called a retarder and one which completely suppresses any detectable reaction is called an inhibitor. The theories which differentiate between the two postulate that an inhibitor reacts with all the primary radicals whereas a retarder is less efficient and does not immediately interfere with the growth of the radical but becomes involved after a certain degree of polymerization has been attained (11)(12). The difference then between a retarder and inhibitor is merely one of degrees.

The mechanism by which the foreign material affects the rate and molecular weight is complicated by a large number of possibilities. A discussion of these possibilities is put forth on the following few pages.

An immediate observation is that the foreign molecule becomes attached to the end of the polymer radical and since the reactivity of the growing radical chain depends only on the end group, both the mechanism and rate of termination will be altered.

$$RM_n\cdot + Q \qquad RM_nQ\cdot$$

$$RM_nQ\cdot + \text{radical} \qquad \text{non radical products.}$$

Where R· represents an initiator fragment, M the monomer unit and Q the foreign molecule.

The $RM_nQ\cdot$ may combine or disproportionate with any of the other radicals that are known to be present. These include other $RM_nQ\cdot$ (13), R· (14), $RM_n\cdot$ (13) and Q· resulting from chain transfer to the Q molecule. Because the termination reaction is bimolecular in all cases, kinetic data cannot give

sufficient evidence as to which of the above reactions predominates. The kinetic information therefore must be supplemented by other observations such as those which may be obtained by judicial use of isotopic tracers.

The reduction in rate due to the foreign Q molecule is possible also if $RM_nQ\cdot$ is not immediately terminated but remains as a relatively stable radical for a period of time after which it adds monomer and polymerizes in the normal fashion (15).

$$RM_nQ\cdot + M \longrightarrow RM_nQM\cdot$$

etc.

If many Q molecules become incorporated into a polymer molecule, this effect is known as copolymerization.

A third method by which the rate of polymerization may be reduced is chain transfer to the Q molecule.

$$RM_n\cdot + Q \longrightarrow RM_n + Q\cdot$$

The $Q\cdot$ formed is capable of further polymerization or of termination with another radical. As larger amounts of Q are added, the incidence of transfer increases thereby lowering the molecular weight and decreasing the rate of reaction.

The rate of polymerization will be completely inhibited if the Q molecules intercept all the primary chain initiating radicals.

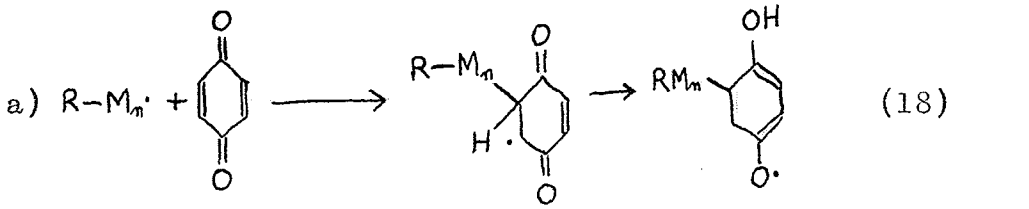
$$\text{Initiator} \longrightarrow 2R\cdot$$

$$R\cdot + Q \longrightarrow RQ\cdot$$

Inhibition of the reaction will take place until all the Q molecules are exhausted. At this point polymerization will proceed at a rate equivalent to that had no inhibitor been initially present (9)(16).

An extensively studied inhibitor is p-benzoquinone. It has been discovered that quinone behaves as a true inhibitor in most cases but for methyl methacrylate (17) and the thermal polymerization of styrene (15) it acts as a retarder.

Although the molecular action of the quinone is not definitely known three of the most logical possibilities are set forth below.



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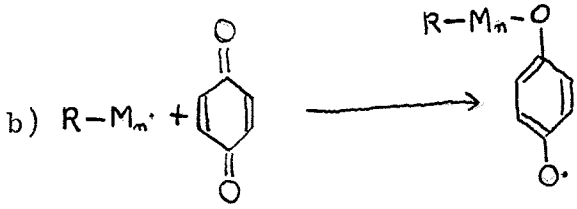

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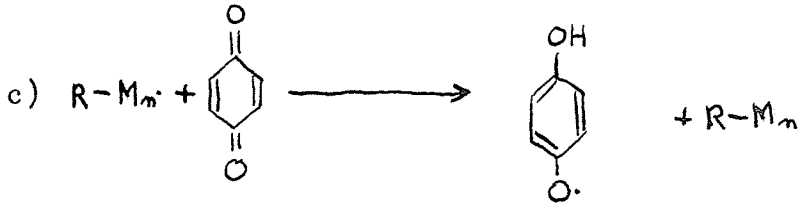


(19)

The products of a p-benzoquinone inhibition for styrene and allyl acetate have been found to be both oxygen and benzene nucleus substituted.

Further proof of "b" has been shown by Bickle and Waters (22) using small R· radicals. Reaction "c" received its justification when hydroquinone was found as a product of quinone inhibition (23)(20). Further discussion of the molecular action of quinone is impossible since the extent to which each of these reactions occur in a polymerization has never been established.

b) Molecular Weight i) Historical

Molecular Weight

An estimation of molecular size was first attempted by Staudinger who stated that the molecular weight of a linear polymer was directly proportional to its intrinsic viscosity in dilute solution (24), $\eta = KM$. Although this relationship is not strictly true, it provided a basis for further theoretical work regarding the viscosity and molecular weight of polymers in solutions. The modified Staudinger equation has a form which equates the intrinsic viscosity to KM^{α}, where K is a constant independent of molecular weight but depends upon the polymer, solvent and temperature. The constant α is dependent upon the shape of the polymer molecules and varies from zero for spheres to two for rigid rods. K and α can only be determined when the values for M are determined by an absolute method.

Cryoscopic and ebullioscopic determinations of molecular weight are very poorly suited for the estimation of the extremely large molecular weights of high polymers. However, number average molecular weights may be determined by measuring the osmotic pressure of a polymer solution with a semi-permeable membrane. Thomas Grahan in 1861 first noticed that the diffusion of polymeric substances is restricted by a semi-permeable membrane but it was not until 1936 that Schulz used this method as a quantitative measure of number average molecular weight (25).

ii) Theoretical

Molecular Weight by Osmotic Pressure

Osmosis is described 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 best 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" (26).

The free energy, chemical potential or activity of solvent molecules is less when in solution with other molecules that it is with molecules of its own kind. For this reason when solute or solution and solvent are placed together, there will be a spontaneous diffusion of solvent to solute in order to obtain a lower energy. A measure of the diffusion taking place is attainable by separating the solution and solvent by a thin film which will permit a ready transfer of solvent but not of solute molecules. A membrane possessing such a property is said to be semi-permeable.

When pure solvent is placed on either side of a membrane there often exists a definite pressure called the asymmetry pressure. One of the very few explanations of this phenomenon 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 may become detached at one end. The asymmetry pressure then is a measure

of the disengaged polymer chains on the two sides (27).

The calculation of molecular weight from osmotic pressures is possible by using the van't Hoff equation for dilute solutions (28).

$$\pi V = \not{n} RT = \frac{WRT}{M}$$

$$\pi = \frac{W}{V}\frac{RT}{M} = C\frac{RT}{M} \qquad M = \frac{RT}{(\pi/c)}$$

Because of polymer-polymer interactions, this equation is absolutely true only at infinite dilution.

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

EXPERIMENTAL PROCEDURE

EXPERIMENTAL

Experimental evidence to decide among the potential mechanisms put forth on the preceeding pages must necessarily be extremely complete. The fulfillment of this essentiality was accomplished by determining four non-independent facts about each polymerization by completely independent methods.

The basic requirements of this or any reaction mechanistic study is a knowledge of the rates of reaction. Accordingly, the effect of increasing concentrations of quinone on the rate was obtained.

The molecular weight of each polymer was determined by osmotic pressure measurements in order to establish the relationship between rate, molecular weight and quinone concentration.

Experimental data concerning the termination mechanism and actual number of quinone molecules in each polymer are factors which drastically limit the number of possible mechanisms. These facts, unaccessible by normal chemical procedures, were obtained by means of a double tracer technique. One set of experiments were performed using C^{14}-p-benzoquinone (BQ) and ordinary $\alpha\alpha'$azobisizobutyronitrile (AIBN) and an identical series of polymerizations were completed using C^{14}-AIBN initiator and normal BQ. (For the latter case, in the absence of any thermal polymerization each polymer would contain either one or two initiator fragments depending on whether disproportionation or combination was the termination mechanism.)

The experimental work was divided into four distinct

groups: preparation and purification of the polymer

kinetic measurements

C^{14} counting

molecular weight determinations.

Each group will be given ample description but considerably more detail on the osmotic pressure determination of molecular weights will be presented in the following pages.

Preparation of Polymers

Monomer purification. Methyl methacrylate monomer (MMA) (Matheson, Coleman and Bell) comes with small amounts of phenolic inhibitor added to prevent polymerization during shipping and storage. This impurity was removed by several washings in 10% NaOH followed by water to remove the NaOH. The monomer was left over $CaSO_4$ and prior to distillation was refluxed at atmospheric pressure in order to remove any last traces of inhibitor by thermal polymerization, Distillation was effected under reduced pressure. The monomer was stored for no more than one week at $-25^{\circ}C$ before it was used.

Initiator purification. The initiator, $\alpha\alpha'$azobisisobutyromitrile (AIBN) containing C^{14} on the CN groups was purchased from the Commissariat a l'Energie Atomique (France). The vacuum sealed vial contained 19.8 mg of AIBN with a total activity of 100 microcuries (μc).

Inactive AIBN (Eastman Organic Chemicals) was crystallized from ether and a portion was added to the active initiator. The dilution was such that one thousand counts per minute would be produced from a polymer assuming a molecular weight of

200,000, one initiator fragment per molecule and a counting efficiency of 50%. This resulted in an activity of 4.4 μc/mg. A stock supply of AIBN was prepared to an activity of 33 μc/mg. The material was purified by three precipitations from toluene.

Retarder purification. p-benzoquinone (BQ) was purchased from Matheson, Coleman and Bell and was purified by recrystallization from ether followed by a sublimation. BQ containing C^{14} was purchased from the Commissariat a l'Energie Atomique (France). One hundred and forty-five (145) mg of BQ having a specific activity of 100 μc were contained within a sealed vial. To 0.0645 grams of active BQ was added 0.4889 grams of inactive BQ thus making an activity of 44.5×10^{-6} μc/gram. Additional dilutions were completed before it was used in any polymerization reaction.

Polymerizations. The small amounts of initiator and retarder were admitted to the polymerization tubes in chloroform solution. The chloroform was distilled off at low temperatures on the vacuum line. Methyl methacrylate monomer was then added to the polymerization tubes and degassed by solidifying the solution in an acetone-dry ice mixture and thawing under vacuum. This procedure was repeated until no gases were observed bubbling from the thawing monomer solution. For polymerizations which were kinetically followed, the monomer solutions were transferred to the dilatometer from an argon atmosphere by a graduated hypodermic syringe into an argon atmosphere in the dilatometer. In this manner no oxygen could come into contact with the monomer.

All polymerizations were conducted at 60 $\pm$ 0.1°C. Blanks, in which the MMA monomer charges contained the small retarder concentrations but no initiator, were simultaneously polymerized to determine whether any thermal polymer would form. (It was thought unnecessary to do this for the more heavily retarded polymerizations.) No thermal polymerization was detected.

The conversion of monomer to polymer was not permitted to exceed ten percent because of "auto-acceleration" effects which are presumably due to the increased viscosity of the solution (29).

Polymer Purification. Polymethylmethacrylate was precipitated in cold 80% methanol. The contents of the polymerization tubes were dissolved in a small amount of methyl-ethyl-ketone (MEK) prior to precipitation in order to obtain a fluffy workable solid. Solution in MEK and precipitation by 80% methanol was repeated three times in order to remove any adsorbed active material which would give an incorrect indication of the number of C^{14} atoms in the polymer.

In order to test whether separation is quantitative an inactive polymer was prepared. Active AIBN and BQ were added and counts were taken after each of three precipitations. The results are tabulated in Table II.

TABLE II Separation of Active AIBN and BQ From Inactive Polymer

	Counts/min/gm.
Active AIBN	
no separation	330,000
1st precipitation	64,200
2nd precipitation	1,596
3rd precipitation	219
Active BQ	
no separation	125,700
2nd precipitation	1,100
3rd precipitation	248

Kinetic Analysis.

The conversion of a monomer to a polymer results in a decrease of volume. This phenomenon allows the progress of polymerization reactions to be followed dilatometrically.

The dilatometer which was used consisted basically of a reaction vessel connected to a capillary tube of known diameter. As polymerization proceeded the volume decreased and the subsequent drop in the capillary level was recorded with a cathetometer. By applying the known relationships between the volume decrease and percent reaction (30), the rates of polymerization were obtained.

Counting.

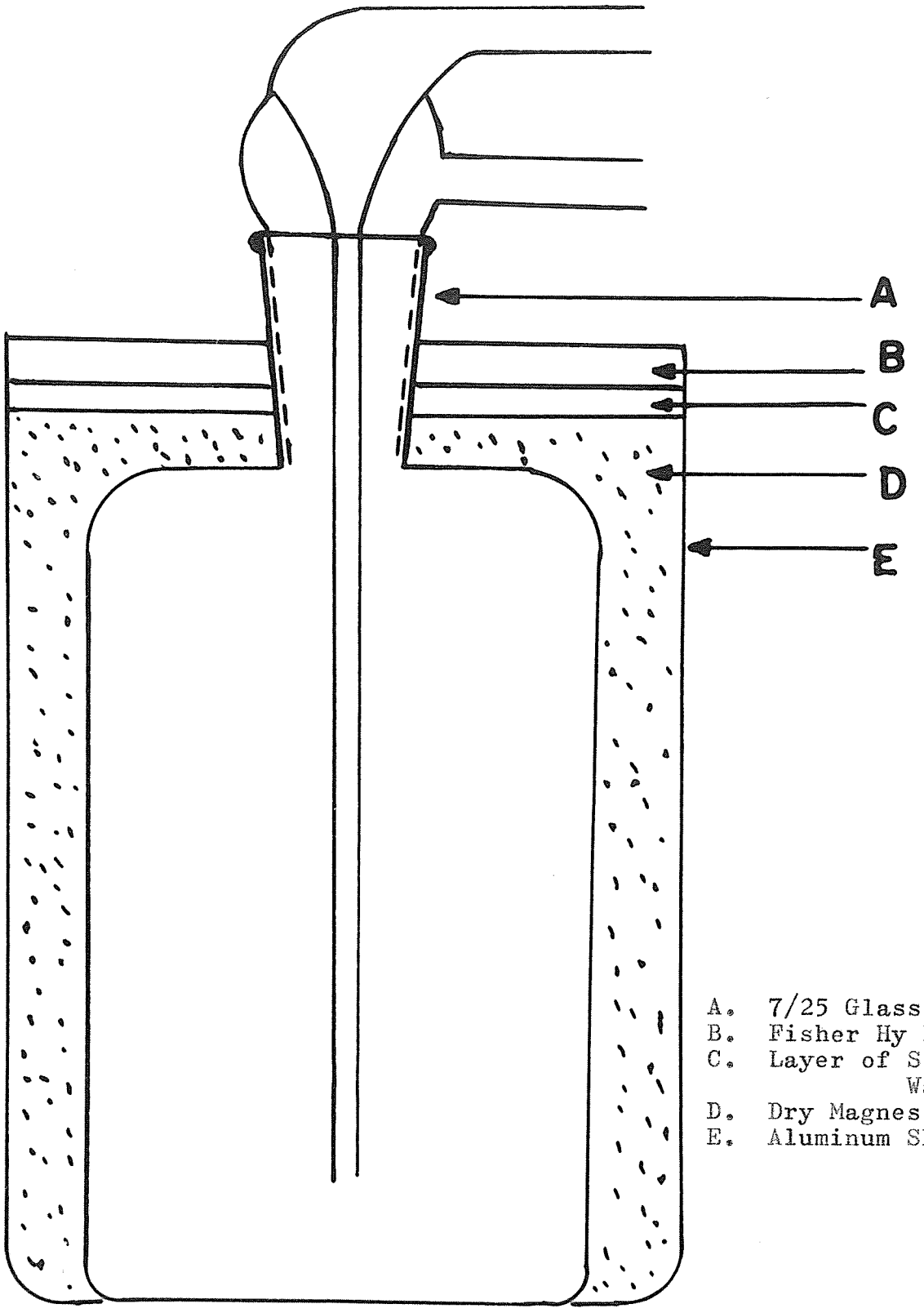
C^{14} was determined by the method of liquid scintillation

counting (31). This method is far superior to the alternate techniques of gas and end-window counting. The gas counting technique requires that the substance be oxidized and the carbon dioxide containing the C^{14} be collected and admitted to geiger tubes. This is of necessity time consuming and because of the relatively large background radiation, less accurate than the scintillation method. End-window counting does not have 4π efficiency and absorption of the weak particles by the window makes it undesirable.

Polymer was dissolved directly in a scintillator solution containing four grams of p-terphenyl and 0.10 grams of 1,4-di(2-(5 phenyloxazole) benzene (POPOP) per litre of toluene (32). Light is quenched by the presence of oxygen (33). For this reason oxygen was removed by bubbling argon through the solution for fifteen minutes before each count by a capillary bubbling device.

All counts were taken on twenty millilitres of solution in the same counting cell (Fig. 1).

The block diagram of the electronic counting apparatus is shown in Figure 2. The electronic equipment was operated from a Sorensen AC voltage regulator. High voltage for the phototube was taken from a Hamner Model N401 power supply. The phototube was an E.M.I. photomultiplier TYPE 9536S especially designed to operate with very low tube noise. Pulses went through a cathode follower at the base of the photomultiplier tube and thence to an "Atomic" linear amplifier model 204C. Amplified signals were put through an integral



A. 7/25 Glass Joint
B. Fisher Hy Pyseal
C. Layer of Sealing Wax
D. Dry Magnesium Oxide
E. Aluminum Shell

Fig. 1 Counting Cell

discriminator unit which blocked off all low energy pulses and finally to an Atomic scalar model 105 where they were counted. This apparatus is able to count approximately all the C^{14} disintigrations because of the low noise tube which was used.

Molecular Weight Determination.

The most important and most difficult experimental fact to determine in this research was the number average molecular weights of the polymer samples. Number average molecular weights are determined by osmotic pressure measurements - a technique which is quite sensitive to many possible sources of error.

Before any work on the osmometers was started a "standard" polymer sample was prepared according to the method of Baysal and Tobolsky (34). The molecular weight of the polymer produced was checked using their intrinsic viscosity - osmotic molecular weight relationship.

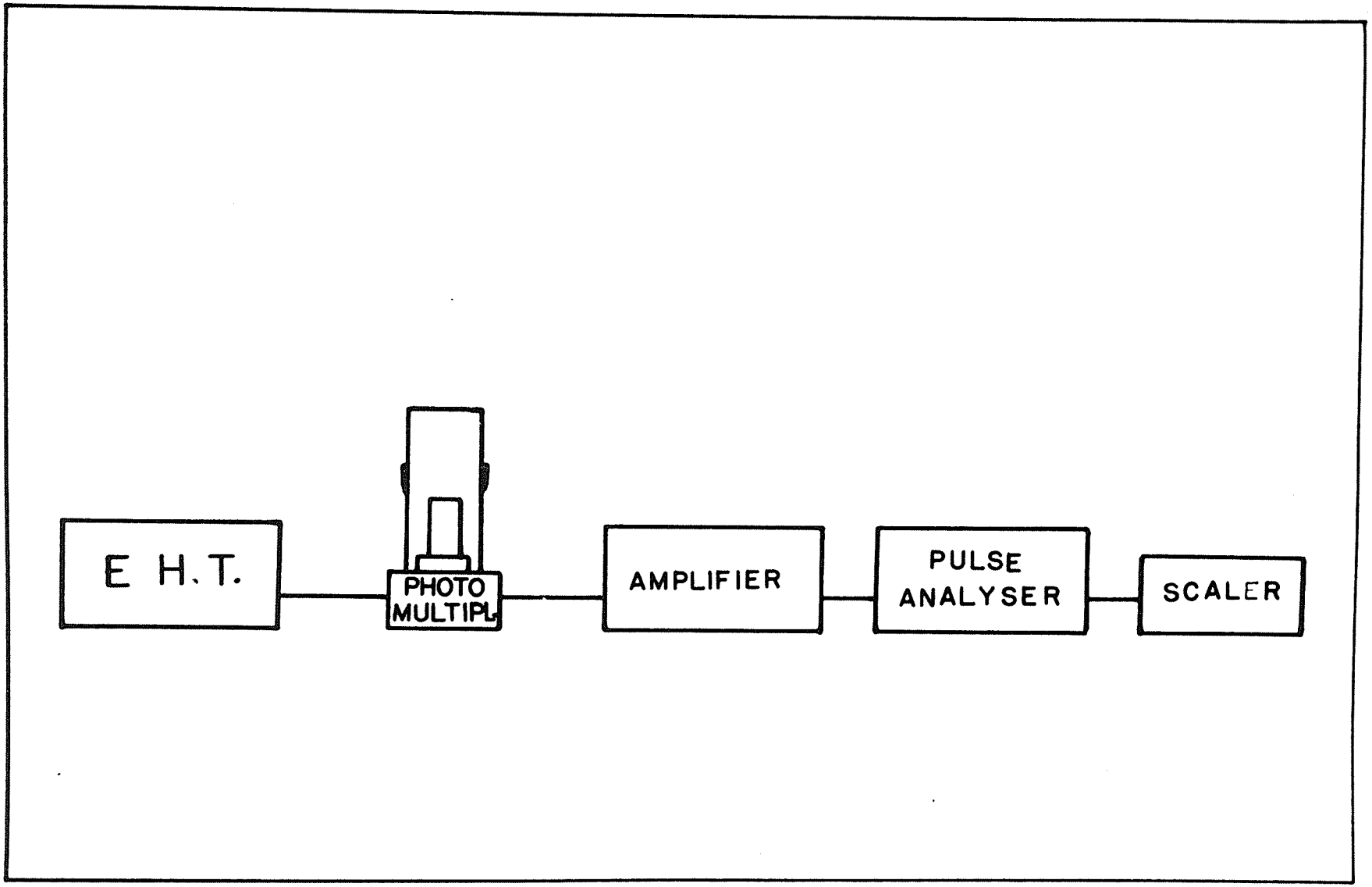
The osmometers were filled with solutions of this polymer and the influence of experimental variables was investigated. When the pressures were reproducible and approximated those predicted by the "known" molecular weight, the osmotic pressures of the unknown polymer samples were determined.

Prior to any osmotic molecular weight determinations the intrinsic viscosities for all the unknown samples were determined by means of an Ubbelohde viscometer (Fig. 3).

From these values the viscosity molecular weight was calculated using the modified Staudinger relationship where:

is the intrinsic viscosity

M is the viscosity molecular weight



BLOCK DIAGRAM OF ELECTRONIC APPARATUS.

Fig. 2

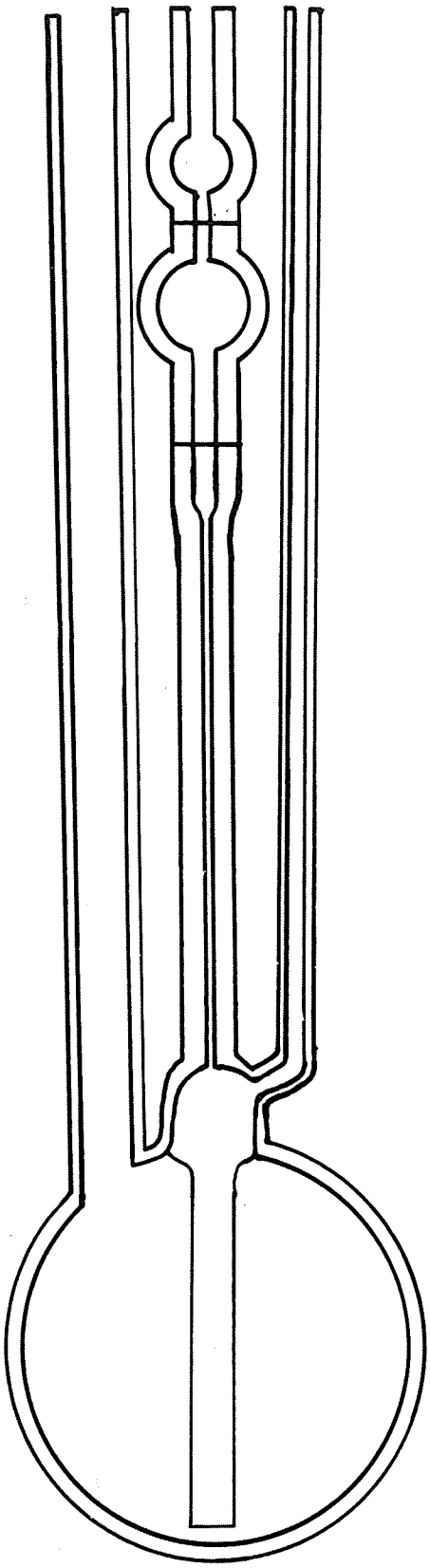


Fig. 3 Ubbelohde Viscometer

K and α are empirically determined constants.

The solvent for the active initiator series was methyl ethyl ketone and for the active retarder series, chloroform.

An operational osmometer consists essentially of a polymer solution separated from the solvent by a semi-permeable membrane. The osmometers used in this research were modified Zimm-Myerson instruments (Fig. 4)(35). Of the initial two osmometers one was commercially manufactured by J. V. Stabin Co., 601 East 19th Street, Brooklyn 26, New York, and the other was constructed locally. (At the time of writing this thesis, five osmometers were in operation - 2 were commercial and 3 were constructed locally.)

The osmometers were placed in a thermostat regulated at 25 $\pm$ .02°C and the pressures which developed were read to $\pm$.001 cm by a Griffin and George Ltd., cathetometer.

Membranes.

The critical constituent of the osmometer is the membrane. A good membrane will contain all polymer molecules but allow a ready transfer of solvent molecules.

The permeability of osmotic membranes can be controlled by the method of conditioning to any particular solvent. Undried gel-cellaphane membranes were obtained from J.V. Stabin Co., American Viscose and Schleicher and Schuell Co. Before conditioning was begun, the membranes were left two days in cold running water to remove salts or other extraneous material which may have been present.

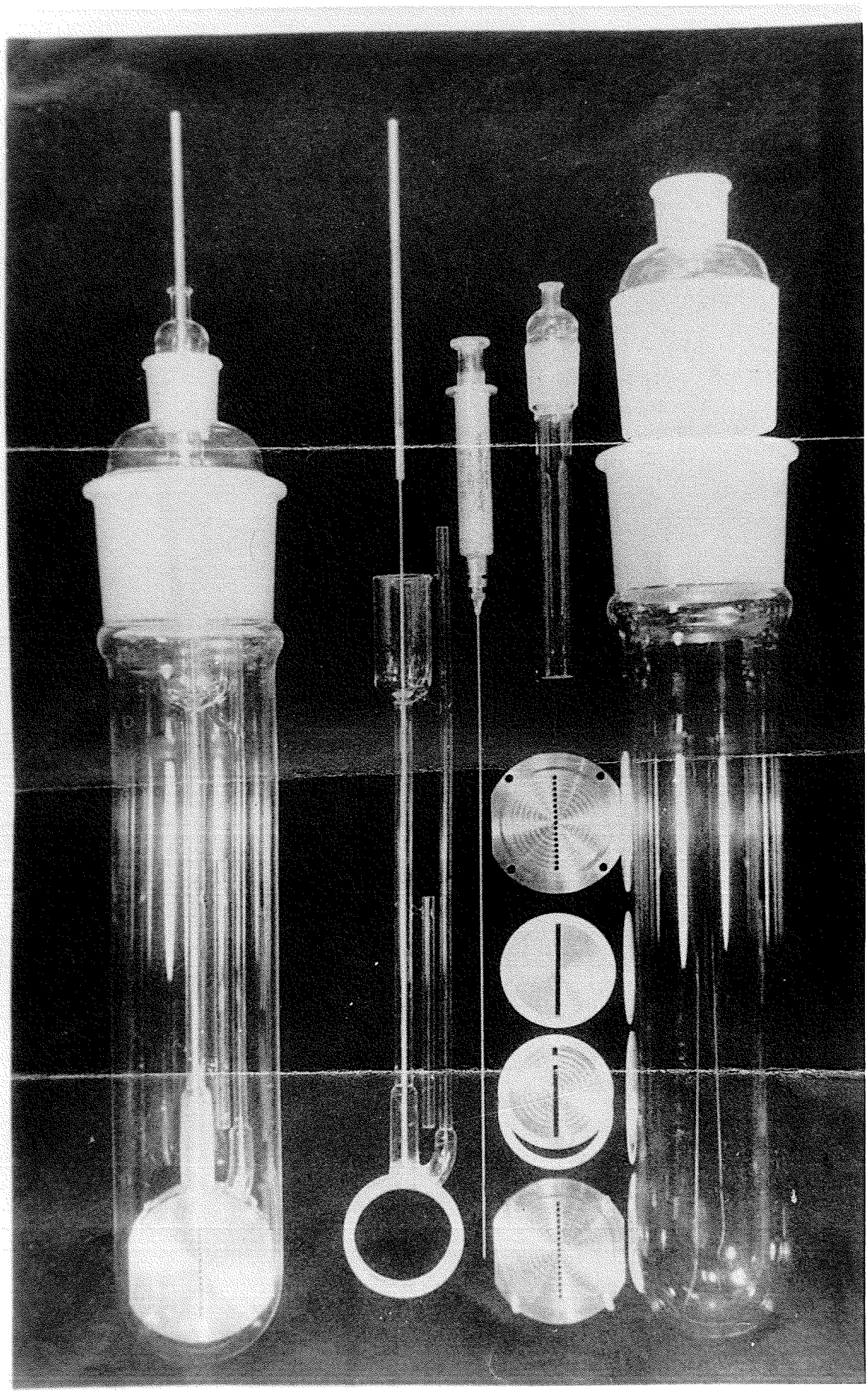


Fig. 4 Modified Zimm-Myerson Osmometer

Three procedures for conditioning the membranes were tested. One method, suggested by Robertson, McIntosh and Grummitt (36) involved treating the membranes with a 4% NaOH solution followed by water, pure ethanol and the organic osmotic solvent. The membranes produced by this procedure were found to be unsatisfactory. The osmotic pressures arising across these membranes were much too low indicating that a considerable amount of polymer was escaping through the membranes. Permeability measurements bear out this conclusion.

A second method of conditioning consisted of transferring the membranes directly from water to ethanol and thence to the desired solvent. This resulted in a totally impermeable membrane due to what was interpreted as a collapse of the highly swollen membrane structure (37).

The conditioning procedure which was eventually used involved gradually replacing the water in the membranes by ethanol followed by a removal of the ethanol by an appropriate solvent (MEK). The membranes were left in each of the following solutions for 15 minutes.

25% ethanol 75% water
50% " 50% "
75% " 25% "
100% " 0% "

75% ethanol 25% MEK
50% " 50% "
25% " 75% "
0% " 100% "

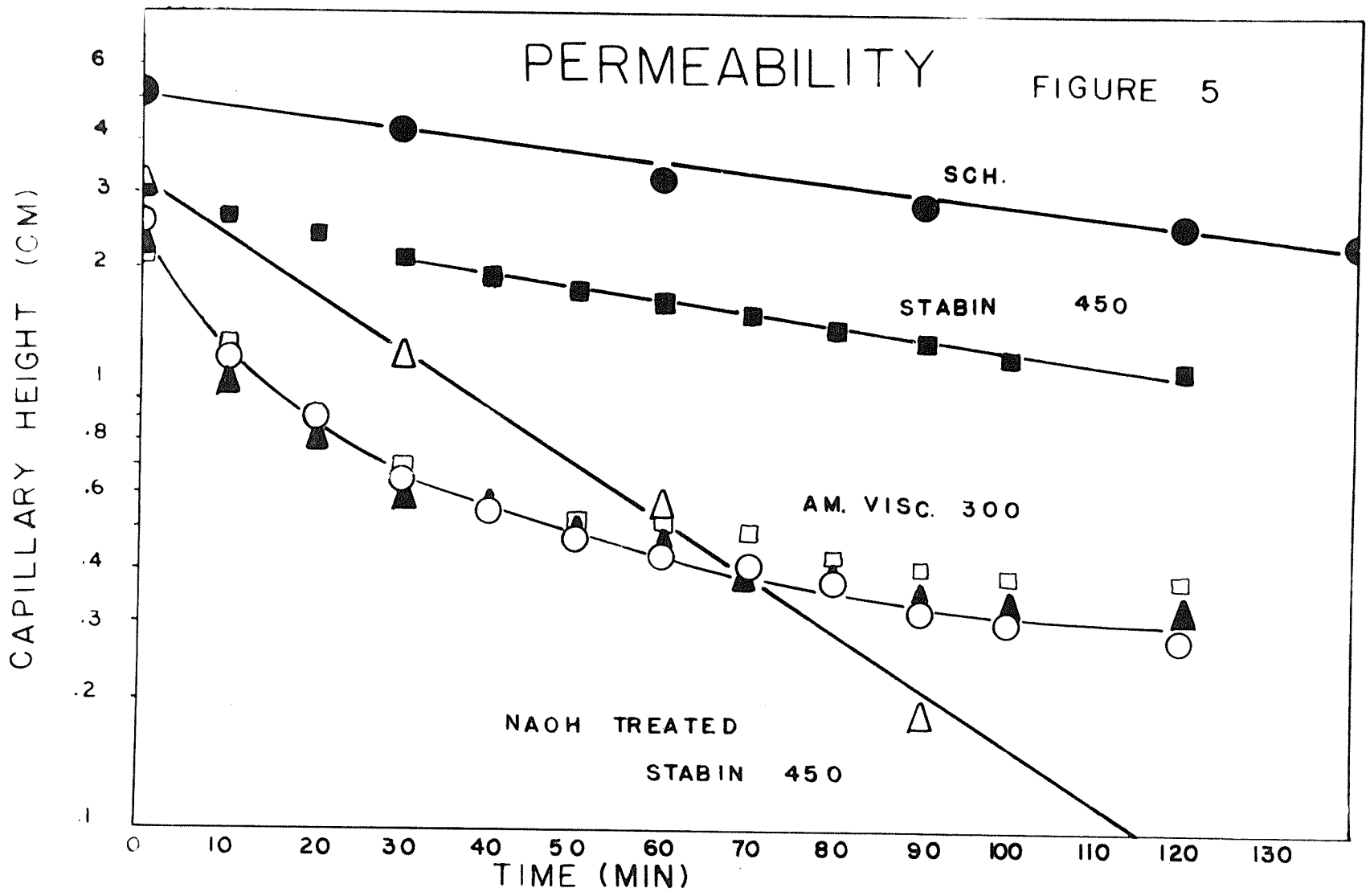

PERMEABILITY
FIGURE 5
SCH.
STABIN 450
AM. VISC. 300
NAOH TREATED
STABIN 450
CAPILLARY HEIGHT (CM)
TIME (MIN)
6
4
3
2
1
.8
.6
.4
.3
.2
.1
0
10
20
30
40
50
60
70
80
90
100
110
120
130

Fig. 5

Two sizes of membranes were tested--#300 and #450 (0.002 and 0.003 inches thick respectively). It was found that both retained polymer to the same extent but that the #300 reached equilibrium at least three times faster than the #450.

Filling.

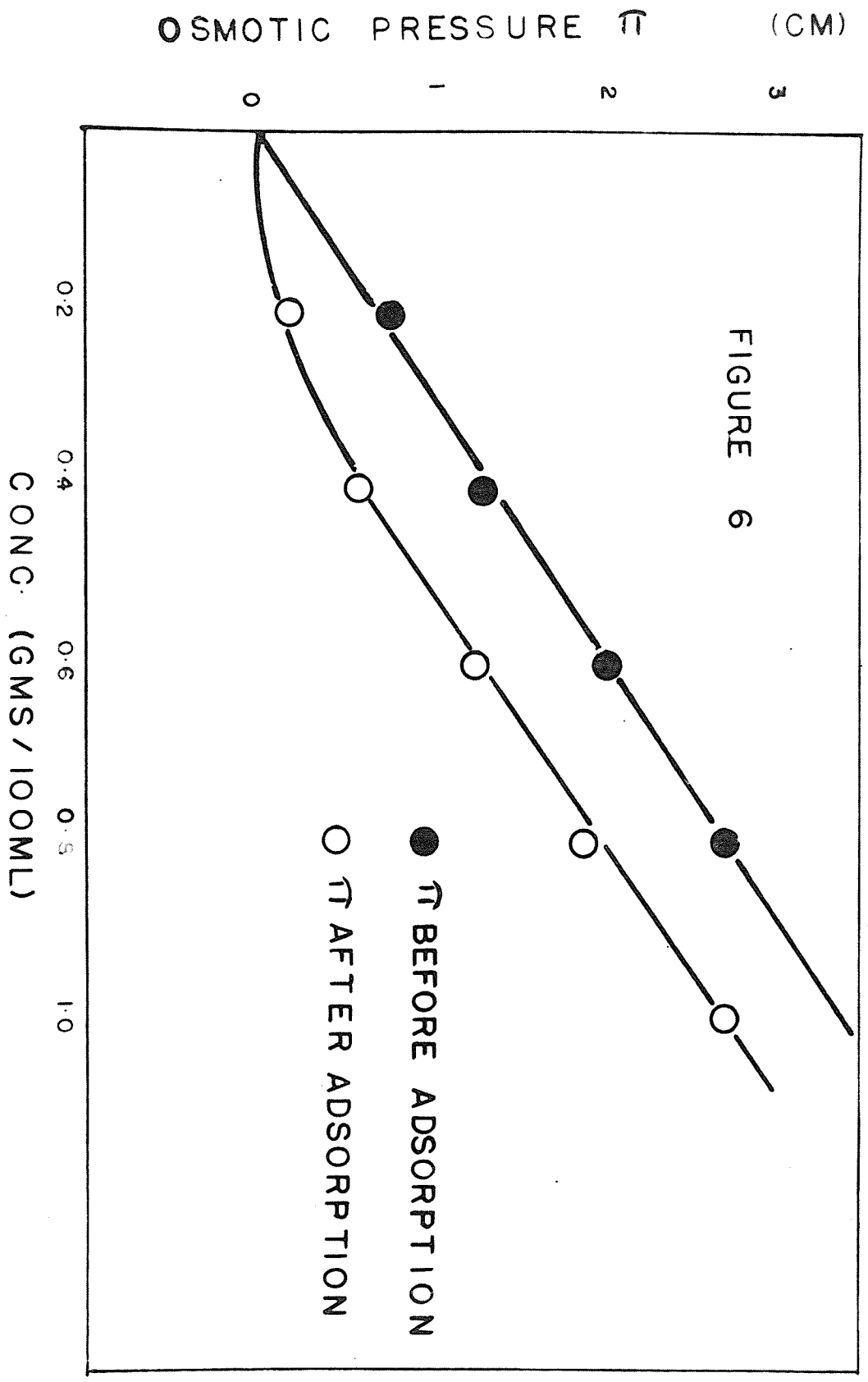
Polymer solutions of concentrations 0.20, 0.40, 0.60, 0.80 and 1.00 grams per 100 ml MEK were put into the osmotic cell by means of a long hypodermic syringe. The solution was sealed in the cell with a tight fitting metal positioning rod. In order to produce a leakproof seal a drop of mercury was placed between the metal and the glass.

The level of the solution in the capillary was adjusted by the metal positioning rod to a value approximating the expected osmotic pressure. Care was taken in this respect to assure that equilibrium was always arrived at from slightly above the final pressure. It was noted that for a considerable movement of the positioning rod there was not the equivalent movement of the liquid level in the measuring capillary. The only possible reason for this effect is a "flapping" of the membrane between its supports. Previously reported (38) slow equilibrium times may be explained by the osmotic pressure being required to "unflap" the membrane before giving a significant value. Variable pressures may have been due to slight leakages through the metal-glass seal which was unaided by mercury.

It has been noted by workers determining osmotic molecular weights that membranes will "improve with age".

This they attribute to a very slight irreversible adsorption of polymer molecules onto the membrane. The author found that after accurately determining the molecular weights of the standard sample on one osmometer, repeated fillings of all five osometers (whose membranes were being continually changed in order to find two with a low asymmetry) resulted in decreasingly lower osmotic pressures. Since for any one reading the value of the osmotic pressure was constant, polymer was not being lost by diffusion through the membrane. The only possible alternative is adsorption. The pressure versus concentration curves before and after the suspected adsorption are shown in Figure 6.

After a suitable pair of membranes were found and "conditioned" to polymer, samples containing the previously indicated concentrations of unknown molecular weight material were added to the osmometers. Osmotic pressures were measured after allowing the solution and solvent sufficient time to come to equilibrium. (Most samples were introduced to the osmometers about 4:00 p.m. and the osmotic pressure values taken at 9:00 a.m. next morning.) The solutions were then removed and replaced with new solutions containing another unknown molecular weight polymer. This procedure was continued without altering in any way the successful pairs of membranes, until the osmotic pressures of all the samples were determined.



Effect of Polymer Adsorption on π

RESULTS AND CALCULATIONS

Results and Calculations.

Kinetic. The results of all kinetic data are shown in Figures 7 and 8.

Every run was initiated by 1.19×10^{-3} moles of AIBN per mole of MMA at 60°C, and the quinone concentration was varied from 0.00 to 45.18×10^{-5} moles per mole of MMA. The rates evaluated from the graphs are shown in Table III.

TABLE III Rate Data

Experiment	BQ conc. Moles/Mole Monomer $\times 10^5$	Rate % Polym. Per Min. $\times 10^3$
0	0.00	60.0
1	9.03	19.5
2	18.07	11.8
3	27.10	5.7
3b or $3\frac{1}{2}$	31.62	---
4	36.14	1.8
4b or $4\frac{1}{2}$	40.65	3.9*
5	45.18	4.1*

*Note: these rates are obtained after a period of inhibition.

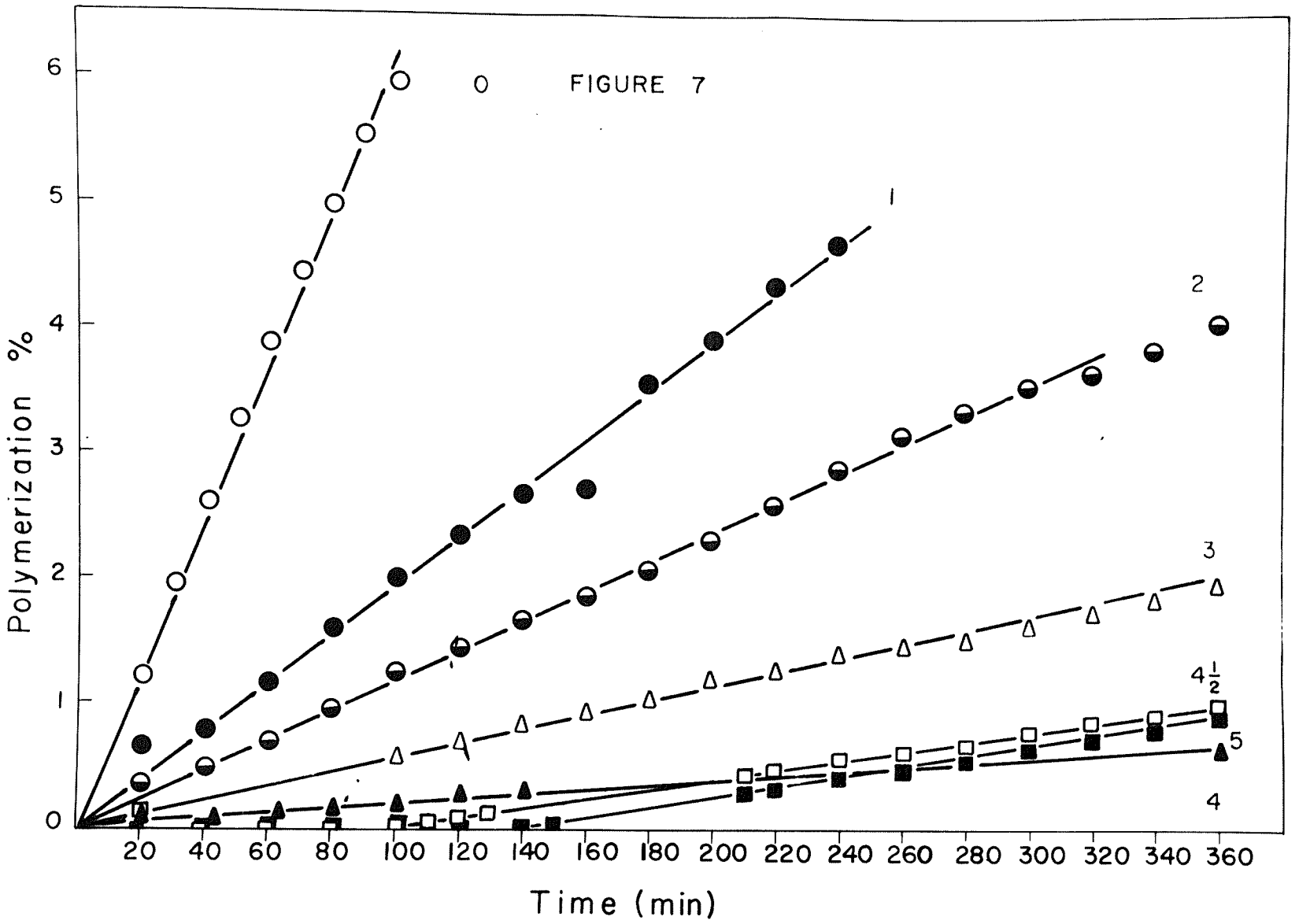
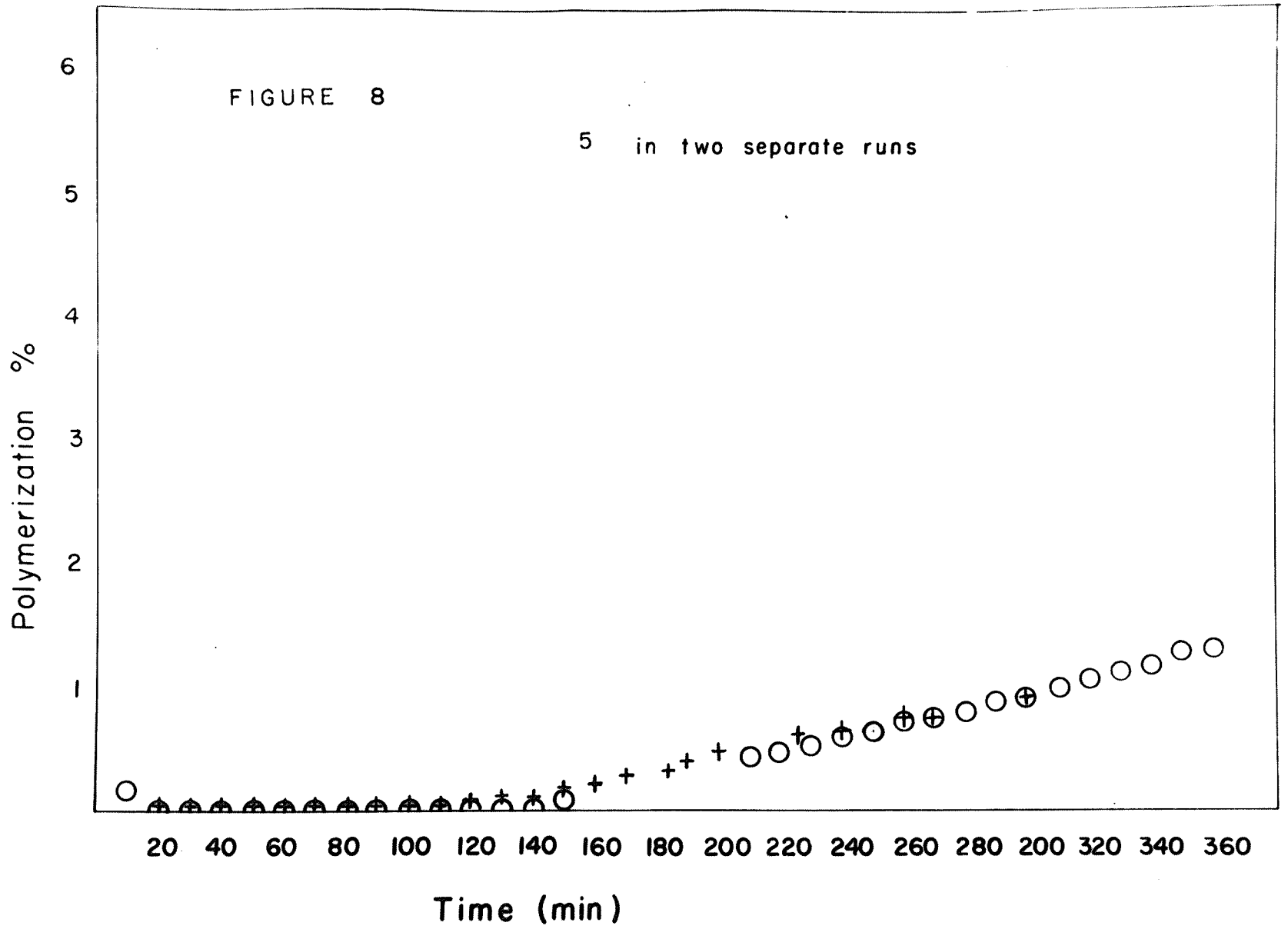


FIGURE 7
Polymerization %
Time (min)
0
1
2
3
4
4½
5
0
1
2
3
4
5
6
20
40
60
80
100
120
140
160
180
200
220
240
260
280
300
320
340
360

FIGURE 8

5 in two separate runs



Kinetic Curves of Sample 5

Molecular weights. Molecular weights of the polymer samples were determined both by viscosity and osmotic pressure measurements. All osmotic molecular weights were determined in MEK at 25 $\pm$ .02°C. The intrinsic viscosities for the series using active initiator were evaluated at 30 $\pm$ .02°C in MEK whereas for the active retarder series, chloroform at 25 $\pm$ .02°C was the solvent.

The molecular weight is calculated from the osmotic pressure by use of the von't Hoff limiting law.

$$M = \frac{RT}{(\pi/C)_o}$$

$(\pi/C)_o$ is the value of π/C at infinite dilution.

π is the osmotic pressure

C is the concentration of polymer in solution.

T is the absolute temperature.

R is a constant.

If π is expressed in centimeters of solvent and C in grams of polymer per 100 millilitres of solvent, then R becomes 848/d where d is the density of the solvent at temperature T.

Therefore $M = \frac{848T}{d(\pi/C)_o}$ and at 25°C $M = \frac{316.45 \times 10^3}{(\pi/C)_o}$

Intrinsic viscosities are determined by measuring the times of flow of polymer solutions and pure solvent. The specific viscosity is then $\eta = \frac{\eta - \eta_o}{\eta_o}$ where η is the viscosity of the polymer solution and η_o the viscosity of pure solvent. The intrinsic viscosity η_i is the $\lim_{c \to 0} (\eta_s/C)$ and is equal to KM^{α}.

If the constants K and α are known, then the molecular weight M may be readily calculated. However, K and α differ from one polymer to another and even from polymers of the same chemical type which have been prepared differently. It is important therefore to determine molecular weights by independent measurements in order to relate them to their viscosities. The values of K and α determined by this research are at the bottom of tables IV and V.

TABLE IV

Molecular Weight - Viscosity Relationship for Active Initiator Series.

Experiment	η_i (MEK at 30°C)	$(\pi/C)_o$ (MEK at 25°C)	Osmotic Molecular Weight
0A	2.030	----	
1A	0.700	0.95	333,000
2A	0.558	1.65	191,800
3A	0.453	1.96	161,400
3bA	0.432	2.14	150,700
4A	-----	2.75	115,100
4bA	0.371	2.40	131,800
5A	0.335	3.25	97,400

$K = 3.1 \times 10^{-5}$

$\alpha = 0.80$

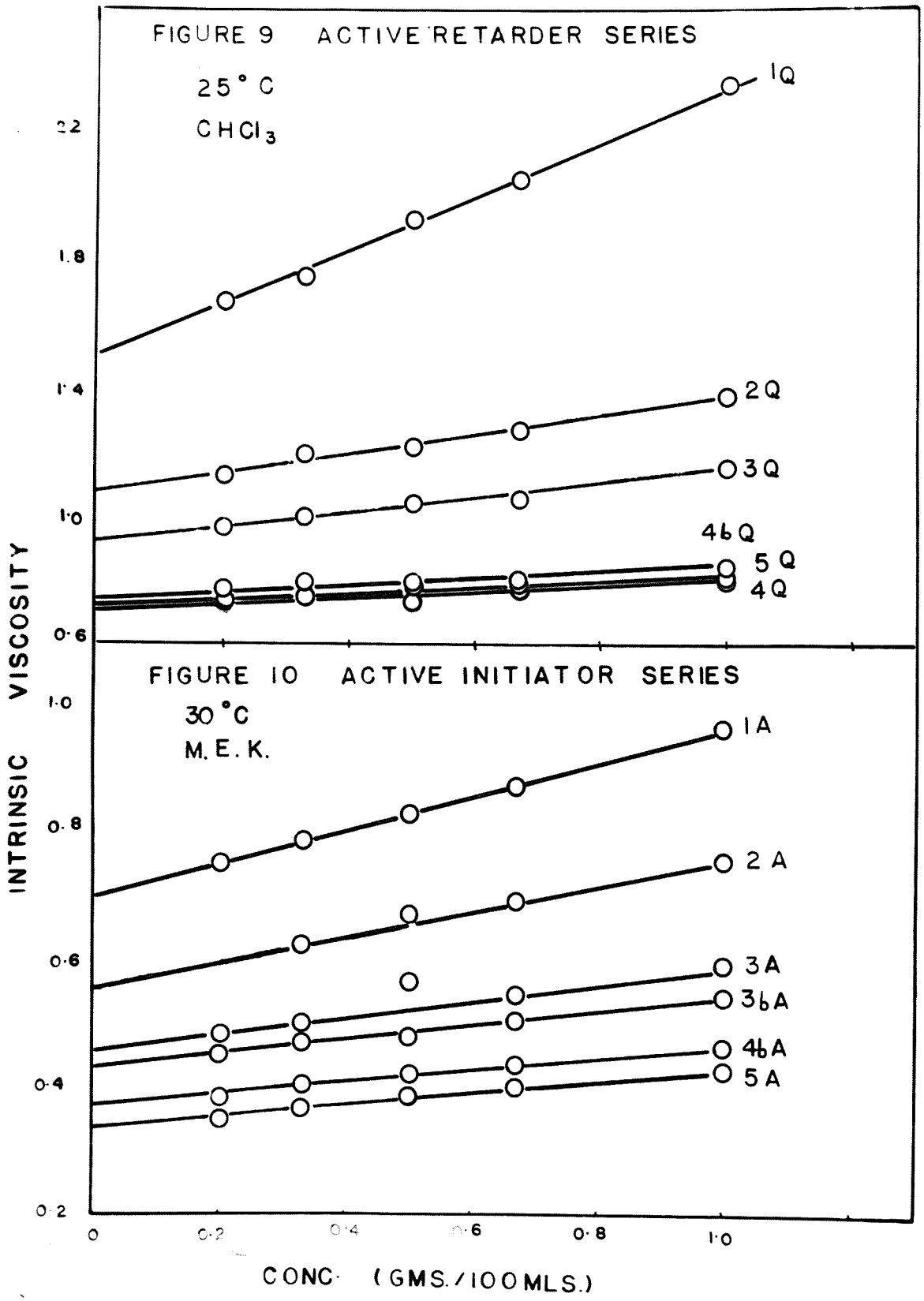


FIGURE 9 ACTIVE RETARDER SERIES
25° C
CHCl3
1Q
2Q
3Q
4bQ
5Q
4Q
FIGURE 10 ACTIVE INITIATOR SERIES
30° C
M.E.K.
1A
2A
3A
3bA
4bA
5A
INTRINSIC VISCOSITY
2·2
1·8
1·4
1·0
0·6
0·8
0·4
0·2
0
0·2
0·4
0·6
0·8
1·0
CONC. (GMS./100MLS.)

TABLE V

Molecular Weight - Viscosity Relationship
for Active Retarder Series

Experiment	$(CHCl_3$ at 25°C)	$(\pi/C)_o$ (MEK at 25°C)	Osmotic Molecular Weight
1Q	1.55	1.14	276,600
2Q	1.08	1.78	178,000
3Q	0.92	2.16	146,000
4Q	0.75	2.92	108,400
4bQ	0.72	2.82	112,000
5Q	0.71	2.87	110,000

$K = 3.82 \times 10^{-5}$

$\alpha = 0.85$

Counting Data

The number of initiator fragments and molecules of p-benzoquinone can be calculated from the specific activity of the initiator or retarder and that of the polymer if the molecular weight of the polymer is known. A sample calculation is shown below (3A).

a) 0.1730 grams of polymer had a count of 41,587 per minute.

b) 1.63×10^{-6} moles of initiator gave 80,873 c/m.

c) There are then $1.63 \times 10^{-6} \times 41,587/80,873 = 8.36 \times 10^{-7}$ moles of initiator present in 0.1730 grams of polymer.

d) The molecular weight is 161,400.

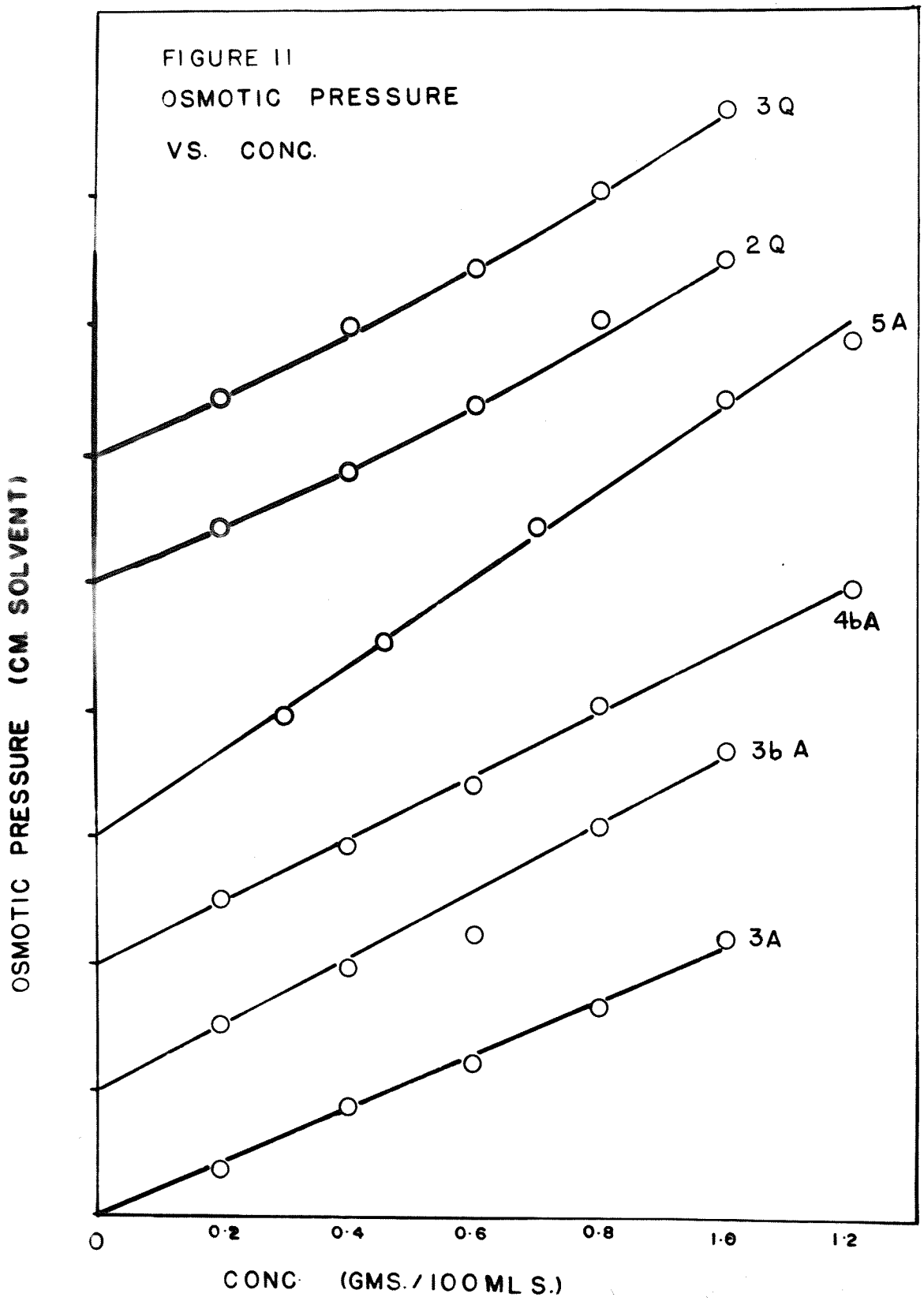


FIGURE II
OSMOTIC PRESSURE
VS. CONC.
3Q
2Q
5A
4bA
3b A
3A
OSMOTIC PRESSURE (CM. SOLVENT)
0
0·2
0·4
0·6
0·8
1·0
1·2
CONC. (GMS./100 ML S.)

e) Moles polymer counted $0.1730/161,400 = 10.72 \times 10^{-7}$.

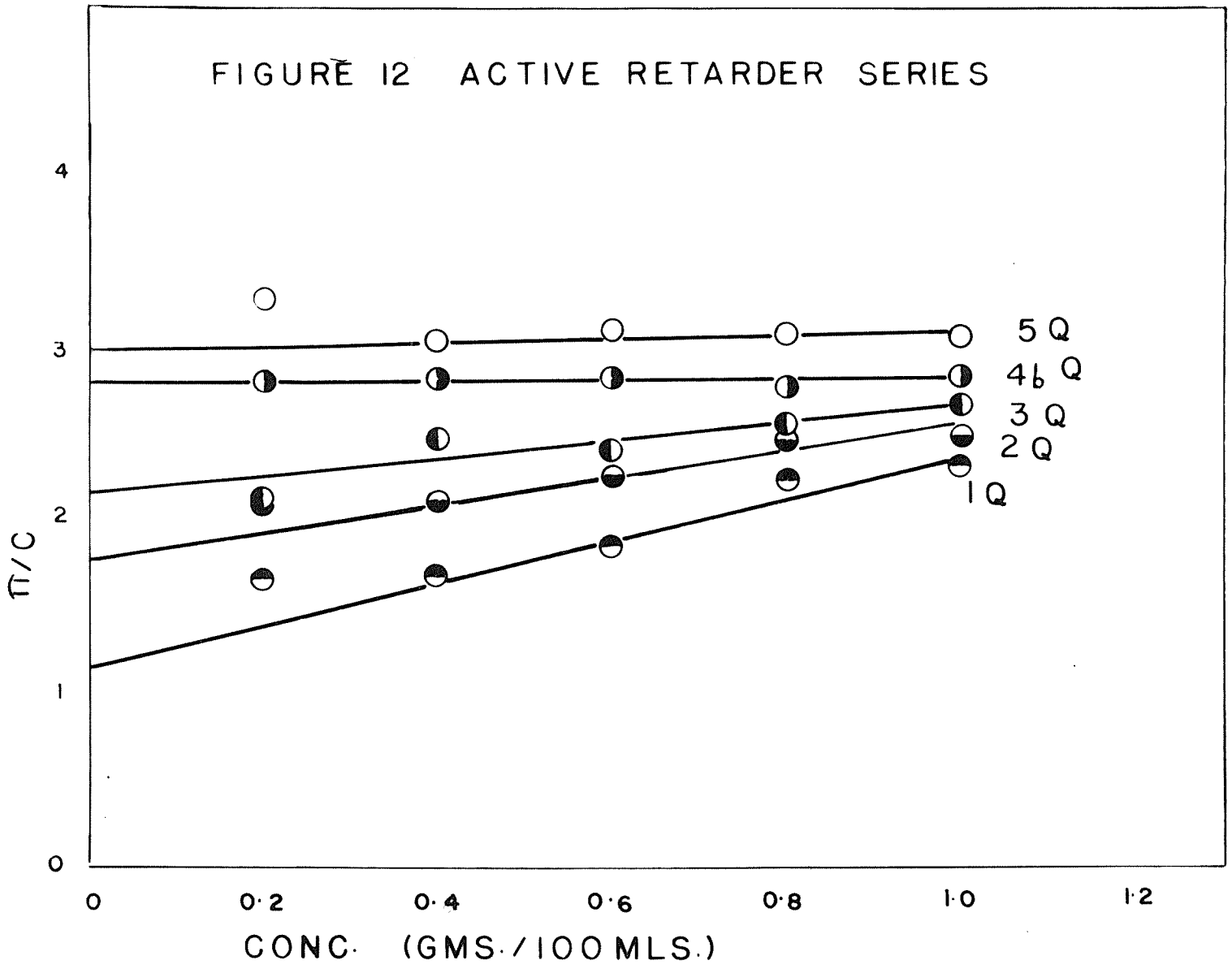
f) Each mole of polymer contains $8.36 \times 10^{-7}/10.72 \times 10^{-7} = 0.78$ moles of initiator.

g) Since each mole of initiator breaks into two fragments (Initiator $\longrightarrow 2R\cdot$), there are $2 \times 0.78 = 1.56$ initiator fragments present in each polymer molecule.

TABLE VI

Results of Active Retarder Series

Experiment	Osmotic Molecular Weight	Weight Counted (grams)	Moles Counted x 10^7	Moles Quinone Present x 10^7	Molecules Quinone per Polymer
1Q	276,000	.1301	4.71	5.18	1.10
2Q	178,000	.1290	7.25	8.66	1.20
3Q	146,000	.1489	10.20	13.4	1.31
4Q	108,400	.1457	13.44	19.8	1.47
4bQ	112,000	.1627	14.53	25.1	1.72
5Q	110,000	.1182	10.75	18.3	1.70



Reduced Osmotic Pressure Curves for Active Retarder Series

TABLE VII

Results of Active Initiator Series

Experiment	Osmotic Molecular Weight	Weight Counted (grams)	Moles Counted x 10^7	Moles Initiator Present x 10^7	Initiator Frag./ Molecule Polymer
0A	-------	.1727		1.25	
1A	333,000	.1727	5.19	4.46	1.72
2A	191,800	.1719	8.96	7.00	1.56
3A	161,400	.1730	10.72	8.36	1.56
3bA	150,700	.1726	11.45	9.13	1.59
4A	115,100	.1350	11.73	8.84	1.51
4bA	131,800	.1719	13.03	10.5	1.61
5A	97,400	.1714	17.60	11.9	1.36
				Average	1.53

Calculations of percent combination and disproportionation

Let x be fraction of molecules with two end groups.

Let y be fraction of molecules with one end group.

n is average number of end groups.

$x + y = 1$

$2x + y = n$

From which $x = n - 1$

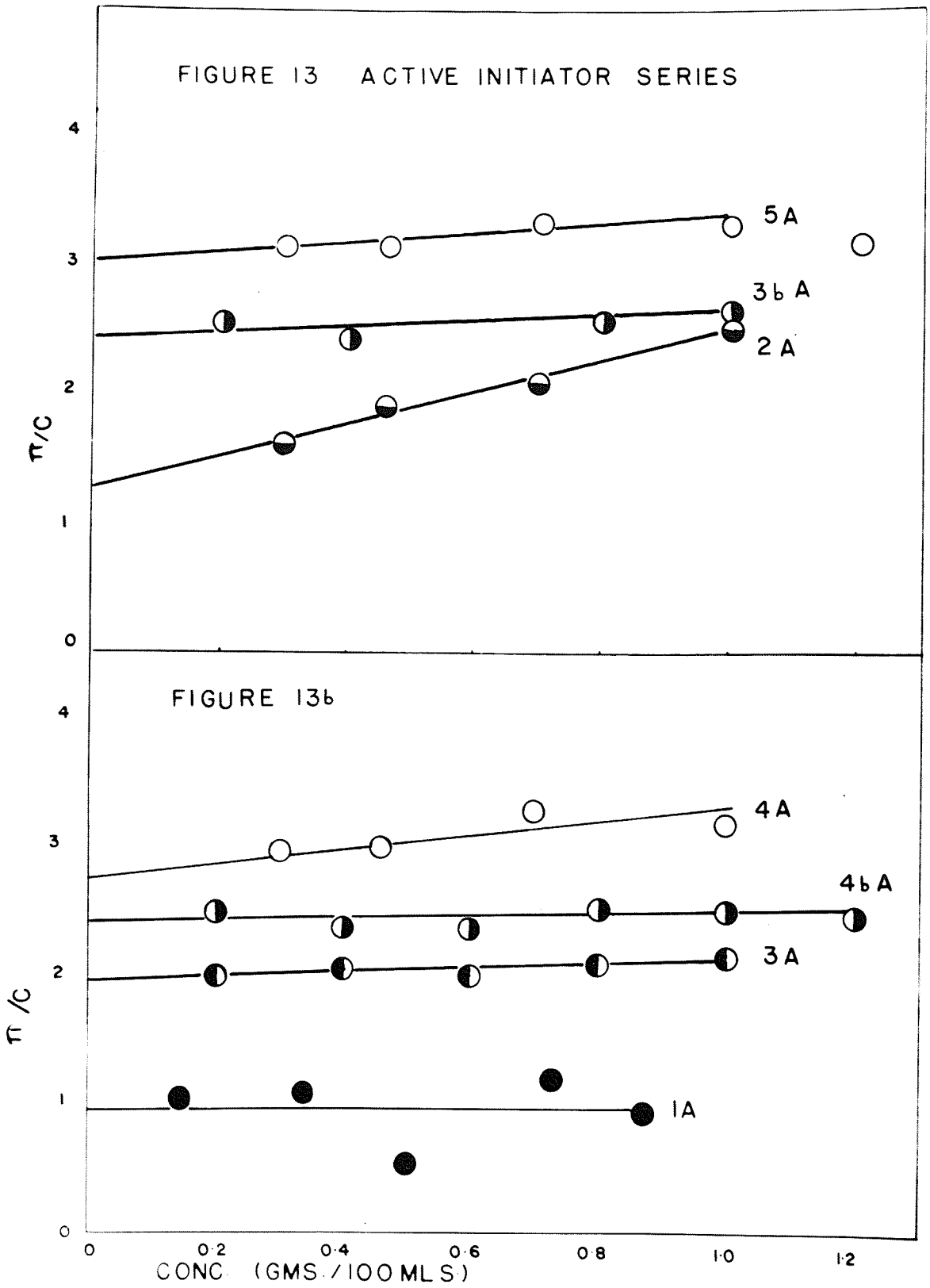
$y = 2 - n$

Therefore the fraction undergoing disproportionation and combination are $\frac{2 - n}{n}$ and $\frac{2(n - 1)}{n}$

In this research n = 1.53

Combination = 69%

Disproportionation = 31%



Reduced Osmotic Pressure Curves for Active Initiator Series

In order to determine whether the amount of quinone in the inhibited polymer varied with time of polymerization, sample 5Q was reprepared and the polymer formed was precipitated, purified and counted after different percentages of polymerization had been attained. The results are shown in Table 8.

TABLE VIII Variation of BQ with Time

Sample 5Q

Polymerization Time (Hours)	Moles Quinone/0.2000 Grams Polymer x 10^7
6	46.0
30	43.6
45	38.0
71	35.7
90	34.6

Kinetic Chain. Another quantity, the kinetic chain length, may be defined as the average number of monomer united comsumed by each chain which has been started.

In Table 6 the number of moles of initiator for each weight of polymer are given. The kinetic chain length, ν, is therefore the total weight counted divided by the molecular weight of the monomer and the moles of initiator found to be present (40).

$$\nu = \frac{\text{(Weight Counted)}}{\text{(Molecular weight of monomer)(Initiator Fragments)}}$$

The weight of a kinetic chain is $\frac{\text{(Weight Counted)}}{\text{(Initiator Fragments)}}$

If the rate of the reaction is known, that is the number of grams of polymer formed per unit time, the number of kinetic chains started in that time can also be determined (Table 9).

TABLE IX Chain Initiation Data

Experiment	$\bar{\nu}$	Rate of Reaction gms/min/l MMA	Rate of Chain Initiation (Chain started/l/min x 10^6)
0A	13810	6.99	5.06
1A	3880	1.75	4.51
2A	2455	1.06	4.32
3A	2070	1.51	2.46
4A	1527	0.16	1.05
$4\frac{1}{2}$A	1635	0.35	2.14
5A	1439	0.37	2.57

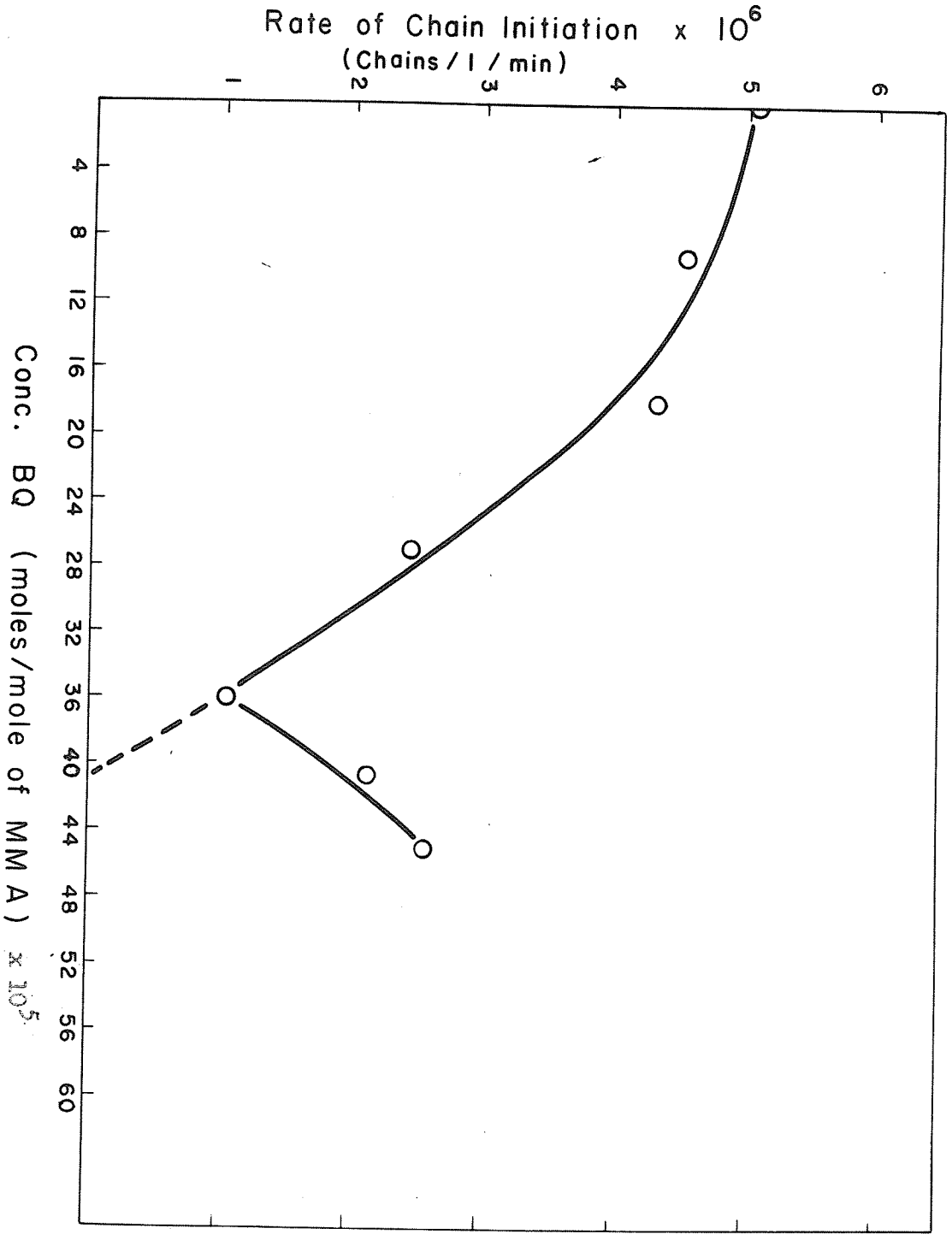


Fig. 14 Chain Initiation

Estimation of Error.

Compared with the error in numberaverage molecular weight determinations and counting data, a negligible amount of error was introduced to the final results by measurements of volume and weight, losses resulting from separations and transfers, impurities and rate measurements. For example, if the uncertainty of a weighing is 0.0002 grams, the error in weighing 0.1500 grams is 0.13%. Similarly the error due to radioactivity occluded on a sample is estimated to be less than 0.20% (page 18).

The accuracy of osmotic molecular weight determinations has been shown to be approximately 90% (42)(43). Molecular weights were independantly measured by a number of laboratories and the deviations determined. It was thus established that the osmotic molecular weights could be obtained with an error of 10%.

The standard deviation in a radioactive count is given by $\sigma = n^{\frac{1}{2}}$ where n is the total number of counts. The error in the count of a sample is $\sigma = (nb + n_s)^{\frac{1}{2}}$ where nb and n_s are the counts of background and sample respectively. For example, samples 2Q had a total activity of 4244 counts per minute of which 77 were due to background. Therefore $\sigma = (4244)^{\frac{1}{2}} = 65.1$. The error in the count is $\frac{65.1}{4167} \times 100 = 1.56\%$

The maximum error in determining the number of initiator fragments and quinone molecules is 13%.

DISCUSSION

DISCUSSION

The purpose of the research was to determine the mechanism by which quinone retards the polymerization of methylmethacrylate from rate and tracer data. The most general observations of this work are listed below:

a) the number of initiator fragments per polymer molecule is not affected by increasing the concentration of quinone in successive polymerization.

b) the number of quinone molecules in each polymer increases to a limiting value as the quinone concentration in successive polymerizations is increased.

c) the rate of chain initiation decreases with increasing quinone concentration.

d) the rates of polymerization decrease with increasing quinone until a definite concentration has been attained, after which periods of inhibition are observed.

e) the molecular weight varies directly with the rate of the retarded reaction.

Although the possible effects of retarder molecules are described in the introduction, the equations for each type of interference are repeated in the following few lines.

(a) Immediate termination of growing chains

$$RM_n\cdot + Q \longrightarrow RM_nQ\cdot$$

$$RM_nQ\cdot + \text{radical} \longrightarrow \text{non-radical products}$$

(b) Copolymerization

$$RM_nQ^{\circ} + M \longrightarrow RM_nQM^{\circ}$$

$$RM_nQM_{n'}^{\circ} + Q \longrightarrow RM_nQM_{n'}Q^{\circ}$$

etc.

(c) Chain transfer

$$RM_n^{\bullet} + Q \longrightarrow RM_n + Q^{\bullet}$$

(d) Initiator-radical capture

$$\text{Initiator} \longrightarrow 2R^{\circ}$$

$$R^{\bullet} + Q \longrightarrow RQ^{\bullet}$$

Copolymerization may be eliminated as a major contribution to the retardation mechanism since it has been found that there are always less than two molecules of quinone present in each polymer molecule. Also, since the number of initiator fragments in the final molecule is constant, chain transfer may be ignored as a principal retarding effect.

In order to fully understand the following argument, consider a pure monomer with terminates predominately by disproportionation. If quinone at radical positions of the growing chains cause combination, increasingly larger amounts of quinone should cause a corresponding change from disproportionation to combination as the termination mechanism. Conversly, if the ratio of combination to disproportionation is constant, then the end radicals of the terminating polymer chains must also be constant. The results of this research indicate that the number of initiator fragments and hence the proportion of

combination to disproportionation remains unchanged when the concentration of quinone is varied. Since the determination of combination to disproportionation is dependent only upon terminating end radicals of the polymer chains, the concentration of quinone at these positions must be constant.

The termination mechanism of methyl methacrylate in the presence of quinone differs from that of unretarded polymerizations (18)(19). Accordingly some quinone must be attached to the end of the polymer radicals and its concentration must remain constant with respect to the total number of radicals present. The number of molecules of quinone in each polymer molecule, however, increases with rising concentrations of the retarder. Quinone is therefore becoming incorporated into the polymer chain at some position other than at its terminus. The conclusion now may be made that reaction "a" occurs to some extent but cannot account for all the retardation exhibited or quinone present.

It has been shown that the number of polymer chains actually initiated per minute decreases when the concentration of quinone is increased (Table 9). The extrapolated value for the quinone concentration at which the rate of initiation will be zero accurately predicts that value at which complete inhibition of polymerization was first detected (Fig. 14). These two very significant facts indicate that a further effect of quinone on the retardation of methyl methacrylate polymerization is to react with the chain initiating radicals. At a high enough retarder concentration all the primary initiating

radicals are intercepted thus completely inhibiting any polymerization.

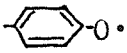
It is generally considered that inhibition is the limiting case of retardation (41). The length of the inhibition period should therefore be comparative to the length of retardation. In this research quinone was added in increasingly larger quantities to successive samples and the measured rate was found to decrease accordingly. The most heavily retarded reaction (Expt. 4) was followed kinetically for 19 hours and showed no sign of increasing its rate in this time. The next two polymerizations (Expts. $4\frac{1}{2}$ and 5) contained slightly greater concentrations of quinone and exhibited inhibition periods. The lengths of inhibition however were considerably shorter than anticipated on the basis of length of retardation of the previous sample.

To account for the very distinct inhibition period followed by an equally distinct and constant rate of polymerization it is necessary to accept one of the following two postulates:

a) the mechanism by which the quinone is being removed from the solution changes drastically at a critical concentration in such a way that the retarder becomes exhausted much faster than it would by ordinary retardation effects. The length of the inhibition period is the time required for the quinone to be reduced to some value low enough for polymerization to resume.

b) the retardation (or inhibition) products formed

by the addition of quinone molecules to the chain initiating radicals are themselves capable of initiating a polymer chain.

The second postulate explaining the inhibition period found, namely that the retardation products can initiate a chain, has some basis in the structures of these products. The radical formed (22) can combine or disproportionate with a growing polymer radical, $RM_n^{\cdot}$, however it is physically impossible for a structure such as R-  -O· to disproportionate with another similar type of radical. Presumably during an inhibition period there are negligibly few $RM_n^{\cdot}$ radicals present; therefore the only way for RQ· to be removed is by combination with other RQ·'s to form R-  O - O-  R. This compound has a relatively weak peroxide linkage which may decompose at the temperature of the reaction and thereby initiate further polymerization.

If the peroxide initiation mechanism is true, then one expects that the polymer formed after the inhibition period would have considerably more quinone incorporated into it than polymer formed from a retarded reaction. This, in fact, has been found (Table 7). One would further expect that after the inhibition period as polymerization proceeds and $RQM_n^{\cdot}$ radicals become more prevalent, the concentration of RQ· in solution would rapidly decrease due to both the peroxide initiation process and bimolecular termination with growing polymer radicals. Therefore polymers formed immediately

after the inhibition period would contain more quinone than those formed later when the RQ· radical concentration is considerably smaller. Confirmation of this prediction was also obtained (Table 8).

Conclusion

It seems highly probable that the quinone molecules are exhibiting a dual behavior in the retardation of methyl methacrylate. Firstly, quinone becomes attached to the end of a growing polymer radical which then rapidly terminates with some other radical in solution. The quinone is simultaneously intercepting initiator radicals.

The presence of a short distinct inhibition period is the result of a high concentration of R-  -O· which combine with other R-  -O· to form the peroxide which later decomposes to initiate polymerization.

A reaction scheme for the retardation of methyl methacrylate polymerization is proposed below.

$$\left.\begin{array}{l} \text{Initiator} \longrightarrow 2R\cdot \\ R\cdot + M \longrightarrow RM\cdot \end{array}\right\} \text{ Initiation}$$

$$RM_n + 1^{\cdot}M \longrightarrow RM_n\cdot \quad \text{Propogation}$$

$$RM_n\cdot + Q \longrightarrow RM_nQ\cdot \quad \text{Retardation}$$

$$RM_nQ\cdot + \text{radical} \longrightarrow \text{non radical products} \quad \text{Termination}$$

$$I\cdot + Q \longrightarrow IQ\cdot \quad \text{Retardation and at high Q concentration, inhibition}$$

$$IQ\cdot + IQ\cdot \longrightarrow IQQI$$

$$RQQR \longrightarrow 2RQ'\cdot$$

$$RQ\cdot' + M \longrightarrow RQ'M\cdot$$

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