SEMIVINYL AND ELECTROLYTIC POLYMERIZATIONS

presented by

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A thesis submitted to the
Faculty of Graduate Studies and Research
in partial fulfillment of the
requirements for the degree of
Doctor of Philosophy

University of Manitoba
March 1963

To My Wife

ACKNOWLEDGMENTS

I am indebted to Dr. Funt for introducing me to the problems, and for his help and advice throughout the investigations. I would also like to record my gratitude to Dr. G. E. Dunn and Dr. W. J. Bierman for many useful discussions. The assistance of the science technical staff, in particular, Mr. G. Epp, Mr. L. Wilkens and Mr. E. Erikson and the occasional assistance of Miss M. Pothorin are acknowledged with thanks.

Finally, I must record my appreciation of the grant awarded by the Defense Research Board of Canada which made this investigation possible.

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ABSTRACT

This investigation was originally directed toward determining the extent of benzene incorporation into various polymers. However, due to the recent severe criticism of this mechanism an experiment was performed which revealed the supposed copolymerization did not take place. Using the same benzene in successive polymerizations the amount of benzene incorporated into a vinyl acetate polymer was found to decrease from an initially high value to less than one benzene molecule per polymer molecule. This value is in agreement with the general observation that very small amounts of halobenzenes are incorporated in polymers prepared in aromatic halogen solvents. A mechanism was suggested which attempted to reconcile the large diminution in rate with the observation that only small amounts of aromatic solvents are incorporated into the polymer. This mechanism involves the termination of three kinetic chains for every reaction with a solvent molecule. An equation was derived from the mechanism which revealed the rate as a complex function of monomer, solvent and initiator concentrations.

In the absence of solvent this equation reduced to the standard rate equation, however, at high solvent concentrations the rate became proportional to the first power of the initiator concentration. An experiment at 10% vinyl acetate in benzene gave the initiator exponent as 0.89.

Anthracene (C^{14}) was synthesized in order to facilitate the kinetic study of its copolymerization with various monomers. During this polymerization, conducted in an emulsion system, the rate curves exhibited an unusual type of retardation. The rate of polymerization was observed to decrease very markedly after a significant degree of conversion had been attained. This very strong retardation was attributed to the formation of a retarder in the monomer-polymer particle during polymerization. This retarder, the copolymer, resulted in almost an inhibition of further polymerization. Verification of this postulate was achieved by a bulk polymerization of styrene containing styrene-anthracene copolymer.

The analysis of the styrene-anthracene copolymers also revealed unusual features. The weight percent anthracene in the polymer remained virtually constant throughout the conversion and was approximately equal to the initial weight percent anthracene charged in the system. These unusual analytical results are related to the observed rate features and a comparison of these results to those of other workers is made.

A method has been suggested whereby a polymerization may be initiated by a material produced electrolytically and originating outside the polymerization medium. The polymerization was activated by sodium amalgam which was prepared by electrolyzing a sodium hydroxide solution over a mercury cathode. The amalgam thus produced was allowed to drop through a solution of methyl methacrylate in dimethylformamide. After a short induction period polymerization proceeded rapidly to completion. The molecular weight of the product obtained was found to be a function of the current passed through the electrolysis cell. A smooth curve of degree of polymerization against various currents was plotted which could be used in the form of a calibration curve for obtaining desired molecular weights. Thus the molecular weight of the polymer may be predetermined through a proper choice of current. The usefulness of this technique over that of other polymerizations involving electrolysis is that the polymerization is no longer necessarily restricted to

polar solvents.

The degree of polymerization was observed to increase with decreasing temperature and increasing monomer concentration. A mechanism was postulated which involved termination by a proton abstraction from solvent.

FOREWORD

The original conception of Chapters I and II of this thesis was the study of "semivinyl" polymerization. This term "semivinyl" polymerization, coined by Bamford (37), refers to the incorporation of small amounts of non-vinyl materials as a random copolymer. The application of this concept to the polymerization of vinyl acetate in benzene (C^{14}) solution was first proposed by Stockmayer and Peebles (21). This work was closely followed by that of Marvel and coworkers (26) (27) (28) (Chapter II) who copolymerized anthracene with styrene and butadiene. These brief reports published in 1953, and one paper in 1958, were the extent of information on this field at the inception of this work. However, during the past 18 to 24 months four publications have appeared on benzene copolymerization, two of which have contradicted the existing theory. These two papers together with our subsequent work have resulted in a revision of the original form of this thesis. It has now been considered advantageous to separate the thesis into three distinct chapters.

CHAPTER I

INTRODUCTION

The discovery and recognition of the free radical as an active intermediate in many organic systems allowed the interpretation of reactions which had previously been baffling. In particular, chain reactions such as autooxidations and polymerizations could be explained on the basis of transitory free radical chain carrying species. The very rapid and universal growth of rubber and plastics industries has resulted in extensive research on free radical polymerizations.

In 1920, Staudinger (1) proposed that a polymer might be a series of covalently linked repeating units, i.e. a linear saturated structure. However, many workers preferred to attribute the unusual properties of polymers to some form of association among the smaller molecules. The free radical character of polymerization processes was confirmed during the 1930's through its sensitivity to light and by the inhibitory effects of certain trace impurities.

In 1937, Flory (2) introduced a kinetic treatment for vinyl polymerizations which laid the foundation for much of the following work. The reaction is basically represented in three steps:

(1) Initiation - the production of radical species capable of attacking the double bond of a vinyl monomer.

$$R\cdot + CH_2 = CHR \longrightarrow R - CH_2 - \dot{C}H - R$$

This step is achieved by thermal or photochemical activation of the monomer itself, or by the addition of a substance capable of producing a free radical.

(2) Propagation - the attack of the growing radical on a monomer unit.

$$M_n\cdot + CH_2 = CHR \longrightarrow M_n - CH_2 - \dot{C}H - R$$

This step forms a polymeric radical one unit longer but chemically identical to the attacking one.

(3) Termination - the destruction of polymeric radicals in the system.

$$M_n\cdot + M_m\cdot \longrightarrow P$$

This usually, but not always, occurs by mutual destruction of two radicals.

Equilibrium concentrations of radicals are normally attained very quickly in such systems, and hence steady state kinetics may be applied to the measured rates. In this way the rate constants and activation energies for the individual steps may be evaluated, giving an insight on the reactivity of a polymeric radical toward its corresponding monomer. Introducing a second monomer resulting in copolymerization, indicates the relative tendency for a given polymeric radical to react with monomer M_1 or monomer M_2. Similarly, the presence of a solvent gives a measure of radical-solvent interaction.

The solvent in a polymerization system may have a marked effect. During the polymerization of certain monomers (e.g. acrylic and methacrylic esters) the reaction rate and molecular weight of the polymer increase with the degree of conversion. This phenomena, known as the "gel" or "Trommsdorf effect", is eliminated by the presence of a good solvent for the polymer. The solvent also assists in dissipating the heat of the reaction.

The molecular weight is invariably reduced by the addition of a solvent due to the process of chain transfer. Certain substances, notably mercaptans, are so efficient in this respect that they are frequently employed for regulating the molecular weight of the polymer where a lower degree of polymerization is required.

Mayo (3) first applied Flory's kinetic scheme to the data of Schulz (4) and Suess (5) on the thermal polymerization of styrene in a variety of solvents. His treatment of their results assumed that the growing polymeric radical attacked the solvent thus terminating the chain, and that the solvent radical so formed was capable of adding monomer and starting a new chain.

The individual steps of this reaction may be written:

initiation	$I \longrightarrow 2\ R\cdot$	k_1
	$R\cdot + M \longrightarrow M\cdot$	k_2
propagation	$M_n\cdot + M \longrightarrow M_{n+1}\cdot$	k_3
transfer to solvent	$M_n\cdot + S \longrightarrow P + S\cdot$	k_4
reinitiation	$S\cdot + M \longrightarrow SM\cdot$	k_5
termination	$M_n\cdot + M_m\cdot \longrightarrow P_{m+n}$	k_6

where M = monomer molecule, $M_n\cdot$ = polymeric radical of n monomer units, P = polymer molecule, S = solvent molecule and $S\cdot$ = solvent radical.

Since $(S\cdot)$ is small and the radical is assumed reactive enough to reinitiate monomer quickly, termination involving this species is neglected.

Applying steady state conditions and assuming the reactivity of the radical is independent of the chain length

$$R_i = 2\ k_1(I) = 2\ k_6(M_n\cdot)^2 \qquad \text{----(1)}$$

The overall rate of reaction is given by

$$R_p = k_3(M\circ)(M) = k_3 \left[\frac{k_1(I)}{k_6}\right]^{1/2} (M) \qquad \text{----(2)}$$

The average degree of polymerization given by

$$\frac{\text{overall rate}}{\text{rate of formation of polymer molecules}}$$

may be represented as

$$\overline{\text{D.P.}} = \frac{k_3(M\cdot)(M)}{k_4(M\cdot)(S) + 2\ k_6(M\cdot)^2} \qquad \text{----(3)}$$

then

$$\frac{1}{\text{D.P.}} = \frac{k_4(S)}{k_3(M)} + \frac{2\ k_6}{k_3(M)} \left[\frac{k_1(I)}{k_6}\right]^{1/2} \qquad \text{----(4)}$$

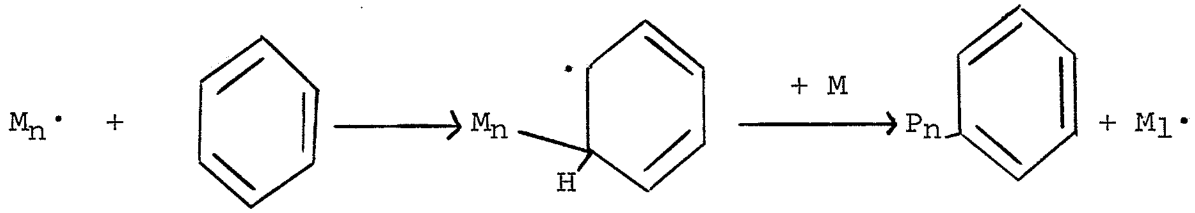
The ratio $\frac{k_4}{k_3}$ is defined as the chain transfer constant (C) of the solvent and can be obtained by plotting $\frac{1}{\text{D.P.}}$ against $\frac{(S)}{(M)}$ for a number of solvent concentrations as long as $\frac{(I)}{(M)}$ is kept constant.

Equation (4) is normally written $\frac{1}{\text{D.P.}} = C\,\frac{S}{M} + \frac{1}{(\text{D.P.})_o}$

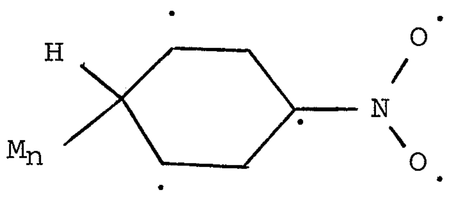
where $(D.P.)_o$ is the average degree of polymerization in the absence of solvent.

Mayo and his coworkers tested this relationship for the thermal polymerization of styrene in a number of solvents (6) and determined the relative susceptibility of these substances to attack by the styryl radical. Using this same relationship Basu, Sen and Palit (7) studied the thermal polymerization of methyl methacrylate in various solvents. In general, the same trend in constants was found for each monomer. Mayo's relationship was modified by Palit, Nandi and Saha (8) to apply to radical initiated polymerizations. The work was then extended to vinyl acetate (9) and methyl methacrylate (10) initiated by $\alpha\alpha$ azobisisobutyronitrile. The variation in C was attributed to the ease with which a hydrogen atom could be abstracted from the solvent.

The transfer constants to benzene for the monomers mentioned above, are among the lowest of any solvent examined. Mayo(3) proposed that the mechanism for this solvent may follow a different course. He suggested that the polymeric radical adds to benzene forming a resonance stabilized adduct which then completes the transfer process by donating a hydrogen atom to the monomer.



This hypothesis was supported by Hey and Waters (11) who demonstrated that radicals derived from azo compounds and peroxides gave substitution products with benzene and its derivatives. Price and Durham (12) proposed a similar scheme to account for the retardation of polymerization by nitrobenzenes. The radical produced by the addition is, in this case, resonance stabilized to a greater extent than the benzene adduct.



The free electron may be placed at any of the five positions specified. Additional nitro-substitution in the meta position, results in even greater radical stability.

The study of chain transfer in halobenzenes has also shown unusual features. Transfer constants to chlorobenzene, for the monomers studied, were found to be only slightly greater than that for benzene. However, Breitenbach (13) polymerized styrene in a large excess of chlorobenzene and found no trace of chlorine in the polymer. This work was extended in 1952 (14), and again, far less halogen was found than would be predicted from chain transfer theory. Breitenbach concluded that a dilution effect was responsible for the observed decrease in molecular weight. Mayo (15) carried out a more detailed investigation of the kinetics and mechanism of the thermal polymerization of styrene in bromobenzene. No significant amounts of bromine were found in the polymer, whereas the chain transfer constant was comparable to those of benzene and chlorobenzene.

The rate of radical initiated polymerization has received an increasing amount of attention although it has not been as universally studied as the degree of polymerization. Experimentally it has been found that the order of a reaction may vary with the monomer concentration and this dependence changes from system to system. However, the overall rate of a polymerization has generally been proportional to the square root of the initiator concentration, thus supporting the normal mutual termination of two chains.

The earliest work on vinyl acetate indicated a second order dependence on monomer concentration. This was a trifle misleading since the highest monomer concentration studied was 4.0 moles per liter. Burnett and Melville (16) made a more detailed study of this monomer in three aliphatic and three aromatic solvents and observed a much more complicated dependence on monomer concentration. The presence of less than 10% chlorobenzene, toluene or benzene gave a strong retardation of the rate. However, the normal relationship between initiator concentrations and rate of polymerization was shown to hold at both 40% and 80% vinyl acetate in toluene. This same effect was observed by Conix (17) for both peroxide and azo initiated polymerizations in benzene, indicating it could not be attributed to any induced decomposition of the former catalyst.

A detailed investigation of polymerizations in benzene was made by Burnett and Loan (18). The rates of polymerization of methyl methacrylate, methyl acrylate and vinyl acetate were measured over the complete concentration range. A first order dependence was found to hold down to 20% monomer for methyl methacrylate. The reaction tended to second order as the concentration was further decreased.

The very high order at high concentrations of vinyl acetate was substantiated. Furthermore, it was observed that the addition of only 2.5% benzene reduced the rate of vinyl acetate polymerization to one-half its bulk rate. The order at low monomer concentrations was observed to be second order as reported by Kamenskaya and Medvedev (19). The normal relationships between initiator concentration and overall rate held down to 25% monomer concentration.

Burnett and Loan (18) developed a kinetic scheme to attempt to account for the variable orders mentioned above. This treatment included the following steps:

$M_n\cdot + S \longrightarrow P + S\cdot$	transfer to solvent
$S\cdot + M \longrightarrow M\cdot$	reinitiation by solvent radicals
$M_n\cdot + M_m\cdot \longrightarrow P$	
$M_n\cdot + S\cdot \longrightarrow P$	inactive products
$S\cdot + S\cdot \longrightarrow X$	

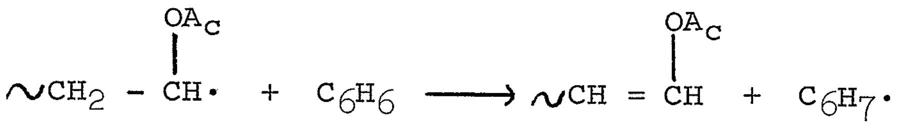
Such an analysis was shown to lead to the following relationship

$$\text{Rate} = k_p(M)^2 R_i^{1/2}\left[k_1(M)^2 + 2\,k_2C(M)(S) + k_3C^2(S)^2\right]^{-1/2}$$

where k_1 = the rate constant for the mutual termination of polymeric radicals; k_2 = the rate constant for termination of unlike radicals; k_3 = the rate constant for the dimerization of solvent radicals.

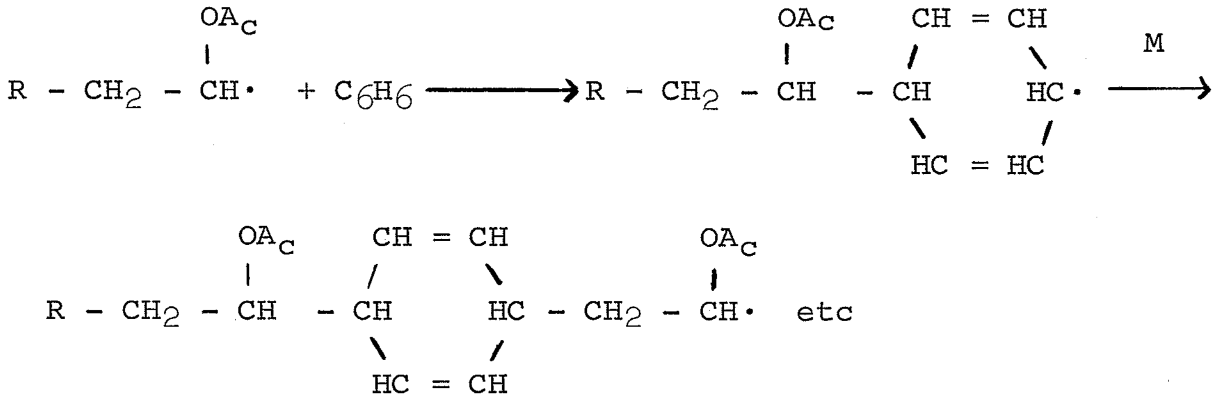
By a choice of suitable rate constants for the steps involved, curves were constructed which reproduced the experimental rate determinations by a variation of C. However, similar curves are also obtained by a variation of the termination constants.

The abstraction of a hydrogen atom from the aromatic nucleus by the growing radical was considered improbable since the resultant phenyl radical is known to be very reactive (20). Furthermore, it is inconceivable that the production of this species would retard polymerization. A transfer in the opposite direction



$$\sim CH_2 - \overset{OAc}{\overset{|}{CH}}\cdot \; + \; C_6H_6 \longrightarrow \sim CH = \overset{OAc}{\overset{|}{CH}} \; + \; C_6H_7\cdot \qquad \text{----(5)}$$

would give a cyclohexadienyl radical of lower reactivity. However, the kinetic scheme demanded a greater frequency of (5) i.e. a higher transfer constant than was indicated by molecular weight studies. Stockmayer and Peebles (21) proposed that the radical added to the benzene nucleus forming a resonance stabilized adduct, which subsequently attacked monomer resulting in copolymerization. They employed C^{14} labelled benzene to determine the solvent incorporation in the polymer chain. Using a benzene to monomer mole ratio of 10.9:1, almost 3% benzene was detected, corresponding to a transfer constant of 2.7×10^{-3}, and about 20 benzene residues per average polymer molecule. The following mechanism was postulated:



However, Stockmayer and Peebles (22) were unable to detect any benzene residues in the polymer by infrared absorption, combustion analysis, or the addition of ICl to a solution of the polymer.

Matsuomoto and Maeda (23) accounted for their kinetic and chain length results by using the copolymerization mechanism, thus indicating that cross termination must predominate, except at high vinyl acetate concentrations, in agreement with Burnett and Loans theory.

The copolymerization of benzene with vinyl acetate was originally published by Stockmayer and Peebles in 1953. A second report appeared in 1960 shortly after the present work was started. Within a period of 12-18 months after this second report three publications appeared concerning polymerization in benzene solution.

Henrici-Olive and Olive (24) used C^{14} labelled benzene in the study of styrene polymerized in benzene solution. Copolymerization of benzene was again obtained with Henrici-Olive and Olive reporting 0.9% incorporation of benzene into the styrene polymer.

Breitenbach (25) severely criticized the copolymerization postulate. A polyvinyl acetate was obtained containing a large quantity of C^{14} labelled benzene. However, no physical evidence could be obtained of any benzene in the polymer. An experiment was then performed in which the same benzene was recycled through several successive polymerizations, the polymer being extracted after each reaction. The percentage benzene in the polymer decreased from an initially high value to less than one molecule per polymer molecule. Breitenbach then attributed the previous copolymerization results to a reactive C^{14} labelled impurity in the benzene.

Henrici-Olive and Olive (26) subsequently supported Breitenbachs conclusion by a study of the variation of reactivity ratios using benzene obtained from different sources.

EXPERIMENTAL

Materials

The scintillation chemicals, p-terphenyl and 1,4 di(2,5 phenyloxazolyl) benzene (POPOP), were obtained from Nuclear Enterprises Ltd. and used without further purification.

Vinyl acetate of 99.9% purity from E. I. Dupont de Nemours and Co. was fractionally distilled and the middle fraction retained. This fraction was polymerized to approximately 10% conversion by the addition of a trace of AZO and the remaining monomer distilled off. The distillate was again fractionated under atmospheric pressure at 72-73° C and the middle fraction collected as the monomer.

Methyl methacrylate from Matheson, Coleman and Bell was washed with four successive portions of 10% NaOH containing NaCl, followed by three successive washings with distilled water. The monomer was dried over anhydrous $CaSO_4$ for 24 hours, then distilled at 32-33° C and 53-54 mm Hg, the middle fraction being collected.

Methyl acrylate from Matheson, Coleman and Bell was washed and dried in the same manner as methyl methacrylate, distilled at 31-32° C and 116 mm Hg, and again the middle fraction collected.

Styrene from the Dow Chemical Co. was washed and dried in the same manner as above, distilled at 61-62° C under a pressure of 53 mm Hg, and the middle fraction collected.

Benzene (C^{14}) purchased from New England Nuclear Corporation was used without further purification. A gas chromatogram obtained from the company indicated the purity was at least 99%.

Benzene (inactive) - Reagent grade benzene was washed successively with concentrated sulfuric acid followed by three washings with distilled water, dried over sodium metal and distilled before use.

αα Azobisisobutyronitrile (AZO) obtained from Eastman Organic Chemicals was purified by recrystallization from toluene.

FIGURE I

Diagram of the vacuum line used for making benzene (C^{14}) transfers.

a,b,c - polymerization tubes

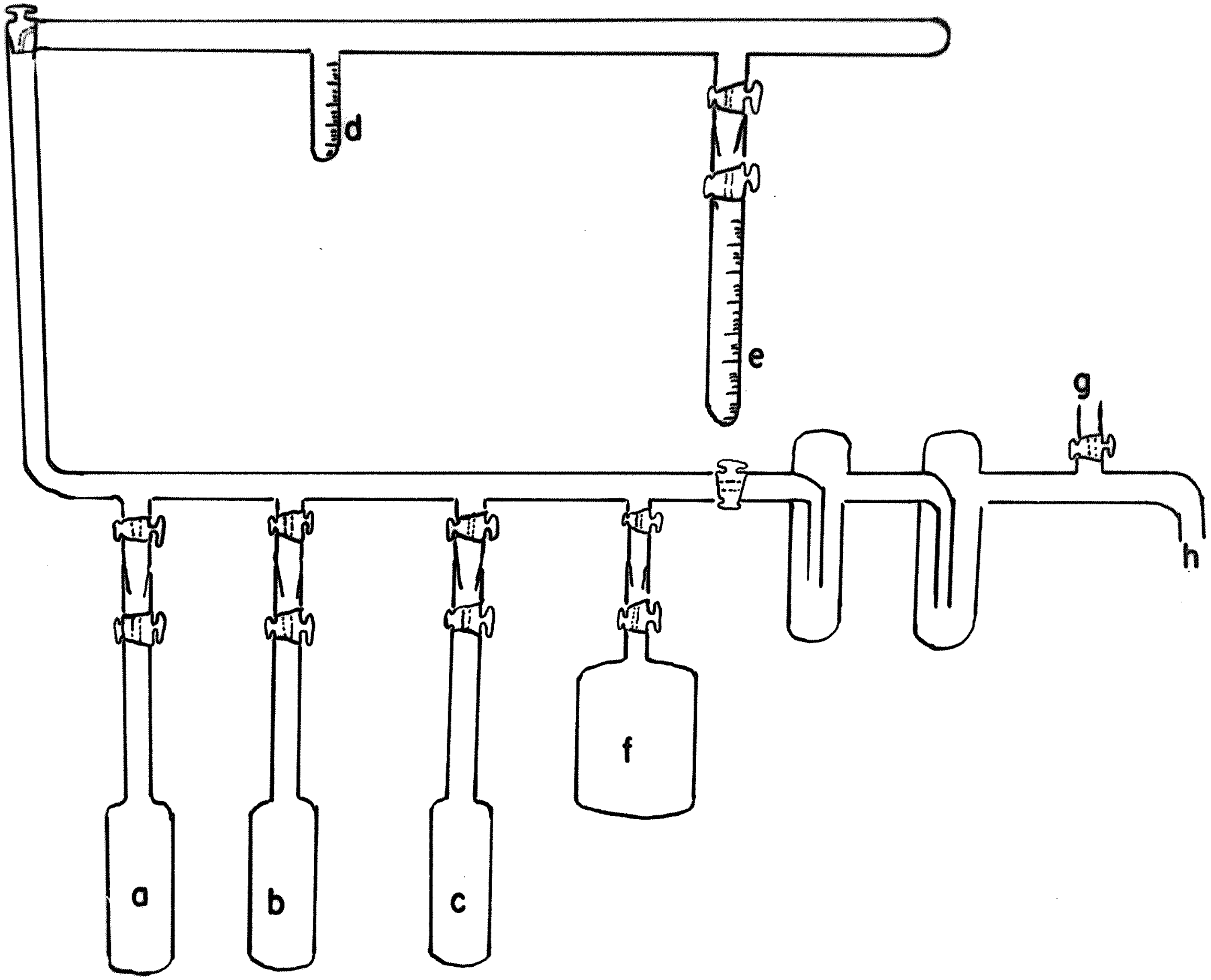
d - calibrated trap

e - calibrated container for benzene (C^{14})

f - storage for residual monomer and benzene

g - to vacuum pump

h - to McLeod gauge


d
e
g
h
a
b
c
f

Procedure

The polymerization tubes a, b and c (Fig. I) were each first charged with monomer, inactive benzene, and initiator to a total volume of approximately 45 ml. These tubes were degassed by four freeze-thawing cycles on the vacuum line. An aliquot of active benzene was then admitted to each tube from the calibrated trap d. Polymerizations were conducted in a constant temperature bath at 60 ± .05° C and were carried to approximately 10% conversion.

Adsorbed benzene was removed by dissolving the polymer in inactive benzene and evaporating the solvent under reduced pressure. This purification procedure was repeated four times, the polymer isolated by precipitation into chilled hexane, and air dried. Table I indicates the efficiency of purification.

Polymerizations involving a constant monomer to benzene ratio, shown in Fig. VI were performed in a similar manner. The appropriate quantities of AZO were admitted to standard polymerization tubes which contained 10% vinyl acetate in benzene by weight, to produce a total volume of

22.6 ml. The tubes were degassed and sealed off on a vacuum line. Polymerizations were again conducted at 60 ± .05° C.

TABLE I

The efficiency of removal of adsorbed benzene from polymers.

Monomer	0 Washing c/sec/g	1st Washing c/sec/g	2nd Washing c/sec/g
Vinyl acetate	359	34.2	6.8
Styrene	99	21.9	11.7
Methyl methacrylate	163	63.0	18.1

The results of the experiment using recycled benzene, shown in Table II were obtained by the following procedure. Vinyl acetate (10 ml) was placed with 90 ml of benzene (C^{14}) and 0.02 g of AZO in a tared 250 ml flask. After gentle refluxing was attained the system was closed and heated in this manner for approximately 30 hours. At the end of this time the benzene and remaining monomer were distilled, in vacuo, into another tared flask cooled with liquid nitrogen. This flask was weighed and the appropriate quantity of monomer and initiator added to return the system to its original concentration. Polymerization was then conducted in the same manner as previously.

Molecular Weight Determinations

The molecular weights of polymers from vinyl acetate, methyl methacrylate and styrene were measured by viscometry at 25 ± .05° C using an Ubbelohde viscometer. The constants employed were those of Wagner (27) for vinyl acetate in acetone, Bishoff (28) for methyl methacrylate in chloroform and Mayo (29) for styrene in benzene.

The molecular weights of methyl acrylate samples were obtained by using a bank of five Zimm-Meyerson Osmometers (30) in a constant temperature bath at 25 ± .05° C with methyl ethyl ketone as solvent.

Analysis

Determinations of radioactivity were performed on a liquid scintillation counter (31)(32). The purified dried polymer was dissolved in a liquid scintillator solution containing 4.0 g p-terphenyl and 0.10 g POPOP per liter of

FIGURE II

Block diagram of liquid scintillation counting assembly

a - power supply

b - potentiometer unit

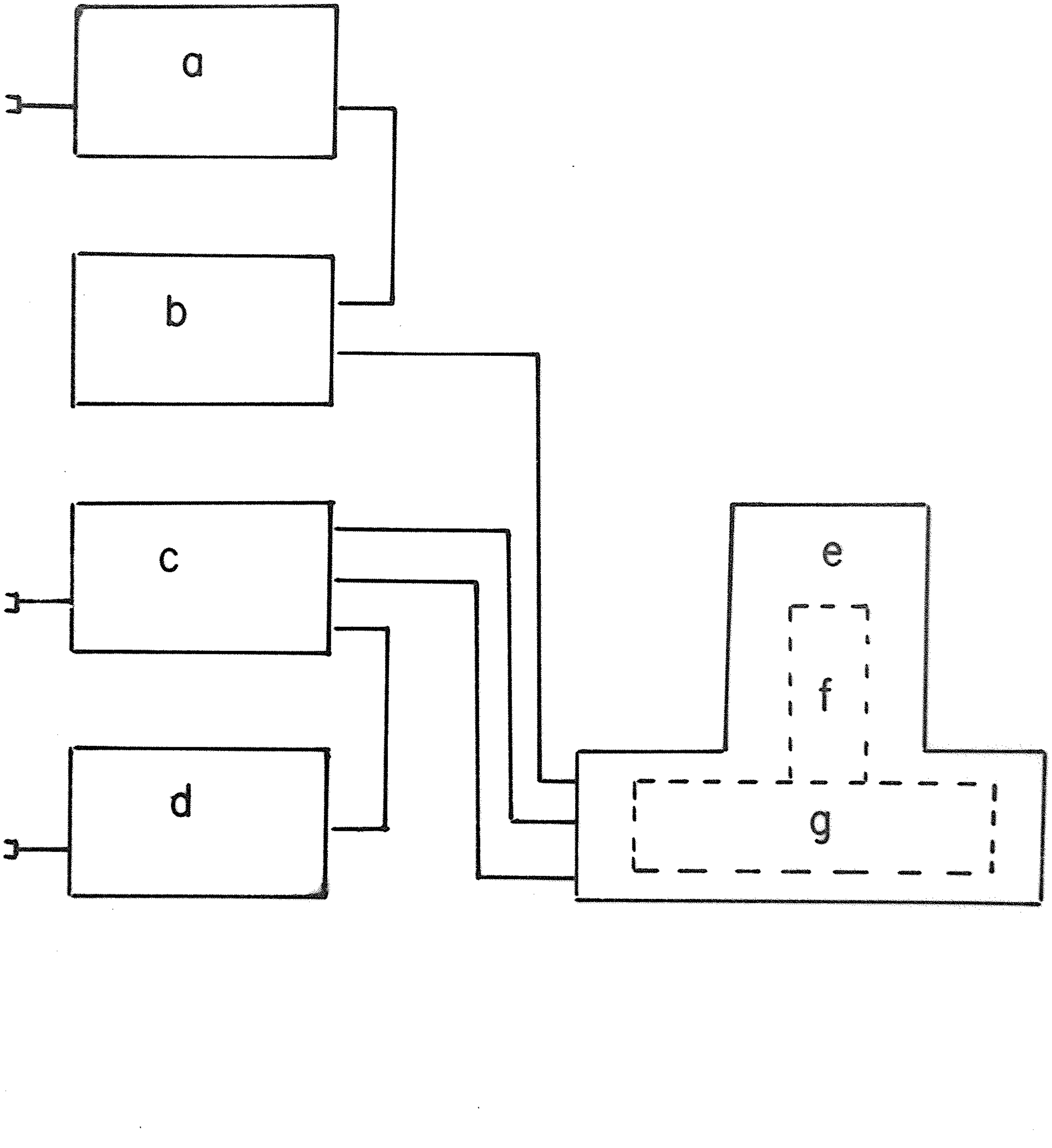
c - linear amplifier with discriminator

d - scaler (model 105)

e - lead castle (2" thickness)

f - photomultiplier tube

g - cathode follower


a
b
c
d
e
f
g

xylene. Argon was bubbled through the solution for fifteen minutes prior to counting to remove oxygen (33). During counting the cell was shielded by a lead castle (Fig. II).

The counting assembly shown in Fig. II, together with the specially selected phototube (EMI 9536 S 5459), was capable of yielding an absolute counting efficiency of 88%.

Benzene (C^{14}), used as an internal standard, revealed that no significant quenching resulted from the presence of low concentrations of polymer in the scintillation solution.

RESULTS AND CALCULATIONS

The data shown in Table III were obtained by polymerization of the monomers specified in C^{14} labelled benzene solution.

The experiment performed by Breitenbach (25) using recycled benzene for successive polymerizations of vinyl acetate was repeated and the data obtained shown in Table II.

TABLE II

Polymerization of Vinyl Acetate in Recycled Benzene

No. of cycles	1	2	3
Activity of polymer (c/min/g)	8050	5100	1710

It is readily apparent that the activity of the polymer (c/min/g) is decreasing with successive cycles. The average molecular weight of the polymer from the third cycle was determined by viscometry. The constants of Wagner (27) gave this molecular weight as 27,150.

The activity of the benzene in the above experiment was determined to be 5.83×10^{7} c/min/mole. Since the activity of the polymer was 1710 c/min/g then 1 g of polymer contained $\frac{1710}{5.83} \times 10^{-7} = 3.02 \times 10^{-5}$ moles benzene. Thus, 27,150 g polymer contain $27{,}150 \times 3.02 \times 10^{-5} = 0.8$ moles of benzene per mole of polymer or, there are only 0.8 molecules of benzene per average polymer molecule. This value agrees with that of Breitenbach who obtained 0.9 molecules of benzene per polymer molecule.

TABLE III

Rates of polymerization and benzene copolymerization data.

Monomer	Wt % monomer in benzene	M.W. of polymer	(I) M/l x 10^3	Base mole monomer per mole benzene	Rate (Rp) M/l/sec x 10^6	Activity of benzene c.p.s./mole	c.p.s./g polymer
Vinyl acetate	5%	17,000	1.31	31	1.34	2.09 x 10^6	787
	10%	58,000	1.16	46	6.64	2.21	558
	20%	68,000	1.06	61	26.5	2.48	471
	30%	100,000	0.98	235	35.4	2.84	141
	40%	118,000	0.86	379	46.4	3.32	102
Styrene	5%	20,000	0.53	85	0.69	2.5 x 10^6	284
Methyl methacrylate	5%	126,000	0.53	147	3.46	2.09 x 10^6	142
	10%	236,000	0.51	215	6.58	2.09	97
Methyl acrylate	5%	158,000	0.87	268	1.06	2.09 x 10^6	91
	15%	422,000	0.78	825	4.64	2.34	33

FIGURE III

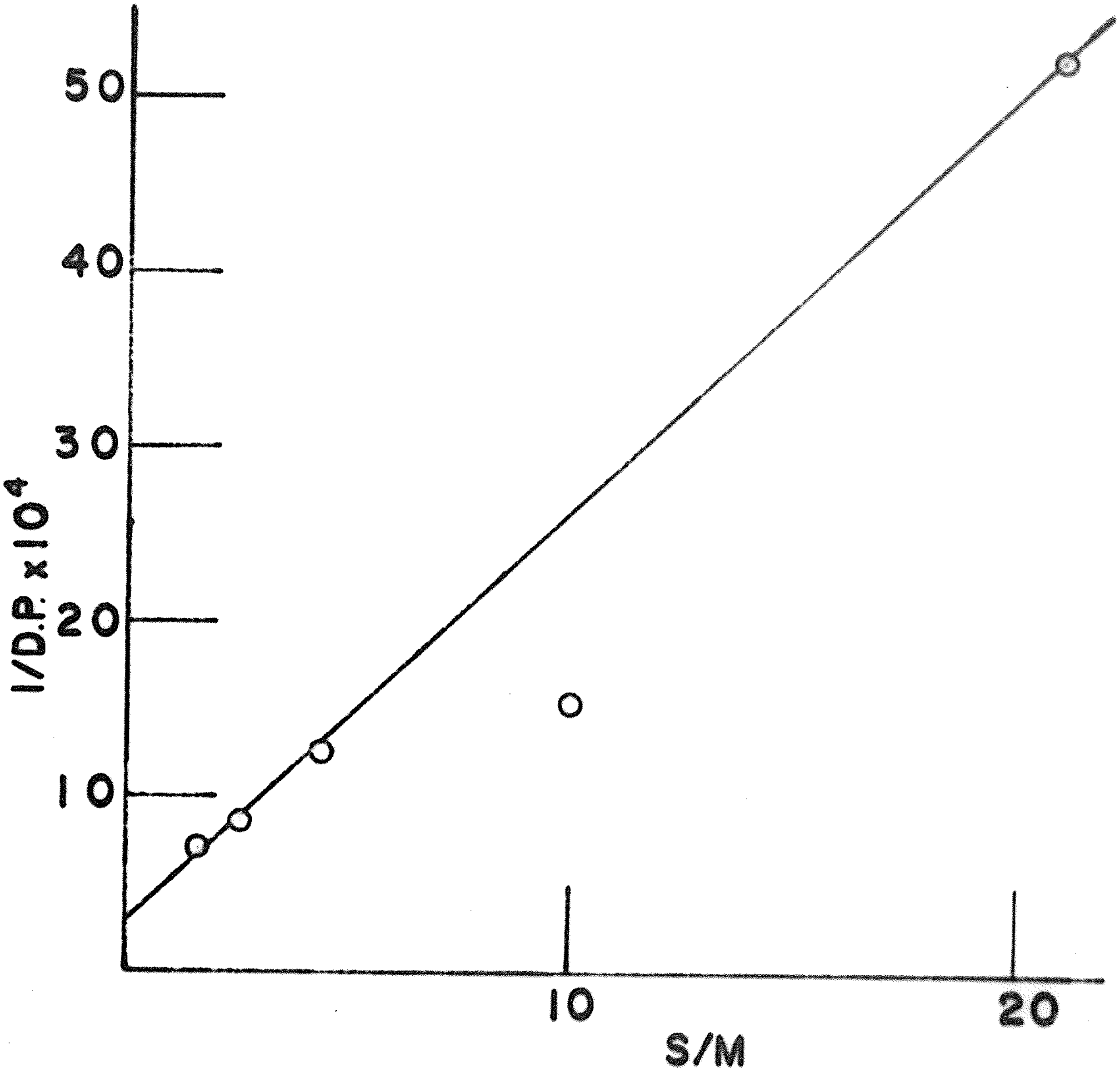
The chain transfer constant of vinyl acetate to benzene (from the slope) = 2.4×10^{-4} at 60° C.

This may be compared to:

Palit and Das (9) - 2.96×10^{-4}

Stockmayer and Peebles (22) - 1.2×10^{-4}

Chadha and Misra (40) - 2.4×10^{-4}



50
40
30
20
10
1/D.P. x 10⁴
10
20
S/M

FIGURE IV

Rates of vinyl acetate polymerization in benzene (from Table III) plotted against $(I)\frac{(M)}{(S)}$.

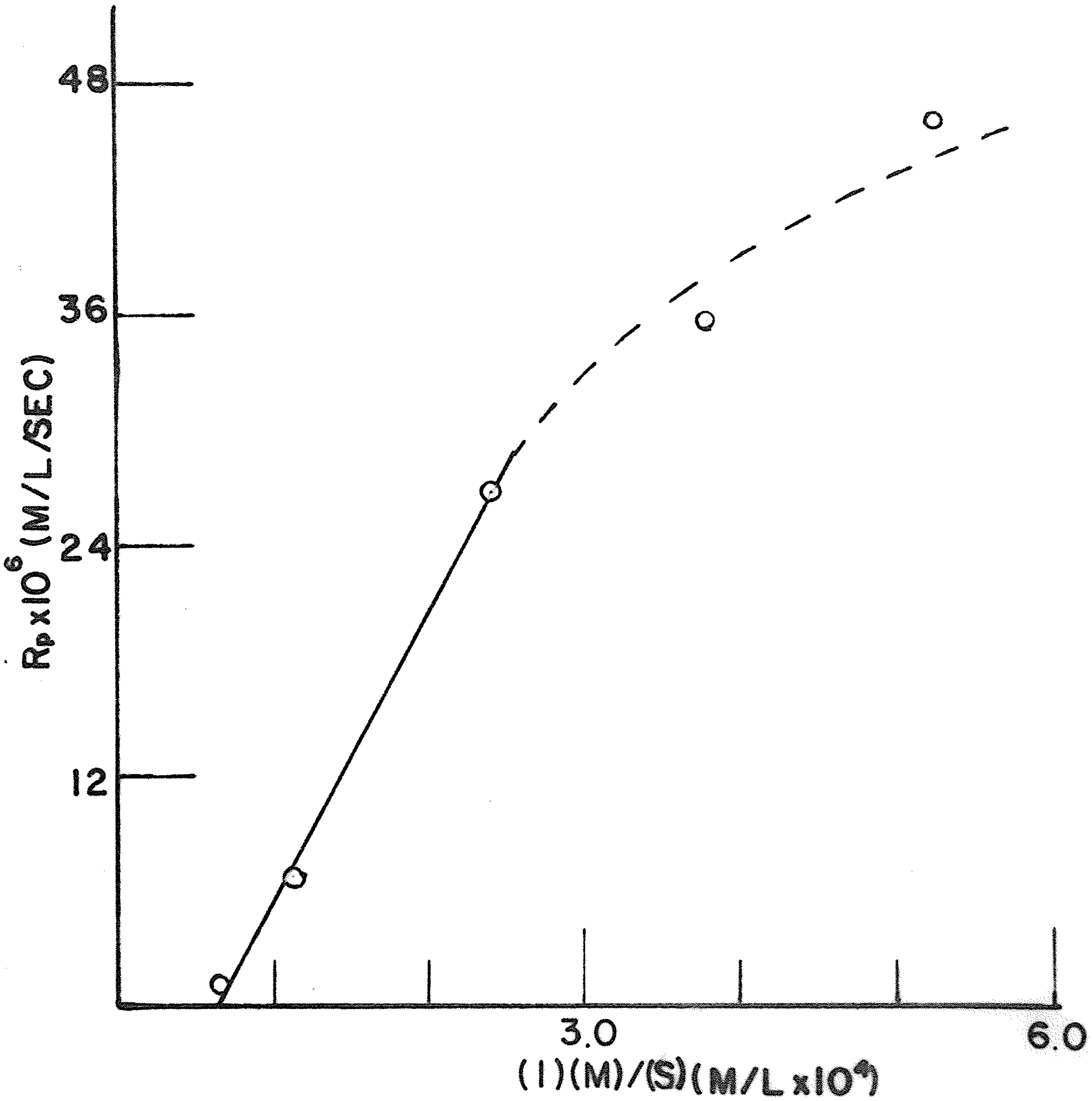

48
36
24
12
$R_p \times 10^6$ (M/L/SEC)
3.0
6.0
(I)(M)/(S)(M/L × 10⁴)

FIGURE V

Rates of vinyl acetate polymerization in benzene (from Stockmayers calculated rates (22)) plotted against $(I)\frac{(M)}{(S)}$.

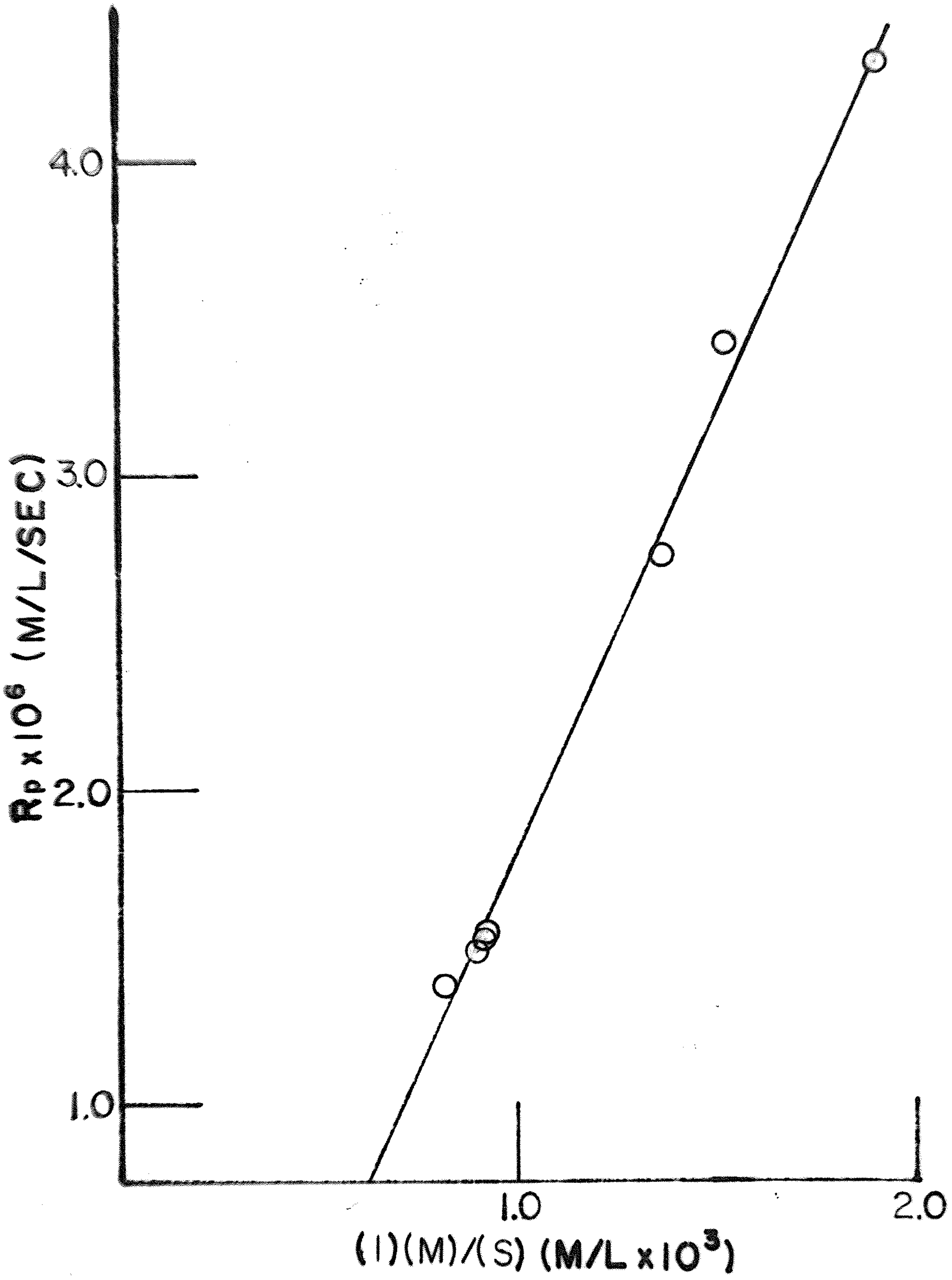
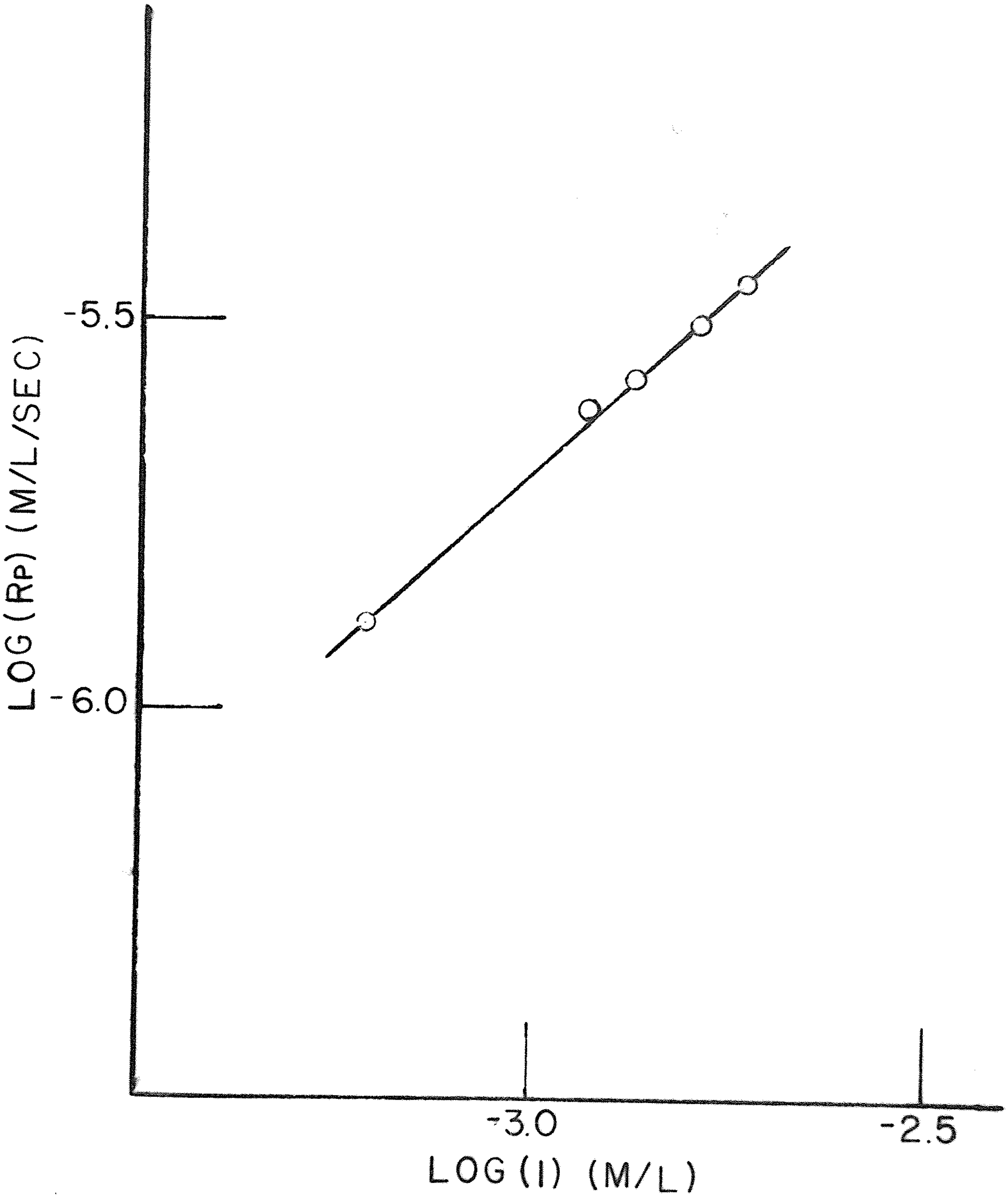

$R_p \times 10^6$ (M/L/SEC)
4.0
3.0
2.0
1.0
1.0
2.0
(I)(M)/(S) (M/L x 10^3)

FIGURE VI

Log (R_p) plotted against log (I) for 10% vinyl acetate in benzene.


LOG (RP) (M/L/SEC)
-5.5
-6.0
-3.0
-2.5
LOG (I) (M/L)

DISCUSSION

Initially this work was based on the supposition that copolymerization of benzene with the various monomers studied, actually occurred. The subsequent investigations of this suggestion by Breitenbach (25), Henrici-Olive and Olive (26) and ourselves (Table II) revealed that the copolymerization hypothesis was actually incorrect. The apparent results were probably due to a reactive radioactive impurity. Consequently, the results tabulated in columns 5, 7 and 8 of Table III are considered invalid.

The fallaciousness of the copolymerization argument thus reopens the question of the polymerization mechanism in aromatic solvents. This mechanism, as mentioned in the introduction, has been particularly troublesome, since very little aromatic solvent has been detected in the polymers (13, 15, 25) and yet the rate with reactive polymeric radicals has been markedly reduced.

The following mechanism attempts to reconcile the unusual features exhibited by polymerizations in aromatic solvents. The aromatic solvents considered here are only those which would result in a phenyl radical if an atom were abstracted from them i.e. benzene, chlorobenzene, bromobenzene etc. Toluene or ethylbenzene, for example, do not fall into this class since abstraction of an H atom from the methyl or ethyl groups results in a resonance stabilized radical.

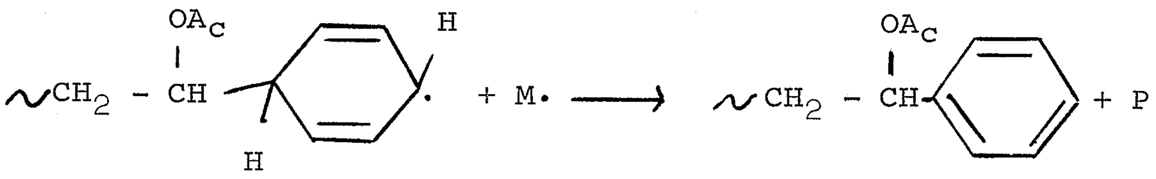
$$\begin{array}{rcll}
I & \xrightarrow{1} & 2\,R\cdot & \text{initiation} \\
R\cdot + M & \xrightarrow{2} & M_1\cdot & \\
M_n\cdot + M & \xrightarrow{3} & \dot{M}_{n+1} & \text{propagation} \\
M_n\cdot + S & \xrightarrow{4} & M_nS\cdot & \text{transfer to solvent} \\
M_nS\cdot + M_m\cdot & \xrightarrow{5} & PS + P & \text{termination} \\
PS + M_m\cdot & \xrightarrow{6} & PS\cdot + P & \text{transfer to polymer} \\
PS\cdot + M_m\cdot & \xrightarrow{7} & P & \text{termination} \\
M_n\cdot + M_m\cdot & \xrightarrow{8} & 2\,P &
\end{array}$$

Vinyl acetate and benzene have been taken as models in the following schematic representations.

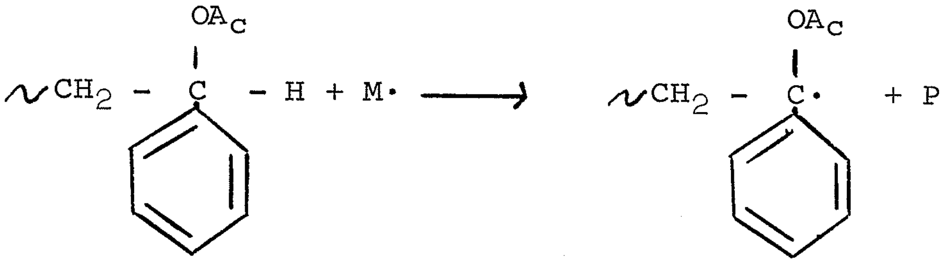
The polymeric radical (M·) is presumed to add to the aromatic nucleus as this has been demonstrated to be the preferred radical reaction with aromatic solvents (34, 35). Furthermore, the abstraction of an atom from the aromatic ring is unlikely as this would leave the extremely reactive phenyl radical (20) and would not result in retardation.

Reinitiation of monomer by the MS· radical is neglected as this would result in copolymerization and the data of Table II show that this does not occur.

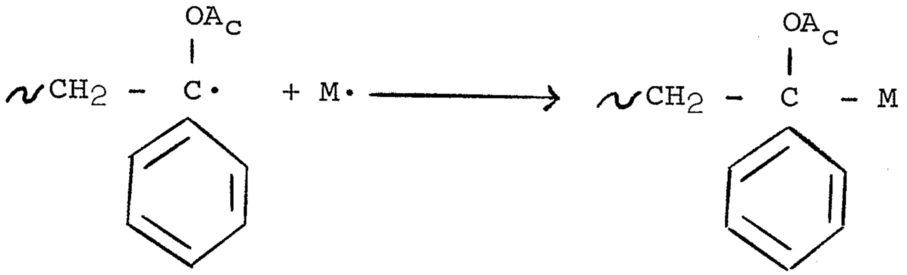
The MS· radical formed in the above step is assumed to react with another radical resulting in termination and rearomatization of the phenyl ring.



This polymer molecule, PS in the above kinetic scheme, has a benzylic type H atom which must be considered reactive toward polymeric radicals. This reaction is represented by the following equation:



The radical formed above, PS· in the kinetic scheme, is considered to undergo cross termination since unlike radicals tend to form stronger bonds (36) and evidence obtained from some copolymerization studies has indicated that cross termination is the preferred reaction (37).



The steps outlined above result in the termination of three kinetic chains for every reaction with an aromatic nucleus. Consequently, since three polymer molecules are formed from every solvent reaction one should expect to detect only about one-third aromatic solvent molecule per polymer molecule. This value has actually been observed experimentally. During the polymerization of low concentrations of styrene in chlorobenzene Breitenbach (14) expected to find 0.27% chlorine if there were one chlorobenzene molecule per polymer molecule. Actually 0.1% chlorine was obtained or about 1/3 chlorobenzene molecule per polymer molecule.

The application of steady state conditions to the above kinetic scheme yields the following equations:

$$-\frac{d(R\circ)}{dt} = o = -2\ k_1(I) + k_2(R\cdot)(M) \qquad \text{----(5)}$$

$$-\frac{d(M\cdot)}{dt} = o = -k_2(R\cdot)(M) + k_4(M\cdot)(S) + k_5(MS\cdot)(M\circ) + k_6(PS)(M\cdot) + k_7(PS\cdot)(M\circ) + k_8(M\cdot)^2 \qquad \text{----(6)}$$

$$-\frac{d(MS\cdot)}{dt} = o = -k_4(M\cdot)(S) + k_5(MS\cdot)(M\cdot) \qquad \text{----(7)}$$

$$-\frac{d(PS)}{dt} = o = -k_5(MS\circ)(M\cdot) + k_6(PS)(M\cdot) \qquad \text{----(8)}$$

$$-\frac{d(PS\cdot)}{dt} = o = -k_6(PS)(M\cdot) + k_7(PS\cdot)(M\cdot) \qquad \text{----(9)}$$

$$-\frac{d(M)}{dt} = k_2(R\cdot)(M) + k_3(M\cdot)(M) \text{ or approximately } k_3(M\cdot)(M) \qquad \text{---(10)}$$

A consideration of equations (7)(8) and (9) indicates that

$$k_4(M\cdot)(S) = k_5(MS\cdot)(M\cdot) = k_6(PS)(M\cdot) = k_7(PS\cdot)(M\cdot)$$

Therefore equation (6) may be written as

$$-\frac{d(M\cdot)}{dt} = o = -k_2(R\cdot)(M) + 4\ k_4(M\cdot)(S) + k_8(M\cdot)^2 \qquad \text{---(11)}$$

The rate of polymerization in the absence of solvent would be given by the standard equation

$$R_a = k_3 \left(\frac{k_1 I}{k_8}\right)^{1/2} Ma \qquad \text{---(12)}$$

However, the presence of an aromatic solvent with its resultant retardation yields a much more complicated expression.

At steady state conditions the rate of initiation is taken equal to the rate of termination or

$$ri = 4\ k_4(M\cdot)(S) + k_8(M\cdot)^2 \qquad \text{---(13)}$$

since $k_4(M\cdot)(S) = k_5(MS\cdot)(M\cdot) = k_6(PS)(M\cdot) = k_7(PS\cdot)(M\cdot)$ from above.

Bevington and Barson (38) have given evidence that the rate of initiation of vinyl acetate is unchanged by the presence of benzene in the system. Consequently equation (13) may be written as:

$$ri = 4\ k_4(M\cdot)(S) + k_8(M\cdot)^2 = k_8(N\cdot)^2 \qquad \text{---(14)}$$

where N· represents the concentration of radicals in the absence of solvent.

The rate of polymerization in the presence of solvent is represented by $R_s = k_3(M\cdot)(M_s)$ and in the absence by $R_a = k_3(N\cdot)(M_a\cdot)$. Substituting these values into equation (14) yields

$$4\ k_4(S)\frac{R_s}{k_3(M_s)} + k_8\left[\frac{R_s}{k_3(M_s)}\right]^2 = k_8\left[\frac{R_a}{k_3(M_a)}\right]^2 \qquad \text{---(15)}$$

rearranging equation (15) gives

$$\left[\frac{R_s(M_a)}{(M_s)R_a}\right]^2 + 4\,\frac{k_3k_4(S)(M_a)}{k_8R_a}\left[\frac{R_s(M_a)}{(M_s)R_a}\right] - 1 = 0 \qquad \text{---(16)}$$

solving equation (16) by the binomial theorem and taking the positive root we have

$$\frac{R_s(M_a)}{(M_s)R_a} = \left[(A^2 + 1)^{1/2} - A\right] \qquad \text{---(17)}$$

which upon rearrangement and substitution for

$$\frac{R_a}{(M_a)} = k_3\left[\frac{k_1(I)}{k_8}\right]^{1/2} \quad \text{yields}$$

$$R_s = k_3\left[\frac{k_1(I)}{k_8}\right]^{1/2}(M_s)\left[(A^2 + 1)^{1/2} - A\right] \qquad \text{---(18)}$$

$$\text{where } A = 2\,\frac{k_3k_4(S)(M_a)}{k_8R_a} = 2\,\frac{k_4(S)}{k_8\left[\frac{k_1(I)}{k_8}\right]^{1/2}} = 2\,\frac{k_4(S)}{\left[k_1k_8(I)\right]^{1/2}} \qquad \text{---(19)}$$

In the absence of solvent (S) in equation (19) = o = A then equation (18) becomes identically $R_s = k_3\left[\frac{k_1(I)}{k_8}\right]^{1/2}(M_s)$ which may be compared to equation (12).

At high concentrations of solvent where A becomes much greater than 1 equation (18) may be rearranged to the form

$$R_s = k_3\left[\frac{k_1(I)}{k_8}\right]^{1/2} (M_s)\ A\ \left[\left(1 + \frac{1}{A^2}\right)^{1/2} - 1\right] \quad \text{and}$$

expanding the root term by the binomial expansion gives

$$R_s\ \alpha (I)^{1/2}\frac{(M_s)}{A}\ \alpha\ (I)^{1.0}\frac{(M_s)}{(S)}$$

Thus the rate is proportional to a power of the initiator concentration which varies from 0.5 to 1.0 at increasing solvent concentrations.

Jenkins (39) derived an equation similar to equation (18) by introducing into the conventional kinetic scheme the assumptions inherent in the previously outlined scheme, i.e. solvent radicals do not reinitiate chains and undergo reaction predominantly by cross termination. By employing the same methods as above Jenkins also indicated the rate should be proportional to a power of the initiator concentration intermediate between 0.5 and 1.0.

This prediction has been verified experimentally. Fig. VI showing a plot of log R_p against log I reveals the exponent of the initiator concentration as 0.89 at 10% vinyl acetate in benzene.

The trend toward first power of the initiator at low monomer concentrations indicates step 8 in the kinetic scheme becomes increasingly less important with lower monomer concentrations. Neglecting this step in the kinetic scheme results in equation (11) becoming

$0 = -k_2(R\cdot)(M) + 4\ k_4(M\cdot)(S)$ and employing equation (5)

$M\cdot = \dfrac{k_1(I)}{2\ k_4(S)}$ which after substituting into equation (10) yields the rate as

$$R_s = \frac{k_1k_3}{2\ k_4}(I)\frac{(M)}{(S)} \qquad \text{---}(20)$$

This equation may only be employed at low monomer concentrations. Fig. IV shows the application of this equation using the rates of Table III. The calculated rates of Stockmayer and Peebles (22), using the above equation, are shown in Fig. V. The failure of these plots to extrapolate to zero probably results from the consistent neglect of the mutual termination step which even at low monomer concentrations, as shown in Fig. VI, cannot be completely ignored. The two points representing 30% and 40% monomer in Fig. IV, show a drift away from linearity which indicates equation (20) actually should not be applied to these points. This is not surprising since a consideration of the assumption involved in deriving equation (20), low monomer concentration with the neglect of step 8 in the kinetic scheme, precludes using it at these concentrations. Equation (18) should be used, however lack of sufficient information regarding the transfer step (constant k_4) makes this very difficult.

A consideration of disproportionation, steps 5 and 6 and combination step 7 indicates a wide molecular weight distribution should be expected at low monomer concentrations. Mayo (15) has noted a wide molecular weight distribution in the polymerization of styrene in bromobenzene at low monomer concentrations.

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CHAPTER II

INTRODUCTION

One of the major techniques of polymerization is by means of an emulsion system. This technique employs the monomer emulsified in a medium, usually water, by means of emulsifying agents such as soaps, alkyl sulfonates, or detergents. The monomer is thus present almost completely in the form of emulsified droplets. At one time it was supposed that most of the polymerization took place in these emulsified droplets, however, it is now known that the emulsified monomer droplet plays only a minor role in the mechanism.

There are several advantages in using an emulsion polymerization. The heat generated during the reaction is dissipated very readily due to the low viscosity of the latex during polymerization. Sticky, rubbery polymers may be easily polymerized by this method since the very active surface agents minimize the tendency of particles to coalesce. Probably the most distinct advantage in using this technique is the rapid rate of conversion combined with a high degree of polymerization. Emulsion systems in this respect are unique among all types of free radical polymerizations, although they are inferior to ionic. This characteristic of emulsion polymerizations is generally attributed to the presence of a large number of small isolated particles which act as loci for the polymerization.

The initiators employed in emulsion systems are generally water soluble materials (e.g. persulfates, peroxides, perborates etc.). Potassium persulfate, perhaps the most frequently used initiator, has received much fundamental study regarding its action as an initiator in the emulsion polymerization of styrene (1 - 6). The nature of the initiating step in the persulfate-styrene system has been established quite conclusively. Rates of thermal decomposition of persulfate in aqueous buffers, determined by Kolthoff and Miller (7), were correlated with rates of free radical formation in the polymerization systems, determined by Smith (6). The agreement between the data was very good indicating that initiation in this system occurs by the following steps:

$$S_2O_8^{=} \longrightarrow 2\ SO_4\cdot^{-}$$

$$SO_4\dot{}^{-} + C_6H_5CH = CH_2 \longrightarrow C_6H_5\dot{C}H - CH_2 - O - SO_3^{-}$$

Various redox systems have also been successfully employed as initiators. Historically, the persulfate-bisulfite system was the first redox system in which the production of free radicals was recognized (8). It has been used successfully as an initiator in various systems (9, 10, 11).

The physical picture we now have of an emulsion polymerization is due principally to the work of Harkins (12, 13, 14), Haward (15), Smith and Ewart (16) and their collaborators.

Beyond a certain critical concentration, soap in water is present in the form of micelles or oriented aggregates of soap. Physically, the micelles are considered to be composed of two layers of soap molecules "back to back" --the hydrocarbon portions close together and the carboxylate portions at the outside in the aqueous phase. Adding liquid monomer to this micellar soap solution results in some soap being transferred from the micelles to the surface of the emulsion droplet, where it acts as a stabilizing agent. Some monomer is transferred to the interior of the micelles (i.e. it is solubilized). This phenomenon of solution of monomer in the micelle is accounted for by the affinity between the hydrocarbon monomer and the hydrocarbon part of the micelle.

Initiation occurs by a reaction between the sulfate radical ion, produced in the aqueous layer, and the monomer solubilized in the micelles. The initiator-monomer adduct grows rapidly by adding monomer to form a polymer chain radical. This chain radical formed in one micelle grows by the addition of monomer which is supplied by diffusion from other micelle and from emulsion droplets. The polymer chain radical rapidly becomes too large to be contained in the detergent micelle and terminates by colliding and combining with another growing radical, forming a polymer particle. Polymer particles so formed are stabilized by the adsorption of emulsifier. The detergent now acts as a protective colloid. The polymer particles are also capable of solubilizing appreciable quantities of monomer. A second sulfate radical ion may collide with a polymer particle swollen with monomer, and initiate further polymerization in this locus of polymer formation.

The proportion of monomer in the polymer particle is probably often controlled by a dynamic balance between the rate of polymerization on one hand and the rate of diffusion of monomer into the particle on the other. However, if the polymerization were very slow the system would be closer to equilibrium where the activity of the monomer in the polymer particle must equal that of the free monomer. Herzfeld, Roginsky, Corrin and Harkins (17) determined the monomer to polymer ratio $(\frac{M}{P})$ during the polymerization of styrene. Due to experimental difficulties however, the $\frac{M}{P}$ ratios were closer to equilibrium values than to the dynamic ones. Meehan (18) has shown that in the emulsion polymerization of butadiene or copolymerization of butadiene with styrene the monomer layer is in equilibrium with the particles.

The importance of the synthetic rubber industries has stimulated much research on the kinetics of emulsion polymerizations. Smith and Ewart (16) discussed the kinetics in terms of free radical reactions in isolated loci--the radicals originating in a medium outside the locus of reaction. Using this model they arrived at the following expression for the rate

$$-\frac{dM}{dt} = kM\left(\frac{N}{2}\right) \qquad \text{----(1)}$$

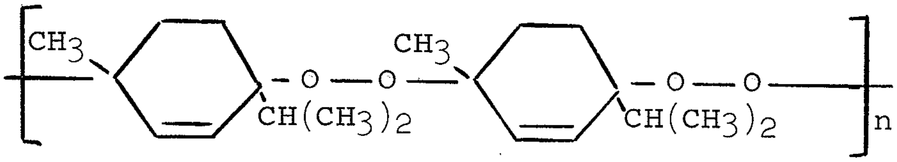
where N = the total number of particles in the system. The mean lifetime of the growing radicals is given by

$$T = \frac{N}{2\ P} \qquad \text{----(2)}$$

where P is the rate of entrance of radicals into the particles. The rate of polymerization and the radical lifetimes are seen to depend only on the number of particles present. This prediction was tested by Smith (5) who found that the overall rate appeared to be directly proportional to the number of particles and essentially independent of their size.

Equation (1) also predicts the rate to be independent of the initiator concentration. Kolthoff and Dale (1) and Price and Adams (3) investigated the polymerization of styrene as a function of initial concentration of potassium persulfate. Both found that the rate appeared to be proportional to the 0.5 power of the initiator concentration and the concentration of persulfate decreased only slightly during polymerization. The effect of changing persulfate concentration after the start of polymerization was tested by Smith (5). The rate was the same with a four fold increase in persulfate concentration as that at the initial concentration. However, the rate did increase slightly with a sixteen fold increase in initiator concentration, but this was attributed to new particle formation.

It has been observed that the introduction of materials normally classed as retarders, frequently results in copolymerization to a minor degree i.e. several retarder molecules may be randomly incorporated into the polymer chain. Breitenbach and coworkers (19) (20) have shown that copolymerization of chloranil with styrene definitely takes place. Bovey and Kolthoff (21) observed a similar behavior in an emulsion system. Oxygen has been shown to copolymerize with α terpinene (22) yielding a material with the structure:



It has also been reported (23) that polystyrene containing some oxygen has been isolated. Bovey and Kolthoff (24) have found that the rate of consumption of oxygen in a well agitated emulsion polymerization of styrene was independent of the oxygen pressure. Magat and Boneme (25) studied the carcinogenic activity of a polymer produced by copolymerizing 2-methyl anthracene with styrene.

In 1953, Marvel and Anderson (26) obtained a copolymer of anthracene with butadiene containing 5% anthracene by weight. Marvel and Anderson subsequently extended this work (27) to other polynuclear aromatic hydrocarbons finding that small amounts of pyrene and trans-stilbene could be copolymerized with butadiene. Marvel and Wilson (28) were able to copolymerize anthracene with styrene and p-chlorostyrene reporting a 10% incorporation of anthracene into the polymer. However, in none of the above systems were the kinetics of the reactions investigated. Thus, no fundamental information regarding the rate at which these "non vinyl" hydrocarbons are incorporated into the polymer has been obtained. Furthermore, Marvel and coworkers admittedly had difficulty analyzing the anthracene content of their polymers. The ultraviolet absorption spectrum of the polymer was compared to that of 9,10-dimethyl-9,10-dihydroanthracene as a standard, assuming no significant shift in the absorption maxima. It has been reported (29) that the length of the alkyl group substituted on an aromatic nucleus has only a small effect in shifting the absorption maxima. However, it is unknown what effect the proximity of the phenyl group from styrene would have on the absorption maxima. Consequently, the use of 9,10-dimethyl-9,10-dihydroanthracene as a standard may result in considerable error in the case of styrene.

The use of C^{14} labelled anthracene would circumvent this difficulty making analysis simple, sensitive, and direct.

EXPERIMENTAL

Materials

Scintillation chemicals, 1,4 di(2,5 phenyloxazolyl) benzene (POPOP), 2,5 diphenyloxazole (PPO), obtained from Nuclear Enterprises, naphthalene from Matheson, Coleman and Bell and Baker analyzed xylene were used without further purification.

Styrene donated by the Dow Chemical Co. was washed with four successive portions of NaOH, followed by three washings with distilled water, and dried by storing over anhydrous $CaSO_4$ for 24 hours. The middle fraction of a distillation conducted at 59° C and 44 mm Hg was collected.

Methyl methacrylate from Matheson, Coleman and Bell was washed successively with 10% NaOH followed by three washings with distilled water. The monomer was dried over anhydrous $CaSO_4$ for 24 hours, distilled at 32-33° C under 53-54 mm Hg and the middle fraction collected.

Methyl acrylate from Matheson, Coleman and Bell was washed and dried as above fractionally distilled under reduced pressure, and the middle fraction stored.

Vinyl toluene from the Dow Chemical Co. was similarly washed, dried, fractionally distilled under reduced pressure and the middle fraction stored.

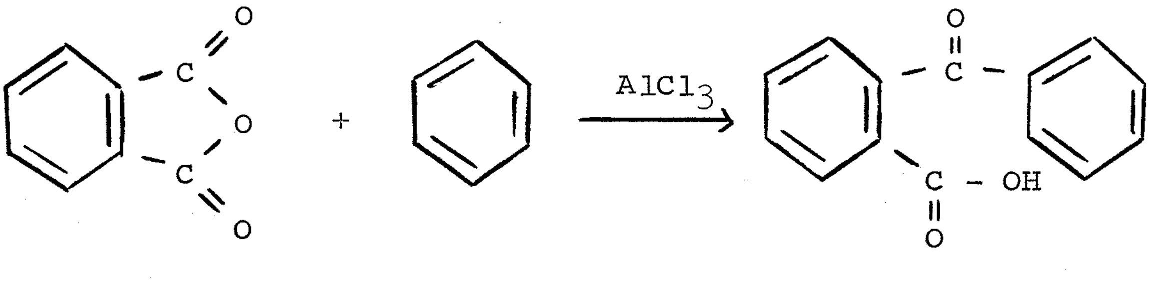
Reagent grade benzene was shaken with successive portions of concentrated sulfuric acid, followed by three washings with distilled water, dried over sodium metal and distilled prior to use.

Potassium laurate, synthesized by neutralizing lauric acid with an equivalent amount of potassium hydroxide, was purified by recrystallization from alcohol.

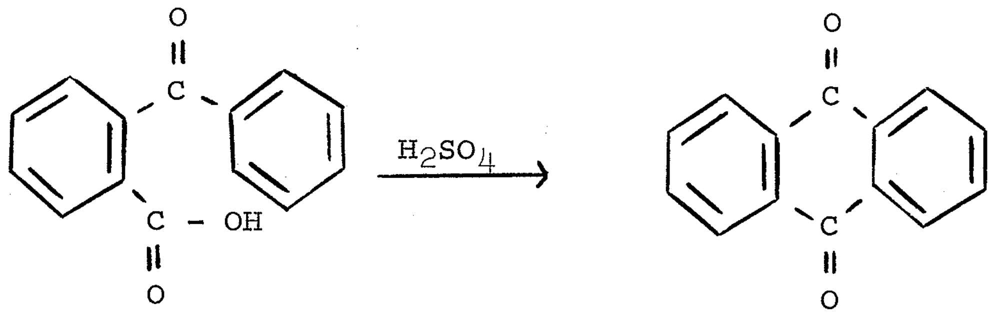
Fisher certified reagent grade $K_2S_2O_8$ and analytical grade $NaHSO_3$ and $CuSO_4$ were used without further purification.

Anthracene (C^{14}) was synthesized in the following manner -

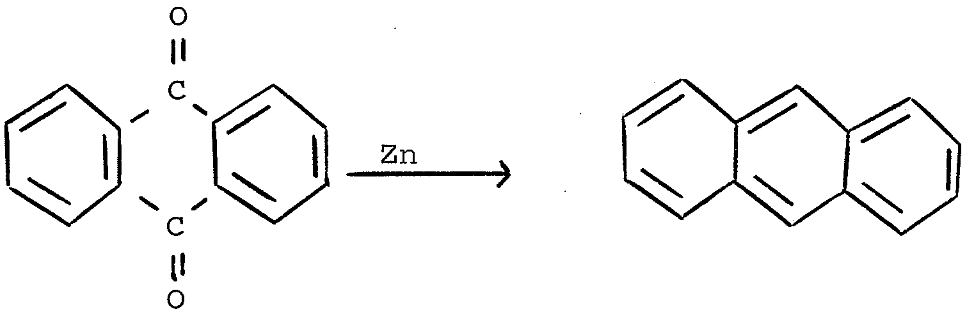
O-benzoyl benzoic acid was prepared according to the directions of Rubidge and Qua (30) using benzene (C^{14})



Fuming H_2SO_4 reacting with this acid formed anthraquinone (31)



Anthracene was formed by reducing the anthraquinone with Zn.



The anthracene obtained via the above procedure was purified by sublimation (m.p. 216° c).

Blue violet anthracene from British Drug Houses was also purified by sublimation (m.p. 214.5° c).

<u>Procedure</u>

Polymerizations were conducted in four ounce screw cap bottles fitted with self sealing gaskets and pierced caps to

FIGURE I

Diagram of emulsion polymerization bath

a - geared motor

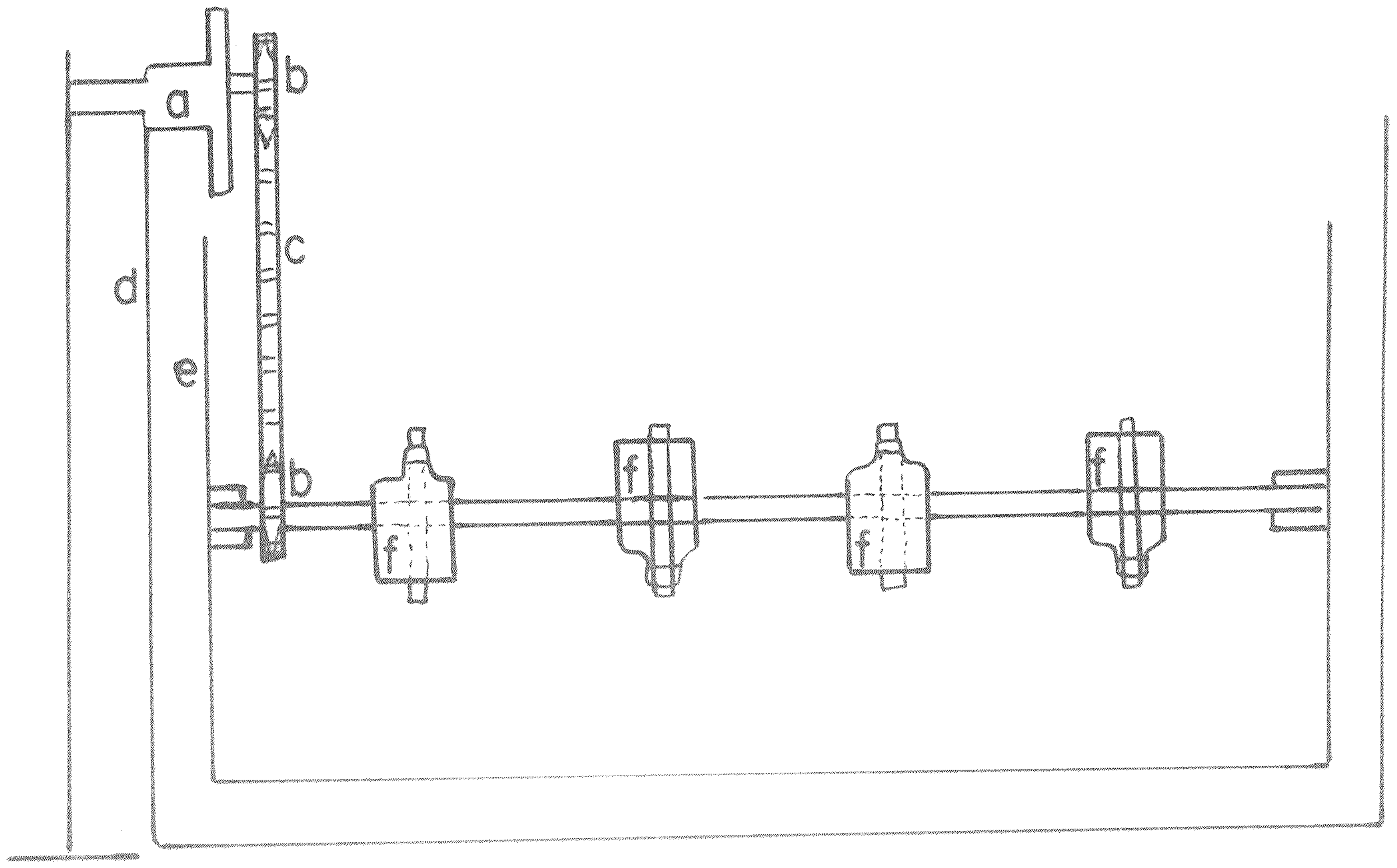
b - sprockets

c - chain

d - insulated box

e - oil bath

f - polymerization bottles


b
a
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f

permit sampling. The bottles were charged with 40 ml of 5% potassium laurate solution, 10 ml benzene, 10 ml monomer, anthracene, and 2 ml of a solution containing 3.67% $NaHSO_3$ and 0.2% $CuSO_4$. Argon was carefully bubbled through the samples for fifteen minutes prior to sealing and placing in the bath (Fig. I) at 50 ± 0.1° C. The bottles were tumbled end over end at 28 r.p.m. for fifteen minutes, to attain thermal equilibrium, before the addition of 2 ml of 2.5% solution of potassium persulfate.

Polymerizations of methyl acrylate were conducted in an identical manner using sodium lauryl sulfate as emulsifier with the system buffered to acid pH.

Samples were periodically withdrawn by means of a 19 gauge 2 inch needle fitted to a 2 cc syringe. The samples were coagulated by the addition of acidified 2-propanol, isolated by filtration and dried in an oven at 50° C.

Bulk polymerizations, shown in Fig. VII, were conducted in a dilatometer over mercury. Prior to filling the dilatometer the styrene monomer was charged with 6.7 g/l polystyrene and 0.122 g/l AZO. In one case, the added polystyrene was obtained from the emulsion polymerization of styrene-anthracene containing 3% anthracene. Polystyrene used in this case was purified by five successive precipitations from dimethylformamide into methanol (see Table I). In the other case, the added polystyrene was obtained by polymerization in the absence of anthracene.

Molecular weights of the polymers were not obtained since they were difficultly soluble in solvents and appeared to have some degree of branching.

Analysis

The radioactive determinations were conducted on a double channel liquid scintillation tri-carb counter (Fig. II). The channels of the instrument were adjusted to yield an $\frac{A}{B}$ ratio which from calibration yielded the efficiency of each count (32).

Purification was effected by two successive precipitations from dimethylformamide solution into stirred methanol, followed by drying in an oven at 50° C.

The purified, dried polymer was dissolved in a liquid scintillator solution containing 5.0 g PPO, 0.1 g POPOP and 70.0 g naphthalene in 1000 ml xylene.

FIGURE II

Tri-carb scintillation counter.

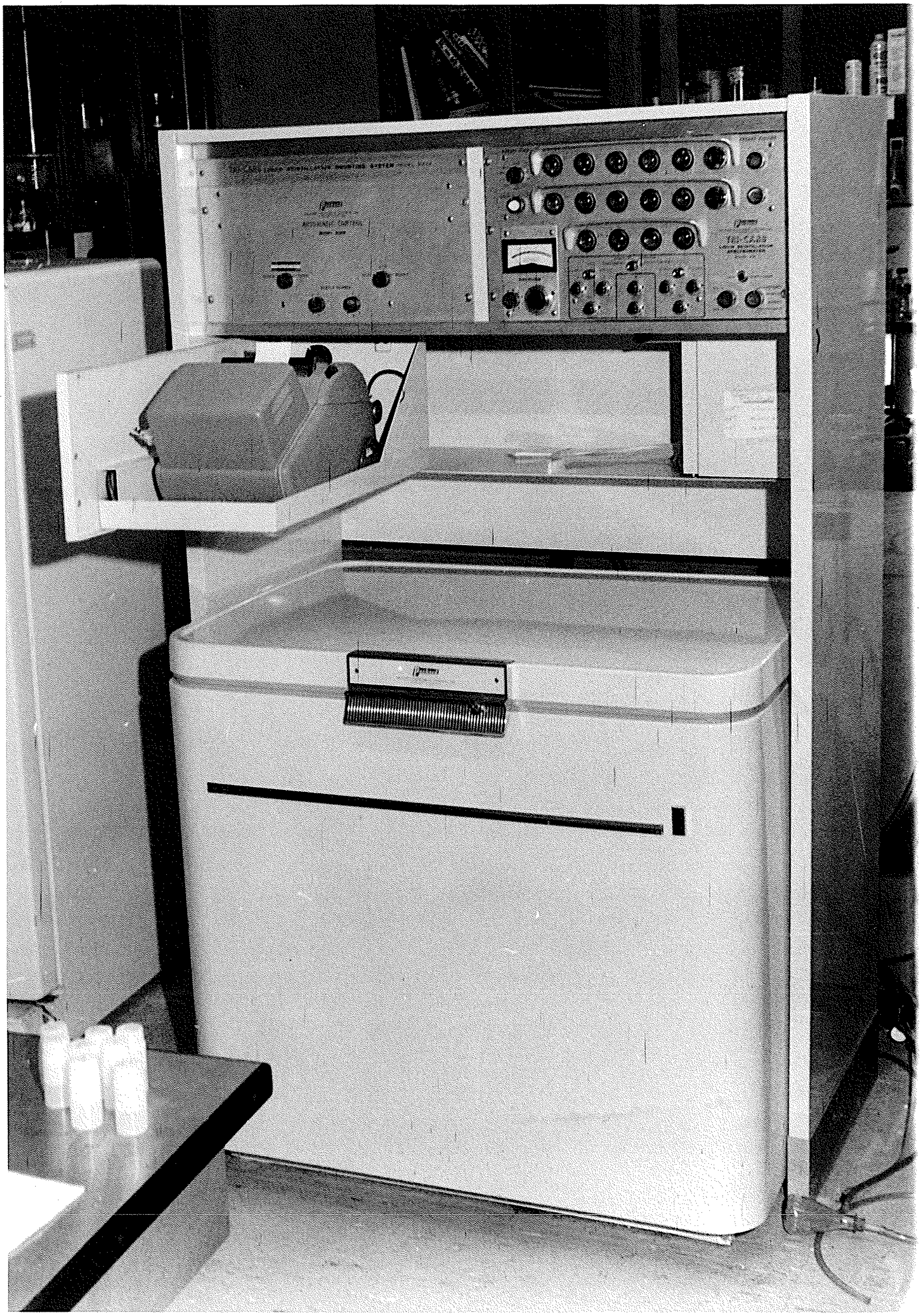

TRI-CARB

TABLE I

Efficiency of Removal of Anthracene from Polymer

No. of Precipitations	Activity of Polymer c/min/g	% Anthracene Remaining
0	1320	1.25%
1	121	0.15%
2	78	0.075%

RESULTS

The rate curves at various concentrations of anthracene in the monomers studied are shown in Fig. III to Fig. VI. All the curves show an unusual type of retardation. Initially, the rate curves appear to exhibit the expected normal type of retardation. At higher anthracene concentrations the initial slopes of the curves are lower, as would be expected. However, the extent of retardation appears to increase with conversion, not decrease as one normally expects. At higher anthracene concentrations this increase in retardation is very marked resulting in almost a cessation of polymerization.

The analytical data of Table II also show unusual features. The percentage anthracene in the polymer seems to remain virtually constant throughout the conversion and is approximately the same as that initially charged in the system. This observation cannot be attributed to improper purification since polymers at low degrees of conversion would then exhibit a higher anthracene content than those at high degrees of conversion. This effect is not observed.

FIGURE III

Rates of styrene polymerization in the presence of -

◒ - 0.1 g anthracene

◐ - 0.2 g anthracene

● - 0.3 g anthracene

◑ - 0.4 g anthracene

○ - 0.5 g anthracene

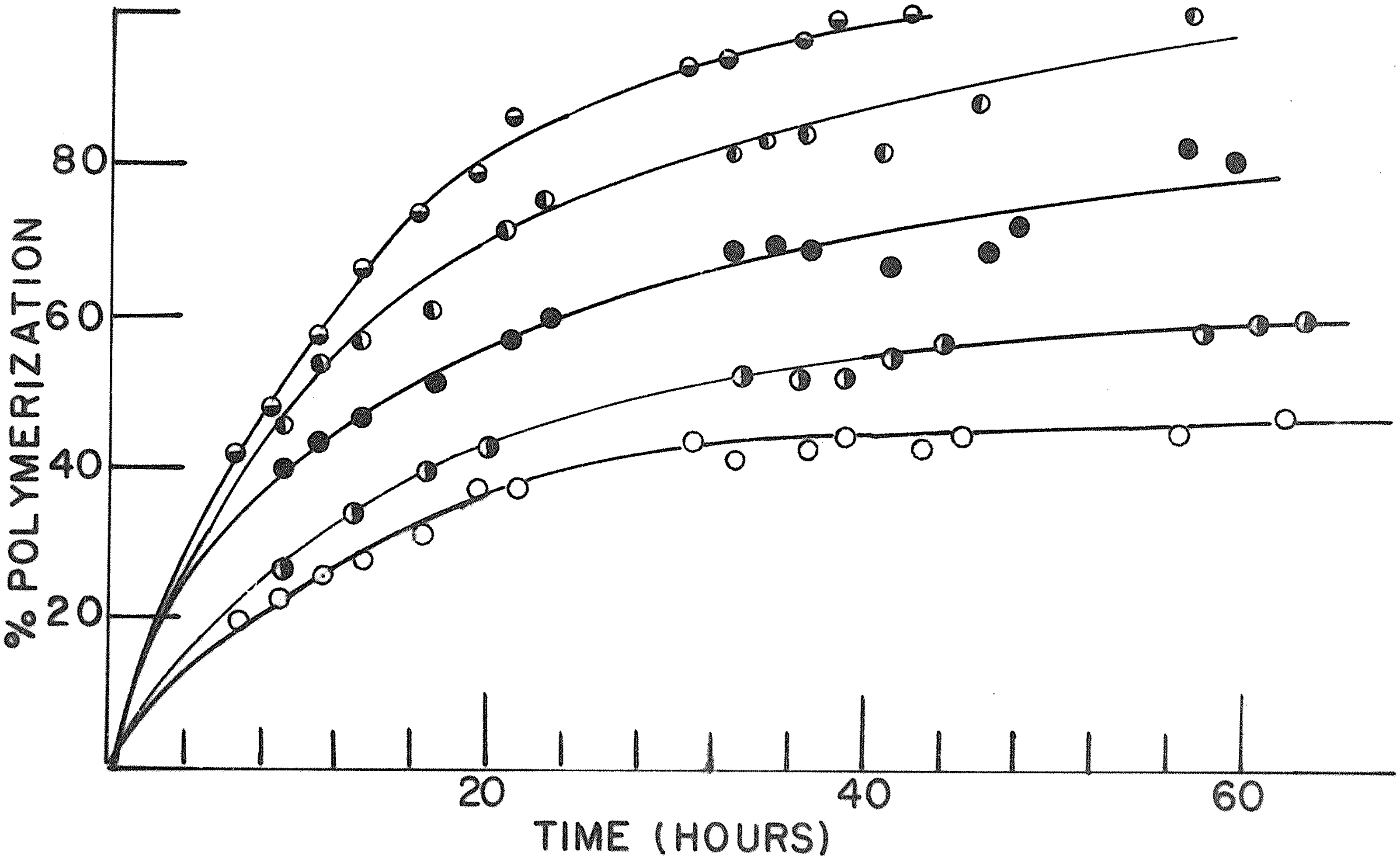

% POLYMERIZATION
20
40
60
80
20
40
60
TIME (HOURS)

FIGURE IV

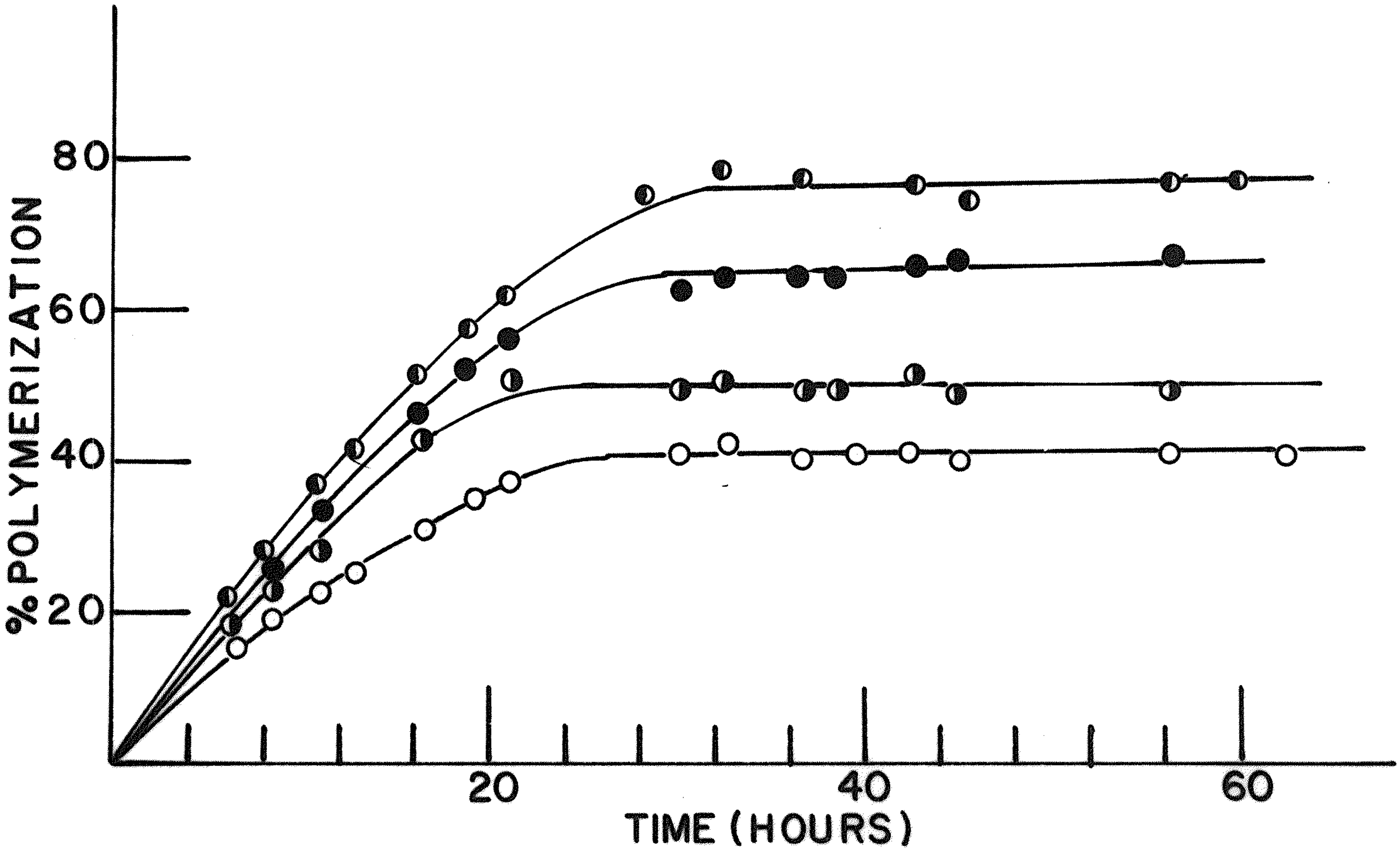
Rates of vinyl toluene polymerization in the presence of -

◐ - 0.025 g anthracene

● - 0.05 g anthracene

◑ - 0.10 g anthracene

○ - 0.20 g anthracene



% POLYMERIZATION
80
60
40
20
20
40
60
TIME (HOURS)

FIGURE V

Rates of methyl methacrylate polymerization in the presence of -

◒ - no anthracene

◐ - 0.25 g anthracene

● - 0.50 g anthracene

◑ - 0.75 g anthracene

○ - 1.0 g anthracene

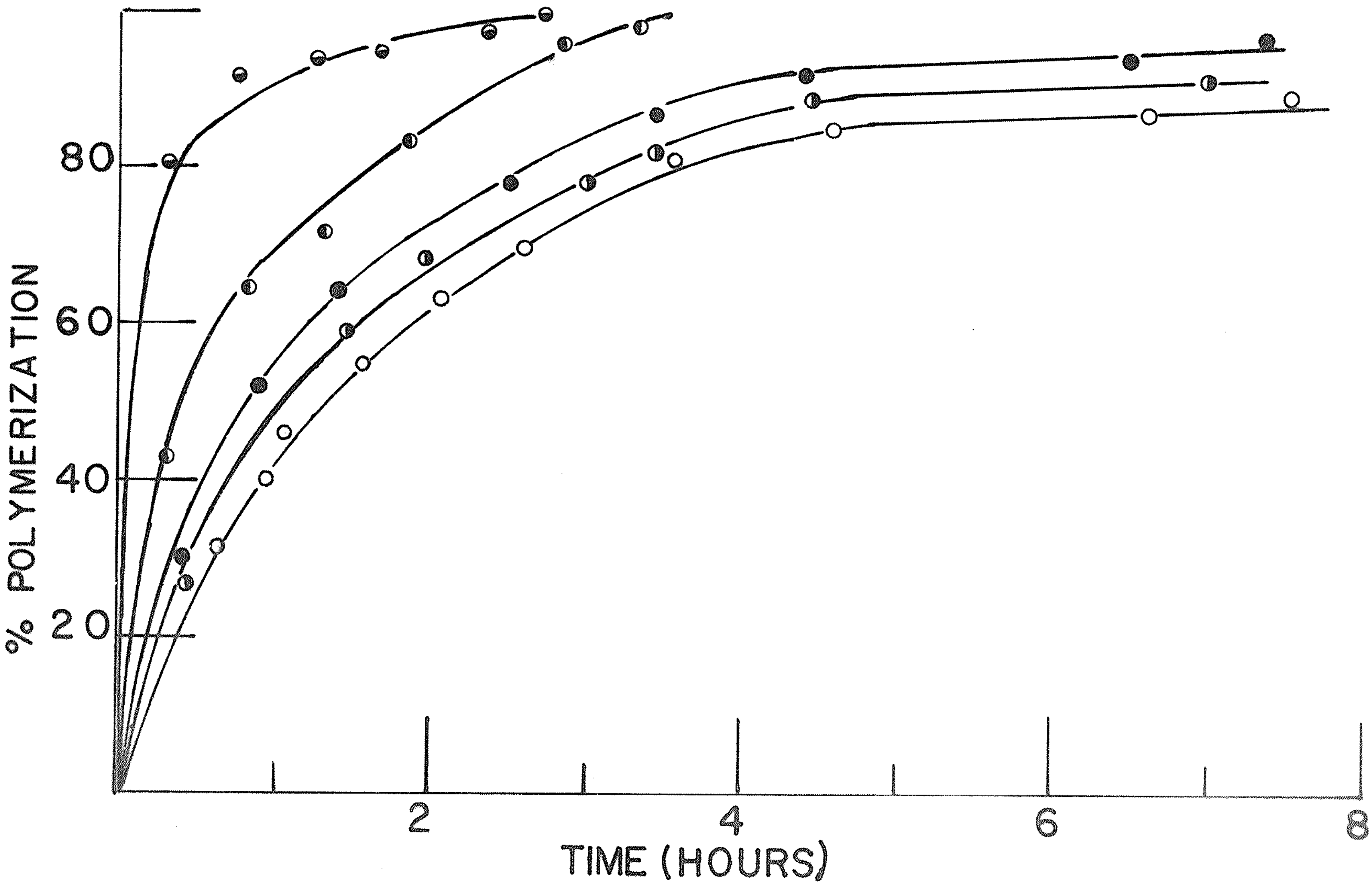

% POLYMERIZATION
20
40
60
80
2
4
6
8
TIME (HOURS)

FIGURE VI

Rates of methyl acrylate polymerization in the presence of -

○ - 0.2 g anthracene

● - 0.4 g anthracene

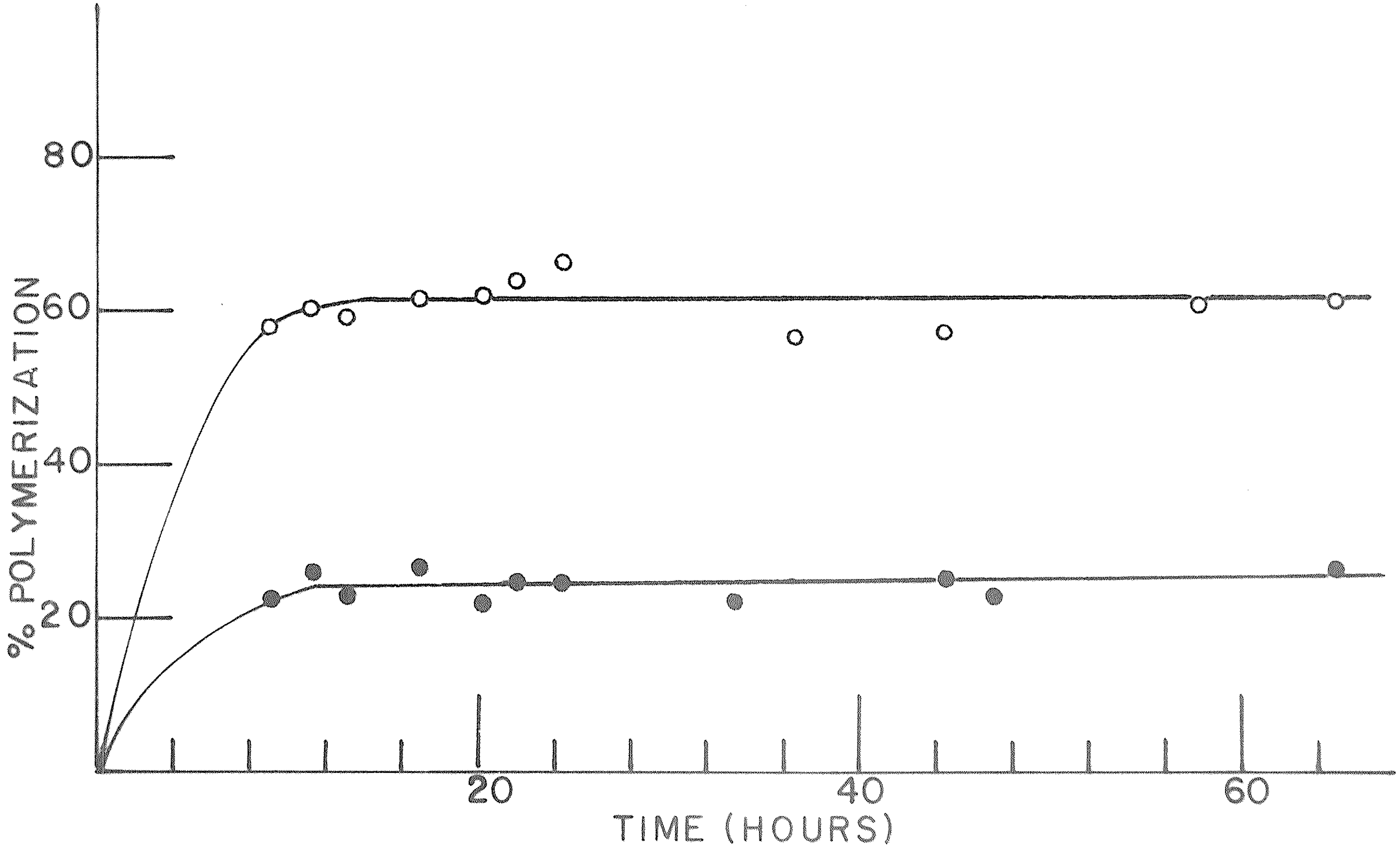
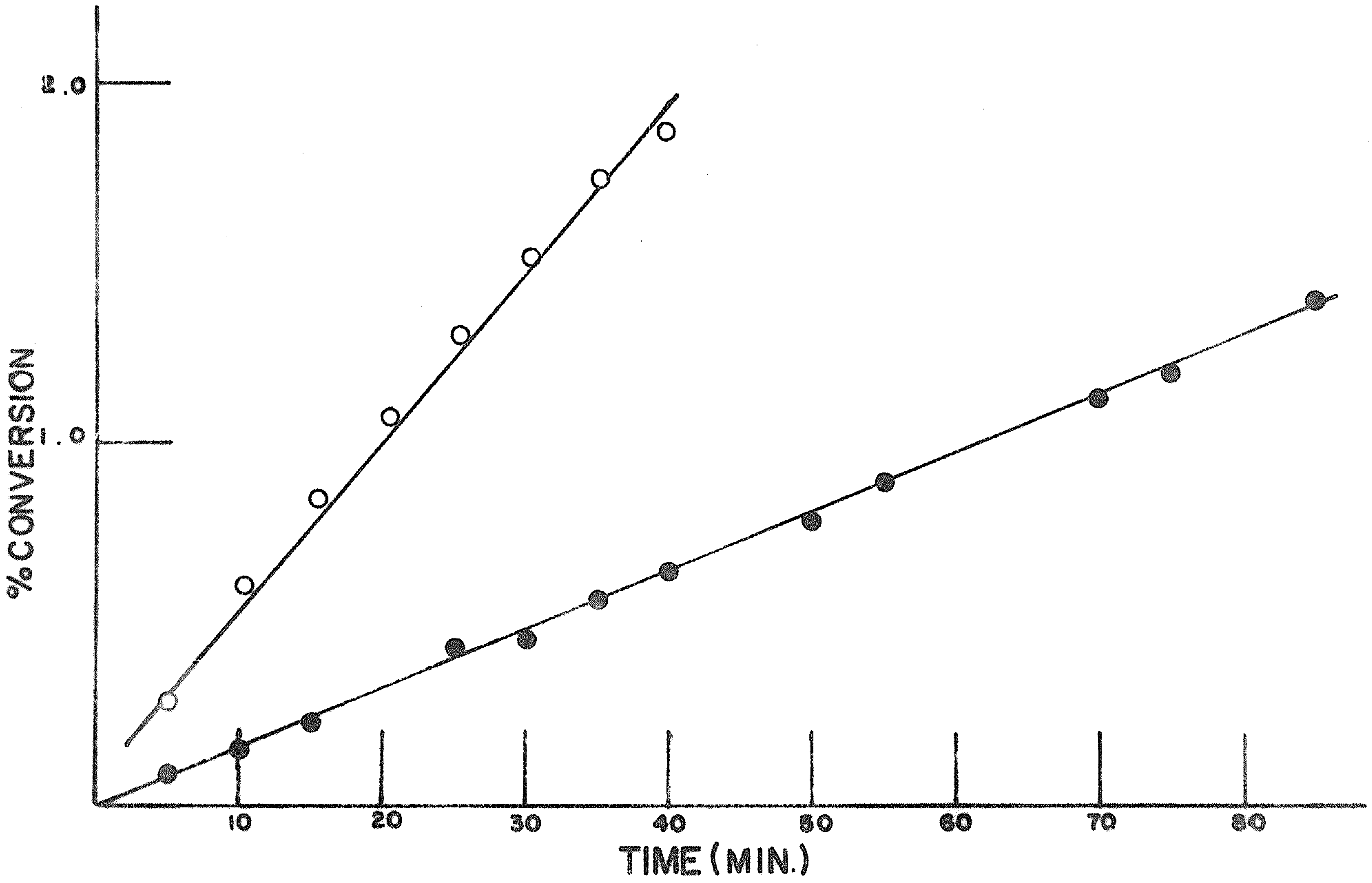

80
60
40
20
% POLYMERIZATION
20
40
60
TIME (HOURS)

FIGURE VII

Rates of bulk polymerization of styrene containing

○ - 6.7 g/l polystyrene

● - 6.7 g/l styrene-anthracene copolymer



2.0
1.0
% CONVERSION
10
20
30
40
50
60
70
80
TIME (MIN.)

TABLE II
Analysis of styrene-anthracene copolymers

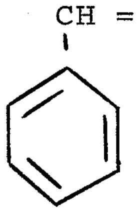
1% Anthracene		2% Anthracene		3% Anthracene		4% Anthracene		5% Anthracene	
% Polymerization	% Anth.	% Polym.	% Anth.	% Polym.	% Anth.	% Polym.	% Anth.	% Polym.	% Anth.
42%	0.98	47%	1.8	43%	2.7	34%	3.9	23%	4.8
48	1.2	50	2.1	49	3.0	35	4.2	25	4.8
57	1.1	55	1.8	55	3.2	39	3.8	28	4.3
74	1.1	58	1.9	58	2.8	43	3.6	31	4.5
79	1.1	67	1.8	59	3.1	46	3.8	37	4.4
86	1.0	69	1.9	60	2.9	49	3.5	39	4.4
93	1.1	70	1.9	61	2.7	51	3.4	39.5	4.4
94	1.1	73	1.8	66	2.8	52	4.4	40	4.5
96	0.91	76	1.9	70	2.7	55	3.6	42	4.7
99	0.91	81	1.8	73	2.7	57	3.8	43	4.7
		83	2.2	77	2.7			45	4.1
		88	1.9					45.2	4.4
		100	1.9					47	4.1

DISCUSSION

The suggestion that anthracene could undergo copolymerization with styrene and butadiene was first put forth by Marvel and coworkers (26)(27)(28). Using 9,10-dimethyl-9,10-dihydroanthracene as a model, U.V. spectrophotometric evidence was obtained indicating the incorporation of a 9,10 disubstituted anthracene into the polymer. Marvel and Anderson (26), using 5 parts anthracene and 95 parts butadiene, obtained 5% anthracene in a polymer taken to 25% conversion. However, Marvel and Wilson (28) using approximately 5 parts anthracene to 95 parts styrene reported a 10% incorporation of anthracene in a polymer taken to 100% conversion. In this latter work either one or other or both of these statements is manifestly wrong. If 10% anthracene were obtained in the polymer, then all of the anthracene must have been incorporated into a polymer taken to only about 50% conversion. In a system taken to 100% conversion it is impossible to incorporate more than about 5% anthracene since this was the initial charge.

The rate data shown in Fig. III to Fig. VI reveal an unusual type of retardation which sets in after a significant degree of polymerization has been obtained. Higher initial concentrations of anthracene result in a lower degree of conversion at which this very strong retardation occurs. This retardation seems to indicate the formation of a retarder in the polymer particle after the onset of polymerization.

Using styrene as a model in the following schematic representations, there are initially only two important species in the system:



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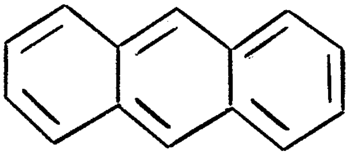
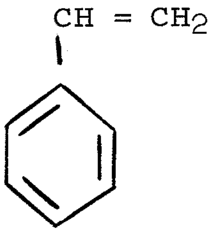
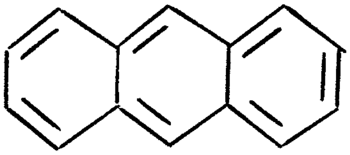


(1)

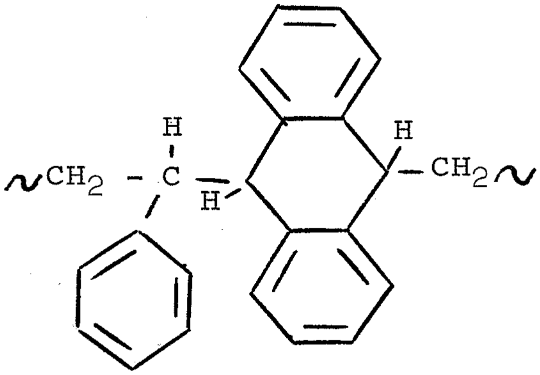
(2)

However, after a significant degree of polymerization there are three species in the polymer particle and the previous two still in the oil phase. The three species are:





and



(1)

(2)

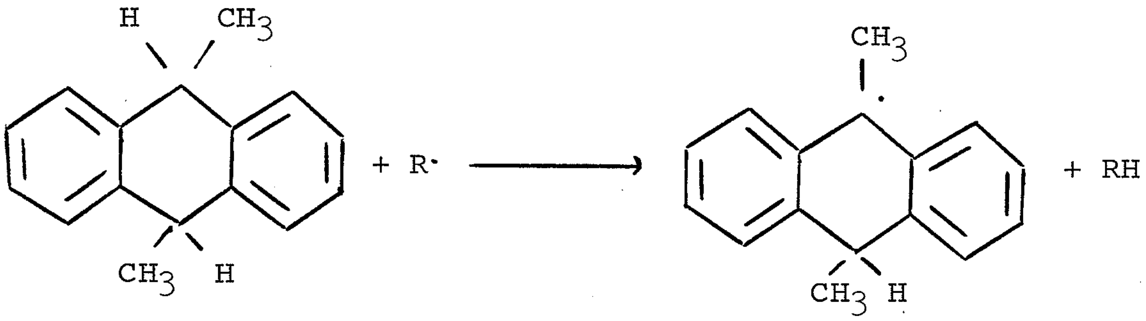
(3)

Since the rate is very low, polymerization must be taking place at essentially equilibrium values, i.e. the rate of polymerization is sufficiently low so that diffusion can maintain the ratio of anthracene to styrene in the polymer particles the same as in the separate organic layer. Consequently, the anthracene concentration of the polymer particles must be approximately the same as the in the oil phase and should therefore remain approximately constant during polymerization. This effect has been noted during polymerizations conducted in emulsions (33)

> "The inference from these different experiments, therefore, is that the monomer ratio in the polymer particles is about the same as in the separate layer of monomers".

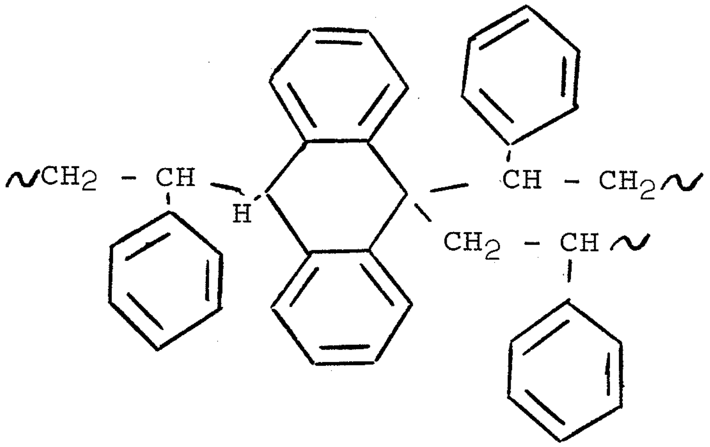
Consequently, the retardation due to anthracene in the particle should remain constant, i.e. if retardation were due only to anthracene the strong increase of retardation after the onset of polymerization would not be observed. This strong decrease in the rate must be due to the styrene anthracene copolymer formed in the reaction. It is readily seen that the concentration of retarding species in the polymer particle must be continually increasing. The anthracene content of the particles remains essentially constant, but the reaction of styrene with anthracene producing (3) results in an increasing concentration of (3) and consequently greater retardation.

Kooyman and coworkers (34) have shown that 9,10-dimethyl-9,10-dihydroanthracene is a strong free radical trap. The mechanism for the reaction, postulated by Kooyman, was H atom abstraction from the 9,10 positions.

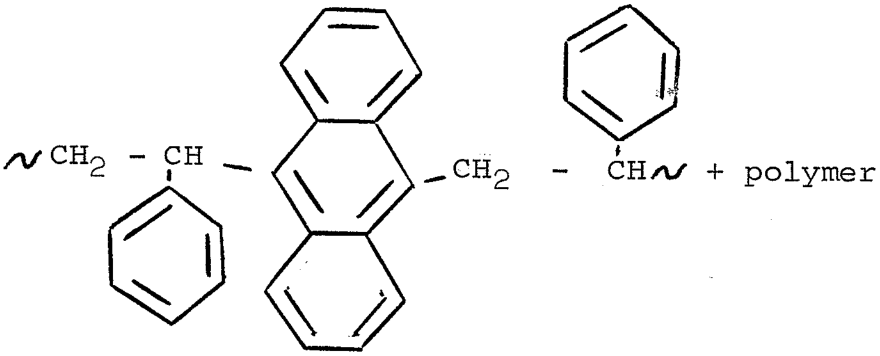


If a reaction as postulated above occurred with 9,10-dialkyl-9,10-dihydroanthracene in the polymer particle, the resultant radical could react in one of two ways.

(a) A second radical could react with the substituted anthracene radical forming a branched polymer with a structure such as -



(b) The second radical may remove the remaining tertiary H atom on the aromatic ring leaving two linear polymers -



If reaction (b) occurred predominantly it is also possible that the 9,10-dialkylanthracene formed here may trap a polymeric radical at a later stage and yield a branched polymer, as noted in the experimental section. In any case it appears the 9,10-dialkyl-9,10-dihydroanthracene formed during polymerization is the species responsible for the marked increase in retardation. This has been verified by polymerizing bulk styrene containing a small quantity of styrene anthracene copolymer. Fig. VII indicates there is a significant retardation due to this polymer.

The rate curves of methyl methacrylate, vinyl toluene and methyl acrylate appear to follow essentially the same pattern as that of styrene. However, methyl methacrylate seems to be much less sensitive to retardation by anthracene than do the others. This probably results from steric hinderance at the reaction site since the radical bearing carbon atom in methyl methacrylate is disubstituted.

It may also be noted that Marvel and Wilson (28) failed to obtain polymer with methyl acrylate and anthracene. However, the use of Rubber Reserve soap (Na palmitate, stearate and oleate) would negate any observations of this system since the alkaline medium produced by this soap would rapidly hydrolyze the ester (35)(36).

The analysis of styrene-anthracene copolymers at various degrees of conversion, shown in Table II, reveal the anthracene content of the polymers as constant and approximately equal to that initially charged in the system. This constancy of anthracene content would be expected since, as mentioned previously, the ratio of monomers in the polymer particles remains essentially the same as that in the oil phase. A consideration of the system containing 1% anthracene shows this constancy to remain virtually throughout the conversion.

The data of Table II are in complete agreement with the results of Marvel and Anderson (26) who reported 5% incorporation of anthracene into polybutadiene. From a consideration of the rate curves and the foregoing arguments this percentage anthracene is exactly what would be predicted. However, it must be concluded that Marvel and Wilson (28), who obtained 10% anthracene in polystyrene, had a much greater error in analysis than they had anticipated.

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CHAPTER III

INTRODUCTION

The fact that monomers could be polymerized by alkali metal surfaces has been known for many years. For example, butadiene and isoprene polymerize very readily in the presence of metallic sodium at ordinary temperatures (1)(2)(3). Alkali metal initiation of butadiene in particular was used commercially for making synthetic rubbers in Europe. Buna 85, a high viscosity polymer of butadiene, was made by potassium catalyzed bulk polymerization and Russian S.K. synthetic rubbers were made by sodium catalysis.

The propagating centers for these polymerizations were presumed to be a carbanionic species based on various pieces of evidence -

(a) Sodium catalyzed polymerization immediately stopped when carbon dioxide was introduced to the system (3)

(b) t-Butyl catechol did not inhibit polymerization (4)

(c) Bright colors frequently developed during polymerization

(d) The copolymerization ratios differed from those of free radical and seemed to be opposite to those for cationic polymerizations

(e) Monomers which underwent this type of polymerization most easily appeared to be those which contained electronegative substitutents.

Beaman (5) has shown that sodium in liquid ammonia is a very effective initiator for methyl methacrylate and methacrylonitrile polymerizations at -75° C. Acrylonitrile (6) was also polymerized at this temperature by sodium in liquid ammonia.

Higginson and Wooding (7) investigated the kinetics of styrene polymerization initiated by potassium amide in liquid ammonia. The rate was observed to be proportional to the amide ion concentration and to the square of the monomer concentration. The degree of polymerization increased approximately as the styrene concentration but was independent of the amide ion. The mechanism proposed for this reaction was -

$$KNH_2 \rightleftarrows K^+ + NH_2^-$$

$$NH_2^- + M \longrightarrow NH_2 - M^-$$

$$NH_2 - M_n^- + M \longrightarrow NH_2 - \bar{M}_n + 1$$

$$NH_2 - M_n^- + NH_3 \longrightarrow NH_2 - M_n - H + NH_2^-$$

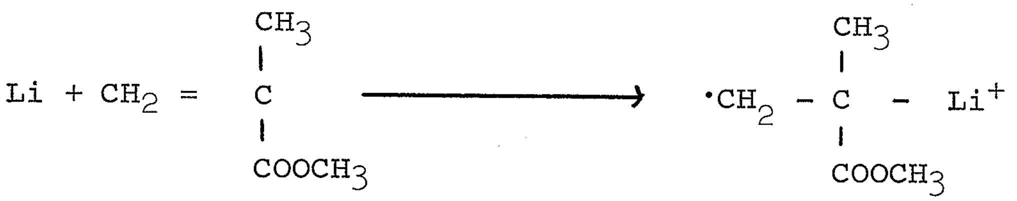
Analysis indicated the presence of approximately one nitrogen atom per polymer molecule and this gave strong support to the mechanism. The termination step is essentially a chain transfer with solvent.

The anionic polymers and copolymers of butadiene, prepared by sodium catalysis, have markedly different structures from those obtained by emulsion polymerizations. These polymers have largely 1,2 addition with many pendant vinyl groups (8)(9). Infrared absorption measurements have confirmed these observations. Potassium initiation gives 15-20% less 1,2 configuration than does sodium (10). Similarly, polyisoprene prepared by sodium polymerization at 50° C contains about 50% of 1,4 units (8)(9)(11) and infrared spectra indicate these are almost exclusively in the trans configuration. Increased temperature results in an increased proportion of 1,4 units (8)(9)(11).

The extensive investigations resulting from the commercial importance of crystalline or stereoregular polymers has brought a greater interest in alkali metal polymerizations, especially with lithium metal. Lithium metal differs from other alkali metals in that it is capable of directing the polymerization of butadiene or isoprene yielding predominantly 1,4 structures. In contrast, the other alkali metals (sodium, potassium, rubidium and cesium) generally yield polyisoprenes containing cis and trans 1,4 structures as well as 1,2 and 3,4 structures. The nature of the solvent also appears to have some effect on the microstructure of the polymer. Adding 0.5 parts of tetraethylene glycol dimethyl ether per 100 parts monomer to the lithium catalyzed polymerization of butadiene increases the 1,2 addition from 12% to 78% and similarly markedly increases the 3,4 addition in isoprene polymerization (11).

Stavely and coworkers of The Firestone Tire and Rubber Company (13) reported the stereoregular polymerization of isoprene by means of lithium metal dispersions. The polymer obtained was almost identical to Hevea, a form of natural rubber. This material, coral rubber, contains slightly less cis 1,4 structure (93.8% in Coral and 97.8% in Hevea) and slightly more 3,4 structure than Hevea. Furthermore, it was noted that while lithium metal gave predominantly a cis structure other alkali metals gave primarily a mixture of structures.

Tobolsky and coworkers (14) have shown that lithium metal polymerizations conducted in tetrahydrofuran yield a mixture of 1,2 and 3,4 structures but no 1,4 structure. Tobolsky (15) also reported that the percentage styrene in styrene-methyl methacrylate copolymers prepared in undiluted monomers, hydrocarbons, tetrahydrofuran, amines and liquid ammonia decreased with increasing basicity of the solvent. In undiluted monomers there was 28% styrene while in liquid ammonia there was no styrene in the polymer. This result was accounted for (16)(17) by assuming the electron transferred to the monomer resulting in a radical ion

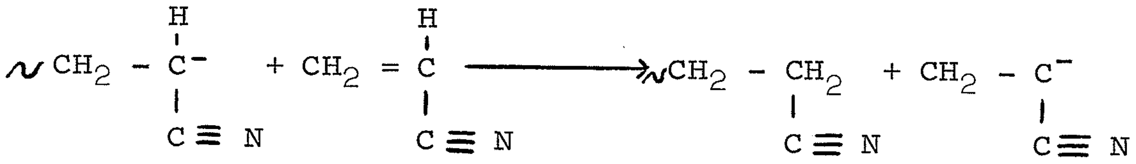


$$\mathrm{Li} + \mathrm{CH_2} = \underset{\mathrm{COOCH_3}}{\overset{\mathrm{CH_3}}{\mathrm{C}}} \longrightarrow \cdot\mathrm{CH_2} - \underset{\mathrm{COOCH_3}}{\overset{\mathrm{CH_3}}{\mathrm{C}}} - \mathrm{Li}^+$$

and propagation took place from both free radical and anionic ends. The free radical would give a copolymer containing 50% styrene and the anionic would yield only methyl methacrylate. This becomes essentially a block copolymer--one half composed of polymethyl methacrylate and the other of a styrene methyl methacrylate copolymer. In contrast sodium metal polymerizations gave exclusively polymethyl methacrylate regardless of the solvent.

A few reports in the literature have indicated that anionic polymerizations may be activated electrolytically (18)(19). The use of electrolysis for initiation has intriguing implications, although there are only scattered reports in the literature concerning this technique. Electrolytic initiation would give control of the rate of initiation which would subsequently have some control of the molecular weight. The disadvantage which has deterred many workers from utilizing electrolysis to a greater extent has been the low molecular weight dimers and trimers which are normally obtained. However, Funt and Yu (20) reported molecular weights of one million from the polymerization of methyl methacrylate in dimethyl sulfoxide solution. This interesting reaction was initiated by the anodic discharge of acetate ions, i.e. the Kolbe reaction. Although free radical in character, this reaction nevertheless indicates that much higher molecular weight materials may be obtained electrolytically.

Funt and Williams (21) made a detailed study of the electrolytically activated polymerization of acrylonitrile in dimethyl formamide solution. The rate of polymerization was found to increase with increasing current and was first order in monomer concentration. However, the molecular weights of the acrylonitrile polymers were very low and evidence was given which supported the chain transfer to monomer termination step suggested by Zilka (22).



$$\sim CH_2 - \overset{H}{\underset{C\equiv N}{C^-}} + CH_2 = \overset{H}{\underset{C\equiv N}{C}} \longrightarrow \sim CH_2 - \underset{C\equiv N}{CH_2} + CH_2 - \underset{C\equiv N}{C^-}$$

The suggested mechanism for the above initiation was a direct electron transfer from the electrode to the monomer. This hypothesis had previously been advanced by Yang, McEwen and Kleinberg (23) for the polymerization of styrene in pyridine using magnesium electrodes. However, the polystyrene obtained in this latter work was also low molecular weight (approximately fifteen hundred to twenty-eight hundred). Polarographic half wave potentials were used by Funt and Williams to confirm the initiation step. Polarography had been utilized by Murphy, Carangelo, Ginaine and Markham (24) to compare polyacrylonitrile produced by electrolytic reduction at a dropping mercury electrode with that from sodium metal initiation.

An intriguing possibility arising from the above work is that of having an electrically controlled polymerization--not necessarily electrolytically initiated, but the initiating species controlled by electrolysis. This might be achieved by the use of reducible organic compounds in the polymerization system. However, this would still necessitate having polymerization proceed in the conducting media containing the electrodes, monomer and reducible organic material. Another possibility is the formation of the initiating species outside the polymerization system, i.e. the polymerization could be conducted in a separate vessel into which the electrically produced initiator could be admitted. This latter possibility has the advantage of electrolytic control and not the disadvantage of requiring the polymerization to take place in the conducting media.

A modification of the Castner-Kellner process may be a means of performing polymerizations in the manner described. This process electrolyzes a concentrated solution of sodium chloride over a mercury cathode, forming a sodium amalgam. The amalgam is allowed to run into a second chamber and react with water resulting in the formation of sodium hydroxide. If the second chamber contained a solution of monomer, instead of water, it might be possible to activate a polymerization by the amalgam.

The only reference known to the author where sodium amalgam has been utilized to initiate polymerization is that of Kern and Quast (25). These authors performed two experiments in which acrylonitrile was initiated by sodium amalgam. However, in both cases the molecular weights of the materials were very low.

EXPERIMENTAL

Materials

Methyl methacrylate from Rohm and Haas was washed with successive portions of 10% NaOH containing NaCl, washed three times with distilled water and dried over anhydrous $CaSO_4$, with occasional shaking, for a period of 48 hours. The monomer was then fractionally distilled at 43-44° C under argon and the middle fraction collected.

NN dimethylformamide (DMF) from Matheson, Coleman and Bell was purified according to the directions of Rochow and Thomas (26). Dimethylformamide was mixed with sodium dried benzene (10% of the total volume of the mixture) and allowed to stand for a short period. The benzene-water azeotrope was distilled from this mixture under atmospheric pressure and at a temperature which was never allowed to go above 81° C. The solvent was stored over BaO for 24 hours, fractionally distilled under argon at a temperature of 74-75° C and the middle fraction collected.

All the mercury used in these experiments underwent

FIGURE I

Diagram of polymerization cell.

A - stopcock (3 mm)

B - stopcock (2 mm)

C - reaction vessel

D - magnetic stir bar

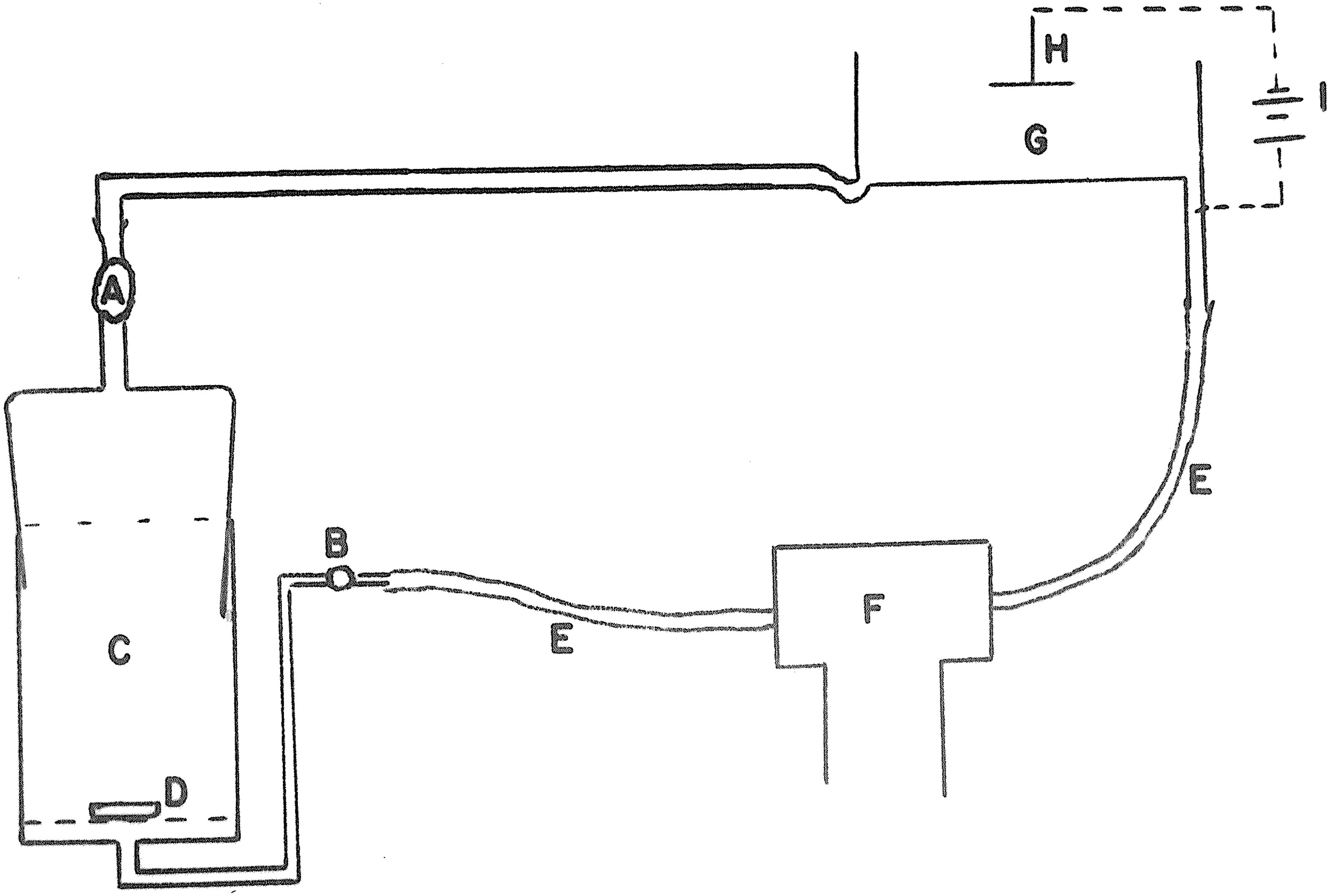
E - tygon tubing

F - sigma motor pump

G - electrolysis section

H - platinum electrode

I - constant current supply


H
I
G
A
E
B
F
E
C
D

an initial purification. The mercury was bubbled with air overnight and the resultant scum filtered off. It was then passed in a fine spray five successive times through a three foot column containing 10% HNO_3 and distilled prior to use.

After the above initial purification the mercury was cleaned after every reaction by being shaken successively with concentrated HCl and distilled water. The mercury was then passed five times through the three foot column containing HNO_3, again shaken with distilled water, then with methanol and dried under vacuum for 24 hours.

U.S.P. sodium hydroxide pellets were used without further purification.

Procedure

All polymerizations, except where temperature was varied, were conducted at room temperature in the cell shown in Fig. I. In all reactions the quantity of mercury placed in the cell was 30 cc (408 g). The reaction part of this cell was stored in an oven at 50° C until one-half hour prior to use, during which time it was placed in an oven at 150° C. A 10 cc syringe used for making transfers was stored in the

FIGURE II a

Constant current supply

FIGURE II b

Diagram of bridge circuit

A - recorder

$R_1 + R_2$ = 5000 ohms (variable resistances)

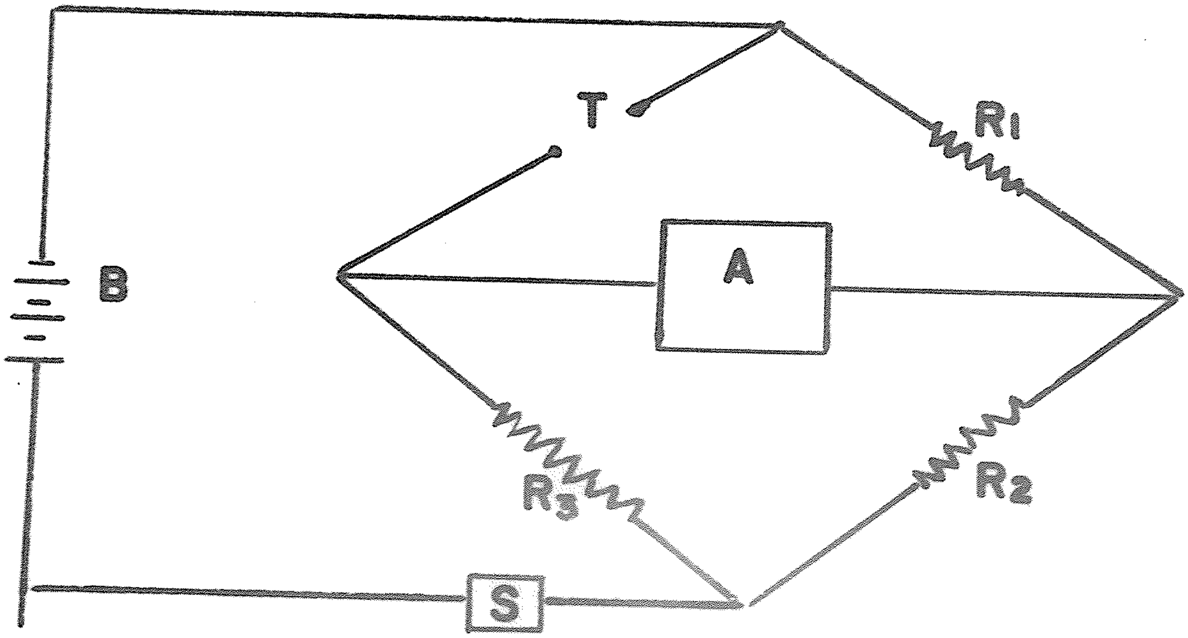
R_3 = 500 ohms

T - thermistor

B - battery (1.5 volts)

S - switch

AC
MA
CURRENT
VOLTAGE
DC−
DC+



T
R1
B
A
R3
R2
S

150° C oven for one hour before use. The cell and syringe were placed in a dry box and transfers of monomer and solvent made under an atmosphere of nitrogen. The total volume of monomer and solvent contained in the cell was 30 cc for runs employing a variation in current and 25 cc for all other experiments. After transfers were completed in the dry box and stopcock A was closed, the cell was set up as shown in Fig. I and the sigma motor pump turned on to circulate the mercury. Stopcock B was left fully open while stopcock A was adjusted to give a continuous flow of mercury. A volume of 140 ml of 40% NaOH was placed in the electrolysis section and the current turned on.

The current was supplied by a constant D.C. current supply shown in Fig. (2a). An x-y recorder was used to observe the very sharp rise in temperature associated with the start of polymerization. This recorder was attached to a sensitive thermistor through the bridge circuit shown in Fig. (2b). The thermistor was fastened to the side of the reaction vessel and insulated by means of heavy insulating glass wool surrounding the reaction vessel. The variable resistances in the circuit were adjusted, in conjunction

FIGURE III

Modification of reaction vessel.

A - stopcock (3 mm)

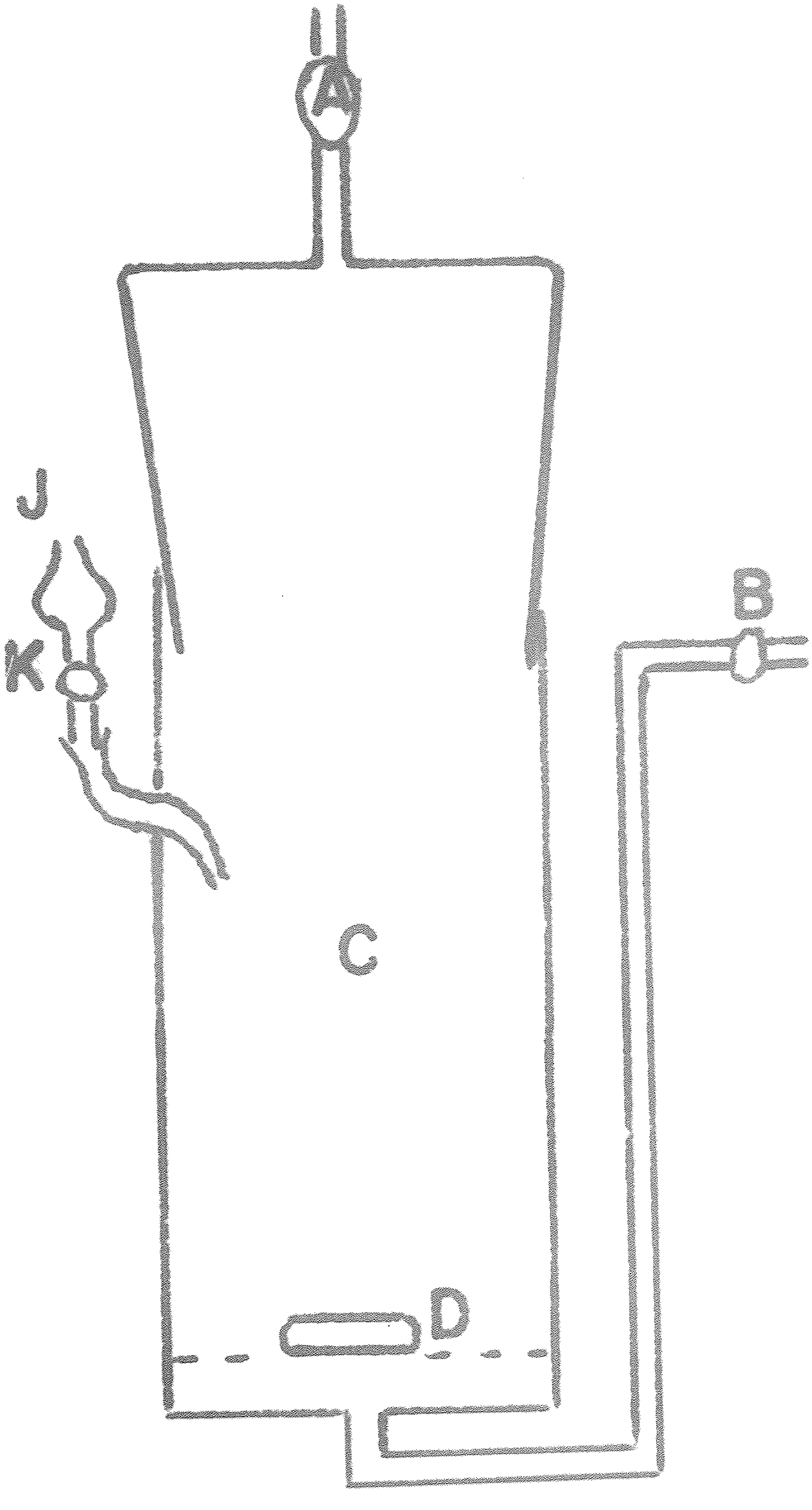
B - stopcock (2 mm)

C - reaction vessel

D - magnetic stir bar

J - bulb for containing HCl

K - stopcock (2 mm)


A
J
B
K
C
D

with the attenuator on the x-y recorder, to give a large deflection with the observed temperature rise.

In order to measure the rates a modification of the cell shown in Fig. I was required. This modification, shown in Fig. III, was the addition of a side arm to the reaction portion of the cell. After a significant conversion had taken place the reaction was quenched by the injection of 2 cc of 3 N HCl contained in the bulb attached to the side arm.

For polymerizations conducted at temperatures below room temperature the reaction cell was immersed in a cooling bath. An ice-water bath was used for 0° C and a crushed ice-salt bath for -10° C.

The polymer was isolated by separating the mercury from the mixture and precipitating the polymer from dimethylformamide solution into methanol. Purification was effected by solution in methyl ethyl ketone followed by precipitation into methanol.

Molecular Weights

All the molecular weights of polymethyl methacrylate were obtained by viscometry using an Ubbelohde viscometer in a constant temperature bath at 25 ± .01° C. The constants of Billmeyer (27) ($K = 6.8 \times 10^{-5}$, $\alpha = 0.72$) for weight average molecular weights were employed in these measurements using methyl ethyl ketone as solvent.

RESULTS

The polymerizations all exhibited the same general phenomena, a short induction period followed by rapid polymerization to completion. The temperature rose quite markedly with the start of the reaction. For example, in the system containing 33% monomer the total rise in temperature was from 27.7° C to 64.9° C.

The general observation in anionic polymerization of increasing molecular weight with decreasing polymerization temperature is shown in Table I.

TABLE I

Variation of Molecular Weight with Temperature

Temperature	Intrinsic Viscosity (η_i)	Molecular Weight
Room temp. (23° C)	0.120	32,300
0° C	0.144	41,700
-10 ± 2° C	0.171	53,700

The above determinations were all made at a monomer concentration of 20% by volume. The current passed through the electrolysis section was 300 m.a. at a potential of 4.0 volts.

The molecular weights of the polymers obtained were observed to increase with increasing monomer concentration. The values for various monomer concentrations are shown in Table II.

TABLE II

Variation of Molecular Weight with Monomer Concentration

Monomer concentration (% by Vol.)	(M)M/l		Molecular Weight
10%	0.936	0.053	10,000
15%	1.41	0.086	20,000
20%	1.87	0.120	32,000
33%	3.02	0.175	55,000
40%	3.72	0.224	79,000

These measurements were all performed at room temperature with 300 m.a. at a potential of 4.0 volts passing through the electrolysis portion of the cell. It may be noted in the above Table that the molecular weight increases quite significantly with monomer concentration. A four fold increase in monomer concentration results in almost an eight fold increase in molecular weight.

The mechanism for this reaction like those of alkali metal polymerization is probably anionic. However, in order to verify that nothing unusual was happening, such as polymerization from the radical end of the radical ion reported by Tobolsky (17), a copolymerization experiment was performed employing 5 ml of styrene (C^{14}) and 5 ml of methyl methacrylate in 20 ml of dimethylformamide. The results of this experiment are shown in Table III.

TABLE III

Styrene-Methyl Methacrylate Copolymerization

No. of Precipitations	1st	2nd	3rd
Activity of polymer (c/min/g)	1267	1108	1040
% Styrene in polymer	2.02%	1.78%	1.68%

Activity of styrene (C^{14}) 6.21×10^4 c/min/g

The percent styrene in the polymer is seen, from the above Table, to be approximately 1-2%. This is in agreement with the general observation that anionic initiation of equal quantities of styrene and methyl methacrylate results in only about 1% styrene in the polymer.

TABLE IV

Molecular Weight and Induction Period at Various Currents

Current (m.a.)	Induction Period (min)		Molecular Weight
100	45	.204	67,000
200	40	.184	60,000
300	34	.175	55,000
400	30	.160	49,000
500	27	.151	45,000

The rate of flow of mercury in two separate determinations was found to be 3 cc per minute.

An experiment was performed at 300 m.a. and the circulation of mercury stopped after 32 minutes before the reaction took place. The solution was separated and methanol added to it. There was no precipitation of polymer, indicating that no polymerization occurred during the induction period.

TABLE V

Rates of Polymerization at Various Monomer Concentrations

(M) M/l	Wt. polymer (g)	Time (sec)	$R_p \times 10^2$
0.936	1.57	88.2	1.1
1.41	2.71	95.6	2.08
1.87	3.31	93.7	2.32
2.34	4.22	84.3	3.54

FIGURE IV

The variation in the degree of polymerization with current.

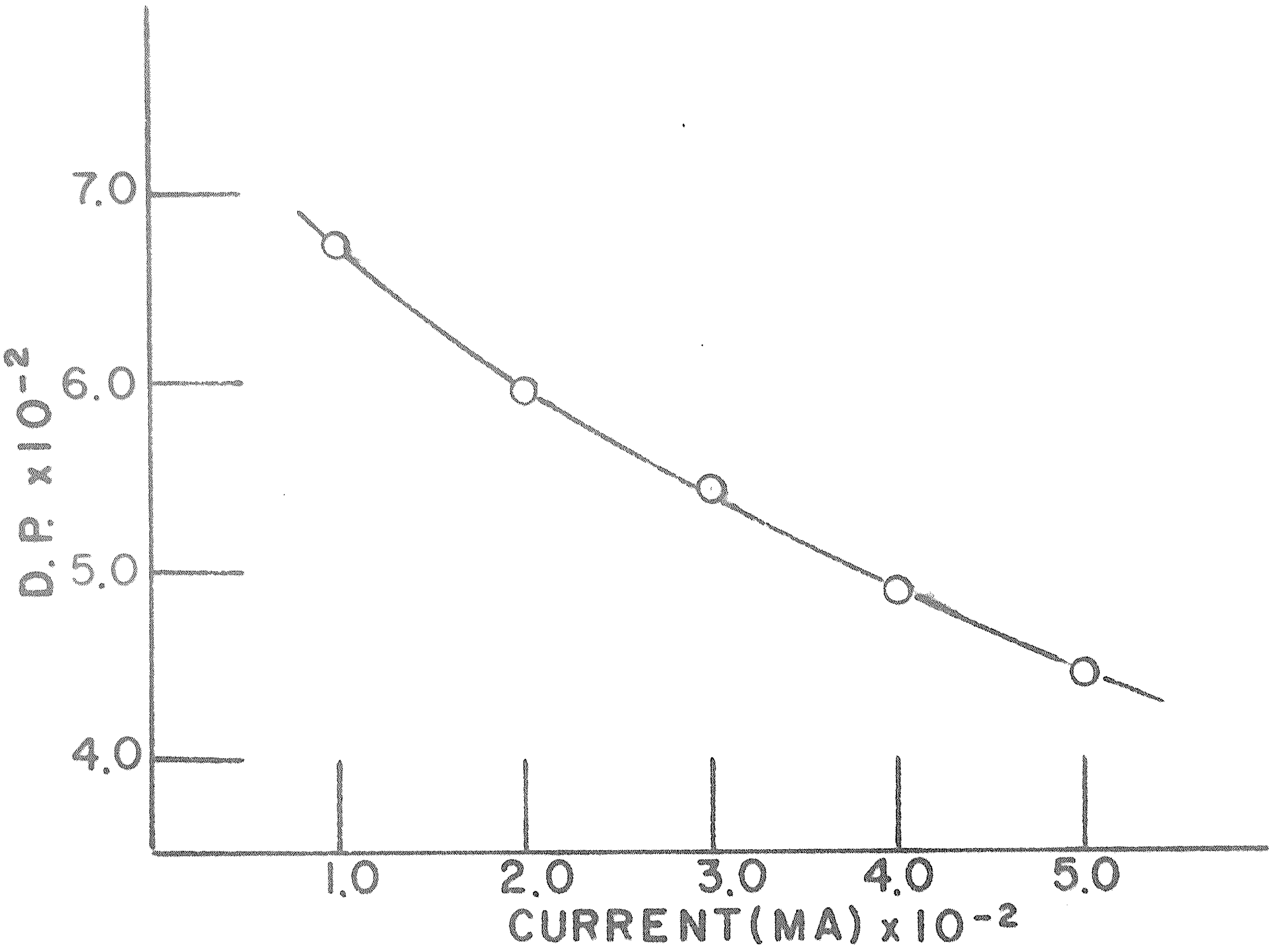
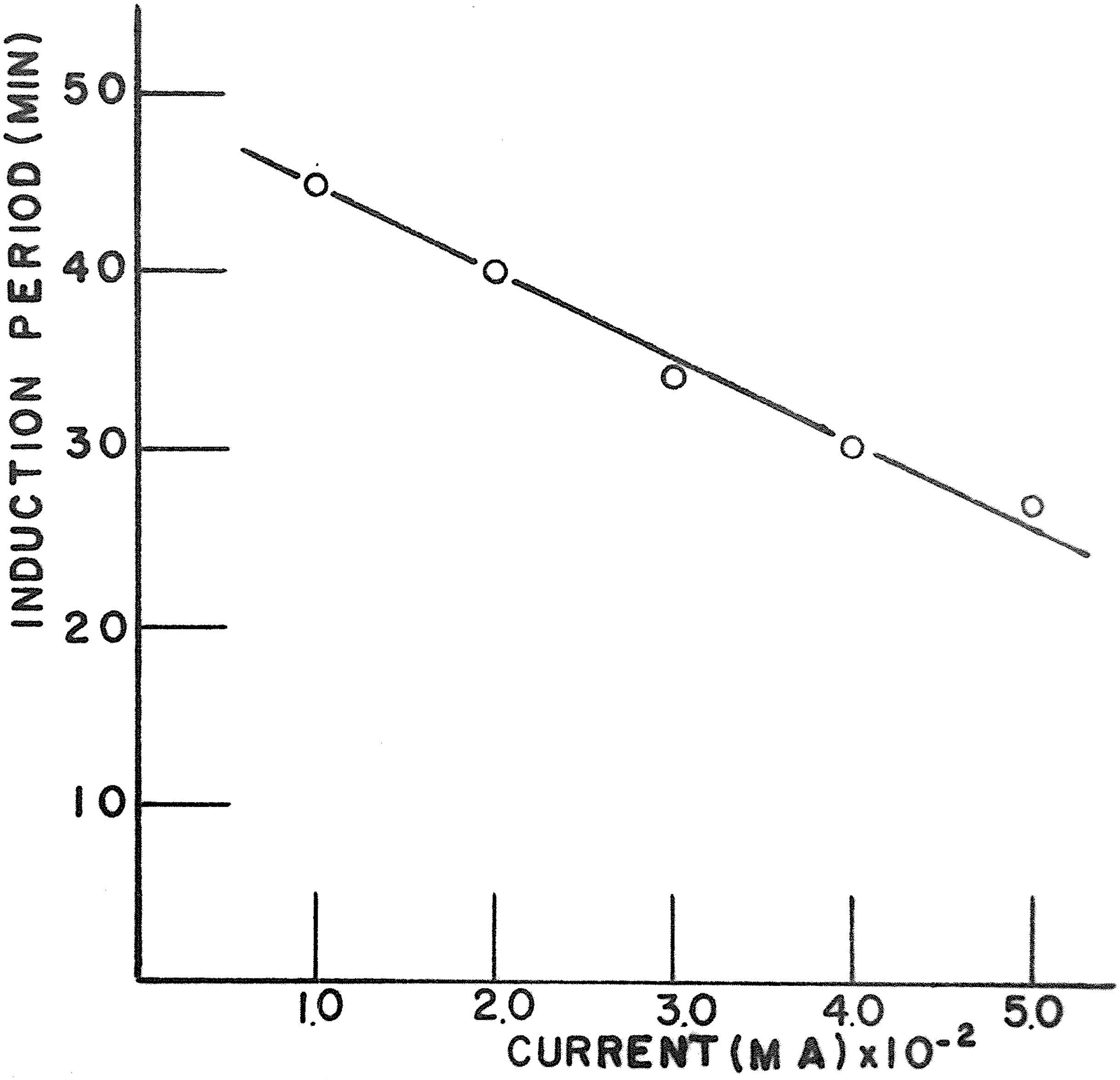

D.P. x10^{-2}
7.0
6.0
5.0
4.0
1.0
2.0
3.0
4.0
5.0
CURRENT (MA) x10^{-2}

FIGURE V

The induction period as a function of current.



INDUCTION PERIOD (MIN)
50
40
30
20
10
1.0
2.0
3.0
4.0
5.0
CURRENT (M A) x10^{-2}

FIGURE VI

Rate of polymerization plotted against monomer concentration.

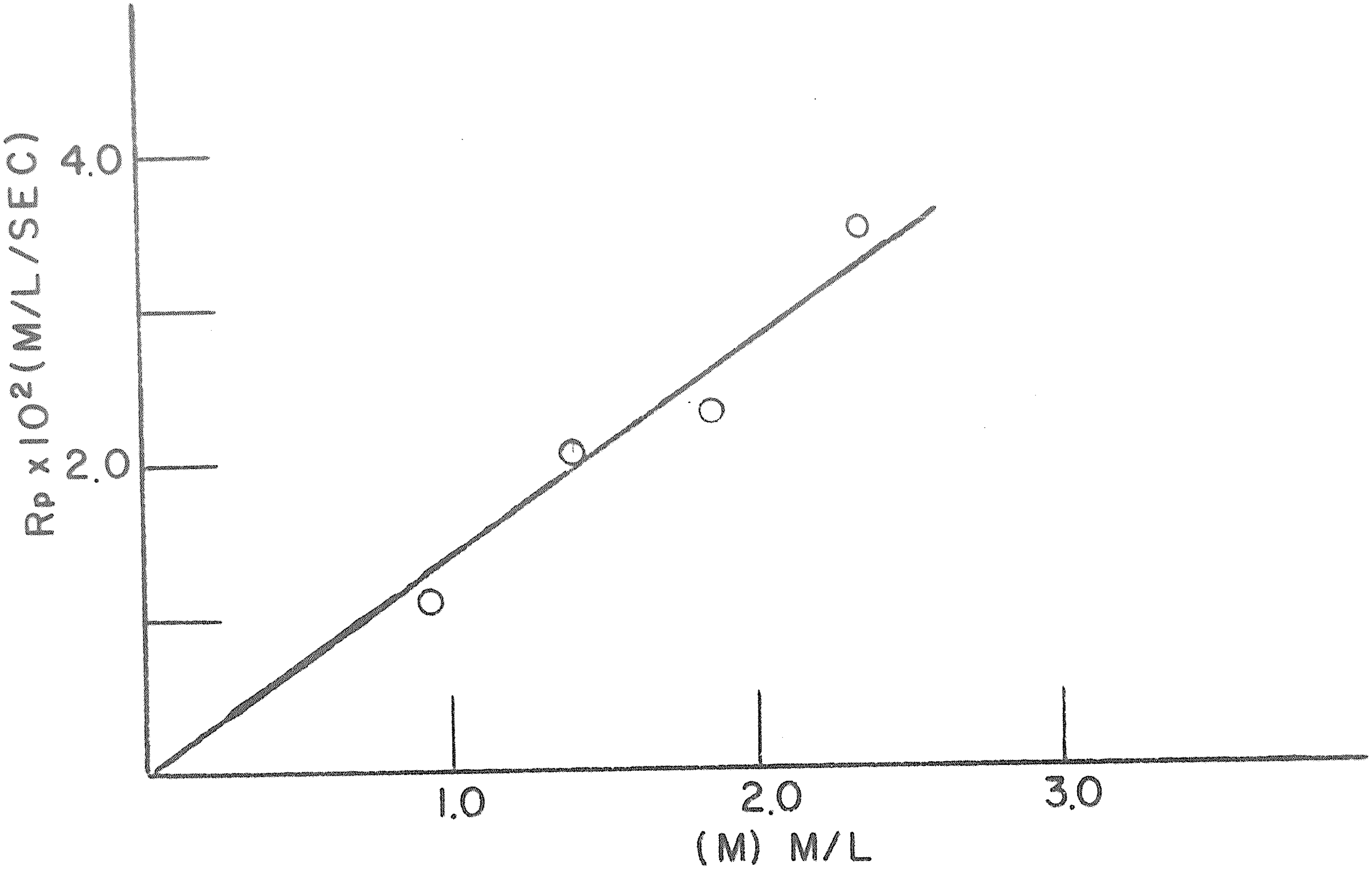
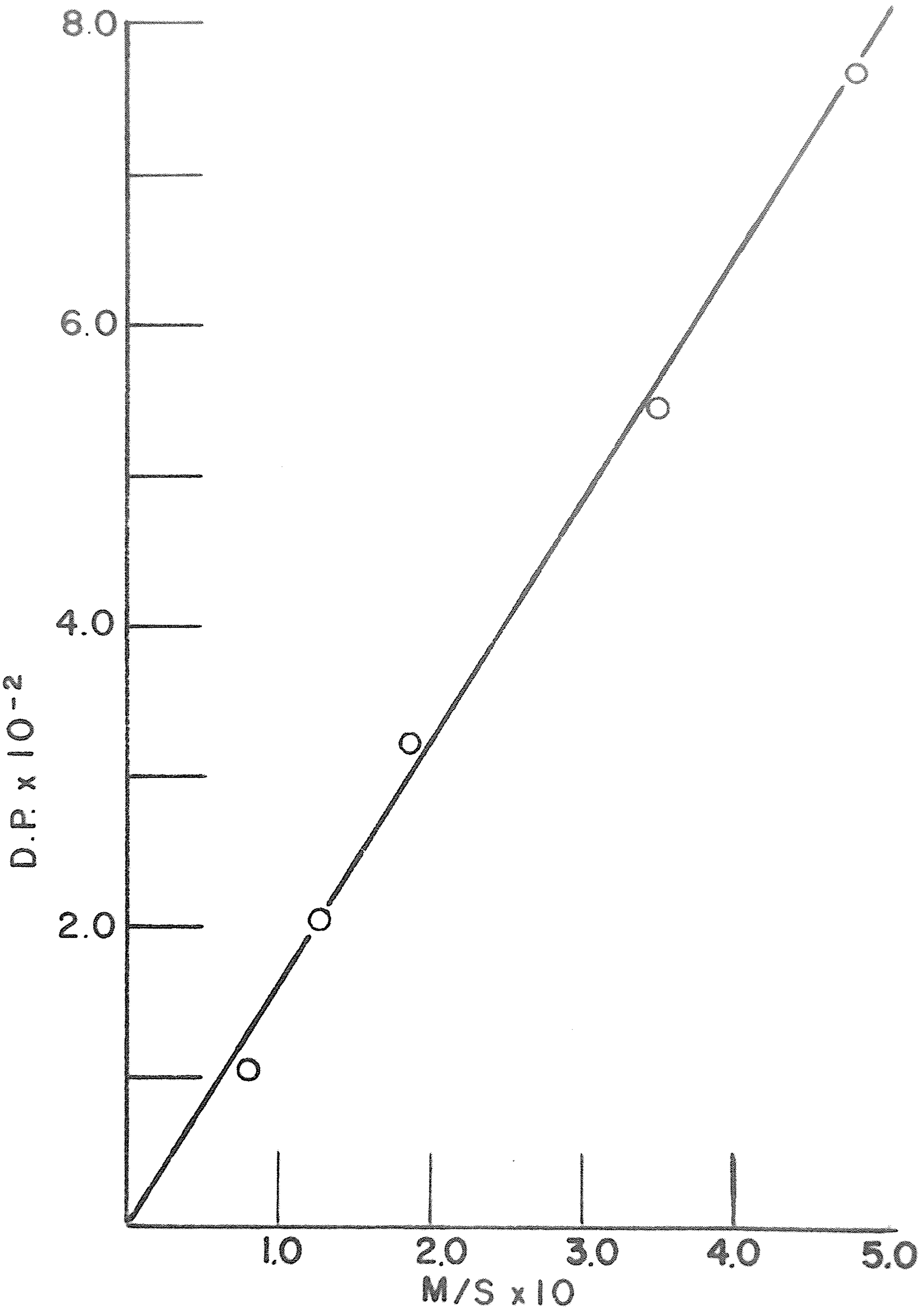

Rp x 10^2 (M/L/SEC)
4.0
2.0
1.0
2.0
3.0
(M) M/L

FIGURE VII

The degree of polymerization plotted against $\frac{M}{S}$ ratio.


8.0
6.0
4.0
2.0
D.P. x 10^-2
1.0
2.0
3.0
4.0
5.0
M/S x 10

DISCUSSION

The present study has been directed toward an attempt to separate the electrolysis and reaction media in an electrolytically initiated polymerization. The advantages in doing this are many, for example, the particular solvent employed need not necessarily conduct a current, possible secondary reactions at the electrode are no longer a problem and the electrolysis section may even consist of an aqueous medium. In addition to the usual variables of temperature and monomer concentration, the unique variable of electrolytic polymerizations, i.e. control of the initiation by means of the current, may still be obtained.

Sodium amalgam produced in the electrolysis section of the cell shown in Fig. I, by electrolyzing a sodium hydroxide solution, is allowed to drop through the reaction part containing monomer and solvent. The amalgam prepared in this manner is controlled by the current and yet the polymerization, occurring in a section separated from that producing the amalgam, is independent of the conditions of amalgam production. Since this reaction is initiated by the amalgam, i.e. sodium metal dissolved in the mercury is the initiating species, the polymerization cannot be regarded as a strictly electrolytic initiation. A more appropriate designation might be--an anionic polymerization with electrolytic production of the initiating species.

One of the major advantages inherent in the use of this method is the ability to control the molecular weight of the product by means of the current passing through the electrolysis section. Fig. IV, a plot of current against the degree of polymerization shows a smooth curve which may be used in the form of a calibration curve. Thus, the current required to produce any desired molecular weight within the bounds of the graph, may be read directly from the curve. This enables the experimenter to predetermine the molecular weight of the polymer. Using different solvents would probably result in a variation of the calibration curve since termination sometimes occurs by a reaction with solvent. Also, using a non polar medium with lithium amalgam may result in a controlled molecular weight stereoregular polymer, since lithium has been shown to direct the propagation step.

Induction periods have frequently been noted in anionic polymerizations (28)(16). These induction periods appear to decrease with increasing temperature and have been suggested to arise from trace impurities in the system. It has been noted that the induction periods are generally shorter the higher the purity of monomer (28). Fig. V, a plot of induction period against current shows this period to decrease with increasing current. This observation could quite easily be explained on the basis of trace impurities in the system. However, recently suggestions have been advanced that methyl methacrylate undergoes an initial slow propagation step followed by a more rapid reaction to completion (29)(30)(31). Although the induction period in the present work probably arises from trace impurities in the system the latter suggestion may also play a part in the reaction.

The variation in viscosity average molecular weight with polymerization temperature is shown in Table I. It is seen that a decrease in temperature of approximately 33° C results in an increase of molecular weight from 32,000 to 53,000. This observation is quite generally observed in anionic polymerization. The same trend was observed by Goode and coworkers (32) for methyl methacrylate polymerizations in liquid ammonia.

A detailed investigation of methyl methacrylate polymerization in toluene revealed unusual complexities in the rate curves (29). There appeared to be an initial slow propagation reaction followed by a more rapid propagation to completion. However, the overall rate of the reaction was reported to be first order in monomer (29)(30)(31). Although conducted in the polar solvent dimethylformamide and initiated by sodium amalgam, the present work also shows the rate to have a first order dependence on monomer (Fig. VI).

Assuming the reactivity of the anion is independent of the chain length, analogous to the assumption made in free radical polymerization, the rate of polymerization may be represented as

$$R_p = k_1(M_n^-)(M) \qquad ---(1)$$

The degree of polymerization is designated by

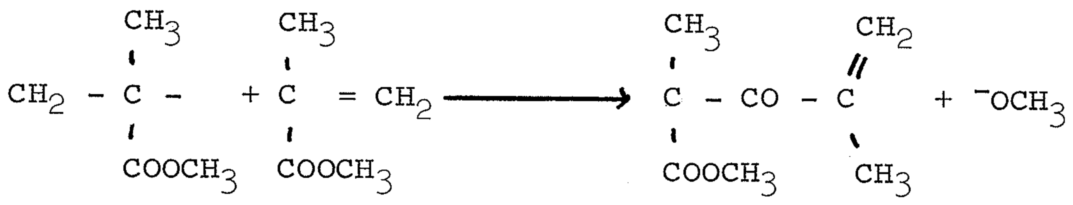
$$\overline{D.P.} = \frac{\text{rate of propagation}}{\text{rate of termination}} = \frac{R_p}{R_t} \qquad ---(2)$$

If the termination reaction is assumed to take place through proton abstraction from a solvent molecule then the degree of polymerization must be represented as

$$\overline{D.P.} = \frac{k_1(M_n^-)(M)}{k_2(M_n^-)(S)} = \frac{K(M)}{(S)} \qquad ---(3)$$

Consequently, a plot of $\overline{D.P.}$ versus $\frac{(M)}{(S)}$ should yield a straight line extrapolating through zero if chain termination were by a reaction with solvent. Fig. VII, shows a plot of $\overline{D.P.}$ against $\frac{(M)}{(S)}$ which extrapolates through zero thus verifying the above assumption.

Suggestions have been advanced that in certain systems termination may occur through carbanion attack on the ester group of the monomer (33).



$$CH_2 - \overset{CH_3}{\underset{COOCH_3}{C}} - \quad + \overset{CH_3}{\underset{COOCH_3}{C}} = CH_2 \longrightarrow \overset{CH_3}{\underset{COOCH_3}{C}} - CO - \overset{CH_2}{\underset{CH_3}{C}} \quad + {}^{-}OCH_3$$

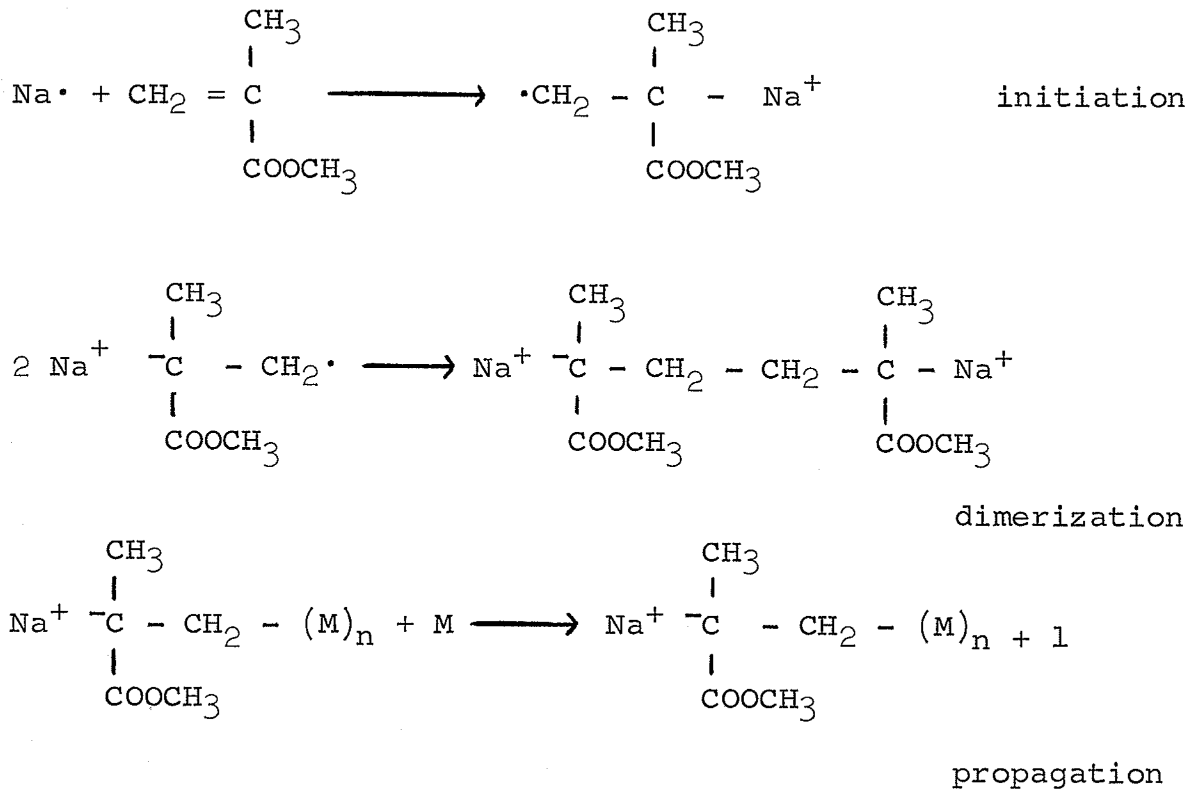
If this reaction were the termination step in the present system then the degree of polymerization would be given by

$$\overline{D.P.} = \frac{k_1(M_n^-)(M)}{k_2(M_n^-)(M)} = K$$

which is independent of monomer concentration (34). Table

II shows the degree of polymerization is not independent of monomer concentration. On the contrary the $\overline{\text{D.P.}}$ increases quite significantly with monomer concentration. The previous arguments are identical to those employed by Zilka (22) for the termination by transfer to monomer observed in the acrylonitrile polymerizations.

The above information suggests the following mechanism for the polymerization.



$$\mathrm{Na\cdot + CH_2 = \underset{COOCH_3}{\overset{CH_3}{C}} \longrightarrow \cdot CH_2 - \underset{COOCH_3}{\overset{CH_3}{C}} - Na^+}$$

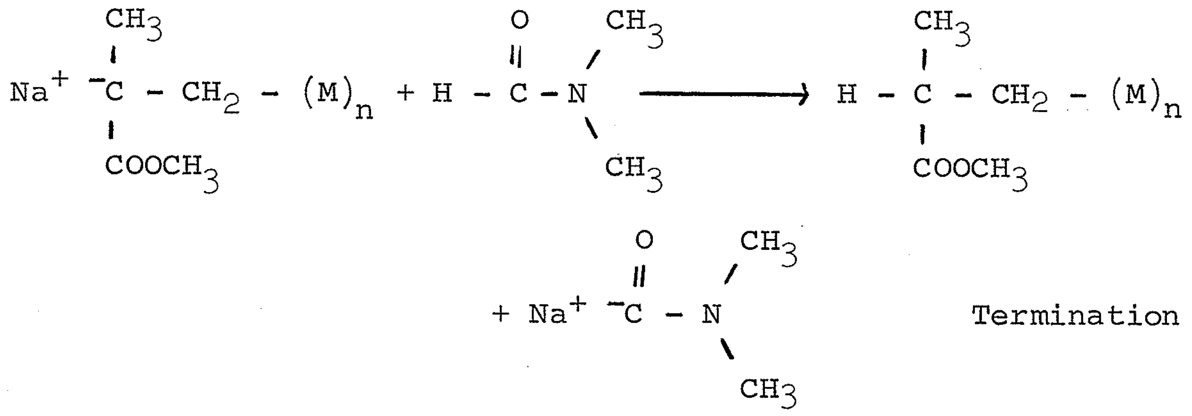
initiation

$$2\ \mathrm{Na^+\ {}^-\underset{COOCH_3}{\overset{CH_3}{C}} - CH_2\cdot \longrightarrow Na^+\ {}^-\underset{COOCH_3}{\overset{CH_3}{C}} - CH_2 - CH_2 - \underset{COOCH_3}{\overset{CH_3}{C}} - Na^+}$$

dimerization

$$\mathrm{Na^+\ {}^-\underset{COOCH_3}{\overset{CH_3}{C}} - CH_2 - (M)_n + M \longrightarrow Na^+\ {}^-\underset{COOCH_3}{\overset{CH_3}{C}} - CH_2 - (M)_n + 1}$$

propagation



$$\mathrm{Na^+\;{}^-C(CH_3)(COOCH_3) - CH_2 - (M)_n + H - C(=O) - N(CH_3)_2 \longrightarrow H - C(CH_3)(COOCH_3) - CH_2 - (M)_n + Na^+\;{}^-C(=O) - N(CH_3)_2}$$

Termination

It is difficult to assess where the dimerization will take place in the reaction. Does it occur with the first radical ion formed, i.e. immediately after the electron transfer from sodium to the monomer, does it take place during the final stages of polymerization or, is it occurring continuously throughout the conversion?

It has been pointed out by Szwarc (35), for initiation through electron transfer, that there is a slow step in the initiation process which must be either dimerization of the radical ions or the addition of monomer to the carbanion. Dimerization of the radicals would be hindered by coulombic repulsion, and since this species is neither a radical nor an ion the carbanion could quite conceivably have a lower reactivity toward monomer. Szwarc suggested that dimerization was the faster reaction during the first period of the initiation step but later monomer addition to the anion might overtake dimerization.

The molecular weights observed in this study have varied from approximately 10,000 to over 70,000 depending on the conditions employed. Molecular weights of this magnitude have not been generally observed, with the exception of Funt and Yu (20), for polymerizations where electrolysis plays a part in the reaction. The electrolytic control of the molecular weight together with the high degree of polymerization observed indicates that this technique may be of considerable use in further investigations.

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CLAIMS TO ORIGINAL WORK AND CONTRIBUTIONS TO KNOWLEDGE

Chapter I

1. A mechanism has been suggested which attempts to reconcile the salient features of polymerizations in aromatic solvents.

2. An equation has been derived from the mechanism which shows the rate of polymerization proportional to the first power of the initiator at high solvent concentrations.

3. The exponent of the initiator concentration at 10% vinyl acetate in benzene has been shown to be 0.89.

Chapter II

1. An unusual retardation has been observed which at high anthracene concentrations results in almost a cessation of polymerization.

2. The styrene-anthracene copolymer formed has been shown to result in retardation of polymerization.

3. The analytical results of the copolymers showed a constant anthracene content of the polymers.

Chapter III

1. A technique for polymerization has been developed which allows the electrolytic control of molecular weight without the necessity of an electric current passing through the monomer solution.

2. A smooth curve representing degree of polymerization against current has been suggested as a calibration curve for predetermining molecular weights of polymers.

3. Initiation by sodium amalgam has been shown to be anionic.

4. The molecular weights obtained in this study have been generally higher than those in previous electrolytic polymerizations.