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# The Inhibition of the Thermal Polymerization of Styrene

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THE INHIBITION OF THE THERMAL  
POLYMERIZATION OF STYRENE

by

William Russell Stoll

A thesis presented to the Department of Chemistry of Union College in partial fulfillment of the requirements for the degree of Bachelor of Science in Chemistry.

By:

William R. Stoll

Approved by:

Howard E. Sheffer

Date:

May 24, 1952

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ABSTRACT

In continuing the work of Cohen (7) and Opitz (10) the percent polymer formed by the inhibition of the thermal polymerization of styrene with chloranil at one hundred degrees is determined to be 0.0025%. The first polymer is precipitated by absolute methanol approximately twenty minutes before the end of the induction period.

For polymer determination an analytical method is developed, which is applicable for concentrations between 0.001% and 0.022% by weight in the presence of the colored inhibitor, and which measures the solution turbidity after precipitation from the monomer. This method can be extended to 0.08% polymer.

Polymer percentages to be measured in this manner greater than 0.02% were diluted with styrene. Polymer percentages greater than one percent were determined by flash distillation.



### INTRODUCTION

Polymerization is considered to be the chemical uniting of several simple molecules together to form a single molecule. Unsaturated vinyl compounds easily unite to form high polymers. Styrene is a phenyl derivative of ethylene, and its polymerization is amply discussed by many authorities.

(1)(8)(9)

The polymerization proceeds somewhat at room temperature, but the rate of polymerization may be accelerated by increasing the energy content of the monomer or by decreasing the necessary energy of activation with catalysts: particularly peroxides.

No catalysts are employed in this work. The polymerization takes place at a favorable rate at one hundred degrees Centigrade.

Foreign materials may be added to the styrene monomer to alter its polymerization. Authorities classify these materials into two groups: inhibitors and retarders.

Ideally, inhibitors prevent the polymerization by reacting preferentially with activated monomer molecules. This causes destruction of the inhibitor to a point where its concentration is no longer effective. After this induction period



the polymerization proceeds at its normal rate, dependent only on the conditions of polymerization.

Retarders, on the other hand, do not prevent polymerization but alter its rate and have effect on the molecular weight of the end product.

Chloranil, as studied by Breitenbach and coworkers (2) (3)(4), Cohen (5), Opitz (10), and other investigators (1) (9), is a very effective but not ideal inhibitor. Furthermore, the deep yellow color of chloranil in styrene solution facilitates colorimetric measurement of its disappearance during the induction period (i.e. the period in which the inhibitor is effective in preventing polymerization). The end of the induction period is indefinite, and the color of the chloranil does not entirely disappear. The end of the induction period may be estimated by plotting chloranil concentration against time and extrapolating the curve to zero time. As this work shows, some polymeric chains are present at this time, and the polymerization is approaching its normal rate.

The purpose of this work is to attempt to establish the point at which measurable polymer is formed and the percent polymer at the end of the induction period.



itating agent, such as absolute methanol. If polymer is present to an extent greater than 0.0005%, opalescence will occur. Ferguson measured the turbidity by a visual turbidimeter and obtained definite, reproducible results. In application of this method to the problem at hand, the turbidity of the solution, after the addition of absolute methanol, is measured by a Fisher electrophotometer. This method is more accurate than the visual method, but it presents several new problems.

The styrene unknown solutions contain varying concentrations of chloranil. The concentration will be small since, as will be shown, no polymer is precipitated until near the end of the induction period, and the solution is diluted by the methanol. However, the absorption of light by the chloranil still is not insignificant. A filter was prepared consisting of a glass cell, one centimeter thick, with a 0.0035 molar solution of chloranil in styrene. This solution absorbs most of the light which ordinarily would be affected by the color of the unknown solutions. See Graph I.

Standard solutions of polymers of different average molecular weights were studied to check the consistency of measurement as the molecular weights vary. Dow resins:



P.S.-3-B, P.S.-15-B, P.S.-65-B. with molecular weights of 15,000, 48,000, and 85,000 respectively \* were used. It was found that the particle size is little affected by the molecular weight. See Graph II.

The major problem results from the particle size itself and the rate of precipitation. It was found that the transmittance increases during the first ten minutes for polymer concentrations greater than 0.05%, and the transmittance decreases for polymer concentrations less than 0.01%. The change from one to the other is gradual and continuous. This is due to two competing factors: the rate of initial precipitation and the later agglomeration and sedimentation. For examples, see Graph IIB.

The technique of precipitation is very important because it determines the particle size. The procedure used throughout this work is adding forty milliliters of absolute methanol all at once (by beaker) to twenty milliliters of the styrene sample, immediately pouring the mixture into the measuring cell.

Measurements of optical density of a particular sample with time gives a smooth curve, which becomes nearly linear after five or six minutes. The linear portion is extrapolated

(\*private correspondence)



back to zero time for the value to be used. There are two reasons for doing this: extrapolation eliminates possible errors from one or two inaccurate time measurements giving a more reproducible value, and the extrapolation makes the optical density versus percent polymer graph more nearly linear with much greater accuracy for the higher polymer percentages in the range of measurement. See the calibration curve, Graph III.

The standard solution is forty milliliters of methanol in twenty milliliters of recently distilled styrene, stabilized by 0.001% tert-butyl catechol. The sensitivity of the electrophotometer is set at letter "A". The cells are rectangular in shape and hold a volume of sixty milliliters. The filter, as mentioned before, is a solution of chloranil in styrene (0.0035 M.); the filter depth is one centimeter.

The measurable range by this method is 0.001% to 0.022% polystyrene in styrene. The error is estimated to be plus or minus 0.0005%. Solutions of greater polymer concentration are brought into this range by dilution with distilled styrene.



### Polymerization Technique

Reaction tubes were made from ten millimeter pyrex tubing, thirty centimeters in length, and sealed at one end. Each tube was cleaned with acetone and dried before use.

The samples, containing fifteen milliliters of the chloranil - styrene solutions, were sealed in the reaction tubes in an atmosphere of nitrogen at one hundred millimeters pressure and approximately -45 degrees Centigrade (dry ice - acetone bath)

The polymerization was carried out in a constant temperature oil bath at  $100 \pm 1$  degrees Centigrade. The polymerization reactions were frozen at the desired time in a dry - ice and acetone freezing bath. The tubes were broken open and allowed to warm to room temperature. The chloranil concentration was measured immediately.

The optical density of the solutions were measured by the Fisher electrophotometer using the micro attachment and the blue filter. The chloranil concentration was determined from the calibration curve used by Opitz (10).

The samples were then measured for percent polymer by either the turbidimetric method or the flash distillation

method as previously described. If the samples were not measured for polymer concentration immediately, 0.001% tert-butyl catechol was added to stabilize the mixture.

#### Purification of Chemicals

The styrene used in this work was obtained through the Schenectady Varnish Company (Dow H-99 styrene). It was distilled in an atmosphere of nitrogen at ten millimeters pressure and forty-two degrees Centigrade. The styrene to be used for standard measurements and for calibration was collected in a flask containing approximately 0.001% tert-butyl catechol for stabilization.

The distilled styrene was tested for the presence of the commercial retarder (tert-butyl catechol). Mixing equal volumes of one percent sodium hydroxide and the styrene gives a red color in the oil layer if significant quantities of tert-butyl catechol are present (6). The chemical reaction is the formation of the ortho quinone from the catechol derivative. The distilled styrene gave completely negative results.

The distilled styrene was also tested for polymer by adding two volumes of absolute methanol to one volume of styrene. The distillate gave no opalescence indicating less



than 0.0005% of polymer was present (6)(7).

The chloranil was obtained from Eastman Kodak Company and was used without further purification (10).

The chloranil and styrene for experimental runs were mixed together, divided into fifteen milliliter aliquots, and sealed into the reaction tubes in apparatus directly connected to the distillation receiver. At no time did the mixture come in contact with the air; thus all effects due to oxygen were eliminated. (1)(8)(9)



DATA

Graph I Optical Density vs. Percent P.S.-15-B. polystyrene  
in styrene. Fisher electrophotometer  
medium cell attachment  
filter: 0.002 M. chloranil in styrene

Part 1

| <u>concentration</u> | <u>opt. density<br/>extrapolated</u> |
|----------------------|--------------------------------------|
|----------------------|--------------------------------------|

no added chloranil to  
polymer solutions

|        |       |
|--------|-------|
| 0.001% | 0.005 |
|--------|-------|

|       |       |
|-------|-------|
| 0.002 | 0.022 |
|-------|-------|

|       |       |
|-------|-------|
| 0.004 | 0.080 |
|-------|-------|

|       |       |
|-------|-------|
| 0.006 | 0.137 |
|-------|-------|

|       |       |
|-------|-------|
| 0.008 | 0.220 |
|-------|-------|

|       |       |
|-------|-------|
| 0.010 | 0.290 |
|-------|-------|

|       |       |
|-------|-------|
| 0.020 | 0.560 |
|-------|-------|

|       |       |
|-------|-------|
| 0.030 | 0.746 |
|-------|-------|

Part 2

| <u>conc.</u> | <u>opt. density<br/>extrapolated</u> |
|--------------|--------------------------------------|
|--------------|--------------------------------------|

chloranil concentration:  
0.002 molar

|        |       |
|--------|-------|
| 0.001% | 0.003 |
|--------|-------|

|        |        |
|--------|--------|
| 0.0025 | 0.0024 |
|--------|--------|

|       |       |
|-------|-------|
| 0.005 | 0.090 |
|-------|-------|

|        |       |
|--------|-------|
| 0.0075 | 0.230 |
|--------|-------|

|       |       |
|-------|-------|
| 0.010 | 0.255 |
|-------|-------|

|       |       |
|-------|-------|
| 0.015 | 0.440 |
|-------|-------|

|       |       |
|-------|-------|
| 0.020 | 0.500 |
|-------|-------|

|       |       |
|-------|-------|
| 0.025 | 0.606 |
|-------|-------|

|       |       |
|-------|-------|
| 0.030 | 0.758 |
|-------|-------|

Graph II      Optical Density vs. percent polystyrene in styrene  
 Fisher electrophotometer  
 Medium cell attachment  
 Filter: 0.002 molar chloranil in styrene  
 no chloranil in standard samples.

| <u>P.S.-3-B. pol- P</u> |                   | <u>P.S.-15-B.</u> |               | <u>P.S.-65-B.</u> |                   |
|-------------------------|-------------------|-------------------|---------------|-------------------|-------------------|
| <u>ystyrene</u>         |                   | <u>polymer</u>    |               | <u>polymer</u>    |                   |
| <u>conc.</u>            | <u>opt. dens.</u> | <u>Conc.</u>      | <u>Op. d.</u> | <u>conc.</u>      | <u>opt. dens.</u> |
| 0.005%                  | 0.136             | 0.001%            | 0.005         | 0.0025%           | 0.062             |
| 0.010                   | 0.250             | 0.002             | 0.022         | 0.005             | 0.146             |
| 0.015                   | 0.388             | 0.004             | 0.080         | 0.0075            | 0.250             |
| 0.020                   | 0.488             | 0.006             | 0.137         | 0.010             | 0.320             |
| c.                      |                   | 0.008             | 0.220         | 0.015             | 0.423             |
|                         |                   | 0.010             | 0.290         | 0.020             | 0.565             |
|                         |                   | 0.020             | 0.560         |                   |                   |
|                         |                   | 0.030             | 0.746         |                   |                   |



Graph II-B      Optical Density vs. time in minutes after  
initial precipitation.

Fisher electrophotometer

optical density times 100

| time: | <u>1</u> | <u>2</u> | <u>3</u> | <u>4</u> | <u>5</u> | <u>6</u> | <u>7</u> | <u>8</u> | <u>9</u> | <u>10</u> | extra. |
|-------|----------|----------|----------|----------|----------|----------|----------|----------|----------|-----------|--------|
| conc. |          |          |          |          |          |          |          |          |          |           | value  |
| .002% | 4.1      | 5.9      | 6.6      | 7.5      | 7.9      | 8.4      | 8.8      | 9.0      | 9.5      | 9.5       | 5.6    |
| .005  | 16.0     | 20.7     | 22.7     | 24.2     | 25.5     | 26.1     | 27.0     | 27.8     | 28.0     | 28.0      | 21.4   |
| .010  | 39.5     | 47.6     | 50.4     | 52.0     | 53.0     | 54.4     | 55.2     | 56.2     | 56.4     | 56.4      | 47.4   |
| .015  | 65.0     | 73.0     | 75.      | 77.      | 78.      | 78.5     | 79.      | 79.      | 79.      | 79.       | 76.0   |
| .022  | 82.      | 88.      | 89.5     | 90.5     | 91.      | 91.      | 90.5     | 90.5     | 90.5     | 90.5      | 91.8   |

From calibration curve; large cell attachment

filter: 0.0035 M. chloranil in styrene

polymer: P.S.-3-B. polystyrene

|       |      |      |      |      |      |      |      |      |      |      |
|-------|------|------|------|------|------|------|------|------|------|------|
| .020% | 23.8 | 24.7 | 24.6 | 24.5 | 24.4 | 24.1 | 24.0 | 23.6 | 23.4 | 25.5 |
| .040  | 45.0 | 44.5 | 43.8 | 43.2 | 42.3 | 41.5 | 40.6 | 40.0 | 39.3 | 46.8 |
| .060  | 61.1 | 59.0 | 57.2 | 56.2 | 54.8 | 54.0 | 52.2 | 51.6 | 51.0 | 61.8 |

with micro cell attachment

filter: 0.002M. chloranil in styrene

polymer: P.S.-3-B. polystyrene

|      |     |     |     |     |     |      |      |      |      |
|------|-----|-----|-----|-----|-----|------|------|------|------|
| .070 | 80. | 77. | 72. | 70. | 69. | 67.4 | 66.6 | 65.2 | 76.2 |
|------|-----|-----|-----|-----|-----|------|------|------|------|

with micro cell attachment

filter: 0.002 M. chloranil in styrene

polymer: P.S.-15-B. polystyrene (with 0.002 M. chloranil)



Graph III

Calibration Curve

Optical Density versus percent polymer by weight

Fisher electrophotometer - large cell attachment

filter: 0.0035 M. chloranil in styrene

P.S.#3-B. polystyrene in styrene, no added chloranil

| <u>Percent<br/>polymer</u> | <u>Opt. Dens.<br/>extrp. val</u> | <u>Percent<br/>polymer</u> | <u>Opt. Dens.<br/>extrp. val</u> |
|----------------------------|----------------------------------|----------------------------|----------------------------------|
| 0.0002%                    | 0.004                            | 0.0090                     | 0.433                            |
| 0.0004                     | 0.008                            | 0.0100                     | 0.474                            |
| 0.0006                     | 0.008                            | 0.0110                     | 0.543                            |
| 0.0008                     | 0.020                            | 0.0120                     | 0.598                            |
| 0.0010                     | 0.020                            | 0.0130                     | 0.635                            |
| 0.0020                     | 0.056                            | 0.0140                     | 0.705                            |
| 0.0030                     | 0.104                            | 0.0150                     | 0.760                            |
| 0.0040                     | 0.137                            | 0.0160                     | 0.794                            |
| 0.0050                     | 0.214                            | 0.0170                     | 0.842                            |
| 0.0060                     | 0.242                            | 0.0180                     | 0.882                            |
| 0.0070                     | 0.310                            | 0.0190                     | 0.918                            |
| 0.0080                     | 0.378                            | 0.0200                     | 0.924                            |

Graphs IV and V Experimental Runs

Induction Period and Percent Polymer

Induction period measured colorimetrically on Fisher electro-photometer, micro attachment, blue filter. Chloranil concentration determined from Opitz's calibration curve (10)

Percent polymer measured in the same manner as in Graph III

Temperature 100 degrees

time      O.D. chlor conc. chl.dilution    O.D.polymer % polymer

Run #1

|        |       |           |      |     |     |
|--------|-------|-----------|------|-----|-----|
| 0 min. | 1.050 | 0.00323 M | none | 0.0 | 0.0 |
| 30 "   | 1.020 | 0.00288   | "    | 0.0 | 0.0 |
| 60 "   | 0.900 | 0.00209   | "    | 0.0 | 0.0 |
| 90 "   | 0.820 | 0.00171   | "    | 0.0 | 0.0 |
| 120 "  | 0.718 | 0.00136   | "    | 0.0 | 0.0 |
| 150 "  | 0.600 | 0.00101   | "    | 0.0 | 0.0 |
| 180 "  | 0.445 | 0.00068   | "    | 0.0 | 0.0 |
| 240 "  | 0.145 | 0.00020   | 2    | 0.0 | 0.0 |

Run #2

|        |       |            |      |       |       |
|--------|-------|------------|------|-------|-------|
| 0 min. | 0.980 | 0.00255 M. |      |       |       |
| 180 "  | 0.292 | 0.00042    | none | 0.0   | 0.0   |
| 210 "  | 0.055 | 0.00006    | 10   | 0.875 | 0.18% |
|        |       |            | 20   | 0.375 | 0.16% |



| <u>time</u> | <u>OR chlor</u> | <u>conc chlor</u> | <u>dilution</u> | <u>OD polymer</u> | <u>% polymer</u> |
|-------------|-----------------|-------------------|-----------------|-------------------|------------------|
|-------------|-----------------|-------------------|-----------------|-------------------|------------------|

Run #2 (con't)

|          |      |  |                            |       |                            |
|----------|------|--|----------------------------|-------|----------------------------|
| 240 min. | 0.00 |  | 100                        | 0.570 | 1.17%                      |
|          |      |  | by flash distillation 1.6% |       |                            |
| 259 "    |      |  |                            |       | by flash distillation 2.7% |
| 281 "    |      |  |                            |       | by flash distillation 4.7% |

Run #3

|        |       |            |      |       |         |
|--------|-------|------------|------|-------|---------|
| 0 min. | 0.990 | 0.00263 M. | none | 0.0   | 0.0     |
| 188 "  | 0.174 | 0.00023    | "    | 0.0   | 0.0     |
| 193 "  | 0.118 | 0.00016    | "    | 0.122 | 0.0036% |
| 200 "  | 0.134 | 0.00018    | "    | 0.0   | 0.0     |
| 210 "  | 0.106 | 0.00014    | 2    | 0.010 | 0.0016% |
| 220 "  | 0.061 | 0.00007    | 10   | 0.140 | 0.039%  |
| 225 "  | 0.056 | 0.00006    | 20   | 0.236 | 0.116%  |

| <u>Run</u> | <u>Induction Period</u> |
|------------|-------------------------|
|------------|-------------------------|

|   |               |
|---|---------------|
| 1 | app. 290 min. |
| 2 | 195 min.      |
| 3 | 215 min.      |

## DISCUSSION OF EXPERIMENTAL RESULTS

### Induction Periods

As shown by Graph IV, the disappearance of chloranil during the induction period is not linear as predicted by Cohen (5). The graphs are somewhat similar to the ones obtained by Opitz, except careful measurements were not made in this work during the early part of the induction period to justify an inflection point.

Theoretical reaction rate considerations between activated styrene molecules with the inhibitor have given several equations: some very complex and others relatively simple (5)(8)(11)(12). The equation developed by Cohen is:

$$Q_t = Q_0 - \frac{1}{2} k_i [M]^2 t \quad (5)$$

$Q_t$  is the chloranil concentration at time "t".  $Q_0$  is the initial chloranil concentration.  $k_i$  is the reaction rate constant of the formation of activated monomer molecules, and  $[M]$  is the initial concentration of the styrene.

Equations of this type should give excellent approximations of chloranil concentrations when they are relatively high. However, as the concentration of the inhibitor is depleted, the probability of effective collisions between the molecules of the inhibitor and the activated monomer decreases. The rate of disappearance of the inhibitor should decrease since the concentration of the monomer is



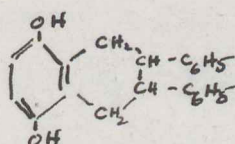
nearly the same.

In other words, although there is no mathematical substantiation for this statement: the rate of disappearance of the inhibitor is not independent of its concentration, and such equations should be derived by statistical methods of probabilities rather than from simple reaction rate considerations alone.

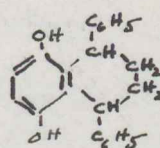
#### Percent Polymer

Breitenbach and Breitenbach (2) assumed from their data that some polymer is formed throughout the induction period. Breitenbach and his co-workers determined the percent polymer by distilling off the monomer under reduced pressure. Bovey and Kohltoff (1) disagree with this conclusion. The work here substantiates their objection since no polymer is precipitated by methanol until the end of the induction period. This is mentioned by Foord (9). He concludes the inhibition is a simple chemical reaction between the active centers and the inhibitor, and no polymer is formed. Breitenbach (3) insisted that Foord and others were wrong: that colored low molecular weight products were formed, which were not detected by the usual viscometric methods. The inhibition products between p-benzoquinone and styrene include quinhydrone and an incompletely identified compound

which probably is either



or



(1).

Breitenbach and Schneider (4) measured the thermal polymerization of styrene in the presence of chloranil at ninety degrees. The initial chloranil concentration in one run was 0.00087 molar (0.0001 mole of chloranil per mole of styrene). At the end of the induction period (three and one half hours) they calculated that 0.26% of the styrene was transformed. Furthermore the ratio of styrene to chloranil in the reaction products was variable. The distillation residue was a brown, viscous material, soluble in methanol. It had a chlorine content of 23%. The reaction products appeared to be able to propagate new chains.

Assuming the conclusions of Breitenbach are true, the inhibition products in this work are not precipitated by the methanol. It appears that the differences in conclusions in the literature result from interpretation of the word "polymer". Breitenbach means all reaction products during the induction period as well as the polystyrene formed afterward. As used here in this work, polymer refers specifically to that material which is precipitated by methanol (viz. polystyrene). This material is white.



A sticky mass is obtained in the flash distillation method of determining the percent polymer in this work. As it is dried it forms a firm, foamy semi-solid. It appears colorless. Attempts to run flash distillations of solutions of percent polystyrene in styrene less than one gave widely varying results.

As Graph V demonstrates, polystyrene is only formed when the chloranil concentration is reduced to such a low point that the probability of reaction with activated molecules is insignificant. This point should be considered the end of the induction period (1).

From Graph V measureable opalescence of styrene and methanol solutions occurs between fifteen and twenty-five minutes before the end of the induction period. The rate of formation of polymer increases until the end of the induction period is reached, where the rate of formation is nearly equal to the normal, uninhibited rate. The percent polymer at this point is between 0.0025% and 0.0030%. The formation of precipitable polystyrene twenty minutes before the end of the induction period is mainly due to insufficient chloranil concentration, but it may also be due in part to chain transfer action by reaction products formed during the induction period.

#### SUGGESTIONS FOR FURTHER WORK

The reaction products formed during the induction period must be studied and identified. Breitenbach's method of separation might be employed (4).

Of particular interest will be the reaction products at the end of the induction period when some polymer is present. The polymer can be separated by precipitation with methanol. The liquid then could be distilled under reduced pressure. The residue then can be examined and compared to Breitenbach's reaction products.

#### SUMMARY

An analytical method of determining percent polymer in styrene at low concentrations is developed, involving the measurement of the turbidity of the solution after the addition of absolute methanol.

It is decided that the end of the induction period of the inhibition of the thermal polymerization of styrene with chloranil at one hundred degrees centigrade is that point where the rate of polymerization of the monomer becomes approximately equal to the normal, uninhibited rate.

Polymer is precipitated with methanol approximately twenty minutes before the end of the induction period.

The percent polymer at the end of the induction period is determined to be nearly 0.0025%.

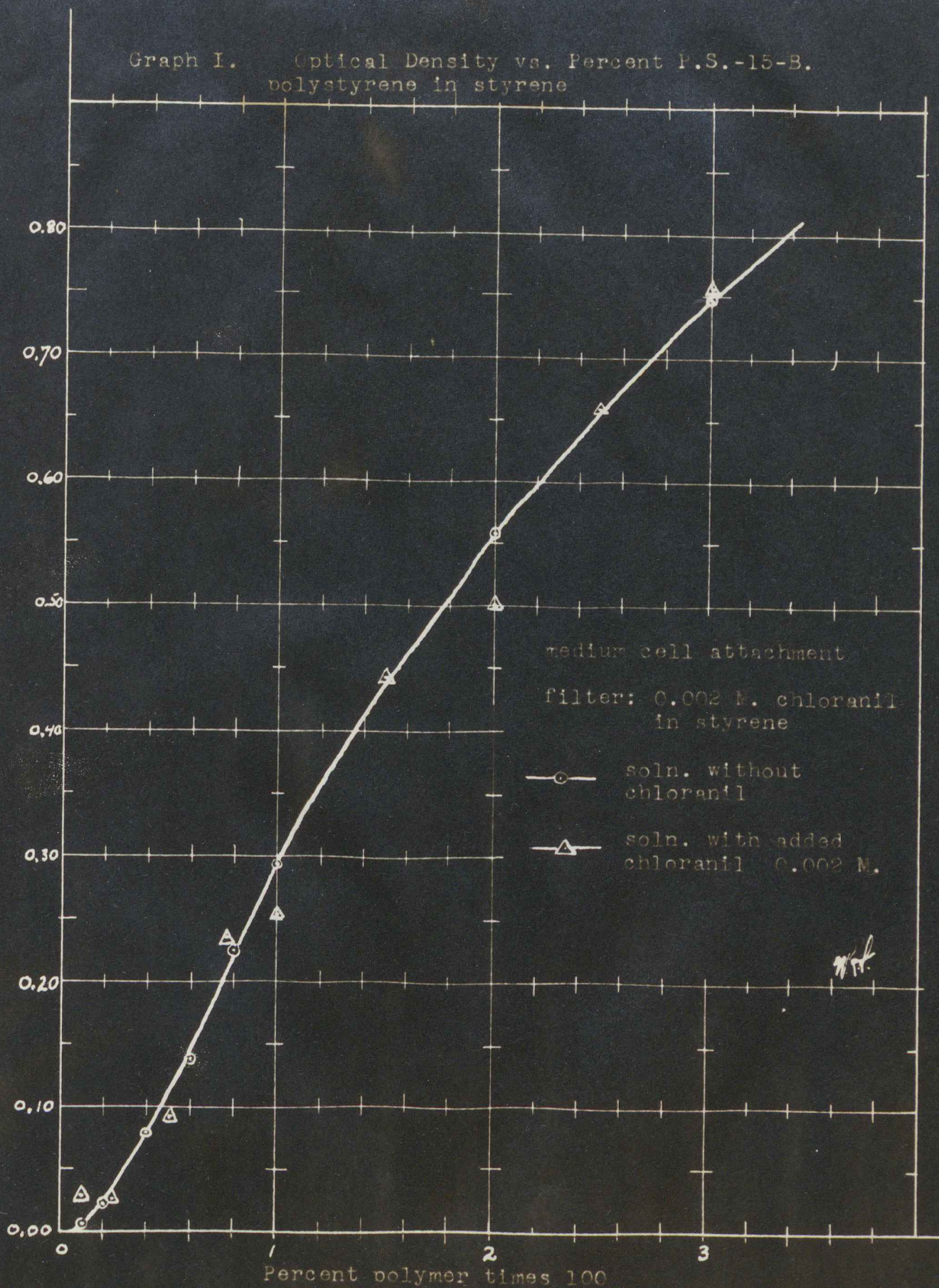


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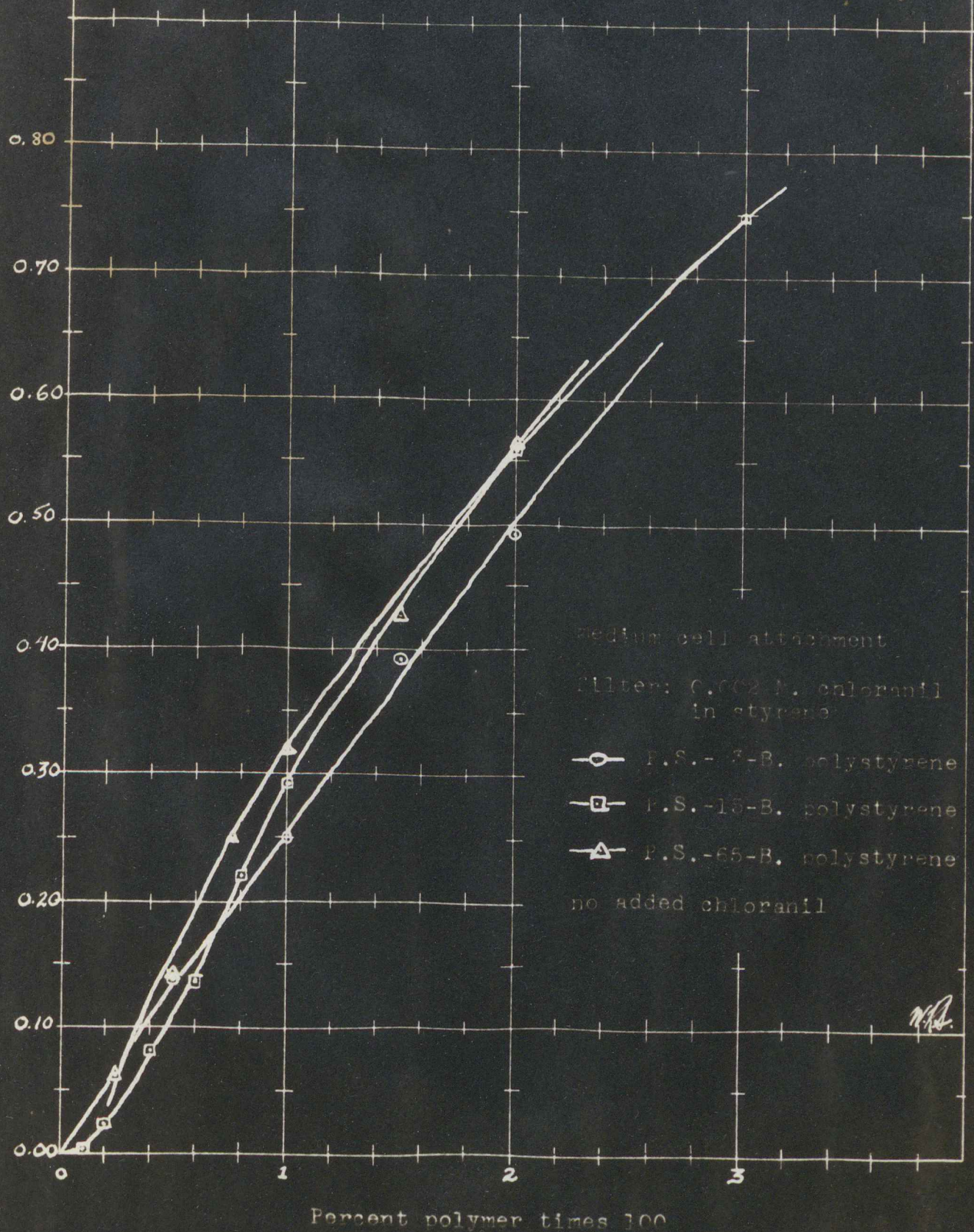


Graph I. Optical Density vs. Percent P.S.-15-B.  
polystyrene in styrene



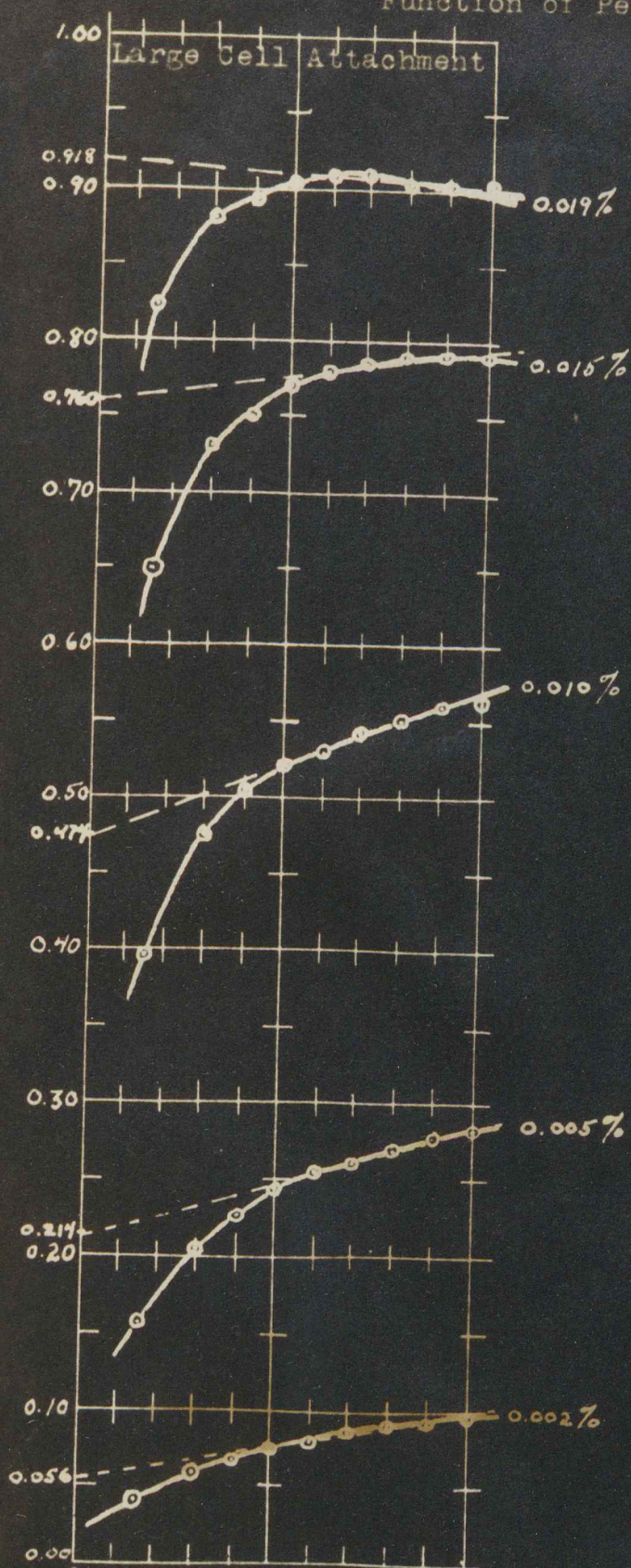


Graph II. Optical Density vs. Percent polystyrene in styrene

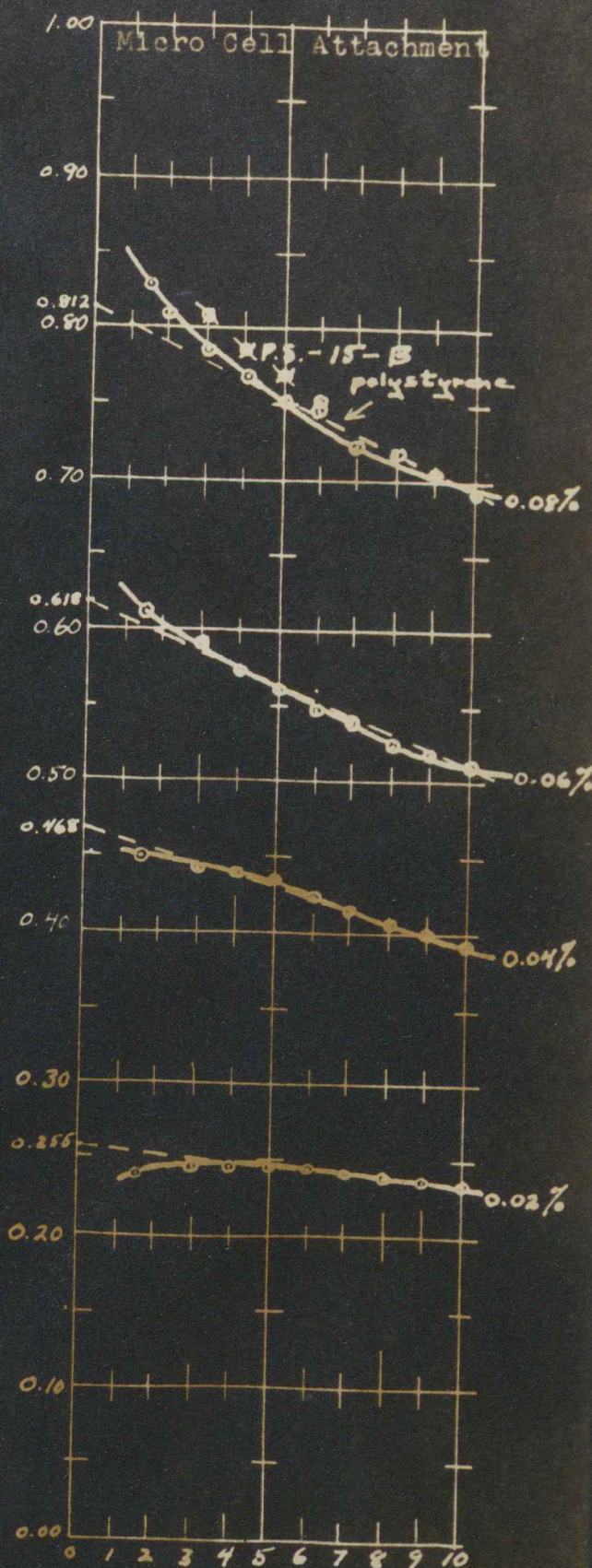




Graph II-B. Optical Density - Time Relationship as a Function of Percent Polystyrene



Time after the addition of methanol  
P.S.-3-B polystyrene  
Filter: 0.0035 M. chloranil

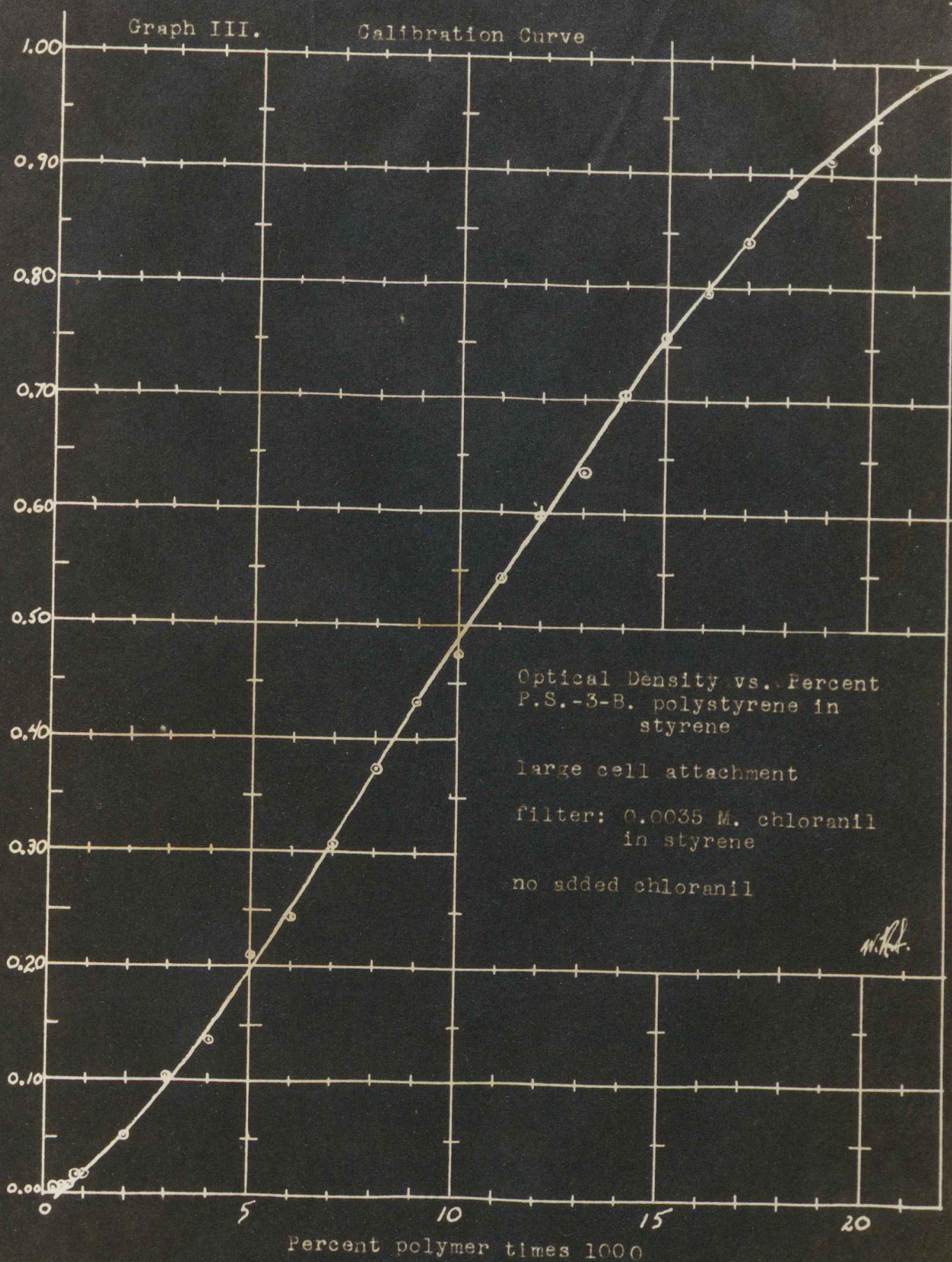


P.S.-3-B. polystyrene  
Filter: 0.002 M. chloranil



Graph III.

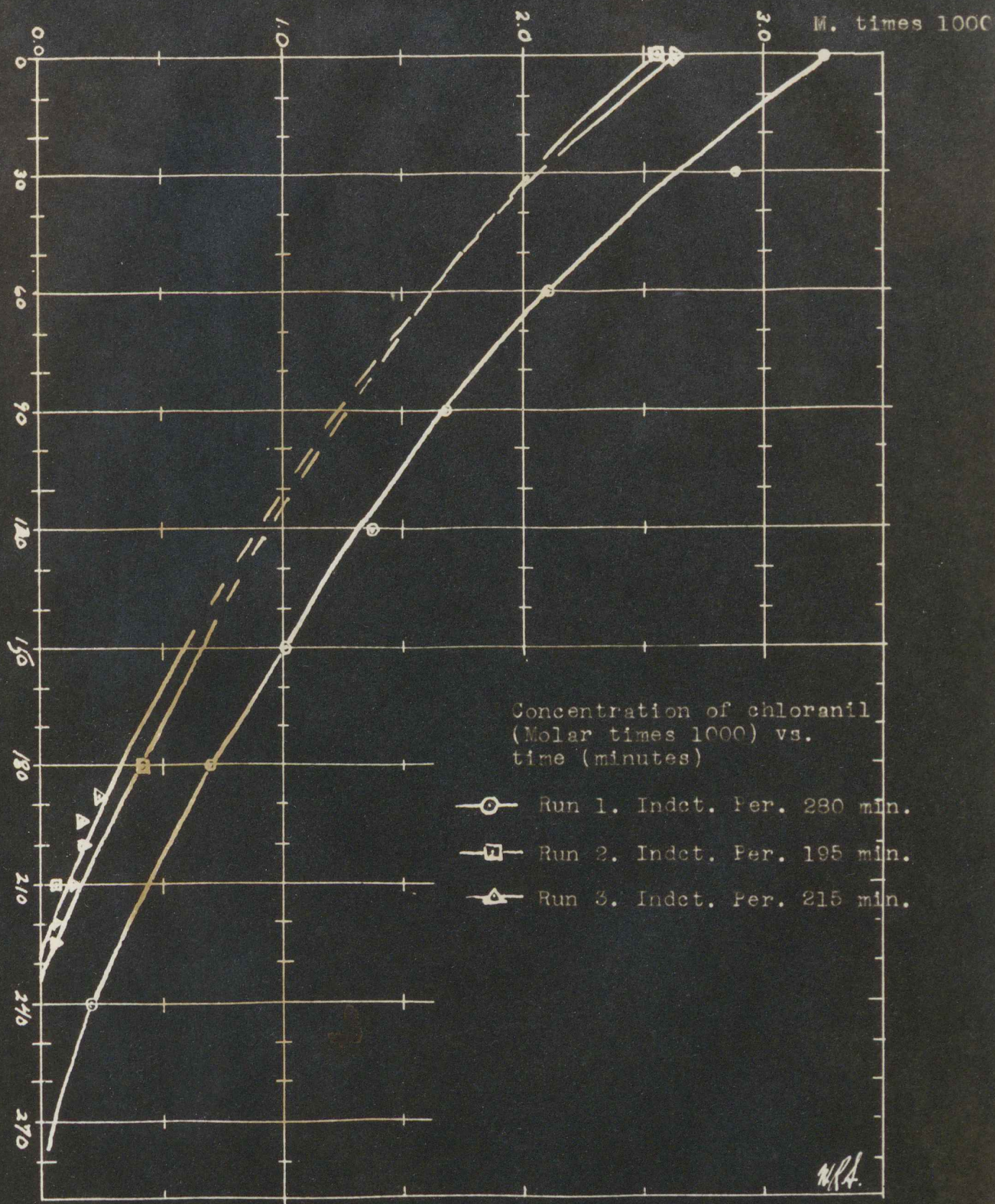
Calibration Curve





Graph IV

## Induction Periods





Graph V. Percent polymer near the end of the induction period

