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The Half-Life of the Styrene Free Radical*

by

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SYNOPSIS

The principle of the method of Paneth and Hofeditz of studying gaseous free radicals has been employed for chain reactions in liquid monomers. The half-life of the photochemically initiated polystyrene free radical has been found to be 0.088 ± 0.015 seconds. A simple extension of the technique should also give absolute values of the propagation rate constant and the chain transfer constant.

I. INTRODUCTION

In recent years ever increasing interest has been shown in the half-life of polymeric free radicals. Notable contributions by Melville (2), Bartlett (1) and Majury (5) have to be noted. The present paper deals with a different approach whose virtue is extreme simplicity of interpretation and relative simplicity of technique.

* This paper contains some of the experimental work done in partial fulfillment of the requirement for the degree of Doctor of Philosophy by one of the authors (Carl Heffelfinger). It was supported in part by the Office of Naval Research and by a research fellowship by the Allied Chemical and Dye Corporation.

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II. PROCEDURE

Paneth and Hofeditz (6) developed a method for the determination of the lifetime of gaseous free radicals. A modification of this method has been adapted to the conditions of liquid phase polymerization reactions.

The apparatus used is pictured in Figure 1. By means of a pressure difference established between the reaction chamber 1 and the pressure bulb 2, 20 ml. of monomer and benzoyl peroxide is forced through the capillary tube 3. The pressure difference is maintained by placing the stopcock 4 in such a position that the pressure in the reservoir 5 and reaction chamber 1 are equal. By the use of stopcocks 6 and 7 predetermined pressures are established in the reaction chamber 1 and pressure bulb 2 and noted on the manometers 8 and 9. The flow is started by turning stopcock 4 in such a position that the pressure in bulb 2 is applied on the solution, forcing it through the capillary in a narrow stream. When approximately one-half of the liquid has left the calibrated reservoir 5, the stopcock 4 is turned to its original position and the flow stopped. The time of flow is measured on an electric timer. The volume of solution reacted is noted on the reservoir 5.

On leaving the capillary, the liquid falls under its initial velocity and gravitational acceleration. At point x, the liquid is exposed to the radiation of a mercury arc, at which point the initiation of polymeric free radicals is assumed to take place.

As the stream falls, the free radicals grow and will end their growth after a period of time. If, however, the chains are terminated prior to natural termination by some other means, the total yield of polymer will decrease. This forced termination is accomplished by means of the stirrer 10 containing a picric acid solution as inhibitor. By varying the distance between reaction chamber 1 and stirrer 10 different flow times can be obtained. Thus the growing free radical is given longer or shorter time to grow before it is forcibly terminated by reaction with the inhibitor molecule. Plotting the yield vs. time of flow a curve is obtained which at first ascends linearly as ever longer time intervals are given for polymerization. Later it curves in a manner to approach asymptotically a maximum yield value obtained by permitting the polymer chains to grow to maturity and terminate by a natural process (Figure 2). This last condition is achieved by replacing the stirrer 10 by a cup in which the polymerizing monomer is permitted to collect.

III. CHEMICALS AND APPARATUS

Styrene - The monomer was obtained from the Dow Chemical Company (N-99) and was purified by the method used by Goldfinger and Lauterbach (3). A 5% solution by weight of benzoyl peroxide in purified styrene was divided into 25 ml. samples and stored in dry ice until used.

Benzoyl peroxide - Eastman Kodak White Label.

Solvents - Benzene, xylene and methanol were distilled before use. The chloroform was used as received.

Picric acid - Merck Reagent Grade picric acid was dried at 105°C. overnight before use. In the stirrer 20 ml. of a 1% solution by weight of picric acid in xylene was used as the inhibitor. In the centrifuge tubes 35 ml. of a 1% solution by weight of picric acid in methanol was used as the inhibitor for the blank samples.

Centrifuge - A Servall Angle Centrifuge (SS-1) was used. The samples were centrifuged at 12,000 r.p.m. in stainless steel tubes for ten minutes before decantation. The supernatant liquid was poured into methanol as a check for complete precipitation of the polymer.

Mercury arc - The source of radiation was a General Electric AH-6 mercury arc. Water flows through the quartz water jacket surrounding the arc at a rate of five quarts per minute. Mounted behind the arc is an aluminum parabolic reflector of focal length 8 mm. The radiation is focused by means of two quartz lenses, so that the radiation converges at the monomer stream. At the point of focus the beam is approximately 3 mm. wide. The arc and optical system are housed in a brass box cooled by an air blower. Entrance of the radiation into the reaction chamber is through a quartz window 25 mm. in diameter. Except for this window all of the reaction chamber is shielded with a brass tube. The

intensity of the arc was monitored with a polaroid filtered Weston photocell Model 594 connected to a millivoltmeter. Variations in intensity from measurement to measurement did not exceed 1%.

Stirrer - The body and rotating member of the stirrer are made of pyrex glass tubing. The tolerance between the rotating member and body is such that the former barely slides into the latter. The rotor of a 1/30 horsepower motor was cut to fit into the rotating member and sealed therein. The field of the same motor was bored to fit over the body of the stirrer and the shading coils enlarged. With 20 ml. of inhibitor solution, the stirrer, operated by 110 volt A.C. current, rotates at 1530 r.p.m., as determined with a stroboscope. The efficiency of stirring was determined by dropping 0.5 M. solution of sodium hydroxide and phenolphthalein from a medicine dropper into the spinning pump, containing 20 ml. of 0.5 M. hydrochloric acid. Complete decoloration occurred in less than $\frac{1}{4}$ revolution. This indicates that complete mixing is achieved in not more than 10 milliseconds.

IV. EXPERIMENTAL PROCEDURE

Fifteen minutes prior to the making of a run, the mercury arc was turned on to allow time for its stabilization. A sample was taken from the dry ice container and warmed to room temperature. The sample tubes were closed

containers made of ground glass standard taper joints. A sample of 20 ml. was then pipetted into the reservoir.

The liquid flow was started and stopped as previously described. At the completion of the run, air was bled into the system, the stirrer was removed, and a 3 ml. sample of the remaining monomer solution was removed as the blank sample. This was precipitated in a centrifuge tube with 35 ml. of the picric acid-methanol solution. The blank indicated the amount of polymer formed thermally.

The contents of the stirrer were poured into an evaporation tube by breaking the glass tips. Four 5 ml. washes of xylene were used to clean the stirrer of any remaining solution. The total volume of material in the evaporation tube was then approximately 50 ml.

For the determination of maximum yield, the stirrer was eliminated and an empty container placed at the bottom of the column. After a lapse of about two minutes, the monomer solution collected was placed in the evaporation tubes with picric acid-xylene solution and treated in the usual way.

In order to handle conveniently the small quantity of polymer dissolved in the contents of the stirrer, concentration through evaporation to dryness was necessary. The solution was placed in an evaporation tube connected through a receiving trap to a high vacuum line. The receiving trap was surrounded by liquid nitrogen and the evaporation tube

by shaved ice. The system was then evacuated by means of an aspirator while a gentle stream of oxygen-free, dry nitrogen was blown over the top of the liquid, thus eliminating bumping. When approximately one-half of the solution had evaporated, the nitrogen flow was turned off and the vacuum increased. The total evaporating time to dryness required five to seven hours.

The residue was dissolved in 3 ml. of xylene and precipitated in a centrifuge tube with 35 ml. of methanol. After centrifugation, this procedure was repeated twice more. No detectable amount of polymer was found in the evaporation tubes after the three washings. The material in the centrifuge tubes was washed twice with methanol, redissolved and reprecipitated, again washed twice with methanol and then dried.

This was accomplished in an all-glass vacuum oven operated at 76°C. The samples were considered dry when a vacuum of 1×10^{-4} mm. of mercury could be maintained in the oven without pumping.

In order to determine the weight of the small amounts of polymer, a spectrophotometer was used. Filtering and weighing proved impractical due to changing atmospheric conditions.

A Beckman Model DU Spectrophotometer was used to determine the amount of polymer obtained. Chloroform was used as the solvent for the polystyrene because of its desirable absorption spectrum.

The calibration of the instrument was accomplished with photopolymerized styrene accelerated by benzoyl peroxide. The region of 2555 Å was chosen for the work. Reproducibility was within 4%. The blank samples were dissolved in 10 ml. of chloroform and the reacted ones in 25 ml. The percent transmission of each at 2555 Å and 0.4 mm. slit width was ascertained. From the calibration curve, the number of milligrams per milliliter of polymer was read and the yield of polymer calculated from the amount of monomer solution reacted and the chloroform dilution.

V. EXPERIMENTAL RESULTS

A total of sixty-four runs were made. Nineteen of these were used for the construction of the curve for the half-life determination. All of these were carried out at $20^{\circ} \pm 1^{\circ}\text{C}$.

Eight runs were omitted because the weight difference between the reacted sample and the blank resulted in negative values. The reasons for this could not be ascertained. However, the most probable explanation is the accidental presence of impurities in the spectrophotometer cell, since in all eight cases the polymer concentration in the blank seemed excessively high. The remaining thirty-seven runs were not included for a variety of reasons. Some were exploratory runs to determine the proper rate of flow, others were invalidated due to sudden failure of the mercury arc or to bumping, and the resultant loss of material during concentration.

The points reported in Table 1 and Figure 2 can be discussed in three groups.

Group I are the six points corresponding to the shortest time elapsed (0.033 sec.) between illumination and termination of the polymer chains. This group presents the greatest spread of values ($\pm 30\%$). This is to be expected since the likelihood of experimental error is the greatest here. The short time elapsed and the low yield result in a relatively large error. The average yield with this time interval is 0.37 mg.

Group II are the nine points representing time intervals of 0.065, 0.102, 0.128 and 0.213 seconds. For the entire group the average error is $\pm 4\%$. The percentage error decreases from $\pm 6\%$ for 0.065 sec. to $\pm 2\%$ for 0.213 sec.

Group III are the four results indicated by horizontal lines on the figure and by time = ∞ in the table. These were obtained by replacing the stirrer and inhibitor solution by a glass container. Here the error is again greater ($\pm 7.5\%$). This is to be expected since in the absence of inhibitor, uncontrollable thermal reactions would slightly increase and the inhibiting effect of the container wall decreases the yield (3).

The purpose of these runs was to determine the maximum conversion obtained, if all chains are permitted to grow until terminated in the natural course of events by mutual

interaction of the radical chains. The average yield of these runs was used as the "YIELD_{Max.}" value. This would be reached asymptotically as ever increasing times were permitted to elapse between illumination and inhibition of the chains.

In calculating the time elapsed between illumination and chain inhibition, the duration of mixing was not taken into account. It can safely be assumed that complete mixing takes less than 10 milliseconds and that no polymerization takes place after mixing has occurred (4). Arbitrarily, 2 to 3 milliseconds were added to the flow time by assuming that mixing does occur exactly when the monomer stream has been carried between the rotor and stator of the stirrer rather than at the point of impact where the stream first strikes the rotor. The error introduced by this uncertainty is easily within the limits of error as reported later.

When the best straight line defined by the lower seven points of the second group is extended to the time axis, it passes within the limits of error but below the average value of the points of group I. It intersects the time axis at 0.006 seconds. This might correspond to a real induction period, the initial reaction step involving the benzoyl peroxide. It will be noted that the band width defining the experimental error spreads broadly over the zero point.

The half-life ($T_{\frac{1}{2}}$) was obtained by finding the time necessary to obtain one-half of the maximum yield. In the

figure the average value is indicated by the bar parallel to the time axis and the average error due to the scattering of the experimental points is indicated by the vertical lines to the right and left of that line defining the average half-life value. The mode of obtaining this result is indicated by the shaded area on the plot.

The half-life determined is 0.088 ± 0.015 seconds, for the entire polymeric styrene chain.

VI. CONCLUSION

From the type of investigation reported, three significant quantities can be obtained, the half-life of polymeric free radicals, the rate constant of the propagation reaction and the rate constant of chain transfer.

Since it has not yet been possible to obtain the average degree of polymerization, only the first of these quantities has been determined.

TABLE 1
EXPERIMENTAL RESULTS

Initial flow rate 352 cm./sec. at the capillary orifice

Run#	Time elapsed between illumination & inhibition	Temperature 20°C.		Yield	
		Yield	Deviation from average	Yield Max	Deviation from average
37	.033 ± .001 seconds	.58mg.	+.21mg.	.29	+.10
41	" " "	.43 "	+.06 "	.21	+.02
48	" " "	.29 "	-.08 "	.15	-.04
50	" " "	.28 "	-.09 "	.14	-.05
51	" " "	.42 "	+.05 "	.21	+.02
64	" " "	.20 "	-.16 "	.10	-.09
Average	" " "	.37 "	±.11 "	.19	±.05
39	.065 ± .002	.71 "	+.04 "	.35	+.02
42	" " "	.63 "	-.04 "	.31	-.02
Average	" " "	.67 "	±.04 "	.33	±.02
46	.102 ± .030	1.11 "	+.04 "	.56	+.02
49	" " "	1.03 "	-.04 "	.51	-.05
Average	" " "	1.07 "	±.04 "	.54	±.05
38	.128 ± .040	1.34 "	-.02 "	.67	-.01
45	" " "	1.31 "	-.05 "	.65	-.03
63	" " "	1.42 "	+.06 "	.71	+.03
Average	" " "	1.36 "	±.04 "	.68	±.02
40	.213 ± .060	2.02 "	+.05 "	1.02	+.02
43	" " "	1.93 "	-.04 "	.98	-.02
Average	" " "	1.97 "	±.05 "	1.00	±.02
58	∞	2.21 "	+.23 "	1.12	+.12
59	" " "	1.86 "	-.02 "	.99	-.01
60	" " "	1.75 "	-.23 "	.88	-.12
61	" " "	2.01 "	+.03 "	1.01	+.01
Average	" " "	1.98 "	±.13 "	1.00	±.07

FIGURE 1

DIAGRAM OF THE APPARATUS

In the actual apparatus, the component parts were placed more compactly than shown in the drawing.

1. Reaction chamber
2. Pressure bulb
3. Capillary tube
4. Stopcock to control monomer flow
5. Reservoir
6. Stopcock to vacuum line
7. Stopcock to vacuum line
8. Manometer
9. Manometer
10. Stirrer
11. Quartz lens
12. Quartz lens
13. AH-6 Mercury arc

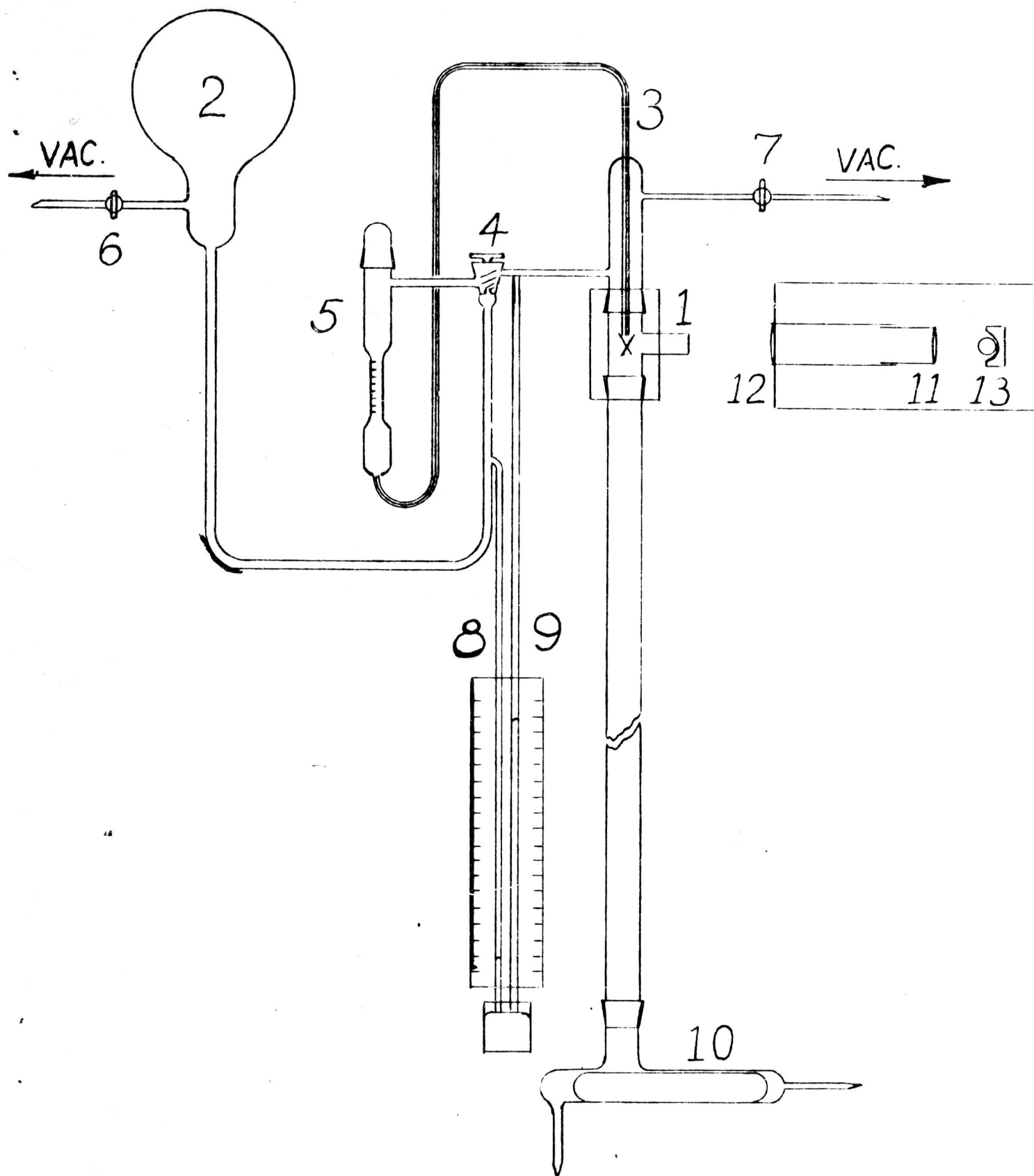
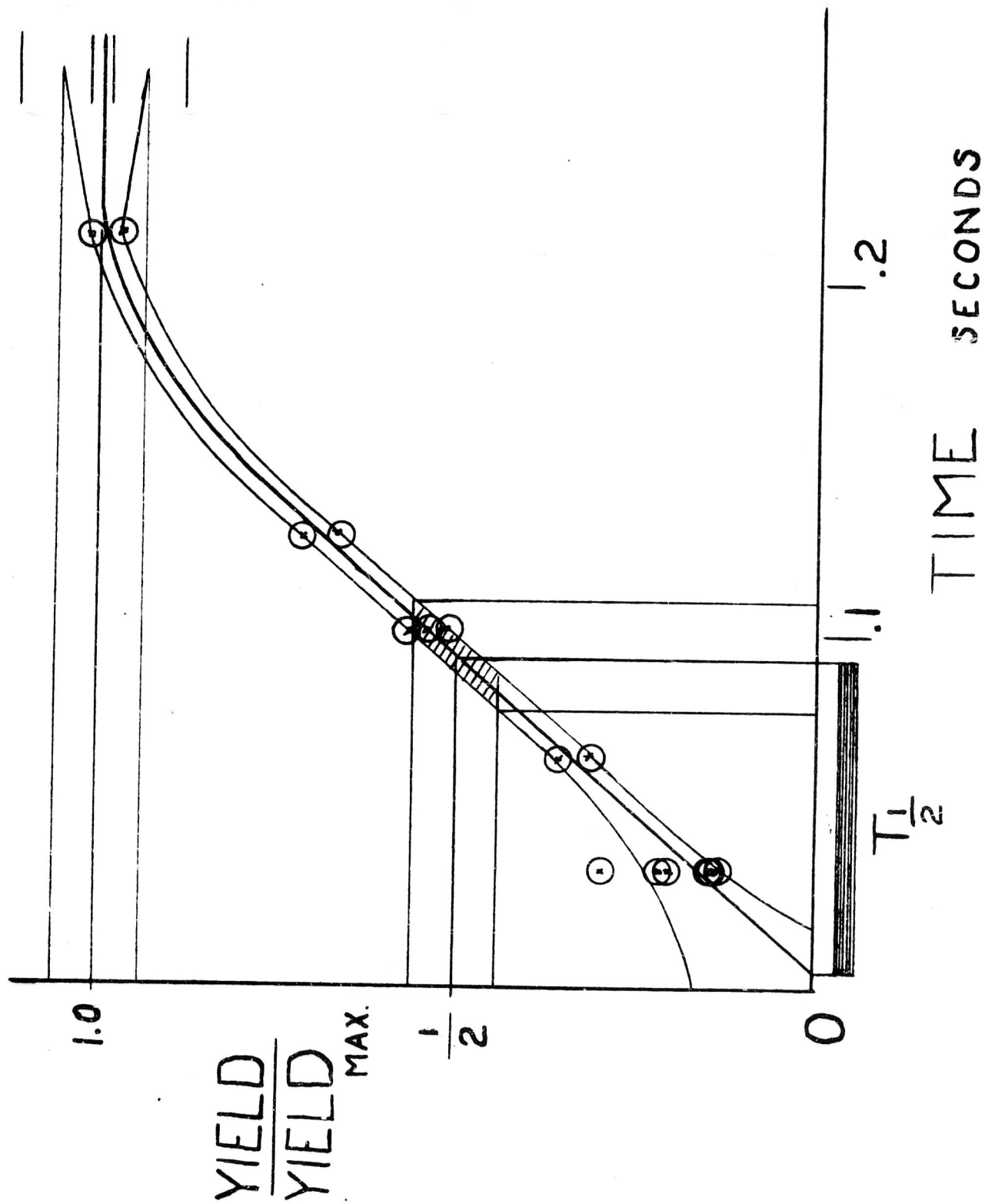


FIGURE 2

PLOT OF $\frac{\text{YIELD}}{\text{YIELD}_{\text{MAX.}}}$ VS. TIME

The half-life of the total
Polymer chain 0.088 ± 0.015 seconds.



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